Development of Zwitterionic Chromophores for Electro-Optic Applications

By
Ying Xiong

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
Carleton University
Ottawa, Ontario, Canada
June 2008

© Copyright, Ying Xiong, Ottawa, Canada, 2008

Library and
Archives Canada

Bibliothèque et
Archives Canada

Published Heritage
Branch

Direction du
Patrimoine de l'édition

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 978-0-494-43916-6

Our file Notre référence

ISBN: 978-0-494-43916-6

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protègent cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Abstract

In order to unlock the full potential of the zwitterionic NLO chromophores for electro-optic (EO) applications, a new series of PeQDM chromophores with large first hyperpolarizabilities ($\beta_0 \sim 600 \times 10^{-30}$ esu) have been designed and synthesized. A large EO coefficient (r_{33}) of 110 pm/V at 1550 nm has been realized with a 5 wt% (corresponding to 3.8 wt% core content) chromophore doped polymer. The EO study of guest-host polymers reveals that dipolar dye aggregation in a less polar medium is responsible for a low chromophore loading and low EO activity. Modification of NLO chromophore by attaching large dendrons can effectively increase the chromophore loading in a host and improve the poling efficiency. Crosslinkable NLO polymers have also been prepared to improve the temporal stability of the poled noncentrosymmetric order. The following are some important highlights from this thesis work.

- (1) A series of thermally stable zwitterionic chromophores (PeQDM) with large first hyperpolarizabilities (β up to -1797×10^{-30} esu) are synthesized in good yields ($\sim 50\%$). The charge-separated ground state is evident by a negative solvatochromism. X-ray crystallographic data further confirms the zwitterionic nature and demonstrates a face-to-face anti-parallel H-aggregation of two monomers due to strong electrostatic interactions between the dipoles.
- (2) PeQDM chromophores are also NIR fluorescent ($\lambda^{PL} \sim 840\text{-}870$ nm in solution) and labile to acid, making them potential candidates for NIR pH sensor applications.
- (3) The hydroxyl-containing PeQDM chromophores are modified with ES-dendron, which exhibit good solubility in solvents and polymers. Self-forming films can be

prepared by direct casting or spin-coating of two dendrons modified chromophores (ES-PeQDM-2 and ES-PeQDM-3), in which the chromophore core contents reach 14.9 and 16.9 wt%, respectively. Compared to ES-PeQDM-2 with two dendrons only at the donor part ($r_{33} = 0$ pm/V), ES-PeQDM-3 with the bulky ES-dendrons anchored at both the donor and acceptor parts can be poled ($r_{33} = 63$ pm/V).

- (4) Crosslinkable NLO polymers can be prepared by grafting PeQDM-C3OH and 5-aminobenzocyclobutenone as a thermal crosslinker onto acid-containing polyethersulfone. The EO coefficient of a crosslinkable NLO polyethersulfone with 4.8 wt% chromophore core content is 37 pm/V.
- (5) The use of a polymer with a high dielectric constant to host PeQDM gives rise to the largest EO coefficient ($r_{33} = 110$ pm/V), due to the well dispersed monomeric chromophores. The J-type chromophore aggregates formed in a less polar polymer host could still contribute to EO activity, if the dissociated monomer intermediate during the J-H aggregate transformation could be oriented under the poling conditions.

Acknowledgements

First of all, I'd like to give my deepest gratitude to my supervisor, Dr. Z. Y. Wang, for his excellent guidance and valuable advices. I am also really appreciated for his critical reading and continous patience during the writing of the thesis. Without his support, this thesis couldn't be completed.

I am greatly thankful to Dr. Jane Gao for her useful suggestions and assistance throughout my thesis work. My particular thank-you also goes to her for her caring about my family in the past few years.

I am also thankful to all my colleagues and the supporting staff at the Department of Chemistry for their help and friendship. It's been a great pleasure for me to work with all of you.

Finally, I'd like to take this opportunity to thank my husband Dr. H. Tang and my son Kuangyi for their continuous encouragement and understanding during my study at Carleton University.

Table of Contents

Abstract.....	I
Acknowledgements	III
Table of Contents	IV
List of Schemes.....	VII
List of Tables	VIII
List of Figures.....	IX
List of Symbols and Abbreviations	XIV
Chapter 1 Introduction to Organic Electro-Optic Materials	1
1. 1. Origin of electro-optic effect	1
1. 2. From molecular hyperpolarizability to macroscopic optical nonlinearity	5
1. 3. Neutral NLO chromophores	9
1. 4. Zwitterionic NLO chromophores.....	13
1. 5. Dendritic NLO chromophores	19
1. 6. NLO polymers	22
1. 7. Poling and EO measurement.....	26
1. 8. Rationale and objectives	29
1. 9. References.....	32
Chapter 2 Synthesis and Characterization of Zwitterionic Chromophores.....	39
2. 1. Introduction.....	39
2. 2. Results and Discussion	43
2. 2. 1. Synthesis of ACQ and PeQDM	43

2. 2. 2. Structural characterization	48
2. 2. 3. X-ray crystallography	50
2. 2. 4. Reaction mechanism	53
2. 2. 5. Negative solvatochromism.....	56
2. 2. 6. Thermal stability	59
2. 2. 7. Acid sensitivity	60
2. 2. 8. Photoluminescence	64
2. 2. 9. Hyperpolarizability study.....	68
2. 3. Conclusions.....	68
2. 4. Experimental	69
2. 5. References.....	80
Chapter 3 Synthesis and Characterization of Dendronized PeQDM	
Chromophores.....	82
3. 1. Introduction.....	82
3. 2. Synthesis and characterization of ES-dendron	83
3. 3. Synthesis and characterization of dendronized chromophores.....	86
3. 4. Conclusions.....	99
3. 5. Experimental	100
3. 6. References.....	103
Chapter 4 Synthesis and Characterization of Crosslinkable NLO Polymers	104
4. 1. Introduction.....	104
4. 2. Synthesis and characterization of PES-Acid.....	105
4. 3. Synthesis and characterization of PES-E	108

4. 4. Synthesis and characterization of crosslinkable NLO polyethersulfone	112
4. 5. Conclusions.....	118
4. 6. Experimental	118
4. 7. References.....	123
Chapter 5 Electro-Optic Properties of NLO Materials.....	124
5. 1. Introduction.....	124
5. 2. Electro-optic properties of zwitterionic chromophores	126
5. 2. 1. Molecular organizations of zwitterionic chromophores in polymers .	126
5. 2. 2. EO properties of PeQDM-Ben doped polymers	129
5. 2. 3. Temporal EO stability of the poled PES-U film.....	133
5. 3. Electro-optic properties of dendronized chromophores.....	134
5. 3. 1. Electro-optic property of ES-PeQDM-1b doped polyethersulfone (PES-U)	135
5. 3. 2. Electro-optic properties of ES-PeQDM-2 and ES-PeQDM-3	137
5. 4. Electro-optic properties of crosslinkable NLO polyethersulfones.....	138
5. 5. Conclusions.....	139
5. 6. Experimental	140
5. 7. References.....	142
Contribution to Knowledge.....	143
Appendices.....	144
Appendix A: X-ray Data of PeQDM-Ben	144
Appendix B: Spectra of Synthesized Reactants and Products.....	154

List of Schemes

Scheme 1.1.	Synthetic route to a side-chain NLO polyimide.....	25
Scheme 2.1.	Synthetic route to PQDM.....	40
Scheme 2.2.	Proposed mechanism for the formation of PQDM and the by-product of TCNQ dianion.....	41
Scheme 2.3.	Synthetic route to ACQ	43
Scheme 2.4.	Synthetic route to PeQDM	46
Scheme 2.5.	Synthetic route to PeQDM-C3OH-E-OH	47
Scheme 2.6.	Resonance structures of PeQDM	52
Scheme 2.7.	Synthetic route to the expected and actual chromophores	53
Scheme 2.8.	Proposed reaction mechanism for the formation of PeQDM.....	55
Scheme 2.9.	Protonation of PeQDM-C2OH and deprotonation of P-PeQDM-C2OH..	61
Scheme 2.10.	Solvolytic dissociation of P-PeQDM-C2OH by DMSO-d ₆	63
Scheme 3.1.	Synthetic route to ES-dendron	83
Scheme 3.2.	Synthetic route to ES-PeQDM-1	87
Scheme 3.3.	Synthetic route to ES-PeQDM-3.....	96
Scheme 4.1.	Synthetic route to PES-Acid	106
Scheme 4.2.	Synthetic route to PES-E.....	109
Scheme 4.3.	Synthetic route to C-NLO-P.....	114
Scheme 4.4.	Thermolysis of benzocyclobutenone (BCBO)	115
Scheme 5.1.	Proposed model for the thermodynamics of H- and J-aggregations during poling process	132

List of Tables

Table 2.1.	Synthesis of PeQDM-2OH under different reaction conditions	45
Table 2.2.	Selected bond lengths of crystallographic data of PeQDM-Ben	51
Table 2.3.	Wavelengths of charge-transfer bands ($\lambda_{\max}$) of PeQDM chromophores in different solvents.....	58
Table 2. 4.	Decomposition temperatures (T_d) determined by TGA.....	60
Table 2.5.	Maximal PL of PeQDMs in DMF solution (excited at 650 nm)	66
Table 2.6.	β values of PQDMs and PeQDMs measured by HRS and the estimated β_0 values	68
Table 3.1.	Decomposition temperatures (T_d) of PeQDM and dendronized PeQDM	90
Table 3.2.	Charge-transfer bands ($\lambda_{\max}$) of PeQDM and ES-PeQDM in DMF	91
Table 4.1.	Decomposition (T_d) and glass transition (T_g) temperatures of PES polymers	112
Table 4.2.	Composition and properties of NLO-P1 and NLO-P2	113
Table 4.3.	Physical properties of C-NLO-P1 and C-NLO-P2	115
Table 5.1.	Glass transition (T_g), poling temperatures (T_p) and EO coefficients (r_{33} , 1550 nm) of 5 wt% PeQDM-Ben doped polymers.....	130

List of Figures

Figure 1.1. A waveguide Mach-Zehnder modulator.....	4
Figure 1.2. A general representative of nonlinear optical chromophores: A-electron-accepting group such as a cyano or nitro group; D- electron-donating group such as an amine.	7
Figure 1.3. Dependence of first hyperpolarizability (β value) on the bond length alternation (BLA).....	8
Figure 1.4. Resonance forms of DANS, 1 and 2	9
Figure 1.5. Some representatives of neutral chromophores.....	10
Figure 1.6. Typical neural FTC and CLD chromophores.....	12
Figure 1.7. Chemical structures and properties of furan-containing [2.2]cyclophenes ...	13
Figure 1.8. Resonance structures of DEMI.....	13
Figure 1.9. NLO properties of DEMI and PQDM	14
Figure 1.10. A pair of covalent-bond linked antiparallel-aligned neutral ground-state chromophore and zwitterionic chromophore.....	15
Figure 1.11. Resonance forms of TICT chromophore.....	16
Figure 1.12. Qualitative state correlation diagrams as a function of twist angle θ and increasing solvent polarity. Panel a represents the gas-phase picture, whereas panels b and c represent the state orderings as the environmental polarity is increased.	17
Figure 1.13. Left: ORTEP drawing of TMC-1 chromophore (Hydrogen atoms are omitted for clarity); Right: A dimer in the unit cell.	18
Figure 1.14. Chemical structures and properties of TMC chromophores.....	18

Figure 1.15. Multiple dendron-modified chromophore	20
Figure 1.16. Multi-chromophore dendrimer	21
Figure 1.17. Multi-CF ₃ -FTC dendrimer.....	22
Figure 1.18. Denronized NLO polymers	26
Figure 1.19. A typical setup for the contact poling.....	27
Figure 1.20. A typical setup for the corona poling	28
Figure 1.21. The optical configuration of the Teng-Man setup	29
Figure 1.22. Potential modification sites for PQDM and new-generation chromophores	31
Figure 2.1. Molecular structures of TCNQ, ACQ and DMCQ.....	42
Figure 2.2. The formation of PeQDM-2OH (entry IV in Table 2.1) monitored by UV-Vis spectroscopy.....	44
Figure 2.3. ¹ H NMR spectrum (400 MHz, DMSO-d ₆) of PeQDM-Ben.....	48
Figure 2.4. ¹³ C NMR spectrum (100 MHz, DMSO-d ₆) of PeQDM-Ben	48
Figure 2.5. IR spectrum (KBr, cm ⁻¹) of PeQDM-Ben	49
Figure 2.6. MS spectrum (ESI, CH ₃ CN, M/Z) of PeQDM-Ben: 394 (M+H ⁺)	50
Figure 2.7. ORTEP drawing of PeQDM-Ben (Hydrogen atoms are omitted for clarity)	51
Figure 2.8. Left: Packing diagram of PeQDM-Ben in the unit cell (Hydrogen atoms are omitted for clarity); Right: Slip angle of the dimmer.	53
Figure 2.9. UV-Vis spectra of PeQDM-Hex in different solvents	57
Figure 2.10. Molecular structure of pyridinium N-phenolate betaine dye.	58
Figure 2.11. TGA traces of PeQDM chromophores.....	59
Figure 2.12. UV-Vis spectra of PeQDM-C2OH in DMF without and with excess HCl..	60
Figure 2.13. IR spectra (KBr, cm ⁻¹) of PeQDM-C2OH and P-PeQDM-C2OH	62

Figure 2.14. ^1H NMR spectra (400 MHz, DMSO- d_6) of P-PeQDM-C2OH and PeQDM-C2OH	62
Figure 2.15. ^{13}C NMR spectra (400 MHz, DMSO- d_6) of P-PeQDM-C2OH (top) and PeQDM-C2OH (bottom)	64
Figure 2.16. Molecular structures of zwitterionic chromophores I ($\lambda_{\text{max}} = 500 \text{ nm}$, $\lambda_{\text{max}}^{\text{PL}} = 565 \text{ nm}$, in 9:1 ethanol-methanol solvent) and II ($\lambda_{\text{max}} = 575 \text{ nm}$, $\lambda_{\text{max}}^{\text{PL}} = 640 \text{ nm}$, in 9:1 ethanol-methanol solvent)	64
Figure 2.17. UV-Vis and PL spectra of PeQDM-C2OH	65
Figure 2.18. Samples of PeQDM-C3OH in aqueous DMF with different pH values	66
Figure 2.19. Left: PL spectra of PeQDM-C3OH aqueous solutions with different pH values; Right: The graph of PL intensity versus pH value.	67
Figure 2.20. Left: UV-Vis spectra of PeQDM-C3OH aqueous solutions with different pH values; Right: The graph of absorption intensity of CT band versus pH value.	67
Figure 3.1. ^1H NMR spectrum (300 MHz, DMSO- d_6) of ES-dendron.....	84
Figure 3.2. IR spectrum (Neat, cm^{-1}) of ES-Dendron.....	85
Figure 3.3. MS spectrum (ESI, CH_3CN , M/Z) of ES-dendron: 736 ($\text{M}+\text{NH}_4^+$).....	85
Figure 3.4. TGA (left) and DSC (right) traces of ES-dendron	86
Figure 3.5. ^1H NMR spectrum (400 MHz, DMSO- d_6) of ES-PeQDM-1a	88
Figure 3.6. IR spectrum (Neat, cm^{-1}) of ES-PeQDM-1a	89
Figure 3.7. MS spectrum (ESI, CH_3CN , M/Z) of ES-PeQDM-1a: 1048 ($\text{M}+\text{H}^+$).....	89
Figure 3.8. DSC traces of ES-PeQDM-1	90
Figure 3.9. Molecular structure of ES-PeQDM-2.....	92

Figure 3.10. ^1H NMR spectrum (300MHz, DMSO-d_6) of ES-PeQDM-2	93
Figure 3.11. MS spectrum (ESI, $\text{THF/CH}_3\text{CN} = 1/1$ (V/V), M/Z) of ES-PeQDM-2: 2030 ($\text{M}+\text{H}^+$).....	93
Figure 3.12. DSC trace of ES-PeQDM-2.....	94
Figure 3.13. UV-Vis spectra of ES-PeQDM-2: (a) film on an ITO coated glass ($\lambda_{\text{max}} =$ 524 nm); (b) DMF solution ($\lambda_{\text{max}} = 691$ nm); (c) THF solution ($\lambda_{\text{max}} = 820$ nm); (d) chloroform solution ($\lambda_{\text{max}} = 660, 787, 870$ nm).....	95
Figure 3.14. ^1H NMR spectrum (300 MHz, DMSO-d_6) of ES-PeQDM-3	97
Figure 3.15. DSC trace of ES-PeQDM-3.....	97
Figure 3.16. UV-Vis spectra of ES-PeQDM-3 in solution: a-DMF ($\lambda_{\text{max}} = 676$ nm), b- acetone ($\lambda_{\text{max}} = 711$ nm), c-1, 2-dichloroethane ($\lambda_{\text{max}} = 780$ nm), d-THF (λ_{max} $= 800$ nm), e-chloroform ($\lambda_{\text{max}} = 656, 789, 849$ nm).	98
Figure 3.17. UV-Vis spectra of spin-coated films: (a) ES-PeQDM-2 and (b) ES-PeQDM- 3.....	99
Figure 4.1. Chemical structure of Ultrason E	105
Figure 4.2. ^1H NMR spectrum (300 MHz, DMSO-d_6) of PES-Acid.....	106
Figure 4.3. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of PES-Acid.....	107
Figure 4.4. TGA (left) and DSC (right) traces of PES-Acid	108
Figure 4.5. ^1H NMR spectrum (300 MHz, CDCl_3) of PES-E-1	110
Figure 4.6. ^{13}C NMR spectrum (75 MHz, CDCl_3) of PES-E-1	110
Figure 4.7. TGA (left) and DSC (right) traces of PES-E.....	111
Figure 4.8. Chemical structures of NLO-P1 and NLO-P2.....	113
Figure 4.9. ^1H NMR spectrum (300 MHz, DMSO-d_6) of C-NLO-P1	116

Figure 4.10. UV-Vis spectra of C-NLO-P1 in DMF (1), C-NLO-P1 (2) and C-NLO-P2 (3) films	117
Figure 4.11. DSC trace of C-NLO-P1	118
Figure 5.1. Explanation of the blue-shifted UV-Vis absorption of H-aggregates of dipolar dyes according to molecular exciton models	125
Figure 5.2. UV-Vis spectrum of PeQDM-Ben crystalline powder.....	127
Figure 5.3. Chemical structures of polymer matrices	128
Figure 5.4. UV-Vis spectra of 5 wt% PeQDM-Ben (3.8 wt% core content) in polymer matrices: a) PES-U, b) APC, c) PES-Met, d) PVPh, e) PES-Hex	128
Figure 5.5. Left: UV-Vis spectra of 5 wt% PeQDM-Ben doped APC: a) before heating, and heating at 167 °C for b) 2 min, c) 12 min, d) 42 min; Right: UV-Vis spectra of 5 wt% PeQDM- Ben doped PES-Hex: a) before heating, b) after heating at 120 °C for 30 min.	131
Figure 5.6. X-ray diffraction pattern of PES-Hex film: A) before heating; B) after heating at 120 °C for 30 min.	133
Figure 5.7. Temporal stability of the poled thin film of PES-U with 5 wt% (3.8 wt% core content) PeQDM-Ben at 80 °C in nitrogen	134
Figure 5.8. Chemical structures of ES-PeQDM-2 and ES-PeQDM-3	135
Figure 5.9. UV-Vis spectra of (1) PeQDM-Ben (3.8 wt% core content) and (2) ES-PeQDM-1b (8.1 wt% core content) doped PES-U films	136
Figure 5.10. X-ray diffraction pattern of ES-PeQDM-2 (left) and ES-PeQDM-3 (right) films	137

List of Symbols and Abbreviations

α	Linear molecular polarizability or first-order polarizability
β	Molecular first hyperpolarizability or second-order polarizability
γ	Molecular second hyperpolarizability or third-order polarizability
μ	Dipole moment
N	Number density
r_{33}	Electro-optic coefficient
T_g	Glass transition temperature
T_d	Decomposition temperature
ACQ	7,8-Di(alkoxycarbonyl)-7,8-dicyanoquinodimethane
APC	Amorphous polycarbonate
ATR	Attenuated total reflection
BLA	Bond length alternation
CT	Charge Transfer
DANS	4-(N,N-dimethylamino)-4'-nitrostilbene
DBU	1,8-Diazobicyclo[5.4.0]undec-7-ene
D(E-OH)CQ	7,8-Di(hydroxyethoxycarbonyl)-7,8-dicyanoquinodimethane
DMAC	N,N-dimethylacetamide
DMAP	4-(N,N-Dimethylamino)pyridine
DMCQ	7,8-Di(methoxycarbonyl)-7,8-dicyanoquinodimethane
DME	1,2-Dimethoxyethane
DMF	N,N-Dimethylformamide

DSC	Differential scanning calorimetry
EDC	1-[3-(2-Dimethylamino)propyl]-3-ethylcarbodiimide
EO	Electro-optic
E _T	Molar electronic transition energy
HRS	Hyper-Rayleigh scattering
ITO	Indium-tin oxide
LDA	Lithium diisopropylamide
LHS	Left-hand-side
M _w	Molecular weight
NIR	Near-infrared
NLO	Nonlinear optical
NMP	N-methylpyrrolidinone
NOE	Nuclear Overhauser enhancement
PES	Polyethersulfone
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
PQDM	Picolinium tricyanoquinodimethane
PVPh	Poly(4-vinylphenol)
RHS	Right-hand-side
TCNQ	7,7,8,8-Tetracyanoquinodimethane
TGA	Thermogravimetric analysis
TICT	Twisted intramolecular charge-transfer
XRD	X-ray diffraction

Chapter 1 Introduction to Organic Electro-Optic Materials

Over the past decades, much attention has been devoted to organic electro-optic (EO) materials due to their paramount advantages in structural versatility, ease of processing, lower dielectric constant and the demonstrated large EO activity over their inorganic counterparts.¹ Devices based on such materials are of considerable importance in hi-tech areas for applications in optical telecommunication and computing, signal processing, data storage, image reconstruction, and electric/optical logic technology.² Recently, great progress has been evidenced by the development of organic EO materials with exceptional high EO coefficients (r_{33}), in the range of 100-400 pm/V,³ which are well beyond that of the traditional inorganic LiNbO₃ crystal ($r_{33} = 31$ pm/V). High-speed EO devices with very broad bandwidth (up to 150 GHz) and low driving voltages (< 1 V) have also been demonstrated in several prototype EO modulators by employing organic EO materials.⁴

1. 1. Origin of electro-optic effect

The active components of the EO materials are dipolar chromophores, most of which are based on an aromatic π -electron system asymmetrically end-capped with electron-donating and electron-accepting groups. The π -electrons of such molecules are weakly bound to nearby nuclei and their locations will be slightly perturbed or polarized by an external electric field. The magnitude of such an induced “polarization” for an isolated molecule can be written:⁵

$$P_i(\omega) = \alpha_{ij}(\omega)E_j(\omega) + \beta_{ijk}(-\omega; \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2) + \gamma_{ijkl}(-\omega; \omega_1', \omega_2', \omega_3')E_j(\omega_1')E_k(\omega_2')E_l(\omega_3') + \dots \quad (1)$$

where the subscripts i, j and k refer to a molecule-based coordinated system, α is the linear molecular polarizability, β is the second-order polarizability and γ is the third-order polarizability. The molecular second-order and third-order response coefficients are also referred as the first and second hyperpolarizabilities, respectively. Energy conservation requires that $\omega = \omega_1 + \omega_2$ and $\omega = \omega_1' + \omega_2' + \omega_3'$. Symmetry requires that all terms of even order in the electric field vanish when the molecule possesses an inversion center. Four different second-order effects can be observed experimentally and they are second-harmonic generation [SHG; $\beta(-2\omega; \omega, \omega)$], sum-frequency generation [SFG; $\beta(-\omega_1 - \omega_2; \omega_1, \omega_2)$], optical rectification [OREC; $\beta(0; \omega, -\omega)$] and linear electro-optic effect [LEOE; $\beta(-\omega; \omega, 0)$]. The linear EO effect is also referred as dc-Pockels effect.

NLO materials owe their macroscopic nonlinear optical responses to the noncentrosymmetric assembly of the individual dipolar chromophores. The macroscopic polarization of the bulk materials is defined by a direct analogy to equation 1:

$$P_I(\omega) = \chi_{IJ}^{(1)}(\omega)E_J(\omega) + \chi_{IJK}^{(2)}(-\omega; \omega_1, \omega_2)E_J(\omega_1)E_K(\omega_2) + \chi_{IJKL}^{(3)}(-\omega; \omega_1', \omega_2', \omega_3')E_J(\omega_1')E_K(\omega_2')E_L(\omega_3') + \dots \quad (2)$$

where I, J and K represent the coordinate system of the bulk materials, $\chi^{(2)}$ and $\chi^{(3)}$ represent the second-order and third-order susceptibilities of the bulk materials, respectively. As in the molecular case, the even-order susceptibility $\chi^{(2)}$ can only come

from noncentrosymmetric media. The bulk second-order susceptibility $\chi^{(2)}$ is related to the corresponding first hyperpolarizability β by local field factor (f) and the molecular number density (N):

$$\chi_{IJK}^{(2)}(-\omega; \omega_1, \omega_2) = N f_I(\omega) f_J(\omega_1) f_K(\omega_2) \langle \beta_{ijk}(-\omega; \omega_1, \omega_2) \rangle_{IJK} \quad (3)$$

where the term $\langle \beta \rangle$ is a weighted sum of various β_{ijk} values, an average over all orientations of the chromophores in the medium.

For the EO effect or Pockels effect of the bulk materials, another tensor $r_{IJ,K}$ is defined related to the corresponding $\chi^{(2)}$. The Pockels effect is a linear change in the index of refraction of the materials in the presence of an external electric field:

$$\Delta\left(\frac{1}{\varepsilon}\right)_{IJ} = \frac{1}{\varepsilon_{IJ}} - \frac{1}{\varepsilon_{IJ}(0)} \approx -\frac{\Delta\varepsilon_{IJ}}{\varepsilon_{IJ}^2} = r_{IJ,K} E_K \quad (4)$$

where $\varepsilon_{IJ}(0)$ is the IJ -th component of the dielectric constant in the absence of the external electric field and r is called the EO coefficient. Equation 4 can be rewritten in terms of the index of refraction:

$$\Delta n = -\frac{n^3}{2} r_{IJ,K} E_K \quad (5)$$

where Δn is the change of the materials' optical index of refraction. The EO coefficient $r_{IJ,K}$ is frequently contracted on the first two subscripts to $r_{\mu,K}$ using the convention (11)→1, (22)→2, (33)→3, (23,32)→4, (13,31)→5, (12,21)→6. The relationship between electro-optic coefficient and $\chi^{(2)}$ (in mks units) is:

$$\chi_{IJK}^{(2)}(-\omega; \omega, 0) = -\frac{1}{2} \varepsilon_{II}(\omega) \varepsilon_{JJ}(\omega) r_{IJ,K}(-\omega; \omega, 0) \quad (6)$$

when all quantities in equation 6 are in esu units, the factor of $1/2$ is replaced by $1/(8\pi)$. Reconciliation of esu and mks in nonlinear optics have been discussed by Skinner and Garth.⁶

Another important parameter for the characterization of EO materials for modulator applications is the half-wave voltage, V_π , which is the voltage required to obtain a π phase shift in the transmitted beam in an appropriated modulator configuration such as a Mach-Zehnder modulator shown in Figure 1.1:

Figure 1.1. A waveguide Mach-Zehnder modulator

Application of an electric field on one arm of the modulator results in a phase retardation ($\Delta\phi$) relative to the signal traversing the second arm:

$$\Delta\phi = 2\pi\Delta nL / \lambda = \pi n^3 r EL / \lambda \quad (7)$$

Thus the applied voltage (V_π) for a π phase shift of the light is:

$$V_\pi = \frac{\lambda}{n^3 r} \frac{d}{L} \quad (8)$$

where d and L are the electrode spacing and the interaction length of the device, respectively. Therefore, the input light split into two arms can be fully turned off via the

destructive interference when the light from both arms is recombined at the output of the device. The higher the EO activity of materials, the lower the V_π of the EO device is. It is estimated that the r_{33} value on the order of 100 pm/V is needed to achieve a sub-1V drive voltage for lossless or transparent communication links.⁷ In comparison, current EO modulators based on LiNbO₃ require a driving voltage typically in a range of 5-10V.^{1,7}

1. 2. From molecular hyperpolarizability to macroscopic optical nonlinearity

For practical EO applications, dipolar chromophores are typically incorporated into glassy polymers for preparation and processing purposes. However, in the polymer hosts, dipolar chromophores are usually well dispersed and their dipoles are randomly ordered, resulting in isotropic materials. To achieve a macroscopic noncentrosymmetric order, an external electric field has to be applied to align the dipole moments of the chromophores along the poling field. In general, calculation of the average $\langle \beta_{ijk} \rangle_{LJK}$ values for a given EO materials is very complicated. Considerable simplification is made by assuming that only one component of the molecular hyperpolarizability β_{zzz} in the direction of the poling electric field is sufficient to describe the nonlinearity of the molecules. Using the simple two-level model suggested by Oudar and Chemla for the molecular hyperpolarizability with one ground state (g) and one excited state (e),⁸ the β value is proportional to the product of the transition dipole moment (μ_{ge}), the difference between the excited and the ground state dipole moments ($\mu_{ee} - \mu_{gg}$) and the transition energy (E_{ge}):

$$\beta \propto \frac{\mu_{ge}^2 (\mu_{ee} - \mu_{gg})}{E_{ge}^2} \quad (9)$$

The relationship between the macroscopic EO coefficient (r_{33}) and the corresponding microscopic nonlinearity is:¹

$$r_{33} = 2Nf\beta \langle \cos^3 \theta \rangle / n^4 \quad (10)$$

where $\langle \cos^3 \theta \rangle$ is the noncentrosymmetric order parameter. Thus, to achieve large EO activity, four parameters have to be optimized: N , f , β and $\langle \cos^3 \theta \rangle$. In the absence of intermolecular electrostatic interactions:

$$\langle \cos^3 \theta \rangle = \mu F / 5\kappa T \quad (11)$$

where μ is the dipole moment of the chromophore, F is the electric poling field felt by the chromophore, κ is the Boltzman constant and T is the Kelvin temperature. Thus,

$$r_{33} = (2NfF) \cdot (\mu\beta) / 5\kappa T n^4 \quad (12)$$

For a given chromophore at a low concentration in a polymer matrix, EO activity will increase in a linear manner with chromophore number density (N), chromophore dipole moment (μ) and poling field strength (F). While at a higher N value, electrostatic interactions between chromophore molecules come into play, usually leading to a tradeoff between the number density and the order parameter.

Therefore, in the development of nonlinear optical (NLO) chromophores for EO applications, only chromophores with large $\mu\beta$ values should be considered, since the following relationship is clear from equation 12:

$$r_{33} \propto \mu\beta \quad (13)$$

For the extensively studied push-pull NLO chromophores (Figure 1.2), an electron donor connects with an electron acceptor through a conjugated bridge. Depending on the nature of the donor, acceptor and the conjugated bridge, a NLO chromophore could be neutral or zwitterionic. A neutral chromophore has a neutral ground state and a positive β value. While a zwitterionic chromophore has a charge-separated ground state and a negative β value.

Figure 1.2. A general representative of nonlinear optical chromophores: A-electron-accepting group such as a cyano or nitro group; D- electron-donating group such as an amine.

In search of high performance NLO chromophores, a simple model has been suggested and proved to be useful to guide the design of chromophores with large first hyperpolarizabilities (β values),⁹ and thus optimization of $\mu\beta$ values. According to this simplified model, β is related to the degree of ground-state polarization and can be maximized with an optimal degree of mixing of the two-limiting resonance forms of the molecule. The degree of ground-state polarization primarily depends on the chemical structure of the chromophore (the π -conjugated bridge and the strength of the donor and acceptor), but also depends on the polarity of the medium. A molecular parameter of bond length alternation (BLA) is defined to describe the relative contribution of the two-limiting forms and related to β value (Figure 1.3).^{9d}

Figure 1.3. Dependence of first hyperpolarizability (β value) on the bond length alternation (BLA)

BLA is defined as the difference between the average carbon-carbon single and double bonds lengths in a polymethine backbone. A neutral resonance form is characterized by a positive BLA and a charged-separated form is characterized by a negative one. For a chromophore with weak donor and acceptor, the neutral resonance form is the dominant contributor to the ground state, resulting in a large positive BLA and a small positive β value. As the strength of the donor and acceptor increases, the contribution of the charge-separated resonance structure increases, resulting in a decreased BLA. On the other hand, β value first increases, arrives a maximum and then decreases with a positive BLA. When both resonance forms contribute equally to the ground-state, the molecule possesses zero BLA, which is also referred as the cyanine limit. Increasing the strength of the donor and acceptor further, the charge-separated ground-state structure dominates, leading to a negative BLA and a negative β value with a reversed pattern. Thus, both neutral and zwitterionic chromophores could yield large β values.

1. 3. Neutral NLO chromophores

For most of the neutral chromophores such as donor-acceptor substituted stilbenes, the degree of ground-state polarization is not sufficient to maximize β value due to the loss of the aromaticity in the charge-separated form upon polarization (Figure 1.4). To solve this problem, a strategy is proposed for the design of dipolar chromophores, in which the loss of aromatic stabilization in one part would be somewhat offset by a gain in aromaticity in the opposite part. On the other hand, this strategy can also result in an increased ground-state dipole moment (μ). This strategy has been validated by introducing acceptor such as 3-phenyl-5-isoxazolone or N, N'-diethyl-thiobarbituric acid, which can gain the aromaticity in the charge-separated form and has the reduced BLA value for an optimal β value (Figure 1.4). The $\mu\beta$ values of **1** ($1,202 \times 10^{-48}$ esu at 1.9 μm) and **2** ($1,457 \times 10^{-48}$ esu at 1.9 μm) are much higher than that of 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS: $\sim 500 \times 10^{-48}$ esu at 1.9 μm), which has the similar conjugation length as **1** and **2**.

Figure 1.4. Resonance forms of DANS, **1** and **2**

Another approach to the increased degree of ground-state polarization is to replace aromatic benzene ring with a heteroaromatic ring such as thiazole or thiophene that has lower delocalization energy than that of benzene and can offer more effective conjugation.¹⁰ Furthermore, the heteroaromatic rings can improve the thermostability of the chromophores. Some examples are given in Figure 1.5. Replacing the benzene ring with a thiophene, the $\mu\beta$ value increases from 1100×10^{-48} esu for chromophore **3** to 1300×10^{-48} esu for chromophore **4** ($n = 1$). Meanwhile, for a given conjugated bridge, using a stronger donor or acceptor could dramatically improve the $\mu\beta$ value. Replacing the dicyanovinyl acceptor in chromophore **4** ($n = 1$) with tricyanovinyl group in chromophore **5** ($n = 1$), the $\mu\beta$ value increases more than five-fold.¹⁰ Moreover, for a given donor-acceptor chromophore, $\mu\beta$ value can be further maximized by increasing the length of the conjugation. For chromophore **5**, the $\mu\beta$ value increases from 6700×10^{-48} to 9100×10^{-48} esu by adding one more ethylene unit.

Chromophores		$\mu\beta$ (10^{-48} esu at 1.9 μm)
3		1100
4		1300 ($n=1$) 2300 ($n=2$) 3800 ($n=3$)
5		6700 ($n=1$) 9100 ($n=2$)

Figure 1.5. Some representatives of neutral chromophores

These strategies have been successfully used to direct the synthesis of some neutral chromophores with large $\mu\beta$ values, which generally have a strong donor-acceptor pair and a long conjugated bridge. However, chromophores with longer unprotected or unsubstituted polyene bridges are thermally and chemically unstable for practical applications in EO devices.¹¹ Furthermore, chromophore aggregation due to

intermolecular electrostatic interactions and π - π stacking prevent the simple scaling of molecular optical nonlinearity into macroscopic EO activity. Therefore, chromophores with large microscopic nonlinearity must also possess high thermostability and suitable molecular shape to prevent aggregation for efficient poling.

The thermostability of chromophores with polyene bridges can be significantly improved by insertion of a heterocycle ring or introducing a ring-locked double bond in the middle of the conjugated bridge. The two examples are FTC¹² and CLD¹³ (Figure 1.6), which among many chromophores has both large $\mu\beta$ values and good thermostability. In FTC, the insertion of a thiophene ring into the conjugated bridge not only results in a large $\mu\beta$ value ($17,600 \times 10^{-48}$ esu at 1.9 μm) but also high thermostability ($T_d = 315$ °C). In CLD, good thermostability ($T_d = 275$ °C) is achieved by ring-locking the long polyene bridge. The introduction of bulky alkyl groups in FTC and CLD also helps improve molecular solubility and render suitable steric hindrance to diminish intermolecular interactions. Large EO coefficients have been realized in FTC (55 pm/V) and CLD (92 pm/V) doped polymer materials. It was also reported that for many chromophores with amine donors, replacement of the alkyl groups on the nitrogen with aryl groups could improve the thermostability dramatically.¹⁴ In the light of a high EO activity of CLD type chromophores, further effort has been made to modify its structure by adjusting the strength of the donor and acceptor and molecular shape. Replacing the TCF acceptor in CLD with a very strong CF_3 -TCF acceptor¹⁵ and changing the alkyl groups on the nitrogen with aryl groups afforded chromophore CF_3 -CLD-1 (Figure 1.6), that lead to an EO material with very large EO activity ($r_{33} = 169$ pm/V) and high thermal stability ($T_d = 237$ °C).^{3b} Having a large pendent group in the middle of the conjugated bridge in CF_3 -

CLD-2 for efficient poling and high chromophore loading, exceptionally large EO activity ($r_{33} = 262$ pm/V) has also been realized.^{3a}

Figure 1.6. Typical neural FTC and CLD chromophores

More recently, inspired by the ultralarge nonlinear optical response of the twisted chromophores (see the following), furan-containing [2.2]cyclophenes with very low polarity have also been synthesized and shown comparable $\mu\beta$ values to that of DANS (Figure 1.7).¹⁶ These cyclophenes have neither particularly strong electron-donating moieties nor electron-withdrawing groups, but they have twisted π -electron systems,

which induce significant enhancement in first hyperpolarizability.

Compound	μ (D)	$\mu\beta$ (10^{-48} esu at 1.9 μm)
	$n = 2$	1.12	232
	$n = 3$	1.23	370
	$n = 4$	1.26	530
	DANS	6.60	450

Figure 1.7. Chemical structures and properties of furan-containing [2.2]cyclophenes

1. 4. Zwitterionic NLO chromophores

According to the BLA theory, there is another kind of chromophores with the charge-separated (zwitterionic) ground states and negative β values. Such chromophores gain aromatic stabilization upon charge separation (Figure 1.8) and have larger dipole moments than the neutral ground-state chromophores.

Figure 1.8. Resonance structures of DEMI

Typical representatives of zwitterionic chromophores are TCNQ adducts such as DEMI¹⁷ and PQDM (Figure 1.9),¹⁸ which have negative β values and much larger dipole moments than that of FTC and CLD chromophores (Figure 1.6). The absolute $\mu\beta$ value of PQDM is even more than four times greater than that of FTC and CLD. However, the very strong intermolecular electrostatic interactions of zwitterionic chromophores make them easily crystallize out of less polar solvents and polymeric matrices or form

aggregates, which will result in low chromophore number density and inefficient poling. The maximum doping level of PQDM in a polar polymer such as polyethersulfone (PES) is only about 2 wt%, much less than that of the FTC and CLD chromophores (>25 wt%).^{3a,b} Other polymers such as polycarbonate and polyimide have been tested, but the doping level is still less than 5 wt%. Until now, the highest EO coefficient ($r_{33} = 65$ pm/V) for PQDM based EO polymer was obtained by doping a hyperbranched oligomer into PES.^{18g}

Figure 1.9. NLO properties of DEMI and PQDM

Recently, a new approach has been explored to simultaneously achieve large β values while providing an adjustable dipole moment by linking a strong neutral ground-state NLO chromophore with a positive β to a zwitterionic chromophore with a negative β (Figure 1.10).¹⁹ It is expected that the dipole-dipole interactions between the two components will provide a force for antiparallel alignment and the overall β value of such a molecular entity will be the sum of the absolute values of the two types of chromophores while the dipole moment will be the difference. Calculations and experimental results confirm that the molecules with an antiparallel-aligned neutral ground-state and zwitterionic chromophores can simultaneously achieve an increased

hyperpolarizability and a decreased dipole moment. The calculated dipole moment is 4.3 D, which is close to the difference of the individual neutral ($\mu = 12.6$ D) and zwitterionic ($\mu = 9.1$ D) chromophores (Figure 1.10). The calculated first hyperpolarizability ($\beta/\beta_{\text{chloroform}} = 2273$) is also about the sum of the absolute values of the neutral ($\beta/\beta_{\text{chloroform}} = 2073$) and zwitterionic ($\beta/\beta_{\text{chloroform}} = -327$) chromophores. Chromophores of this sort can be considered as a way to optimally tune the dipole moment for acentric order under poling conditions because intermolecular dipolar interactions can be reduced for a high poling efficiency.

Figure 1.10. A pair of covalent-bond linked antiparallel-aligned neutral ground-state chromophore and zwitterionic chromophore

More recently, twisted intramolecular charge-transfer (TICT) molecules have been demonstrated as a new generation of NLO chromophores having tunable nonlinear optical properties according to a twist angle and a polarizing environment such as an external applied field or polar solvent.^{3c,20} In contrast to the almost planar π -system of the common NLO chromophores, the π -conjugation is broken in the twisted biaryl molecules. Theoretical study and experimental results suggested that the ground-state electronic configuration of TICT chromophore is diradicaloid (**D**) and the first excited

state is zwitterionic (**Z**) in the gas phase (Figure 1.11).

Figure 1.11. Resonance forms of TICT chromophore

For a TICT chromophore with a large twist angle ($\theta \sim 90^\circ$), the calculated first hyperpolarizability is extremely large and the $\mu\beta$ ($\sim 70,000 \times 10^{-48}$) value can be 2 orders of magnitude larger than that of the DANS. Meanwhile, the energy difference between the **D** and **Z** state is small and the state ordering of the chromophore is sensitive to environmental polarity (Figure 1.12). At an applied field strengths below 0.002 a.u. (or $\epsilon_0 \sim 3$ in the solvent dielectric model), the ground state is **D** and the first excited state is **Z**. Increasing the applied field to 0.002 a.u. leads to the degeneracy of the ground-state and excited-state energies. Beyond an applied field of 0.002 a.u., the energy ordering of **D** and **Z** is reversed. Since most experimental characterization studies of TICT chromophores are performed in solvents with a significantly higher dielectric constant and even a solid-state polymer constructed from TICT building blocks would have a dielectric constant of at least 4, TICT chromophores always exhibited properties (such as negative β value) associated with a zwitterionic (**Z**) ground state.

Figure 1.12. Qualitative state correlation diagrams as a function of twist angle θ and increasing solvent polarity. Panel a represents the gas-phase picture, whereas panels b and c represent the state orderings as the environmental polarity is increased.

In agreement with the theoretical predication, the recently reported TMC chromophores have large twist angles and exhibited exceptional $\mu\beta$ values.^{3c} The twist angle (θ) in TMC-1 is 89.6 °C determined by X-ray diffraction (Figure 1.13). In the solid state, the two monomers of TMC-1 are antiparallel to each other like the planar chromophores due to the strong electrostatic interactions involving their large dipole moments. However, the intermolecular distance of 8.232 Å is considerably larger than that of the planar π -system such as DEMI (3.35 Å),^{17b} which is the result of the difficulty in closely face-to-face packing the aromatic rings in the twisted molecules. Unlike the conventional planar chromophores, TICT chromophores with large optical nonlinearity can be as simple as two connected arene rings such as TMC-1 (Figure 1.14), hence less susceptible to thermal/oxidative/photochemical degradation. Therefore, the TMC chromophores exhibited good thermostability ($T_d > 300^\circ\text{C}$). TMC-1 has a $\mu\beta$ ($-24,000 \times 10^{-48}$) value in the same order as the planar ones such as CLD, DEMI and PQDM. By extending the

conjugated length, TMC-2 exhibited an ultralarge $\mu\beta$ ($-488,000 \times 10^{-48}$ esu) which is the largest value ever achieved and is one order of magnitude larger than that of the best planar chromophores. Large EO activity ($r_{33} = 330$ pm/V) was also achieved by doping only 5 wt% of TMC-2 in poly (4-vinylphenol) (PVPh).

Figure 1.13. Left: ORTEP drawing of TMC-1 chromophore (Hydrogen atoms are omitted for clarity); Right: A dimer in the unit cell.

Figure 1.14. Chemical structures and properties of TMC chromophores

Clearly, the ultralarge nonlinear optical response of the twisted chromophores with small numbers of π electrons couldn't be explained by the simple two-level model. The complete electron transfer upon twisting may be responsible for the large NLO response.

1. 5. Dendritic NLO chromophores

For EO applications, NLO chromophores can be doped in or covalently attached onto polymers. However, chromophores with large first hyperpolarizabilities usually have large dipole moments (>12 D) and the strong electrostatic interactions between the dipoles will compete with electric-field forces during poling process, leading to low chromophore loading and poling efficiency. Many EO chromophores with large $\mu\beta$ values were reported to have low EO activities, except for a few examples with the r_{33} values over 100 pm/V. Zwitterionic chromophores may have dipole moments as large as 50 D and are often insoluble in low polar solvents and polymers. Their strong electrostatic interactions limit the choices of polymer hosts for doping and the loading of chromophores (less than 5 wt%). Experimental and theoretical studies²¹ have suggested that the poling efficiency can be enhanced by modification of chromophores with bulky substitutes as spacers to prevent stacking. Dendritic chromophores are considered to be spherical in shape, which can be poled more effectively.

For example, a multiple dendron-modified chromophore was reported to be three times better ($r_{33} = 30$ pm/V) than the pristine analog ($r_{33} = 10$ pm/V) (Figure 1.15).²² In the study, the pristine and the dendritic chromophores had the same doping level (12 wt%) of the active component in polymer. The introduction of the highly fluorinated dendrons was also aimed to achieve high thermostability and low optical loss. It is the encapsulation effect of three highly fluorinated dendrons that allowed chromophores to be spatially separated, thus decreasing chromophore electrostatic interactions and accounting for a higher poling efficiency. Furthermore, the site-isolation effect resulted in higher thermostability ($T_d = 265$ °C) compared to the small molecule ($T_d = 245$ °C).

Figure 1.15. Multiple dendron-modified chromophore

Another advantage of dendritic approach is that dendrimers are large enough to form films for EO applications without further incorporation into polymer matrices. A multi-chromophore dendrimer (Figure 1.16) with a molecular weight (M_w) of 4664 Dalton synthesized by connecting three smaller dendritic chromophores to a central core can be directly spin-coated and has demonstrated large optical nonlinearity ($r_{33} = 60\text{ pm/V}$) and long-term alignment stability (retaining $>90\%$ of its original r_{33} value at $85\text{ }^{\circ}\text{C}$ for more than 1000 h).²³ The excellent temporal stability is achieved by locking in the poling induced polar order through sequential cross-linking the peripheral trifluorovinyl ethers on the dendrons.

Figure 1.16. Multi-chromophore dendrimer

Recently, $\text{CF}_3\text{-FTC}$ chromophore has also been modified as a multi-chromophore dendrimer²⁴ (Figure 1.17) to minimize unwanted attenuation of EO activity at a high chromophore loading. Except for improved thermostability, the optimized r_{33} value of the $\text{CF}_3\text{-FTC}$ dendrimer arrives 140 pm/V,^{24c} which is more than twice of the $\text{CF}_3\text{-FTC}$ doped polymer ($r_{33} = 52$ pm/V).^{24a} The dendrimer exhibited a high poling efficiency ($r_{33}/E_p = 1.42$ (nm/V)²), while that of the parent chromophore was only 0.45 (nm/V)². Furthermore, the experimental and theoretical study first revealed a linear dependence of EO activity (r_{33}) on number density in dendrimer doped polymers and even in pure materials.

Figure 1.17. Multi-CF₃-FTC dendrimer

1. 6. NLO polymers

NLO chromophores are generally doped in or covalently bonded onto polymers, and then polymer films are subjected to an externally applied electric field at or near the glass transition temperature (T_g) of the films. At the T_g , the polymer becomes rubbery and the chromophores can be orientated in the direction of the applied electric field. Upon cooling while applying the electric field, then the induced noncentrosymmetric order of the dipoles can be frozen in place, yielding a material with second-order nonlinearity.

Guest-host NLO polymers

The guest-host system is the most convenient for studying EO activities of materials. In this system, NLO chromophores are simply mixed with commercially available or synthetic polymers. The commonly used polymers include poly(methyl methacrylate) (PMMA),^{13,25} polyimide,²⁶ polyquinoline,²⁷ amorphous polycarbonate (APC),^{13b,22}

polyethersulfone (PES)^{18g,h} and poly(4-vinylphenol) (PVPh).^{3c} Although the guest-host system is easy to formulate, the doping level is usually low and phase separation often occurs. For low T_g polymers, the induced optical nonlinearity decays quickly and temporal stability of EO activities is rather poor at elevated temperatures. For practical applications, if the T_g of the polymer is at 200 °C or higher, the decay of the orientation would be negligible over the device lifetime. Thus, high T_g polymers such as polyimide ($T_g = 320$ °C), polyquionoline ($T_g = 265$ °C), PES ($T_g = 225$ °C) and APC ($T_g = 205$ °C) are ideal candidates as hosts. To date, the largest EO activity (r_{33}) realized in guest-host polymer is 330 pm/V at 1310 nm in PVPh.^{3c}

Main-chain NLO polymers

In order to increase the number density, prevent phase separation and improve temporal stability, NLO chromophores can be covalently incorporated into a polymer backbone. Thus, the decay of the poled order can be significantly inhibited since large segmental motions of the polymer backbone are required. According to the chromophore dipole arrangements along the polymer backbone, main-chain NLO polymers can be classified as head-to-tail, head-to-head and random polymers. The early studied main-chain polymers are “head-to-tail” polymers,²⁸ in which the arrangement of the molecular dipole moments might result in a coherent enhancement of the NLO properties. However, no such an enhancement was observed in polymer films due to possible chain entanglements and the sum of the dipole moments might also lead to insoluble polymers. As for the “head-to-head” and “random” polymers, the dipole moments of the NLO chromophores seem to cancel out if being viewed in an extended configuration. Nevertheless, these polymers can still exhibit some NLO properties,²⁹ although poling is much difficult for

main-chain NLO polymers due to the large segmental motions of the polymer backbones. Thus, they receive relatively little attention compared to side-chain NLO polymers.

Side-chain NLO polymers

In side-chain NLO polymers, chromophores are attached as the pendent groups in a higher number density. They can be synthesized either by copolymerization of chromophore-containing monomers or by grafting polymers containing the functional groups. The former method may require a tedious synthesis and purification of chromophore-containing monomers that may have to withstand the harsh conditions for polymerization, as seen for some side-chain NLO polyimides.³⁰ With the latter method, a wide variety of NLO chromophores can be introduced into the polymer system under mild conditions.

In order to stabilize the induced polar order, high T_g polymers such as polyquinolines,^{27b,31} polyimides^{30,32} and polyethersulfones³³ are often employed. Among them, polyimides are more favored for practical EO applications. In addition to their high T_g , good mechanical strength and low optical loss, polyimides have good compatibility with highly polar NLO chromophores such as PQDM.^{18f} Side-chain NLO polyimides can be readily synthesized by condensation of hydroxyl containing polyimides with hydroxyl NLO chromophores through the Mitsunobu reaction (Scheme 1.1).³⁰ The obtained polymer not only has a high T_g , but also has a high chromophore loading level (45 wt%). The poled EO activity can retained >90% of its original value ($r_{33} = 34$ pm /V) at 100 °C for more than 400 h.

Scheme 1.1. Synthetic route to a side-chain NLO polyimide

In order to further improve thermal stability and mechanical properties of NLO polymers for device fabrication and temporal stability, NLO polymers that can undergo a subsequent crosslinking reaction during or after the poling process have been explored.^{18f,23,34} However, a significant reduction of EO activity is often observed in hardened polymers. This is because that lattice-hardening and poling process are often preceded together and the steadily crosslinked network increases the difficulty in aligning the dipolar chromophores. Recently, an improved poling efficiency has been realized by employing a new crosslinkable system based on a thermally reversible Diels-Alder reaction, in which the crosslinking reaction was separated well from and happened after the poling process.³⁵ The poling efficiency of side-chain NLO polymers is usually lower than that of the guest-host polymers due to the restriction of chain entanglements and intermolecular electrostatic interactions among NLO chromophores.

Dendritic shielding effect was also explored in side-chain polymers for improvement of the poling efficiency.³⁶ By grafting the dendronized CLD-type chromophores onto a polystyrene backbone, large EO activities ($r_{33} = 97\text{--}111\text{ pm/V}$) were achieved (Figure 1.18). However, the poling-induced polar order decayed quickly upon heating due to the low T_g (90 °C) temperature of the polystyrene backbone. When the dendronized CLD-type chromophore was attached onto a high-temperature polyimide, the poled film has exhibited the combined advantages of both high poling efficiency ($r_{33} = 71\text{ pm/V}$) and excellent temporal stability.³⁷

Figure 1.18. Dendronized NLO polymers

1. 7. Poling and EO measurement

Contact poling

Nonlinear optical materials require a noncentrosymmetric structure, which is generally achieved by aligning chromophores in polymer matrices into a noncentrosymmetric order through the application of an external electric field at an elevated temperature. To date, two commonly used electric field poling methods are the contact poling and the corona

poling. In contact poling (Figure 1.19),²⁵ a polymer film is sandwiched between two parallel electrodes, a strong electric field is applied across the film when the material is heated up to its glass transition temperature (T_g), and then the polymer film is cooled to room temperature to lock in the noncentrosymmetric order while the field is still applied. A high quality of film is often required because even a single pinhole defect can result in a catastrophic short circuit due to the large cover areas and high lateral conductivity of the poling electrodes. Moreover, electric breakdown often occurs at elevated temperatures when a high voltage is applied on. The poling voltage is usually controlled in a range of 50-100 V/ μm across the film.

Figure 1.19. A typical setup for the contact poling

Corona poling

For corona poling, the polymer film can be poled without deposition of the electrode or with only one electrode.^{5a,38} In a typical corona poling setup (Figure 1.20), a sharp needle, wire, or grid is charged to several kilovolts to ionize the surrounding atmosphere and the produced ions will be deposited on the surface of the polymer film, producing an electric field in the bulk of the film. Depending on the polarity of the corona needle, either positive or negative ions can be produced, but the positive corona is more stable than the negative one. A high field exceeding 4 MV/cm (400 V/ μm) can be obtained in this technique, which is very difficult to achieve using contact electrode poling, and the

larger poling fields possible with corona poling lead directly to larger nonlinearities. Polymer films with some defects could also be poled because the low surface conductivity localizes the damages. For these reasons, corona poling has become very popular for second-harmonic generation applications. However, induced surface damage is a major concern for corona poling since a variety of chemically reactive and physically energetic species are present during the corona discharge.³⁹

Figure 1.20. A typical setup for the corona poling

EO measurement

The methods for measuring electro-optic coefficients of NLO materials include Mach-Zehnder interferometer,⁴⁰ attenuated total reflection (ATR),⁴¹ simple reflection⁴² and transmission⁴³ techniques and so on. One of the most popular measurement techniques is the simple reflection technique introduced by Teng and Man. The Teng-Man setup simply takes advantage of a relative phase-shift difference between the *s*- and *p*-polarized waves of a single laser beam reflected from the sample when a modulating voltage is applied across two parallel-plate electrodes (Figure 1.21). The EO coefficient of a poled polymer film is calculated by:

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2 \theta)^{\frac{3}{2}}}{(n^2 - 2\sin^2 \theta) \sin^2 \theta} \quad (14)$$

where θ is the incident angle, λ is the optical wavelength, I_m is the amplitude of the modulation, I_c is the half of the maximum output laser intensity, n is the index of refraction of the polymer materials and V_m is the modulating voltage. In our experimental setup, θ is set at 20° , λ equals 1550 nm and V_m equals 48.5 V. The measured variables are I_m and I_c .

Figure 1.21. The optical configuration of the Teng-Man setup

1. 8. Rationale and objectives

To date, neutral and zwitterionic chromophores with large $\mu\beta$ values have been developed according to the established theories and computational predictions. Neutral chromophores have been extensively studied from synthesis, functionalization and optimization of molecular shape to highly active NLO dendrimers and polymers (e.g., $r_{33} > 100$ pm/V). However, optimization of the $\mu\beta$ value of a neutral chromophore such as CLD (section 1.3: $\mu\beta = 14,065 \times 10^{-48}$ esu) usually require the extension of the length of the conjugation and changes of the donors and acceptors, which definitely involves

tedious synthesis and purification. Moreover, the long conjugated bridge would be fragile to the attack of heat, light and O₂. In contrast, a zwitterionic chromophore such as PQDM with a much shorter conjugation could have a larger $\mu\beta$ value (section 1.4: $-77,200 \times 10^{-48}$ esu). Furthermore, the $\mu\beta$ value of a recently reported zwitterionic TMC-2, $-488,000 \times 10^{-48}$ esu, is even one order of magnitude larger than that of CLD. However, zwitterionic chromophores are much less studied than the neutral NLO chromophores, possibly due to their poor solubility in polymers.

Our group is particularly interested in zwitterionic NLO chromophores. Over the past several years, the one-step synthesis of PQDM chromophores has been optimized with the yield up to 97%.^{18e} The EO activities of PQDM chromophores were steadily improved from 21 pm/V of a guest-host polymer,^{18h} 45 pm/V of a side-chain polyimide^{18f} to 65 pm/V of a hyperbranched PQDM doped polymer.^{18g} However, these values are still much less than a theoretical prediction (210 pm/V).⁴⁴ Indeed, a tradeoff between the number density and the macroscopic optical nonlinearity were observed due to aggregation,^{18f,g} preventing simply scaling molecular nonlinearity.

Since a spherical molecular shape has been demonstrated to be effective for a high poling efficiency^{24c} as a result of reducing strong electrostatic interactions, the full potential of PQDM chromophores would be unlocked by using the same strategy. However, the bulky or functional groups could be readily introduced only on one side of PQDM molecule (Figure 1.22) and chromophore aggregation is still possible. The unprotected negative charge residing on the acceptor still has a great opportunity to interact with the positive charge of another molecule to form aggregates. Therefore, it is necessary to explore a new generation of PQDM chromophores, in which bulky or

functional groups can be readily introduced also at the acceptor part. Replacing one cyano group of the PQDM acceptor with an ester group would have little effect on the degree of the ground-state polarity, leading to a new generation of chromophores having the dipole moments (μ) and first hyperpolarizabilities (β) similar to PQDM chromophores. Once the positive and negative charges are well “shielded”, the new-generation chromophores should be more soluble in organic solvents and polymers and are less able to form aggregates.

Figure 1.22. Potential modification sites for PQDM and new-generation chromophores

Accordingly, the objectives of this thesis are:

1. To explore the synthesis of a new-generation NLO chromophores, dendritic NLO chromophores and NLO polymers.
2. To systematically study the structure-property relationships in order to achieve a high poling efficiency and thus a large EO activity.

1. 9. References

- (1) Dalton, L. R. *J. Phys.: Condens. Matter* **2003**, *15*, R897.
- (2) Nalwa, H. S.; Miyata, S. *Nonlinear Optics of Organic Molecules and Polymers*, CRC press, Boca Raton, FL, **1997**.
- (3) (a) Kim, T.-D.; Luo, J.; Ka, J.-W.; Hua, S.; Tian, Y.; Shi, Z.; Tucker, N. M.; Jang, S.-H.; Kang, J.-W.; Jen, A. K.-Y. *Adv. Mater.* **2006**, *18*, 3038. (b) Cheng, Y.-J.; Luo, J.; Hau, S.; Bale, D. H.; Kim, T.-D.; Shi, Z.; Lao, D. B.; Tucker, N. M.; Tian, Y.; Dalton, L. R.; Reid, P. J.; Jen, A. K.-Y. *Chem. Mater.* **2007**, *19*, 1154. (c) Kang, H.; Facchetti, A.; Jiang, H.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C.; Liu, Z.; Ho, S.; Brown, E. C.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 3267.
- (4) (a) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. (b) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, 388, 845. (c) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119. (d) Lee, M.; Katz, H. E.; Erben, C.; Gill, D. M.; Gopalan, P.; Heber, J. D.; McGee, D. J. *Science* **2002**, *298*, 1401. (e) Kajzar, F.; Lee, K.-S.; Jen, A. K.-Y. *Adv. Polym. Sci.* **2003**, *161*, 1.
- (5) (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
- (6) Skinner, I. M.; Garth, S. J. *Am. J. Phys.* **1990**, *58*, 177.
- (7) Dalton, L. *Adv. Polym. Sci.* **2002**, *158*, 1.
- (8) (a) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (b) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

-
- (9) (a) Marder, S. R.; Beratan, D. N.; Cheng, L. T. *Science*, **1991**, 252, 103. (b) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. *J. Am. Chem. Soc.* **1994**, 116, 10703. (c) Bourhill, G.; Brédas, J. L.; Cheng, L. T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc.* **1994**, 116, 2619. (d) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science*, **1994**, 263, 511. (e) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature*, **1997**, 388, 845.
- (10) (a) Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater.* **1990**, 2, 700. (b) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. (c) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.*, **1993**, 1118. (d) Cai, C.; Liakatas, I.; Wong, M.-S.; Bösch, M.; Bosshard, C.; Günter, P.; Concilio, S.; Tirelli, N.; Suter, U. W. *Org. Lett.* **1999**, 1, 1847.
- (11) Zhang, C.; Ren, A. S.; Wang, F.; Zhu, J.; Dalton, L. R.; Woodford, J. N.; Wang, C. H. *Chem. Mater.* **1999**, 11, 1966.
- (12) (a) Robinson, B. H.; Dalton, L. R.; Harper, A. W.; Ren, A.; Wang, F.; Zhang, C.; Todorova, G.; Lee, M.; Aniszfeld, R.; Garner, S.; Chen, A.; Steier, W. H.; Houbrecht, S.; Persoons, A.; Ledoux, I.; Zyss, J.; Jen, A. K.-Y. *Chem. Phys.* **1999**, 245, 35. (b) Dalton, L.; Harper, A.; Ren, A.; Wang, F.; Todorova, G.; Chen, J.; Zhang, C.; Lee, M. *Ind. Eng. Chem. Res.* **1999**, 38, 8. (c) Dalton, L. R.; Steier, W. H.; Robinson, B. H.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L.; Phelan, G.; Kincaid, C.; Amend, J.; and Jen, A.

-
- J. Mater. Chem.*, **1999**, *9*, 1905. (d) Robinson, B. H.; Dalton, L. R. *J. Appl. Phys.* **2000**, *104*, 4785.
- (13) (a) Liakatas, I.; Cai, C.; Bösch, M.; Jäger, M.; Bosshard, C.; Günter, P.; Zhang, C.; Dalton, L. R. *Appl. Phys. Lett.* **2000**, *76*, 1368. (b) Zhang, C.; Dalton, L. R.; Oh, M.-C.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043. (c) Wang, C. H.; Woodford, J. N.; Zhang, C.; Dalton, L. R. *J. Appl. Phys.* **2001**, *89*, 4209.
- (14) (a) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 12599. (b) Jen, A. K.-Y.; Cai, Y.; Bedworth, P. V.; Marder, S. R. *Adv. Mater.* **1997**, *9*, 132. (c) Spraul, B. K.; Suresh, S.; Sassa, T.; Herranz, M. Á.; Echegoyen, L.; Wada, T.; Perahia D.; Smith Jr. D. W. *Tetrahedron Lett.* **2004**, *45*, 3253.
- (15) Liu, S.; Haller, M. A.; Ma, H.; Dalton, L. R.; Jang, S.-H.; Jen, A. K.-Y. *Adv. Mater.* **2003**, *15*, 603.
- (16) Lin, H.-C.; Lin, W.-Y.; Bai, H.-T.; Chen, J.-H.; Jin, B.-Y.; Luh, T.-Y. *Angew. Chem. Int. Ed.* **2007**, *46*, 897.
- (17) (a) Szablewski, M. *J. Org. Chem.* **1994**, *59*, 954. (b) Cole, J. C.; Howard, J. A. K.; Cross, G. H.; Szablewski, M. *Acta Crystallogr. Sect. C* **1995**, *C51*, 715. (c) Cross, G. H.; Bloor, D.; Szablewski, M. *Nonlinear Opt.* **1995**, *14*, 219. (d) Cole, J. C.; Cole, J. M.; Cross, G. H.; Farsari, M.; Howard, J. A. K.; Szablewski, M. *Acta Crystallogr. Sect. B* **1997**, *B53*, 812. (e) Szablewski, M.; Thomas, P. R.; Thornton, A.; Bloor, D.; Cross, G. H.; Cole, J. M.; Howard, J. A. K.; Malagoli, M.; Meyers, F.; Brédas, J.-L.; Wenseleers, W.; Goovaerts, E. *J. Am. Chem. Soc.* **1997**, *119*, 3144. (f) Cross, G. H.; Hackman, N.-A.; Thomas, P. R.; Szablewski, M.; Pålsson,

-
- L.-O.; Bloor, D. *Opt. Mater.* **2003**, *21*, 29. (g) Szablewski, M.; Robson, J. H.; Newberry, T.; Cross, G. H. *Nonlinear Opt. Quantum Opt.* **2005**, *34*, 21.
- (18) (a) Metzger, R. M.; Heimer, N. E.; Ashwell, G. J. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 133. (b) Akhtar, S.; Tanaka, J.; Metzger, R. M.; Ashwell, G. J. *Mol. Cryst. Liq. Cryst.* **1986**, *139*, 353. (c) Ashwell, G. J. *Thin Solid Film* **1990**, *186*, 155. (d) Ashwell, G. J.; Jefferies, G.; Dawnay, E. J. C.; Kuczyński, A. P.; Lynch, D. E.; Gongdata, Y.; Bucknall, D. G. *J. Mater. Chem.*, **1995**, *5*, 975. (e) Weir, C. A. M.; Hadizad, T.; Beaudin, A. M. R.; Wang, Z. Y. *Tetrahedron Lett.* **2003**, *44*, 4697. (f) Song, N.; Men, L.; Gao, J. P.; Bai, Y.; Beaudin, A. M. R.; Yu, G.; Wang, Z. Y. *Chem. Mater.* **2004**, *16*, 3708. (g) Bai, Y.; Song, N.; Gao, J. P.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. Y. *J. Am. Chem. Soc.* **2005**, *127*, 2060. (h) Beaudin, A. M. R.; Song, N.; Men, L.; Gao, J. P.; Wang, Z. Y.; Szablewski, M.; Cross, G.; Wenseleers, W.; Campo, J.; Goovaerts, E. *Chem. Mater.* **2006**, *18*, 1079.
- (19) Liao, Y.; Bhattacharjee, S.; Firestone, K. A.; Eichinger, B. E.; Paranj, R.; Anderson, C. A.; Robinson, B. H.; Reid, P. J.; Dalton, L. R. *J. Am. Chem. Soc.* **2006**, *128*, 6847.
- (20) (a) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 3155. (b) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 11174. (c) Keinan, S.; Zojer, E.; Brédas, J.; Ratner, M. A.; Marks, T. J. *THEOCHEM* **2003**, *633*, 227. (d) Kang, H.; Facchetti, A.; Zhu, P.; Jiang, H.; Yang, Y.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C. L.; Liu, Z.; Ho, S.-T.; Marks, T. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 7922. (e)

- Isborn, C. M.; Davidson, E. R.; Robinson, B. H. *J. Phys. Chem. A* **2006**, *110*, 7189.
- (f) Brown, E. C.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem. B* **2008**, *112*, 44.
- (21) (a) Robinson, B. H.; Dalton, L. R. *J. Phys. Chem. A* **2000**, *104*, 4765. (b) Harper, A. W.; Sun, S.; Dalton, L. R.; Garner, S. M.; Chen, A.; Kalluri, S.; Steier, W. H.; Robinson, B. H. *J. Opt. Soc. Am. B* **1998**, *15*, 329.
- (22) (a) Luo, J.; Ma, H.; Haller, M.; Jen, A. K.-Y.; Barto, R. R. *Chem. Commun.*, **2002**, 888. (b) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2002**, *12*, 565.
- (23) Ma, H.; Chen, B.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 986.
- (24) (a) Liao, Y.; Anderson, C. A.; Sullivan, P. A.; Akelaitis, A. J. P.; Robinson, B. H.; Dalton, L. R. *Chem. Mater.* **2006**, *18*, 1062. (b) Sullivan, P. A.; Akelaitis, A. J. P.; Lee, S. K.; McGrew, G.; Lee, S. K.; Choi, D. H.; Dalton, L. R. *Chem. Mater.* **2006**, *18*, 344. (c) Sullivan, P. A.; Rommel, H.; Liao, Y.; Olbricht, B. C.; Akelaitis, A. J. P.; Firestone, K. A.; Kang, J.-W.; Luo, J.; Davies, J. A.; Choi, D. H.; Eichinger, B. E.; Reid, P. J.; Chen, A.; Jen, A. K.-Y.; Robinson, B. H.; Dalton, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 7523.
- (25) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248.
- (26) (a) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. *Appl. Phys. Lett.* **1991**, *58*, 225. (b) Wong, K. Y.; Jen, A. K.-Y. *J. Appl. Phys.* **1994**, *75*, 3308.
- (27) (a) Cai, Y. M.; Jen, A. K.-Y. *Appl. Phys. Lett.* **1995**, *67*, 299. (b) Jen, A. K.-Y. Wu, X.; Ma, H. *Chem. Mater.* **1998**, *10*, 471.

-
- (28) (a) Green, G. D.; Hall, H. K., Jr.; Mulvaney, J. E.; Noonan, J.; Williams, D. J. *Macromolecules* **1987**, *20*, 716. (b) Green, G. D.; Weinschenk, J. I., III; Mulvaney, J. E.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 722. (c) Katz, H. E.; Schilling, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 7554. (c) Hall, H. K., Jr.; Kuo, T.; Leslie, T. M. *Macromolecules* **1989**, *22*, 3525. (d) Kohler, W.; Robello, D. R.; Willand, C. S.; William. D. J. *Macromolecules* **1991**, *24*, 4589.
- (29) (a) Lindsay, G. A.; Stenger-Smith, J. D.; Henry, R. A.; Hoover, J. M.; Nissan, R. A.; Wynne, K. J. *Macromolecules* **1992**, *25*, 6075. (b) Xu, C.; Wu, B.; Becker, M. W.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Chem. Mater.* **1993**, *5*, 1439.
- (30) (a) Yu, D.; Gharavi, A.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 11680. (b) Saaden, H.; Gharavi, A.; Yu, D.; Yu, L. *Macromolecules* **1997**, *30*, 5403.
- (31) Ma, H.; Jen, A. K.-Y.; Wu, J.; Wu, X.; Liu, S.; Shu, C.-F.; Dalton, L. R.; Marder, S. R.; Thayumanavan, S. *Chem. Mater.* **1999**, *11*, 2218.
- (32) Chen, T. A.; Jen, A. K.-Y.; Cai, Y. *J. Am. Chem. Soc.* **1995**, *117*, 7295.
- (33) Lu, Z.; Li, J.; Hua, J.; Li, X.; Qin, J.; Qin, A.; Ye, C. *Syn. Met.* **2005**, *152*, 217.
- (34) (a) Zhang, C.; Wang, C.; Yang, J.; Dalton, L. R.; Sun, G.; Zhang, H.; Steier, W. H. *Macromolecules* **2001**, *34*, 235. (b) Zhang, C.; Wang, C.; Dalton, L. R.; Zhang, H.; Steier, W. H. *Macromolecules* **2001**, *34*, 253. (c) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *2*, 167. (d) Jin, Y.; Carr, S. H.; Marks, T. J.; Lin, W.; Wong, G. K. *Chem. Mater.* **1992**, *4*, 963. (e) Hubbard, M. A.; Marks, T. J.; Lin, W.; Wong, G. K. *Chem. Mater.* **1992**, *4*, 965. (f) Yu, L.; Chan, W.; Bao, Z. *Macromolecules* **1992**, *25*, 5609. (g) Yu, L.; Chan, W.; Dikshit, S.;

-
- Bao, Z. *Appl. Phys. Lett.* **1992**, *60*, 1655. (h) Ma, H.; Wu, J.; Herguth, P.; Chen, B.; Jen, A. K.-Y. *Chem. Mater.* **2000**, *12*, 1187.
- (35) Haller, M.; Luo, J.; Li, H.; Kim, T.-D.; Liao, Y.; Robinson, B. H.; Dalton, L. R.; Jen, A. K.-Y. *Macromolecules* **2004**, *37*, 688.
- (36) (a) Luo, J.; Liu, S.; Haller, M.; Liu, L.; Ma, H.; Jen, A. K.-Y. *Adv. Mater.* **2002**, *14*, 1763. (b) Luo, J.; Haller, M.; Ma, H.; Liu, S.; Kim, T.-D.; Tian, Y.; Chen, B.; Jang, S.-H.; Dalton, L. R.; Jen, A. K.-Y. *J. Phys. Chem. B* **2004**, *108*, 8523.
- (37) Luo, J.; Haller, M.; Li, H.; Tang, H.; Jen, A. K.-Y. *Macromolecules* **2004**, *37*, 248.
- (38) (a) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733. (b) Giacometti, J. A.; Fedosov, S.; Costa, M. M. *Brazilian J. Phys.* **1999**, *29*, 269.
- (39) Tang, H.; Taboada, J. M.; Cao, G.; Li, L.; Chen, R. T. *Appl. Phys. Lett.* **1997**, *70*, 538.
- (40) Singer, K. D.; Kuzyk, M. G.; Holland, W. R.; Sohn, J. E.; Latama, S. J.; Comizzoli, R. B.; Katz, H. E.; Schilling, M. L. *Appl. Phys. Lett.* **1998**, *53*, 1800.
- (41) Dentan, V.; Lévy, Y.; Dumont, M.; Robin, P.; Chastaing, E. *Opt. Commun.* **1989**, *69*, 379.
- (42) Teng, C. C. and Man, H. T. *Appl. Phys. Lett.* **1990**, *56*, 1734.
- (43) Ma, C. B.; Xu, D.; Ren, Q.; Lv, Z. H.; Yang, H. L.; Meng, F. Q.; Zhang, G. H.; Guo, S. Y.; Sang, L. X.; Wang, Z. G. *J. Mater. Sci. Lett.* **2003**, *22*, 49.
- (44) Cross, G. H.; Hackman, N. A.; Thomas, P. R.; Szablewski, M.; Passon, L. O.; Bloor, D. *Opt. Mater.* **2002**, *21*, 29.

Chapter 2 Synthesis and Characterization of Zwitterionic Chromophores

2. 1. Introduction

As an important part in the whole EO system, NLO chromophores play a key role in the exhibition of EO activity. There are two types of NLO chromophores, which include neutral ground-state¹ or so-called left-hand-side (LHS) chromophores, and highly polar zwitterionic chromophores^{2,3} or so called right-hand-side (RHS) chromophores (see chapter 1).

We are particularly interested in the design and functionalization of zwitterionic chromophores such as the reported picolinium tricyanoquinodimethane (PQDM) chromophores (Scheme 2.1). They have very large figure of merit ($\mu\beta$ value),^{2b-d} being comparable to some well studied neutral ground state chromophores and can be prepared in the fairly short synthetic routes, making them the most competitive candidates for practical application. However, these highly polar dyes often fail to exhibit the expected large EO activities in polymer matrices, either in a doped polymer system or in a covalently bonded polymer system. It is generally considered that chromophore-chromophore aggregation due to strong electrostatic interactions between the dipoles is responsible for the loss of EO activity of NLO materials.⁴

In order to realize the full potential of PQDM chromophores, our group carried out a series of studies on the synthesis and functionalization of PQDM chromophores. Dendritic NLO polymers have been demonstrated to show larger EO coefficients due to site isolation⁵ that diminishes or completely prevents the chromophore-chromophore aggregation. The synthesis of PQDM chromophores were first reported by a

condensation reaction between a picolinium salt and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with low yields (15-30%) over very long reaction time (5-14 days).⁶ Later the optimized synthetic conditions with up to 97% yield and shortened reaction time (14-30 h) were reported by our group by using lithium-TCNQ adduct instead of TCNQ and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) as the base (Scheme 2.1).^{2c} The molar ratio for the higher yield is Li-TCNQ / DBU / picolinium salt = 2: 2: 1.

Scheme 2.1. Synthetic route to PQDM

Based on the experimental results, a reaction mechanism for the formation of PQDM was proposed (Scheme 2.2).^{2c} First, one equiv. of DBU deprotonates the picolinium salt to form a neutral compound, which reacts with two equiv. of Li-TCNQ consecutively to form a charge-separated intermediate. Then the second equiv. of DBU is required to attack the acidic proton to form the central double bond with the loss of one of the central cyano group. Therefore, there are three cyano groups presented in the molecular structure of PQDM, which exhibit apparent different IR absorption peaks. Cyano group connected to the central double bond has a weak absorption at $\sim 2220\text{ cm}^{-1}$, while the other two cyano groups show strong absorptions at $\sim 2150\text{ cm}^{-1}$ due to the neighboring negative charge.

Scheme 2.2. Proposed mechanism for the formation of PQDM and the by-product of TCNQ dianion

A series of PQDM derivatives with the different R groups,^{2d} linear and hyperbranched polymers containing PQDM chromophores were reported by our group.⁷ To date, the functionalization of PQDM has mainly focused on the donor part (pyridinium ring) of the chromophore. In order to further diminish the chromophore interaction by site isolation, we intended to introduce additional functional groups on the middle (π -conjugated bridge) and acceptor parts of chromophores. Therefore, the functional groups in three parts of chromophores can be present, which allows for further encapsulation of the chromophore in order to prevent the deleterious chromophore-chromophore aggregations. Considering the structural similarity between TCNQ and 7,8-di(alkoxycarbonyl)-7,8-dicyanoquinodimethane (ACQ) (Figure 2.1), 7,8-di(methoxycarbonyl)-7,8-dicyanoquinodimethane (DMCQ) can be used to replace TCNQ in the reaction with picolinium salts. According to the proposed mechanism for the

formation of PQDM, the product should have the ester groups in the middle and acceptor parts. By further replacing the methyl group of the ester with the hydroxyethyl group, up to three hydroxyl groups can be introduced into the chromophore.

Figure 2.1. Molecular structures of TCNQ, ACQ and DMCQ

This chapter describes the synthesis, structural characterization, x-ray crystallographic analysis, reaction mechanism, thermostability, acid sensitivity, photoluminance (PL) and microscopic nonlinear optical properties of a new generation of zwitterionic chromophores PeQDM (Scheme 2.4). The synthesis and characterization of dendronized NLO chromophores and crosslinkable NLO polymers will be introduced in chapters 3 and 4, respectively. EO properties of the zwitterionic PeQDM, dendronized PeQDM and NLO polymers will be discussed in the last chapter.

2. 2. Results and Discussion

2. 2. 1. Synthesis of ACQ and PeQDM

7,8-Di(alkoxycarbonyl)-7,8-dicyanoquinodimethane (ACQ) including DMCQ can be easily prepared from p-xylylene dichloride in quantitative yield (Scheme 2.3) according to the reported method.⁸

Scheme 2.3. Synthetic route to ACQ

Attempts to make Li-DMCQ similar to Li-TCNQ failed because DMCQ readily polymerizes when reacting with lithium iodide. On the other hand, when the reaction of DMCQ with picolinium salt was carried out in acetonitrile, the decomposition of the resulting chromophore was observed as indicated by the UV-Vis spectroscopic analysis. Surprisingly, when the reaction was carried out in methanol at reflux, a pure product was obtained as dark blue precipitates from the reaction mixture. In order to investigate the optimal reaction conditions, the synthesis of chromophore PeQDM-2OH was done with different molar ratios of the starting materials.

Figure 2.2. The formation of PeQDM-2OH (entry IV in Table 2.1) monitored by UV-Vis spectroscopy

The reaction was monitored by taking the UV-Vis spectra of aliquots of the reaction mixture in DMF (Figure 2.2). Like TCNQ, DMCQ can readily form $\text{DMCQ}^{\cdot-}$ radical anion by one-electron transfer from Lewis base DBU (see reaction mechanism for the formation of PeQDM in Scheme 2.8). At the beginning, the very intense peaks at 426, 437, 742 and 836 nm of $\text{DMCQ}^{\cdot-}$ were formed immediately. During the course of the reaction, the relative intensity of these peaks gradually decreased and saturated within 5 h, indicating the end of reaction. On the other hand, the relative intensity of the peaks at 676 nm and 320 nm belonging to the resulting chromophore became much stronger than that of the radical anion peaks. After 4-5 h, the reaction mixture was cooled down to room temperature, then filtered and washed with methanol three times. A pure product was obtained, displaying the expected peaks cleanly in the NMR and UV-Vis spectra.

Table 2.1. Synthesis of PeQDM-2OH under different reaction conditions

Entry	Mass of DMCQ (g)	Equiv. of Picolinium Salt	Equiv. of DBU	Reaction Time (h)	Yield (g, %)
I	0.50	1	0.5	24	incomplete
II	0.50	1	0.8	24	incomplete
III	0.50	1	1	4-5	0.26, 44% ^a
IV	0.50	0.5	1	4-5	0.28, 48%
V	0.50	0.25	1	30	incomplete

^a The yield was calculated according to 0.5 equiv. of picolinium salt.

From the collected experimental data (Table 2.1), the optimal conditions for the best yield was found from entry IV or 1 equiv. of DMCQ, 1 equiv. of DBU and 0.5 equiv. of picolinium salt. The yield was 48% based on picolinium salt and the reaction time was less than 5 h. In entry III, the use of an excess of picolinium salt didn't affect the reaction much as almost the same amount of chromophore (44% yield based on 0.5 equiv. of picolinium salt) was obtained. It was also found that the reaction couldn't go to completion after more than one day with less than 0.5 equiv. of picolinium salt (entry V) and less than 1 equiv. of DBU (entries I and II). When using an excess of DBU (more than 1 equiv.), the resulting chromophore decomposed.

The optimized reaction conditions were applied to the synthesis of a series of chromophores (Scheme 2.4) with the yield in a range of 44%-50% (see experimental section). Chromophores containing the alkyl and benzyl groups are designed as model compounds for hyper-Rayleigh scattering (HRS) experiments and doping studies. Hydroxyl-containing PeQDM chromophores were pursued so that they could be further functionalized or grafted onto a polymer having pendent acid groups. The diol-containing chromophores are potential monomers for making linear and hyperbranched NLO polyesters and polyurethanes. Furthermore, the synthesis of PeQDM-2OH was

scaled up in 4 g per batch and PeQDM-C2OH in 8 g per batch in ~50% yields. Therefore, a simple synthetic method has been established for the large scale synthesis of the new generation chromophores with good yields.

Scheme 2.4. Synthetic route to PeQDM

In addition to the functional groups at the donor part of the chromophores just like the reported PQDM chromophores, this reaction also allows for introduction of another functional group in the acceptor part. Thus, chromophore PeQDM-C3OH-E-OH with two functional groups at both the donor and acceptor parts was synthesized by using 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyanoquinodimethane [D(E-OH)CQ] according to the following reactions (Scheme 2.5).

Scheme 2.5. Synthetic route to PeQDM-C3OH-E-OH

In the first step, 1,4-phenylenediacetonitrile reacted with excess of lithium diisopropylamide (LDA) and ethylene carbonate at -78 °C to provide 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyano-p-xylylene, which can be purified by recrystallization from chloroform as white solids in 51% yield. Different bases such as butyl lithium and sodium hydride were also used, but the yields were less than 20%. The main by-product of the reaction is the monosubstituted product, which can be separated and reused for the same reaction. Oxidation by bromine gave 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyanoquinodimethane, which was separated from the reaction mixture by filtration as yellow solids in 50% yield. The low yield was due to the polymerization of the resulting product during the oxidation. Although the overall yield from 1,4-phenylenediacetonitrile to chromophore is low (10.7%), the yield in the last step (42%) is still comparable to those for other PeQDM chromophores (44%-49%).

2. 2. 2. Structural characterization

All the chromophores have been characterized by ^1H NMR, ^{13}C NMR, IR and MS (see experimental section).

Figure 2.3. ^1H NMR spectrum (400 MHz, DMSO-d_6) of PeQDM-Ben

As an example, the ^1H NMR spectrum of PeQDM-Ben (Figure 2.3) displays proton resonances (ppm) at 9.05 (d, $J = 6.8$ Hz, 2H), 8.33 (d, $J = 6.8$ Hz, 2H), 7.84 (s, 1H), 7.69 (br, 2H), 7.43-7.59 (m, 7H), 5.75 (s, 2H) and 3.51 (s, 3H). One methoxy group is assigned to the resonance at 3.51 ppm.

Figure 2.4. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of PeQDM-Ben

In its ^{13}C NMR spectrum (Figure 2.4), carbon resonances (ppm) at 167.3, 149.8, 147.2, 144.1, 134.3, 129.2, 129.1, 128.6, 126.7, 125.2, 124.8, 121.1, 120.7, 119.9, 116.8, 62.4, 61.1 and 49.1 were observed. Only one carbonyl carbon ($\text{C}=\text{O}$) of ester group at 167.3 ppm and one aliphatic carbon ($\text{C}-\text{O}$) at 49.1 ppm were found. The information provided by both ^1H NMR and ^{13}C NMR spectra indicates that there is only one ester group and two cyano groups presented in this chromophore. The IR and MS spectra further support this finding.

In the IR spectrum of PeQDM-Ben (Figure 2.5), two different cyano groups appeared. One of them was at 2226 cm^{-1} , assigned to the one connected to a double bond. While another one was at lower wavenumber (2146 cm^{-1}) and the intensity of the peak was strikingly high, which is the characteristic of the cyano group connected to an electro-rich group bearing a negative charge. Also there was just one stretching frequency of the carbonyl at 1750 cm^{-1} . These information strongly support the molecular structure of PeQDM.

Figure 2.5. IR spectrum (KBr , cm^{-1}) of PeQDM-Ben

In the MS spectrum (Figure 2.6), the molecular ion peak at M/Z 426 for $C_{26}H_{22}O_4N_2$ (with one cyano and two ester groups) was not observed, instead of a $M+H$ peak at M/Z 394 for $C_{25}H_{19}O_2N_3$ (with two cyano and one ester groups). Peak at M/Z 453 may be attributed to a small quantity of reaction intermediate **B** (see Scheme 2.8), which has the molecular weight of 453.

Figure 2.6. MS spectrum (ESI, CH_3CN , M/Z) of PeQDM-Ben: 394 ($M+H^+$)

2. 2. 3. X-ray crystallography

The molecular structure of PeQDM was further confirmed by the X-ray crystallography of PeQDM-Ben. Single crystals of PeQDM-Ben were grown by slow diffusion of methanol into a concentrated DMF solution of PeQDM-Ben at room temperature. Detailed x-ray data are presented in appendix. ORTEP drawing of PeQDM-Ben and selected bond lengths of the crystals are shown in Figure 2.7 and Table 2.2, respectively.

Figure 2.7. ORTEP drawing of PeQDM-Ben (Hydrogen atoms are omitted for clarity)

The zwitterionic structure of the chromophore is clearly demonstrated by the double bond between C14 and C17 (1.354 Å) and the single bond between C5 and C8 (1.455 Å). The bond distance between C5 and C8 (1.455 Å) as well as accompanying shortened C-CN (1.411 Å), CH₃OOC-C (1.417 Å) bonds and elongated C≡N (1.157 Å) bond compared with the central C≡N bond (1.142 Å), indicating the negative charge is localized on (CH₃OOC)-C-(CN) group. The localization of the negative charge is also supported by the lower wavenumber and higher intensity of IR stretching frequency of C≡N (2146 cm⁻¹) of (CH₃OOC)-C-(CN) group compared to that of the central C≡N bond (2226 cm⁻¹).

Table 2.2. Selected bond lengths of crystallographic data of PeQDM-Ben

Cn-Cm	Å	Cn-Cm	Å	Cn-Cm	Å	Cn-Nm	Å
C3-C5	1.417(3)	C11-C12	1.403(3)	C17-C18	1.455(3)	C6-N7	1.157(3)
C5-C6	1.411(3)	C12-C13	1.371(3)	C18-C19	1.399(3)	C15-N16	1.142(3)
C5-C8	1.455(3)	C13-C8	1.415(3)	C19-C20	1.363(3)	C20-N21	1.345(3)
C8-C9	1.409(3)	C11-C14	1.471(3)	C18-C23	1.397(3)	C22-N21	1.341(3)
C9-C10	1.375(3)	C14-C15	1.449(3)	C22-C23	1.369(3)		
C10-C11	1.402(3)	C14-C17	1.354(3)				

Although the bond lengths in the bridge and acceptor parts clearly suggest a zwitterionic molecular structure, the bond lengths of the pyridinium ring and the benzene ring connecting to the (CH₃OOC)-C-(CN) group are quinoidal rather than aromatic,

respectively. Similar phenomena have also been reported for several TCNQ adducts such as DEMI and P₃CNQ and it was found that the central cyano group is necessary for retention of the quinoidal character in the molecule and it was suggested that conventional Kekulé structure can not adequately depict the structural characteristics of such a molecule.^{2a,9} Therefore, the best description of the ground-state structure of such a chromophore is the combination of the two limiting forms (Scheme 2.6): zwitterionic and neutral forms with predominantly zwitterionic structure, which is also supported by negative solvatochromism.

Scheme 2.6. Resonance structures of PeQDM

The extended π -system between the donor and the acceptor is almost planar, as evident by a small torsional angle (10.38°) between the pyridinium and the phenylene groups. The coplanarity of the π -electron structure and very large ground-state dipole moment should facilitate the positive charge center overlapping with the negative charge centre to form anti-parallel packing. As expected, the crystal cell contains a complete dimer and the two monomers overlap anti-parallel to each other with a large slip angle ($\theta = 64.5^\circ$), which is characteristic of the face-to-face H-aggregation (Figure 2.8).¹⁰ The strong electrostatic interactions between chromophores make this kind of molecules only soluble in some polar solvents such as DMF, DMAC, DMSO, NMP, etc.

Figure 2.8. Left: Packing diagram of PeQDM-Ben in the unit cell (Hydrogen atoms are omitted for clarity); Right: Slip angle of the dimer.

2.2.4. Reaction mechanism

It had been expected that two methyl ester groups (Scheme 2.7) would be introduced into the molecular structure of chromophore by reacting DMCQ with picolinium salt if the reaction follows the same pathway as proposed for the formation of PQDM after eliminating one cyano group during the reaction (Scheme 2.2). However, only one methyl ester group was present in the molecular structure of PeQDM, as confirmed by NMR, IR, MS and X-ray data. In addition, the yield for the synthesis of PeQDM was low (~50%), which is about half of the highest yield for PQDM (97%).

Scheme 2.7. Synthetic route to the expected and actual chromophores

Considering the spectroscopic data collected during the course of reaction and the required molar ratio for the best yield (DMCQ / DBU / Picolinium Salt = 2: 2: 1), a possible mechanism for the formation of PeQDM is proposed (Scheme 2.8). The reaction is mediated by radicals and the first half is very similar to the mechanism for PQDM. First, DBU transfers one-electron to DMCQ to form a radical anion ($\text{DMCQ}^{\cdot-}$) and a radical cation ($\text{R}_3\text{N}^{\cdot+}$). Then the second equiv. of DBU is required to deprotonate picolinium salt to form a neutral compound that reacts with $\text{DMCQ}^{\cdot-}$ to form an intermediate **A**. The radical of **A** will be abstracted by the radical cation ($\text{R}_3\text{N}^{\cdot+}$) to form an intermediate **B** and regenerate one equiv. of base. The base cleavages the O-methyl bond followed by the decarboxylation to form an intermediate **C**. Experimentally it has been found that if less DBU is presented, the reaction can not go to the completion even with the extended reaction time (See Table 2.1: entries I and II). The possibility of hydrolysis of the methyl ester was ruled out, since the same results were obtained by running the reactions in anhydrous methanol and reagent-grade methanol. After the cleavage of the methyl ester, the second equiv. of DMCQ is required to receive one electron from the intermediate **C** to form **D** and the radical anion ($\text{DMCQ}^{\cdot-}$). $\text{DMCQ}^{\cdot-}$ continues to abstract the hydrogen radical from the intermediate **D** to form $\text{HDMCQ}^{\cdot-}$ and the final product PeQDM.

Scheme 2.8. Proposed reaction mechanism for the formation of PeQDM

According to the proposed mechanism, H₂DMCQ should be a major by-product. In order to isolate this by-product, the filtrate for the reaction (PeQDM-C2OH) was acidified and extracted with ethyl acetate. After column chromatography (silica gel, hexane/ethyl acetate), H₂DMCQ was obtained as white crystals, which was characterized

by NMR, MS and IR: ^1H NMR (400 MHz, CDCl_3): δ 3.83 (s, 6H), 4.78 (s, 2H), 7.55 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.9, 131.1, 129.1, 115.0, 54.2, 43.1; MS (EI, M/Z): 272 (M^+); IR (Neat, cm^{-1}): 2253 ($\nu_{\text{C}\equiv\text{N}}$), 1749 ($\nu_{\text{C}=\text{O}}$).

Although this proposed mechanism can explain the formation of PeQDM and the required molar ratio of the reactants for the best yield, the reason for the low yield is still unclear.

2. 2. 5. Negative solvatochromism

Solvatochromism is the ability of a chemical substance to change color due to a change in solvent polarity. A hypsochromic (or blue) shift of the UV/Vis/Near-IR absorption band with increasing solvent polarity is called negative solvatochromism, which is mainly observed with dyes having a charge-separated (or zwitterionic) ground-state structure. The corresponding bathochromic (or red) shift with increasing solvent polarity is called positive solvatochromism, which is mainly observed with dyes having a neutral ground-state structure.

Solvent polarity is used to be defined with some macroscopic physical parameters such as the relative permittivity (ϵ_r), the permanent dipole moment (μ) and the refractive index (n). But these parameters often fail to give a correct correlation due to the oversimplification of the idealized electrostatic approach without considering solute/solvent interactions. For example, although solvents have the following polar order determined by the relative permittivities: Acetone (20.7) < Methanol (32.7) < DMF (36.7) < Acetonitrile (37.5), the UV-Vis absorptions of PeQDM-hex in these solvents didn't show the corresponding either the same (red-shift) or the reversed (blue-shift) order (Figure 2.9).

Figure 2.9. UV-Vis spectra of PeQDM-Hex in different solvents

Some other empirical parameters of solvent polarity with considering solute/solvent interactions have been introduced such as E_{T30} , which is a well selected, strongly solvent-dependent spectral absorption parameter.¹¹ E_{T30} values are based on the negatively solvatochromic pyridinium N-phenolate betaine dye (Figure 2.10) as a probe molecule, and they are defined as the molar electronic transition energies (E_T) of dissolved dyes, measured in kcal mol^{-1} at room temperature (25 °C) and normal pressure (1 bar) according to equation: $E_{T30} (\text{kcal mol}^{-1}) = h c N_A / \lambda_{\text{max}} = 28591 / \lambda_{\text{max}}$. A high E_{T30} value corresponds to a high solvent polarity. E_{T30} values range from 30.7 for tetramethyl silane up to 63.1 kcal / mol for water.

Figure 2.10. Molecular structure of pyridinium N-phenolate betaine dye.

By using the E_T30 parameter as the index of solvent polarity, the previous mentioned solvents have a different polarity order: Acetone < DMF < Acetonitrile < Methanol. Meanwhile, a reversed order of $\lambda_{\max}$ of PeQDM-Hex was observed in the corresponding solvents: 704 nm (in acetone) > 674 nm (in DMF) > 666 nm (in Acetonitrile) > 621 nm (in Methanol) (Figure 2.9), which is the characteristic of a negative solvatochromism.

All chromophores exhibit the similar negative solvatochromism, the solvatochromic data of the chromophores are summarized in Table 2.3. Negative solvatochromism indicates that PeQDM chromophore has a charge separated (or zwitterionic) ground state, which is consistent with information obtained from IR and X-ray results.

Table 2.3. Wavelengths of charge-transfer bands ($\lambda_{\max}$) of PeQDM chromophores in different solvents

Solvent (E_T30) ^a	$\lambda_{\max}$ (nm)			
	Acetone (42.2)	DMF (43.2)	Acetonitrile (45.6)	Methanol (55.4)
PEQDM-Hex	704	674	660	621
PeQDM-C2OH	702	668	660	619
PeQDM-C3OH	705	671	662	628
PeQDM-2OH	712	677	669	627
PeQDM-Ben	727	691	676	630
PeQDM-BenOH	725	691	679	642
PeQDM-C3OH-E-OH	691	669	655	611

^a The polarities of the solvents are given by the E_T30 parameters.¹¹

2. 2. 6. Thermal stability

For EO applications, NLO chromophores are usually doped in or covalently bonded onto polymers, followed by poling under an externally applied electric field at the glass transition temperature (T_g) of the materials in order to achieve a noncentrosymmetric order. Therefore, thermostability of the chromophore is a key parameter for the selection of polymer and poling temperature.

Figure 2.11. TGA traces of PeQDM chromophores

The thermostability of a chromophore is determined by thermogravimetric analysis (TGA) as the onset temperature (T_d) for 5% weight loss in nitrogen. TGA traces of the chromophores are shown in Figure 2.11 and the T_d values are summarized in Table 2.4. All the chromophores are thermally stable above 200 °C, except for PeQDM-C3OH-E-OH having a hydroxyethyl ester at the acceptor part.

Table 2. 4. Decomposition temperatures (T_d) determined by TGA

Chromophore	T_d ($^{\circ}\text{C}$)	Chromophore	T_d ($^{\circ}\text{C}$)
PeQDM-Hex	228	PeQDM-Ben	250
PeQDM-C2OH	215	PeQDM-BenOH	222
PeQDM-C3OH	238	PeQDM-C3OH-E-OH	183
PeQDM-2OH	234		

2. 2. 7. Acid sensitivity

As the active component of an EO device, chemical stability of a chromophore is also important for selecting appropriate solvents and polymer matrices. In our study, we found that zwitterionic chromophores are sensitive to acids such as H_2SO_4 , HCl , acetic acid and even the acid vapor at room temperature, but fairly stable in basic media at room temperature. When an excess of acid is present, the solution of chromophore turns colorless immediately. The original color comes back by adding an excess of base. For example, a blue DMF solution of PeQDM-C2OH became colorless when an excess of HCl was added and resumed the blue color by adding an excess of NaOH (Figure 2.12). This reversible color-changing process is due to the protonation by acid and deprotonation by base at the acceptor part of the chromophore (Scheme 2.9).

Figure 2.12. UV-Vis spectra of PeQDM-C2OH in DMF without and with excess HCl

Scheme 2.9. Protonation of PeQDM-C2OH and deprotonation of P-PeQDM-C2OH

The structure of the protonated product P-PeQDM-C2OH prepared by adding an excess of HCl to the DMF solution of PeQDM-C2OH (see experimental section) was confirmed by FT-IR, ^1H NMR, ^{13}C NMR and MS analyses.

By comparing the IR spectrum of P-PeQDM-C2OH with that of PeQDM-C2OH (Figure 2.13), the position and intensity of $\nu_{\text{C}\equiv\text{N}}$ at the acceptor part changed noticeably after protonation. Before protonation, $\nu_{\text{C}\equiv\text{N}}$ was at a lower wavenumber (2167 cm^{-1}) with high intensity due to the adjacent negative charge. After protonation, $\nu_{\text{C}\equiv\text{N}}$ moved to a higher wavenumber (2252 cm^{-1}) with a much lower intensity, which is typical for $\text{C}\equiv\text{N}$ connected to the neutral saturated carbon atom. For the central $\text{C}\equiv\text{N}$ connected to double band, no apparent difference was observed. Therefore, the proton was added to the carbon with a negative charge. After protonation, all resonance signals in the ^1H NMR spectrum (see experimental section) were shifted to a lower field (Figure 2.14).

Figure 2.13. IR spectra (KBr, cm⁻¹) of PeQDM-C2OH and P-PeQDM-C2OH

Figure 2.14. ¹H NMR spectra (400 MHz, DMSO-d₆) of P-PeQDM-C2OH and PeQDM-C2OH

However, it is difficult to determine the resonance peak of the add-on proton from the ^1H NMR spectrum of P-PeQDM-C2OH. One possible reason is the proton exchange with H_2O in DMSO-d_6 due to the stronger acidity of this proton, which causes the proton signal overlapping with that of H_2O and broadening at ~ 3.5 ppm (Figure 2.14, top). The strong acidity of this proton is also possibly to cause solvolytic dissociation by DMSO-d_6 as shown in Scheme 2.10, which was evident by the blue color of the solution. Spectroscopically, P-PeQDM-C2OH in DMF appears almost the same ($\lambda_{\text{max}} = 669$ nm) as PeQDM-C2OH ($\lambda_{\text{max}} = 668$ nm in DMF).

Scheme 2.10. Solvolytic dissociation of P-PeQDM-C2OH by DMSO-d_6

P-PeQDM-C2OH also gave the apparently different ^{13}C NMR spectrum (Figure 2.15), especially in the range for the aliphatic carbons, in which four peaks are observed. For PeQDM-C2OH, only three peaks are observed. The observation of **d'** was due to nuclear Overhauser enhancement (NOE) effect after protonation.

MS ($\text{ESI}+\text{H}^+$) spectrum of P-PeQDM-C2OH gave a base peak at 348 M/Z , which is the same as the $\text{M}+1$ ($\text{ESI}+\text{H}^+$) peak found for PeQDM-C2OH.

Figure 2.15. ^{13}C NMR spectra (400 MHz, DMSO-d_6) of P-PeQDM-C2OH (top) and PeQDM-C2OH (bottom)

2.2.8. Photoluminescence

It has been reported that some zwitterionic chromophores are photoluminescent (Figure 2.16).¹²

Figure 2.16. Molecular structures of zwitterionic chromophores I ($\lambda_{\text{max}} = 500 \text{ nm}$, $\lambda_{\text{max}}^{\text{PL}} = 565 \text{ nm}$, in 9:1 ethanol-methanol solvent) and II ($\lambda_{\text{max}} = 575 \text{ nm}$, $\lambda_{\text{max}}^{\text{PL}} = 640 \text{ nm}$, in 9:1 ethanol-methanol solvent)

Since PeQDM chromophores absorb at longer wavelengths up to 900 nm in polar solvents (negative solvatochromism), they are likely to exhibit near-infrared (NIR, 750-900 nm) photoluminescence (PL). NIR dyes are widely used in biomedical studies to increase detection sensitivity and depth of light penetration in tissue because the autofluorescence and light absorption by tissue are low in the NIR region.¹³

Indeed, PeQDM chromophores are found to be NIR photoluminescent (Figure 2.17) with the maximal wavelength at ~860 nm in DMF when being excited at 650 nm. The optimal concentration for PL measurement is $\sim 3 \times 10^{-5}$ mol/L and the results are summarized in Table 2.5. Stokes shifts in DMF solution are less than 200 nm, while the one in more polar environment is about 300 nm (PeQDM-C3OH in aqueous solution: $\Delta\lambda = 840 - 542 = 298$ nm). The increased Stokes shift in polar solvent can be attributed to the higher degree of solvent stabilization effect on the ground-state energy than on the excited state, indicating the ground-state dipole moment is significantly larger than the one in the excited state, which is also consistent with information obtained from IR, X-ray and negative solvatochromism results.

Figure 2.17. UV-Vis and PL spectra of PeQDM-C2OH

Table 2.5. Maximal PL of PeQDMs in DMF solution (excited at 650 nm)

Chromophore	PeQDM-Hex	PeQDM-C2OH	PeQDM-C3OH	PeQDM-2OH	PeQDM-Ben	PeQDM-BenOH
λ^{PL} (nm)	856	860	862	860	860	866
$\Delta\lambda$ (nm) ^a	182	192	191	183	169	175

^a $\Delta\lambda = \lambda^{PL} - \lambda_{max}$ (λ_{max} : See Table 2.3)

Considering that PeQDM chromophores are also acid sensitive, they should be able to be used as an NIR optical pH sensor. The PL spectra of PeQDM-C3OH in aqueous solution with different pH values were then taken.

The stock solution (2.88×10^{-4} M) was prepared by dissolving PeQDM-C3OH in DMF. The sample solutions for PL measurements were prepared by adding 0.2 mL of stock solution to 2 mL of buffer solution with a given pH value. Going from acidic to basic, the color of the sample solution changes from colorless to purple (Figure 2.18, $\lambda_{max} = 542$ nm).

Figure 2.18. Samples of PeQDM-C3OH in aqueous DMF with different pH values (a: pH = 4.00, b: pH = 4.67, c: pH = 5.13, d: pH = 5.41, e: pH = 6.07, f: pH = 7.00)

When the sample solution was at pH < 4, the solution was colorless and no photoluminescence was detected (excitation at 540 nm). With increase of the pH value, the intensity of the PL ($\lambda_{max}^{PL} = 840$ nm) increased until reaching the maximum at pH = 6

(Figure 2.19). In comparison, the UV-Vis spectra of sample solutions were also taken (Figure 2.20) at a given pH range. The sensitivity to pH change can then be determined as $\Delta A/\Delta pH$, where ΔA is a change in absorption intensity, and as $\Delta I/\Delta pH$, where ΔI is a change in the PL intensity. Accordingly, $\Delta A/\Delta pH$ and $\Delta I/\Delta pH$ were found to be 0.017/0.1pH and $\Delta I/\Delta pH = 1.0/0.1pH$, indicating the PL is very sensitive to a pH change within a narrow range of pH (4.0-6.0).

Figure 2.19. Left: PL spectra of PeQDM-C3OH aqueous solutions with different pH values; Right: The graph of PL intensity versus pH value.

Figure 2.20. Left: UV-Vis spectra of PeQDM-C3OH aqueous solutions with different pH values; Right: The graph of absorption intensity of CT band versus pH value.

2. 2. 9. Hyperpolarizability study

First hyperpolarizabilities (β values) of NLO chromophores were measured by hyper-Rayleigh scattering (HRS) in DMF solution at 1.07 μm wavelength by a physical group at Antwerpen University in Belgium.^{2d} In DMF solution, PQDM and PeQDM showed the almost consistent microscopic nonlinearity and the results are summarized in Table 2.6.

Table 2.6. β values of PQDMs and PeQDMs measured by HRS and the estimated β_0 values

Chromophore	PQDM-Met	PQDM-C3OH	PeQDM-2OH	PeQDM-Hex	PeQDM-C2OH	PeQDM-Ben
$\beta (\times 10^{-30} \text{esu})$	-1865 ^{2d}	-1930 ^{2d}	-1660	-1700	-1729	-1797
$\beta_0 (\times 10^{-30} \text{esu})^a$	595	598	599	602	590	670

^a β_0 was calculated by the following equation according to two-level model:¹⁴

$$\beta = \beta_0 \frac{\lambda^4}{(\lambda^2 - \lambda_{\text{max}}^2)(\lambda^2 - 4\lambda_{\text{max}}^2)}$$

λ is the wavelength of the optical field (1070 nm) and λ_{max} is the wavelength of the CT band. PQDM-Met: $\lambda_{\text{max}} = 654$ nm in DMF; PQDM-C3OH: $\lambda_{\text{max}} = 658$ nm in DMF.^{2d}

2. 3. Conclusions

A series of novel zwitterionic chromophores (PeQDM) have been designed and synthesized. Optimal synthetic conditions have been established and a plausible reaction mechanism is offered. X-ray crystallographic data and solvent-dependent Stokes shift along with negative solvatochromism and IR data confirm the highly charge-separated (zwitterionic) ground state of these chromophores in the solid state and in solution. In the solid state, chromophores form face to face anti-parallel H-aggregation with a large slip angle ($\theta = 64.5^\circ$) due to the stronger electrostatic interactions. Although PeQDM

chromophores show the larger first hyperpolarizabilities ($\beta_0 \sim 600 \times 10^{-30}$ esu) similar to those of PQDM chromophores, the most important feature is an additional functional group at the acceptor part, which makes complete site-isolation of chromophores possible by further functionalization of the donor and acceptor parts. Chromophores are also NIR fluorescent and sensitive to pH changes, which make them potential candidates for optical pH sensor applications.

2. 4. Experimental

Materials. 7,8-Di(methoxycarbonyl)-7,8-dicyanoquinodimethane (DMCQ) was synthesized according to the literature method.⁸ All other reagents and solvents were purchased from Aldrich and used as received. Britton-Robinson (BR) buffers were prepared by mixing appropriate amount of 0.2 M NaOH aqueous solution to a mixture including equimolar amount of orthophosphoric acid, acetic acid and boric acid aqueous solutions (0.04 M each).

Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Bruker AMX 400 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 or a Bomen Michelson 120 FTIR spectrometer. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer. Thermogravimetric analysis (TGA) was carried out in nitrogen on a TA DSC Q100 and Hi-Res TGA 2950 thermogravimetric analyzer.

Preparation of 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyanoquinodimethane [D(E-OH)CQ]

1,4-Phenylenediacetonitrile (6.24 g, 40 mmol) was dissolved in 140 mL of anhydrous tetrahydrofuran and then the mixture was cooled down to -78°C . To the mixture, LDA (2M, 60 mL, 120 mmol) solution was added slowly with mechanical stirring, and then anhydrous tetrahydrofuran solution (80 mL) of ethylene carbonate (9.00 g, 100 mmol) was slowly added. The reaction was continued until it warmed up to room temperature. The reaction mixture was acidified with 2N hydrochloric acid. The organic phase was separated and the water layer was extracted with ethyl acetate twice. The organic phases were combined and washed with saturated sodium chloride solution three times and dried over anhydrous sodium sulfate. After the solvent was removed in vacuum, the product was recrystallized from chloroform to afford 5.50 g of white solids (51% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.55 (s, 4H), 5.74 (s, 2H), 4.88 (br, 2H), 4.18 (m, 4H), 3.59 (t, $J = 4.8$ Hz, 4H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 165.2, 131.6, 129.9, 116.5, 68.3, 58.5, and 42.0. IR (Neat, cm^{-1}): 3422 ($\nu_{\text{O-H}}$), 2255 ($\nu_{\text{C}\equiv\text{N}}$), 1746 ($\nu_{\text{C=O}}$). 7,8-Di(hydroxyethoxycarbonyl)-7,8-dicyano-*p*-xylene was oxidized according to the literature method⁸ to yield 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyanoquinodimethane as yellow solids in 50% yield. This compound is not stable and can polymerize easily in

solution. Therefore, the yellow solids were subjected for IR and MS analyses. IR (KBr, cm^{-1}): 3407 ($\nu_{\text{O-H}}$), 2210 ($\nu_{\text{C}\equiv\text{N}}$), 1717($\nu_{\text{C=O}}$); MS (EI, M/Z): 330(M^+).

Preparation of picolinium halides

N-Hexyl-4-methylpyridinium bromide

A solution of 4-picoline (4.65 g, 50 mmol), 1-bromohexane (9.90 g, 60 mmol) and 30 mL of acetonitrile was refluxed for three hours and then cooled to room temperature. Then the cooled viscous mixture was slowly added into 100 mL of ethyl ether with vigorously stirring. Then the resulting mixture was kept standing for a while and the upper ether layer was decanted. The residual viscous liquid was dissolved in 10 mL of acetonitrile and dispersed into 100 mL of ethyl ether again. This dissolve-disperse procedure was repeated two more times in order to remove residual starting materials. The resulting viscous liquid was dried in vacuum and the product as off-white wax was obtained (11.82 g, 92% yield). This product is highly hygroscopic and needs to be preserved in a desiccator. ^1H NMR (400 MHz, DMSO-d_6): δ 9.07 (d, $J = 6.6$ Hz, 2H), 8.04 (d, $J = 6.2$ Hz, 2H), 4.61 (t, $J = 7.4$ Hz, 2H), 2.63 (s, 3H), 1.90 (m, 2H), 1.28 (m, 6H), 0.85 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.6, 143.7, 128.2, 59.7, 30.5, 30.4, 24.9, 21.7, 21.3, 13.7.

N-Hydroxyethyl-4-methylpyridinium bromide

The similar procedure for the synthesis of N-hexyl-4-methylpyridinium bromide: a mixture of 4-picoline (12.66 g, 136 mmol), 2-bromoethanol (17.00 g, 136 mmol) and 60 mL of acetonitrile was refluxed for three hours to afford the product as off-white wax (29.01 g, 98% yield). This product is also highly hydroscopic and needs to be preserved in a desiccator. ^1H NMR (400 MHz, DMSO- d_6): δ 8.89 (d, J = 6.7 Hz, 2H), 8.00 (d, J = 6.4 Hz, 2H), 5.21 (br, 1H), 4.62 (t, J = 5.0 Hz, 2H), 3.84 (t, J = 5.0 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 158.7, 144.0, 127.8, 62.1, 59.9, 21.3.

N-Hydroxypropyl-4-methylpyridinium bromide

The similar procedure for the synthesis of N-hexyl-4-methylpyridinium bromide: a mixture of 4-picoline (12.66 g, 136 mmol), 3-bromopropanol (18.90 g, 136 mmol) and 60 mL of acetonitrile was refluxed for three hours to afford the product as viscous liquid (30.00 g, 95% yield). This product is also highly hydroscopic and needs to be preserved in a desiccator. ^1H NMR (300 MHz, DMSO- d_6): δ 8.96 (d, J = 6.0 Hz, 2H), 7.98 (d, J = 6.0 Hz, 2H), 4.62 (t, J = 6.0 Hz, 2H), 3.42 (t, J = 6.0 Hz, 2H), 3.40 (br, 1H), 2.60 (s, 3H), 2.04 (p, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 159.1, 144.4, 128.7, 58.2, 57.5, 33.7, 21.8.

N-Benzyl-4-methylpyridinium chloride

A solution of benzyl chloride (2.53 g, 20 mmol), 4-picoline (1.86 g, 20 mmol) and 20 mL of acetonitrile was refluxed for three hours and then cooled to room temperature and frozen in a refrigerator. Pale pink crystals precipitated from the solution were filtered and washed with ethyl ether three times (3×5 mL) to afford 4.09 g of product (92% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.17 (br, 2H), 8.02 (d, $J = 6.2$ Hz, 2H), 7.55 (d, $J = 6.2$ Hz, 2H), 7.43 (m, 3H), 5.86 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 159.0, 143.5, 134.3, 128.9, 128.8, 128.4, 61.9, 21.1.

N-(4-Hydroxymethyl)benzyl-4-methylpyridinium chloride

A solution of 4-(chloromethyl)benzyl alcohol (3.00 g, 19.2 mmol), 4-picoline (2.25 g, 24.1 mmol) and 20 mL of acetonitrile was refluxed for three hours and then cooled to room temperature. After the upper colorless liquid was decanted, 5 mL of methanol was added to dissolve the residual pale pink solid. Then the methanol solution was dispersed into 50 mL of ethyl ether to precipitate the product, which was collected and washed with ethyl ether three times (3×5 mL) to be 4.60 g (96% yield). ^1H NMR (300 MHz, DMSO- d_6): δ 9.19 (d, $J = 6.6$ Hz, 2H), 8.00 (d, $J = 6.3$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 5.85 (s, 2H), 5.43 (br, 1H), 4.47 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 159.7, 144.4, 144.2, 133.3, 129.1, 129.0, 127.5, 62.7, 62.5, 21.9.

1-2OH-4-methylpyridinium bromide

This compound was synthesized according to the reported method.^{7b} This product is also highly hygroscopic and needs to be preserved in a desiccator. ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.23 (s, 2H), 8.96 (d, *J* = 6.0 Hz, 2H), 7.94 (d, *J* = 6.0 Hz, 2H), 6.91 (d, *J* = 6.0 Hz, 4H), 6.67 (d, *J* = 6.0 Hz, 4H), 4.62 (t, *J* = 6.0 Hz, 2H), 4.03 (t, *J* = 6.0 Hz, 2H), 2.54 (s, 3H), 2.14-2.23 (m, 4H), 1.87 (t, *J* = 6.0 Hz, 2H), 1.43 (s, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 173.4, 159.3, 155.5, 144.4, 139.6, 128.7, 128.2, 115.2, 61.6, 58.1, 44.2, 36.5, 30.1, 29.9, 27.8, 21.8.

Synthesis of PeQDM chromophores (with an example of PeQDM-Hex)

PeQDM-Hex

To a refluxed suspension of DMCQ (0.5000 g, 1.85 mmol), N-hexyl-4-methylpyridinium bromide (0.2387 g, 0.925 mmol) and 25 mL of anhydrous methanol, 5 mL of methanol solution of DBU (0.2812 g, 1.85 mmol) was added drop-wise in 30 min. The reaction was monitored by UV-Vis spectra of the reaction mixture in DMF and typically the reaction can be finished within 4-5 h after completion of adding the DBU

solution. To do this, a small amount of reaction mixture was taken out and dissolved in DMF for UV-Vis measurement. The reaction was stopped when the charge-transfer band of chromophore (~670 nm) was much stronger than the characteristic peaks of the radical anion (~430, 740 and 830 nm). After the reaction mixture was cooled to room temperature, the solid collected by filtration was washed with methanol and ethyl ether three times, respectively, to afford 0.17 g of product (48% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 8.96 (d, J = 6.7 Hz, 2H), 8.31 (d, J = 6.7 Hz, 2H), 7.84 (s, 1H), 7.69 (br, 2H), 7.57 (d, J = 9.1 Hz, 2H), 4.49 (t, J = 7.3 Hz, 2H), 3.50 (s, 3H), 1.92 (m, 2H), 1.30 (s, 6H), 0.87 (t, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 167.4, 149.5, 147.2, 144.1, 126.7, 125.3, 125.0, 121.2, 120.8, 119.8, 116.9, 59.9, 49.1, 30.6, 30.4, 25.1, 21.8, 13.8; MS (ESI, CH_3CN , M/Z): 388 ($M+H^+$); IR (KBr, cm^{-1}): 2227 and 2155 ($\nu_{\text{C}\equiv\text{N}}$), 1752 ($\nu_{\text{C}=\text{O}}$).

PeQDM-C2OH

The same procedure as PeQDM-Hex: N-hydroxyethyl-4-methylpyridinium bromide (0.20 g, 0.925 mmol) was used to afford 0.14 g of product (44% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 8.89 (d, J = 6.9 Hz, 2H), 8.31 (d, J = 6.9 Hz, 2H), 7.86 (s, 1H), 7.69 (br, 2H), 7.57 (d, J = 9.2 Hz, 2H), 5.27 (t, J = 5.3 Hz, 1H), 4.55 (t, J = 4.6 Hz, 2H), 3.86 (m, 2H), 3.50 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 167.4, 149.6, 147.0, 144.5, 126.6, 125.3, 125.0, 124.7, 121.1, 120.7, 119.7, 116.8, 62.3, 59.9, 49.0; MS (ESI,

CH₃CN/DMF: v/v = 8/1, M/Z): 348 (M+H⁺); IR (KBr, cm⁻¹): 2226 and 2161 (ν_{C≡N}), 1751(ν_{C=O}).

P-PeQDM-C2OH

P-PeQDM-C2OH was prepared by adding an excess of HCl to the DMF solution of PeQDM-C2OH and precipitated from ethyl ether. The yield was quantitative. ¹H NMR (400 MHz, DMSO-d₆): δ 9.17 (d, J = 6.5 Hz, 2H), 8.49 (d, J = 6.5 Hz, 2H), 8.45 (s, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 5.91 (s, 1H), 4.71 (br, 2H), 3.90 (t, J = 4.5 Hz, 2H), 3.76 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆): δ 165.4, 148.8, 145.6, 137.5, 133.6, 132.8, 129.3, 127.5, 126.3, 118.5, 116.4, 115.9, 63.0, 53.8, 42.0; MS (ESI, Methanol, M/Z): 348 (M+H⁺); IR (KBr, cm⁻¹): 2252 and 2224 (ν_{C≡N}), 1752(ν_{C=O}).

PeQDM-C3OH

The same procedure as PeQDM-Hex: N-hydroxypropyl-4-methylpyridinium bromide (0.22 g, 0.925 mmol) was used to afford 0.16 g of product (48% yield). ¹H NMR (300 MHz, DMSO-d₆): δ 8.93 (d, J = 6.9 Hz, 2H), 8.29 (d, J = 6.9 Hz, 2H), 7.83 (s, 1H), 7.68 (br, 2H), 7.56 (d, J = 9.3 Hz, 2H), 4.77 (t, J = 4.8 Hz, 1H), 4.57 (t, J = 6.9 Hz, 2H), 3.44-3.50 (m, 5H), 2.07 (m, 2H); ¹³C NMR (75 MHz, DMSO-d₆): δ 167.9, 149.5, 147.6, 144.9, 127.2, 125.8, 125.5, 125.4, 121.6, 121.3, 120.2, 117.4, 61.3, 58.3, 57.7, 49.6, 33.5;

MS (ESI, CH₃CN/DMF: v/v = 8/1, M/Z): 362 (M+H⁺); IR (KBr, cm⁻¹): 2229 and 2148 (ν_{C≡N}), 1749 (ν_{C=O}).

PeQDM-Ben

The same procedure as PeQDM-Hex: N-benzyl-4-methylpyridinium chloride (0.20 g, 0.925 mmol) was used to afford 0.17 g of product (47% yield). ¹H NMR (400 MHz, DMSO-d₆): δ 9.05 (d, J = 6.8 Hz, 2H), 8.33 (d, J = 6.8 Hz, 2H), 7.84 (s, 1H), 7.69 (br, 2H), 7.43-7.59 (m, 7H), 5.75 (s, 2H), 3.51 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆): δ 167.3, 149.8, 147.2, 144.1, 134.3, 129.2, 129.1, 128.6, 126.7, 125.2, 124.8, 121.1, 120.7, 119.9, 116.8, 62.4, 61.1, 49.1; MS (ESI, CH₃CN, M/Z): 394 (M+H⁺); IR (KBr, cm⁻¹): 2226 and 2146 (ν_{C≡N}), 1750(ν_{C=O}).

PeQDM-BenOH

The same procedure as PeQDM-hex: N-(4-hydroxymethyl)benzyl-4-methylpyridinium chloride (0.23 g, 0.925 mmol) was used to afford 0.19 g of product (49% yield). ¹H NMR (300 MHz, DMSO-d₆): δ 9.01 (d, J = 6.3 Hz, 2H), 8.28 (d, J = 6.3 Hz, 2H), 7.79 (s, 1H), 7.67 (br, 2H), 7.55 (d, J = 9.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H),

5.71 (s, 2H), 5.25 (t, $J = 5.7$ Hz, 1H), 4.50 (d, $J = 5.7$ Hz, 2H), 3.49 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 167.9, 150.3, 147.7, 144.5, 144.4, 133.1, 130.0, 129.1, 127.6, 127.3, 125.7, 125.4, 121.7, 121.3, 120.4, 117.3, 62.9, 61.7, 49.7; MS (ESI, $\text{CH}_3\text{CN}/\text{DMF}$: v/v = 1/1, M/Z): 424 ($M+H^+$); IR (KBr, cm^{-1}): 2219 and 2157 ($\nu_{\text{C}\equiv\text{N}}$).

PeQDM-2OH

The same procedure as PeQDM-hex: 1-2OH-4-methylpyridinium bromide (0.46 g, 0.925 mmol) was used to afford 0.28 g of product (48% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.20 (s, 2H), 8.94 (d, $J = 6.8$ Hz, 2H), 8.30 (d, $J = 7.2$ Hz, 2H), 7.82 (s, 1H), 7.70 (br, 2H), 7.58 (d, $J = 9.3$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 4H), 6.64 (d, $J = 8.7$ Hz, 4H), 4.55 (t, $J = 6.9$ Hz, 2H), 4.06 (t, $J = 5.7$ Hz, 2H), 3.50 (s, 3H), 2.16-2.25 (m, 4H), 1.91 (t, $J = 8.0$ Hz, 2H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 172.7, 167.3, 154.9, 149.5, 147.1, 144.3, 139.0, 127.6, 126.7, 124.9, 124.7, 121.1, 120.7, 119.8, 116.8, 114.6, 61.0, 57.6, 49.0, 43.6, 35.9, 29.5, 29.2, 27.1; MS (ESI, CH_3CN , M/Z): 630 ($M+H^+$); IR (KBr, cm^{-1}): 2226 and 2155 ($\nu_{\text{C}\equiv\text{N}}$), 1733 ($\nu_{\text{C}=\text{O}}$).

PeQDM-C3OH-E-OH

The same procedure as PeQDM-Hex: a mixture of N-hydroxypropyl-4-methylpyridinium bromide (0.232 g, 1mmol), D(E-OH)CQ (0.660 g, 2 mmol) and DBU (0.304 g, 2mmol) was refluxed to afford 0.162 g of product (42% yield). ^1H NMR (300 MHz, DMSO- d_6): δ 8.93 (d, J = 6.0 Hz, 2H), 8.28 (d, J = 6.0 Hz, 2H), 7.82 (s, 1H), 7.68 (d, J = 9.0 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 4.77 (t, J = 6.0 Hz, 1H), 4.67 (t, J = 6.0 Hz, 1H), 4.56 (t, J = 6.0 Hz, 2H), 3.96 (t, J = 6.0 Hz, 2H), 3.53 (m, 2H), 3.45 (m, 2H), 2.06 (m, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 167.7, 149.9, 147.6, 144.8, 127.2, 125.7, 125.5, 125.3, 121.6, 121.4, 120.2, 117.4, 61.3, 60.4, 58.3, 57.7, 33.5; MS (ESI, Methanol/DMF: v/v = 1/1, M/Z): 392 ($\text{M}+\text{H}^+$); IR (KBr, cm^{-1}): 2225 and 2150 ($\nu_{\text{C}\equiv\text{N}}$), 1751 ($\nu_{\text{C}=\text{O}}$).

2. 5. References

- (1) (a) Robinson, B. H.; Dalton, L. R.; Harper, A. W.; Ren, A.; Wang, F.; Zhang, C.; Todorova, G.; Lee, M.; Aniszfeld, R.; Garner, S.; Chen, A.; Steier, W. H.; Houbrecht, S.; Persoons, A.; Ledoux, I.; Zyss, J.; Jen, A. K.-Y. *Chem. Phys.* **1999**, *245*, 35. (b) Zhang, C.; Dalton, L. R.; Oh, M.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043. (c) Spraul, B.; Suresh, S.; Sassa, T.; Ángeles Herranz, M.; Echegoyen, L.; Wada, T.; Perahia, D.; Smith, D. *Tetrahedron Lett.* **2004**, *45*, 3253.
- (2) (a) Szablewski, M.; Thomas, P. R.; Thornton, A.; Bloor, D.; Cross, G. H.; Cole, J. M.; Howard, J. A. K.; Malagoli, M.; Meyers, F.; Brédas, J.; Wenseleers, W.; Goovaerts, E. *J. Am. Chem. Soc.* **1997**, *119*, 3144. (b) Metzger, R. M.; Heimer, N. E.; Aswell, G. *J. Mol. Cryst. Liq. Cryst.* **1984**, *107*, 133. (c) Weir, C. A. M.; Hadizad, T.; Beaudin, A. M. R.; Wang, Z. Y. *Tetrahedron Lett.* **2003**, *44*, 4697. (d) Beaudin, A. M. R.; Song, N.; Men, L.; Gao, J. P.; Wang, Z. Y.; Szablewski, M.; Cross, G.; Wenseleers, W.; Campo, J.; Goovaerts, E. *Chem. Mater.* **2006**, *18*, 1079. (e) Kay, A. J.; Woolhouse, A. D.; Zhao, Y.; Clays, K. *J. Mater. Chem.* **2004**, *14*, 1321.
- (3) Kang, H.; Facchetti, A.; Jiang, H.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C.; Liu, Z.; Ho, S.; Brown, E. C.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 3267.
- (4) (a) Würther, F.; Yao, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 1978. (b) Würther, F.; Yao, S.; Debaerdemaeker, T.; Wortmann, R. *J. Am. Chem. Soc.* **2002**, *124*, 9431.

-
- (5) (a) Luo, J.; Liu, S.; Haller, M.; Liu, L.; Ma, H.; Jen, A. K.-Y. *Adv. Mater.* **2002**, *14*, 1763. (b) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2002**, *12*, 565.
- (6) (a) Ashwell, G. J. *Thin Solid Films* **1990**, *186*, 155. (b) Ashwell, G. J. Eur. Patent EP 0 391 631 A1, 1990.
- (7) (a) Song, N.; Men, L.; Gao, J. P.; Bai, Y.; Beaudin, A. M. R.; Yu, G.; Wang, Z. Y. *Chem. Mater.* **2004**, *16*, 3708. (b) Bai, Y.; Song, N.; Gao, J. P.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. Y. *J. Am. Chem. Soc.* **2005**, *127*, 2060.
- (8) (a) Iwatsuki, S.; Itoh, T.; Nishihara, K.; Furuhashi, H. *Chem. Lett.* **1982**, *4*, 517. (b) Hall, H. K., Jr.; Cramer, R. J.; Mulvaney, J. E. *Polym. Bull.* **1982**, *7*, 165. (c) Iwatsuki, S.; Itoh, T.; Iwai, T.; Sawada, H. *Macromolecules* **1985**, *18*, 2726.
- (9) Cole, J. C.; Cole, J. M.; Cross, G. H.; Farsari, M.; Howard, J. A. K.; Szablewski, M. *Acta Cryst.* **1997**, *B53*, 812.
- (10) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.
- (11) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
- (12) Smith, G. J.; Dunford, C. L.; Kay, A. J.; Woolhouse, A. D. *J. Photochem. Photobiol. A: Chem.* **2006**, *179*, 237.
- (13) (a) Zhang, Z.; Achilefu, S. *Org. Lett.* **2004**, *6*, 2067. (b) Zhang, Z.; Achilefu, S. *Chem. Commun.* **2005**, 5887.
- (14) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

Chapter 3 Synthesis and Characterization of Dendronized PeQDM

Chromophores

3. 1. Introduction

EO materials are routinely prepared by chromophore doping or covalently bonding into a polymer matrix and then poled to achieve a noncentrosymmetric order. There are two major problems encountered in developing high-performance EO materials containing zwitterionic chromophores: low chromophore loading and aggregate formation in a polymer. At a low loading level, the maximal EO activity (r_{33}) can not be high since it increases linearly with chromophore number density (Equation 1) when intermolecular interactions are weak.¹ On the other hand, re-orientation of aggregates by poling to achieve macroscopic nonlinearity is often inefficient due to the strong electrostatic interactions between the dipoles and possible π - π stacking.

$$r_{33} = 2Nf\beta \langle \cos^3 \theta \rangle / n^4 \quad (1)$$

N is the chromophore number density, f accounts for local field factors from the dielectric nature of the environment surrounding the chromophores, β is the molecular first hyperpolarizability, $\langle \cos^3 \theta \rangle$ represents noncentrosymmetric order parameter and n is the index of refraction.

One of the strategies aimed at enhancing EO activity is introduction of bulky substituent groups into the chromophore to prevent aggregation. These bulky substituents are also designed to impact solubility to chromophores without sacrifice of their thermostability. Moreover, with large bulky groups such as dendritic substituents, it is possible for the chromophores to form films. This chapter describes further

functionalization of the PeQDM chromophores with large dendrons. Furthermore, solubility and aggregation behavior of single dendron-modified and double dendron-modified chromophores will be discussed.

3. 2. Synthesis and characterization of ES-dendron

It was found by our group that high-quality films can be prepared by doping PQDM into a commercially available polymer, polyethersulfone (PES), at only the 1 wt% doping level.² The same was true for PeQDM as the doping level could not be over 5 wt% in PES (see chapter 5). Since like dissolves like, an ethersulfone (ES)-dendron with a pendent acid group was designed for structurally modifying all the PeQDM chromophores having the hydroxyl groups.

ES-dendron was synthesized according to the method for the preparation of PES containing a pendent acid group³ (Scheme 3.1). ES-dendron was characterized by ¹H NMR, ¹³C NMR, IR and MS analyses.

Scheme 3.1. Synthetic route to ES-dendron

Figure 3.1. ^1H NMR spectrum (300 MHz, DMSO-d_6) of ES-dendron

The ^1H NMR spectrum of ES-dendron (Figure 3.1) displays proton resonances (ppm) at 12.10 (br, 1H), 7.91-7.95 (m, 8H), 7.54-7.70 (m, 6H), 7.25 (d, $J = 8.7$ Hz, 4H), 7.04-7.12 (dd, $J = 8.7$ Hz, 8H), 2.35 (t, $J = 7.8$ Hz, 2H), 2.01 (t, $J = 7.8$ Hz, 2H), 1.59 (s, 3H). Acidic proton was assigned to the resonance at 12.10 ppm. In its ^{13}C NMR spectrum, all the expected 17 resonances of the carbons were observed at 174.9, 162.0, 152.9, 145.7, 142.0, 135.2, 134.0, 130.5, 130.2, 129.4, 127.6, 120.3, 118.3, 45.3, 36.6, 30.3 and 27.4 ppm. The carbon of the carbonyl group was found at 174.9 ppm. The IR and MS data also support the molecular structure of ES-dendron. The $\nu_{\text{C=O}}$ of ES-dendron was observed at 1710 cm^{-1} (Figure 3.2). MS spectrum (Figure 3.3) showed a base peak at 736 M/Z , corresponding to the molecular ion (+18) peak of ES-dendron.

Figure 3.2. IR spectrum (Neat, cm⁻¹) of ES-Dendron

Figure 3.3. MS spectrum (ESI, CH₃CN, M/Z) of ES-dendron: 736 (M+NH₄⁺)

ES-dendron was found to be thermally stable up to 386 °C and had a glass transition temperature (T_g) of 86 °C (Figure 3.4). By modifying a zwitterionic chromophore with ES-dendron, it is highly possible for a dendronized chromophore to have a T_g . EO materials with a high T_g are expected to have better temporal stability.

Figure 3.4. TGA (left) and DSC (right) traces of ES-dendron

3. 3. Synthesis and characterization of dendronized chromophores

The ester bond was formed between ES-dendron and PeQDM chromophore at room temperature in the presence of a coupling reagent, 1-[3-(2-dimethylamino)propyl]-3-ethylcarbodiimide (EDC), and 4-(N,N-dimethylamino)pyridine (DMAP). Three types of dendronized PeQDM were synthesized: ES-PeQDM-1, ES-PeQDM-2 and ES-PeQDM-3. The first two have one or two ES-dendrons anchored only at the donor part of the chromophores. The third one has an ES-dendron anchored at both the donor and acceptor parts. If high-quality films could be made from the dendronized PeQDM chromophores, they would have the highest number density of active chromophore components.

Synthesis and characterization of ES-PeQDM-1

The first series of dendronized PeQDM (ES-PeQDM-1) were prepared by reacting ES-dendron with the corresponding PeQDM-C2OH, PeQDM-C3OH and PeQDM-BenOH chromophores, respectively (Scheme 3.2). All the dendronized PeQDM have been characterized by ^1H NMR, ^{13}C NMR, IR, MS and UV-Vis analyses.

Scheme 3.2. Synthetic route to ES-PeQDM-1

As an example, the ^1H NMR spectrum of ES-PeQDM-1a (Figure 3.5) displays proton resonances (ppm) at δ 8.94 (d, J = 6.7 Hz, 2H), 8.29 (d, J = 6.7 Hz, 2H), 7.93-7.95 (m, 8H), 7.79 (s, 1H), 7.53-7.70 (m, 10H), 7.05-7.23 (m, 12H), 4.77 (br, 2H), 4.49 (br, 2H), 3.52 (s, 3H), 2.31 (t, J = 6.8 Hz, 2H), 2.10 (t, J = 7.7 Hz, 2H), 1.57 (s, 3H). Protons on

pyridyl ring, double bond and aliphatic chain are assigned (Figure 3.5); any other unlabelled peaks are for the aromatic protons. The resonances of the acid (at 12.10 ppm) and hydroxyl (at 5.27 ppm) protons of the starting materials disappeared (Figure 3.5). Its ^{13}C NMR spectrum also displays the expected peaks. The IR spectrum (Figure 3.6) shows $\nu_{\text{C=O}}$ at 1736 cm^{-1} for the ester, rather than $\nu_{\text{C=O}}$ at 1710 cm^{-1} for the acid. MS (ESI+ H^+) spectrum (Figure 3.7) shows a base peak at 1048 M/Z, corresponding to the M+1 peak of ES-PeQDM-1a.

Figure 3.5. ^1H NMR spectrum (400 MHz, DMSO-d_6) of ES-PeQDM-1a

Figure 3.6. IR spectrum (Neat, cm⁻¹) of ES-PeQDM-1a

Figure 3.7. MS spectrum (ESI, CH₃CN, M/Z) of ES-PeQDM-1a: 1048 (M+H⁺)

This series of dendronized chromophores exhibited T_g in a range of 120 °C to 138 °C (Figure 3.8). It was found that the T_g is related to the linking spacer between ES-dendron and chromophore. Going from a two-carbon spacer (ES-PeQDM-1a) to a three-carbon spacer (ES-PeQDM-1b), the T_g decreases from 138 °C to 120 °C. With a benzyl ring, the T_g is up to 129 °C (ES-PeQDM-1c). ES-PeQDM-1s also have good thermostability (Table 3.1).

Figure 3.8. DSC traces of ES-PeQDM-1

Table 3.1. Decomposition temperatures (T_d) of PeQDM and dendronized PeQDM

PeQDM	T_d^a (°C)	Dendrimer	T_d^a (°C)
PeQDM-C2OH	215	ES-PeQDM-1a	199
PeQDM-C3OH	238	ES-PeQDM-1b	215
PeQDM-BenOH	222	ES-PeQDM-1c	208
PeQDM-2OH	234	ES-PeQDM-2	236
PeQDM-C3OH-E-OH	183	ES-PeQDM-3	238

^a Determined by 5% weight loss by the thermogravimetric analysis (TGA) with a heating rate of 5 °C min⁻¹ under nitrogen atmosphere.

It was found that the absorptions ($\lambda_{\max}$) of ES-PeQDM-1a and ES-PeQDM-1b were red-shifted compared to PeQDM (Table 3.2). This is likely due to a lower dielectric environment created by the ES-dendron compared to DMF. Meanwhile, it was also found that the doping level of ES-PeQDM-1 in PES can be greatly increased (see chapter 5). However, they still have rather poor solubility in common organic solvents such as THF, 1,2-dichloroethane and chloroform and can not form high-quality of films, which indicate that it is necessary to introduce more ES-dendron in order to further improve the solubility and film-forming property.

Table 3.2. Charge-transfer bands ($\lambda_{\max}$) of PeQDM and ES-PeQDM in DMF

PeQDM	$\lambda^1_{\max}$ (nm)	Dendrimer	$\lambda^2_{\max}$ (nm)	$\Delta\lambda = \lambda^2 - \lambda^1$ (nm)
PeQDM-C2OH	668	ES-PeQDM-1a	691	23
PeQDM-C3OH	671	ES-PeQDM-1b	680	9
PeQDM-BenOH	691	ES-PeQDM-1c	691	0
PeQDM-2OH	677	ES-PeQDM-2	691	14
PeQDM-C3OH-E-OH	669	ES-PeQDM-3	676	7

Synthesis and characterization of ES-PeQDM-2

By introducing one more dendron to the donor part of PeQDM (Figure 3.9), ES-PeQDM-2 was prepared by reacting ES-dendron with PeQDM-2OH.

Figure 3.9. Molecular structure of ES-PeQDM-2

ES-PeQDM-2 has been characterized by ^1H NMR, ^{13}C NMR, IR, MS and UV-Vis methods. ^1H NMR spectrum of ES-PeQDM-2 (Figure 3.10) displays proton resonances (ppm) at δ 8.93 (d, $J = 6.6$ Hz, 2H), 8.24 (d, $J = 6.6$ Hz, 2H), 7.91-7.95 (m, 16H), 7.77 (s, 1H), 7.53-7.69 (m, 16H), 7.29 (d, $J = 8.7$ Hz, 8H), 6.98-7.15 (m, 24H), 4.56 (br, 2H), 4.07 (br, 2H), 3.47 (s, 3H), 2.18-2.42 (m, 4H), 1.89 (br, 2H), 1.65 (s, 6H), 1.52 (s, 3H). Proton resonances of the acid and hydroxyl groups of the two starting materials were not observed, indicating the formation of the ester bond. MS ($\text{ESI}+\text{H}^+$) spectrum (Figure 3.11) shows the $M+1$ peak of ES-PeQDM-2 at 2030 M/Z .

Figure 3.10. ^1H NMR spectrum (300MHz, DMSO-d_6) of ES-PeQDM-2

Figure 3.11. MS spectrum (ESI, $\text{THF/CH}_3\text{CN} = 1/1$ (V/V), M/Z) of ES-PeQDM-2: 2030 ($\text{M}+\text{H}^+$)

ES-PeQDM-2 was also investigated by TGA method, showing its decomposition temperature up to 236 °C (Table 3.1). Its glass transition temperature (T_g) determined by DSC analysis was found to be 132 °C (Figure 3.12), indicating that unlike PeQDM, ES-PeQDM-2 is amorphous in the solid state.

Figure 3.12. DSC trace of ES-PeQDM-2

As expected, ES-PeQDM-2 exhibited the largely enhanced solubility in the aforementioned common organic solvents in comparison with PeQDM and ES-PeQDM-1 and could form thin films by direct casting or spin-coating. Subsequently, ES-PeQDM-2 was characterized by UV-Vis spectroscopy in solutions and as a thin film (Figure 3.13). A similar red shift in absorption ($\Delta\lambda = 14$ nm) was observed for ES-PeQDM-2 (Table 3.2). A negative solvatochromism is clearly shown for ES-PeQDM-2 (Figure 3.13), indicating that ES-dendron doesn't affect the zwitterionic nature of chromophore. Instead of one charge-transfer band in DMF and THF, there are three peaks in less polar chloroform, which is due to the head-to-tail J-aggregation of the chromophore (see

chapter 5 for definition). Interestingly, the film spin-coated from the chloroform solution displays a blue shift in absorption ($\lambda_{\text{max}} = 524 \text{ nm}$), which can be attributed to the face-to-face anti-parallel H-aggregation (see chapter 5 for more discussion)).⁴ Therefore, ES-PeQDM-2 can still form aggregates both in solution and in the solid state, even with two dendrons attached. Either J or H-aggregation adversely affects the poling efficiency, which is generally considered as a reason for the loss of the EO activity.⁵

Figure 3.13. UV-Vis spectra of ES-PeQDM-2: (a) film on an ITO coated glass ($\lambda_{\text{max}} = 524 \text{ nm}$); (b) DMF solution ($\lambda_{\text{max}} = 691 \text{ nm}$); (c) THF solution ($\lambda_{\text{max}} = 820 \text{ nm}$); (d) chloroform solution ($\lambda_{\text{max}} = 660, 787, 870 \text{ nm}$)

Synthesis and characterization of ES-PeQDM-3

As previously discussed, although ES-PeQDM-2 with two ES-dendrons can form a good film, the observed H-aggregation needs to be eliminated for EO applications. It seems that the introduction of ES-dendrons only at the donor part of the chromophore is

not enough to keep polar chromophores apart from each other. Therefore, ES-dendron was introduced at both the donor and acceptor parts of PeQDM (Scheme 3.3).

Scheme 3.3. Synthetic route to ES-PeQDM-3

The ^1H NMR spectrum of ES-PeQDM-3 (Figure 3.14) displays proton resonances (ppm) at δ 8.95 (d, $J = 6.0$ Hz, 2H), 8.26 (d, $J = 6.0$ Hz, 2H), 7.92 (m, 16H), 7.77 (s, 1H), 7.50-7.65 (m, 16H), 7.21 (m, 8H), 6.97-7.09 (m, 16H), 4.58 (br, 2H), 4.16 (br, 2H), 4.08 (br, 2H), 2.20-2.45 (m, 6H), 2.11 (br, 2H), 1.97 (br, 2H), 1.57 (s, 3H), 1.55 (s, 3H). The formation of the new ester bond was indicated by disappearance of proton resonances of the acid and hydroxyl groups, and supported by the IR and ^{13}C NMR data (see experimental section). ES-PeQDM-3 exhibits a higher thermostability with T_d up to 238 $^\circ\text{C}$ compared to PeQDM-C3OH-E-OH ($T_d = 183$ $^\circ\text{C}$) (Table 3.2). The T_g (122 $^\circ\text{C}$) of ES-PeQDM-3 (Figure 3.15) is close to that of ES-PeQDM-1b ($T_g = 120$ $^\circ\text{C}$). Considering the

structural difference between ES-PeQDM-1b and ES-PeQDM-3, it seems that the linking spacer at the donor part affects the T_g the most. Thus, the higher T_g (132 °C) of ES-PeQDM-2 compared to ES-PeQDM-3 is due to a more rigid spacer.

Figure 3.14. ^1H NMR spectrum (300 MHz, DMSO-d_6) of ES-PeQDM-3

Figure 3.15. DSC trace of ES-PeQDM-3

Like ES-PeQDM-2, ES-PeQDM-3 is also soluble in common organic solvents. The similar J-aggregation was also observed in chloroform for ES-PeQDM-3 (Figure 3.16). However, the spin-coated film of ES-PeQDM-3 displays the absorption ($\lambda_{\max}$) at 614 nm, which is red-shifted 102 nm compared to ES-PeQDM-2 (Figure 3.17). Apparently, molecular interactions are different for ES-PeQDM-2 and ES-PeQDM-3 and there is definitely no H-aggregation for the film of ES-PeQDM-3 (see chapter 5 for more discussion). In the UV-Vis spectrum of ES-PeQDM-3, there is a shoulder at the longer wavelength (~ 750 nm), which is possibly due to a small amount of J-aggregation.

Figure 3.16. UV-Vis spectra of ES-PeQDM-3 in solution: a-DMF ($\lambda_{\max} = 676$ nm), b-acetone ($\lambda_{\max} = 711$ nm), c-1, 2-dichloroethane ($\lambda_{\max} = 780$ nm), d-THF ($\lambda_{\max} = 800$ nm), e-chloroform ($\lambda_{\max} = 656, 789, 849$ nm).

Figure 3.17. UV-Vis spectra of spin-coated films: (a) ES-PeQDM-2 and (b) ES-PeQDM-

3

3. 4. Conclusions

All the hydroxyl-containing PeQDM chromophores (chapter 2) have been further modified with ES-dendron. The dendronized PeQDMs exhibit glass transition temperatures and higher thermostability and are more soluble in organic solvents or in a polymer matrix (PES) than PeQDM. The more ES-dendron is introduced, the more soluble of a dendronized PeQDM is. Introduction of bulky ES-dendron only at the donor part of PeQDM can not effectively diminish strong electrostatic interactions or J-aggregation in solution and H-aggregation in the solid state. With ES-dendron anchored at both the donor and acceptor parts, anti-parallel H-aggregation is completely eliminated in the solid state, although J-aggregation still exists.

3. 5. Experimental

Materials. All the reagents and solvents were purchased from Aldrich and used as received unless otherwise stated. Anhydrous N,N-dimethylacetamide (DMAC) and N-methyl pyrrolidinone (NMP) were dried by calcium hydride; vacuum distilled and stored over 4 Å molecular sieves.

Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Bruker AMX 400 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 or a Bomen Michelson 120 FTIR spectrometer. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in nitrogen on a TA DSC Q100 and Hi-Res TGA 2950 thermogravimetric analyzer.

Preparation of ES-dendron

4-Chlorophenyl phenyl sulfone (3.00 g, 11.9 mmol), 4,4'-bis(4-hydroxyphenyl)valeric acid (1.43 g, 5.0 mmol), anhydrous potassium carbonate (2.07 g, 15 mmol), 20 mL of DMAC and 40 mL of toluene were charged in a 100 mL of three-necked flask. The reaction mixture was purged with nitrogen for half an hour at room temperature and was then heated to reflux with stirring while water was removed by azeotropic distillation with toluene. After the reaction mixture was heated for two days at 180 °C, it was cooled to room temperature and acidified with HCl (1M) and extracted with ethyl acetate. The

crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford 2.45 g of white solids (68% yield). ^1H NMR (300 MHz, DMSO- d_6): δ 12.10 (br, 1H), 7.91-7.95 (m, 8H), 7.54-7.70 (m, 6H), 7.25 (d, J = 8.7 Hz, 4H), 7.04-7.12 (dd, J = 8.7 Hz, 8H), 2.35 (t, J = 7.8 Hz, 2H), 2.01 (t, J = 7.8 Hz, 2H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 174.9, 162.0, 152.9, 145.7, 142.0, 135.2, 134.0, 130.5, 130.2, 129.4, 127.6, 120.3, 118.3, 45.3, 36.6, 30.3, 27.4; MS (ESI, CH_3CN , M/Z): 736 ($M+\text{NH}_4^+$); IR (Neat, cm^{-1}): 1710 ($\nu_{\text{C=O}}$).

Preparation of ES-PeQDM (with an example of ES-PeQDM-1a)

ES-PeQDM-1a. A mixture of PeQDM-C2OH (347 mg, 1.0 mmol), ES-dendron (789 mg, 1.1 mmol), DMAP (201 mg, 1.6 mmol), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (288 mg, 1.5 mmol) and 9 mL of NMP was stirred at room temperature for 1 day. The mixture was then precipitated into an excess of methanol and the crude product was collected by centrifugation. The crude product was washed by methanol and ethyl acetate three times, consecutively, to give 0.65 g of pure product in 62% yield. ^1H NMR (400 MHz, DMSO- d_6): δ 8.94 (d, J = 6.7 Hz, 2H), 8.29 (d, J = 6.7 Hz, 2H), 7.93-7.95 (m, 8H), 7.79 (s, 1H), 7.53-7.70 (m, 10H), 7.05-7.23 (m, 12H), 4.77 (br, 2H), 4.49 (br, 2H), 3.52 (s, 3H), 2.31 (t, J = 6.8 Hz, 2H), 2.10 (t, J = 7.7 Hz, 2H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 172.2, 167.3, 161.4, 152.4, 149.9, 147.3, 144.9, 144.6, 141.4, 134.6, 133.5, 130.0, 129.6, 128.8, 127.0, 126.8, 124.9, 124.7, 121.1, 120.8, 120.0, 119.8, 117.7, 116.8, 62.3, 61.2, 58.5, 49.1, 44.6, 35.7, 29.5, 26.8; MS (ESI, CH_3CN , M/Z): 1048 ($M+\text{H}^+$); IR (Neat, cm^{-1}): 2219 and 2161 ($\nu_{\text{C}\equiv\text{N}}$), 1736 ($\nu_{\text{C=O}}$).

ES-PeQDM-1b. Yield: 65%. ^1H NMR (300 MHz, DMSO- d_6): δ 8.94 (d, J = 6.9 Hz, 2H), 8.27 (d, J = 6.9 Hz, 2H), 7.92-7.96 (m, 8H), 7.80 (s, 1H), 7.52-7.71 (m, 10H), 7.03-7.23 (m, 12H), 4.56 (t, J = 6.3 Hz, 2H), 4.08 (t, J = 5.4 Hz, 2H), 3.50 (s, 3H), 2.23-2.31 (m, 4H), 1.95-2.00 (m, 2H), 1.57 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 173.0, 167.9, 161.9, 152.9, 150.1, 147.7, 145.4, 144.9, 142.0, 135.2, 134.0, 130.5, 130.2, 129.3, 127.6, 127.2, 125.4, 125.3, 121.6, 121.3, 120.4, 120.3, 118.3, 117.4, 61.7, 61.6, 58.2, 49.6, 45.1, 36.2, 30.0, 29.7, 27.4; MS (ESI, DMF/Methanol: v/v = 1/1, M/Z): 1062 ($M+H^+$); IR (KBr, cm^{-1}): 2219 and 2160($\nu_{\text{C}\equiv\text{N}}$), 1737 ($\nu_{\text{C}=\text{O}}$).

ES-PeQDM-1c. Yield: 65%. ^1H NMR (300 MHz, DMSO- d_6): δ 9.01 (d, J = 6.9 Hz, 2H), 8.30 (d, J = 6.6 Hz, 2H), 7.92-7.95 (m, 8H), 7.81 (s, 1H), 7.40-7.74 (m, 14H), 7.04-7.26 (m, 12H), 5.73 (br, 2H), 5.05 (br, 2H), 3.50 (s, 3H), 2.40 (t, J = 7.5 Hz, 2H), 2.15 (t, J = 7.5 Hz, 2H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 173.1, 167.9, 161.9, 152.9, 150.4, 147.8, 145.5, 144.6, 142.0, 137.8, 135.2, 134.5, 134.0, 130.5, 130.2, 129.4, 129.1, 127.6, 127.3, 125.7, 125.4, 125.3, 121.7, 121.3, 120.5, 120.3, 118.3, 117.3, 65.5, 62.6, 49.6, 45.3, 36.3, 30.1, 27.4; MS (ESI, Acetonitrile, M/Z): 1124 ($M+H^+$); IR (KBr, cm^{-1}): 2218 and 2159($\nu_{\text{C}\equiv\text{N}}$), 1733 ($\nu_{\text{C}=\text{O}}$).

ES-PeQDM-2

Similar procedure for the synthesis of ES-PeQDM-1a using PeQDM-2OH. Yield: 75%. ^1H NMR (300 MHz, DMSO- d_6): δ 8.93 (d, J = 6.6 Hz, 2H), 8.24 (d, J = 6.6 Hz, 2H), 7.91-7.95 (m, 16H), 7.77 (s, 1H), 7.53-7.69 (m, 16H), 7.29 (d, J = 8.7 Hz, 8H), 6.98-7.15 (m, 24H), 4.56 (br, 2H), 4.07 (br, 2H), 3.47 (s, 3H), 2.18-2.42 (m, 4H), 1.89 (br, 2H), 1.65 (s, 6H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 173.0, 172.1, 167.9, 162.0,

152.9, 150.1, 148.9, 147.7, 146.1, 145.5, 144.9, 142.0, 135.2, 134.0, 130.5, 130.2, 129.4, 128.3, 127.6, 127.3, 125.7, 125.4, 125.3, 121.8, 121.6, 121.3, 120.4, 118.3, 117.4, 60.2, 49.6, 45.3, 45.1, 36.2, 30.3, 27.5, 14.5; MS (ESI, THF/CH₃CN = 1/1 (V/V), M/Z): 2030 (M+H⁺); IR (Neat, cm⁻¹): 2222 and 2158 ($\nu_{\text{C}\equiv\text{N}}$), 1747 ($\nu_{\text{C}=\text{O}}$).

ES-PeQDM-3

Similar procedure to the synthesis of ES-PeQDM-1a using PeQDM-C3OH-E-OH. Yield: 69%. ¹H NMR (300 MHz, DMSO-d₆): δ 8.95 (d, J = 6.0 Hz, 2H), 8.26 (d, J = 6.0 Hz, 2H), 7.92 (m, 16H), 7.77 (s, 1H), 7.50-7.65 (m, 16H), 7.21 (m, 8H), 6.97-7.09 (m, 16H), 4.58 (br, 2H), 4.16 (br, 2H), 4.08 (br, 2H), 2.20-2.45 (m, 6H), 2.11 (br, 2H), 1.97 (br, 2H), 1.57 (s, 3H), 1.55 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆): δ 173.2, 172.0, 167.2, 162.0, 161.9, 152.9, 152.8, 150.0, 147.5, 145.6, 145.4, 144.9, 142.0, 135.2, 135.1, 134.0, 130.5, 130.2, 129.4, 129.3, 128.3, 127.6, 127.2, 125.7, 125.4, 125.2, 121.8, 121.5, 120.3, 118.3, 118.2, 117.3, 65.4, 63.5, 61.7, 60.2, 59.6, 58.2, 45.2, 45.1, 36.4, 36.2, 30.3, 30.0, 29.7, 27.4, 15.6, 14.5; IR (Neat, cm⁻¹): 2213 and 2161($\nu_{\text{C}\equiv\text{N}}$), 1733 ($\nu_{\text{C}=\text{O}}$).

3. 6. References

- (1) Dalton, L. R. *J. Phys.: Condens. Matter* **2003**, *15*, R897.
- (2) Beaudin, A. M. R.; Song, N.; Men, L.; Gao, J. P.; Wang, Z. Y.; Szablewski, M.; Cross, G.; Wenseleers, W.; Campo, J.; Goovaerts, E. *Chem. Mater.* **2006**, *18*, 1079.
- (3) Esser, I. C. H. M.; Parsons, I. M. *Polymer* **1993**, *34*, 2836.
- (4) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.
- (5) (a) Würther, F.; Yao, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 1978. (b) Würther, F.; Yao, S.; Debaerdemaeker, T.; Wortmann, R. *J. Am. Chem. Soc.* **2002**, *124*, 9431.

Chapter 4 Synthesis and Characterization of Crosslinkable NLO

Polymers

4. 1. Introduction

A commonly used strategy to develop NLO polymers is covalently bond NLO chromophores as sidechain to polymer mainchain in order to physically prevent polar chromophores from forming aggregates while eliminating any possible phase separation as often occurs in a guest-host system. However, noncentrosymmetric order in poled polymers tends to decay very quickly in low- T_g polymers at ambient to elevated temperatures. Thus, chromophores are usually incorporated into high- T_g polymers to improve temporal stability of EO activity. Generally speaking, if the T_g of a polymer is at 150 to 200 °C, the decay of the poled optical nonlinearity would be negligible over time.¹ If the T_g of a polymer is too high, a higher poling temperature will be required, which may cause chromophore decomposition. Therefore, a solution is to introduce cross-linking groups to a low- T_g NLO polymer, which can be poled and cross-linked consecutively to lock the poling-induced nonlinearity. Cross-linked NLO polymer is insoluble in common organic solvents and environmentally more stable. Cross-linking should also be beneficial for EO device fabrication since the active NLO layer should be chemically inert to the solvent used for deposition of the upper cladding layer.

To date, a wide variety of polymer matrices have been exploited for development of EO materials and device, such as PMMA,² polycarbonate,² polyurethane,³ polyimide,⁴ polyethersulfone (PES)⁵ and sol-gel.⁶ For highly polar chromophores such as PQDM and PeQDM, it has been found by our group that they must be incorporated into polymers with high polarity such as polyimide and PES in order to achieve a higher chromophore

loading and form high-quality films. Crosslinkable NLO polyimide based on PQDM chromophore has been studied by a former student in our group.^{4b} Doping of PQDM and its hyper-branched oligomer into a commercially available PES has also been reported by our group.^{5c} An approach by covalently bonding these zwitterionic chromophores onto PES has not been studied yet.

This chapter describes the synthesis and characterization of crosslinkable NLO polyethersulfone based on PeQDM chromophores. The choice of the polymer mainchain structure, the effect of sidechain on the T_g of the polymer and preliminary investigation into the chromophore loading are also discussed. Their EO properties will be discussed in chapter 5.

4. 2. Synthesis and characterization of PES-Acid

By doping PeQDM chromophore into a commercially available PES (commercial trade name: Ultrason E), high-quality films can be prepared. The chemical structure of Ultrason E is shown in Figure 4.1.

Figure 4.1. Chemical structure of Ultrason E

In order to covalently attach a hydroxyl-containing PeQDM chromophore onto PES, polyethersulfone with a pendent acid group (PES-Acid) was synthesized according to a known procedure⁷ (Scheme 4.1). PES-Acid was characterized by ¹H NMR, ¹³C NMR and IR methods. Its thermostability and glass transition temperature have been investigated by TGA and DSC. Molecular weight of PES-Acid has also been estimated.

Scheme 4.1. Synthetic route to PES-Acid

Figure 4.2. ^1H NMR spectrum (300 MHz, DMSO-d_6) of PES-Acid

The ^1H NMR spectrum of PES-Acid (Figure 4.2) displays proton resonances (ppm) at 12.08 (s, 1H), 7.89 (d, $J = 8.7$ Hz, 4H), 7.23 (d, $J = 8.7$ Hz, 4H), 7.01-7.10 (m, 8H), 2.34 (t, $J = 6.9$ Hz, 2H), 2.00 (t, $J = 6.9$ Hz, 2H), 1.58 (s, 3H). Acid proton is assigned to the resonance at 12.08 ppm. In its ^{13}C NMR spectrum (Figure 4.3), all 13 resonances of

carbons are observed at 174.9, 161.8, 152.9, 145.6, 135.6, 130.3, 129.4, 120.2, 118.3, 45.2, 36.5, 30.3 and 27.4ppm. The carbonyl carbon is assigned to the peak at 174.9 ppm. Its IR spectrum shows $\nu_{\text{C=O}}$ at 1717 cm^{-1} (see experimental part).

Figure 4.3. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of PES-Acid

Although the molecular weight of PES-Acid was not directly measured, it was estimated to be high for the following facts. First of all, the molecular weight (M_w) of the ester (PES-E-2) (see Scheme 4.2), which was derived from PES-Acid, was determined by GPC to be 3.22×10^5 relative to polystyrene standard. PES-Acid can be precipitated from water and methanol as fibers or sheets and form high-quality, free-standing film on glass.

PES-Acid had a good thermostability with T_d of $408\text{ }^\circ\text{C}$ for 5% weight loss in nitrogen (Figure 4.4: left) and a glass transition temperature of $230\text{ }^\circ\text{C}$ (Figure 4.4: right).

Figure 4.4. TGA (left) and DSC (right) traces of PES-Acid

4. 3. Synthesis and characterization of PES-E

When PES-Acid was fully grafted with PeQDM-C2OH, the obtained product could not be dissolved in any available solvents and had no T_g by DSC analysis up to 300°C , which is beyond the decomposition temperature of PeQDM-C2OH. This is mainly attributed to the largely enhanced polarity of the polymer due to the presence of the zwitterionic moiety. Thus, PES-Acid should only be partially grafted with highly polar PeQDM chromophores. Since PeQDM chromophore is sensitive to acid (see chapter 2), the residual acid group in a grafted polymer must be blocked with other groups. Such a blocking group should be less polar than PeQDM, in order to allow the NLO polymer have a suitable T_g for poling.

The ester derivatives (Scheme 4.2) were synthesized according to the same method for the dendronized chromophores (see chapter 3). PES-E is characterized by ^1H NMR, ^{13}C NMR, IR, TGA and DSC methods. The molecular weight of PES-E-2 was measured by GPC.

Scheme 4.2. Synthetic route to PES-E

The ^1H NMR spectrum of PES-E-1 (Figure 4.5) displays proton resonances (ppm) at 7.87 (d, $J = 9.0$ Hz, 4H), 7.23 (d, $J = 8.7$ Hz, 4H), 6.95-7.04 (m, 8H), 3.65 (s, 3H), 2.48 (t, $J = 7.5$ Hz, 2H), 2.16 (t, $J = 7.2$ Hz, 2H) and 1.65 (s, 3H). The disappearance of the acid proton resonance of PES-Acid at a lower field (12.08 ppm) and the appearance of the resonance at 3.65 ppm for the methoxy group indicate the formation of the ester bond. IR provides further evidence, with the carbonyl stretching frequency at 1735 cm^{-1} compared to the acid at 1717 cm^{-1} . Its ^{13}C NMR spectrum (Figure 4.6) displays all 14 resonances (ppm) at 173.9, 161.8, 153.1, 145.1, 135.5, 129.7, 128.9, 119.9, 117.8, 51.7, 45.2, 36.5, 30.0 and 27.7. The peak at 173.9 ppm is assigned to the carbonyl carbon of the ester, while the one at 51.7 ppm is assigned to the methoxy carbon.

Figure 4.5. ^1H NMR spectrum (300 MHz, CDCl_3) of PES-E-1

Figure 4.6. ^{13}C NMR spectrum (75 MHz, CDCl_3) of PES-E-1

Thermostability and glass transition temperatures of PES-E were investigated by TGA and DSC (Figure 4.7 and Table 4.1). Among them, PES-E-1 has the highest thermostability with a decomposition temperature ($T_d = 401\text{ }^{\circ}\text{C}$) close to that of PES-Acid ($T_d = 408\text{ }^{\circ}\text{C}$), indicating the methyl ester bond is thermally stable. The lower thermostability of PES-E-2 ($T_d = 376\text{ }^{\circ}\text{C}$) compared to PES-E-1 is due to the long aliphatic side chain. PES-E-3 and PES-E-4 have the same decomposition temperature ($T_d = 319\text{ }^{\circ}\text{C}$), implying that the aromatic ester is less thermally stable than aliphatic one in this case. Despite of these differences, all PES-E polymers show good thermostability with T_d over $300\text{ }^{\circ}\text{C}$. As expected, the glass transition temperatures of PES-E polymers ($T_g = 103\text{ }^{\circ}\text{C} - 160\text{ }^{\circ}\text{C}$) are much lower than that of PES-Acid ($T_g = 230\text{ }^{\circ}\text{C}$). By changing the length of the side chain, going from one carbon (PES-E-1) to six carbons (PES-E-2), the T_g of the polymer decreases from $158\text{ }^{\circ}\text{C}$ to $103\text{ }^{\circ}\text{C}$.

Figure 4.7. TGA (left) and DSC (right) traces of PES-E

Table 4.1. Decomposition (T_d) and glass transition (T_g) temperatures of PES polymers

Polymer	T_d^a (°C)	T_g^b (°C)
PES-Acid	408	230
PES-E-1	401	158
PES-E-2	376	103
PES-E-3	319	148
PES-E-4	319	160

^a The decomposition temperature (T_d) was determined by 5% weight loss by TGA with a heating rate of 5 °C min⁻¹ in nitrogen. ^b The glass transition temperature (T_g) was determined by DSC with a heating rate of 5 °C min⁻¹ in nitrogen.

All the PES-E polymers and the NLO polymers were prepared from the same batch of PES-Acid. The molecular weight of PES-E-2 was determined by GPC to be 3.22×10^5 ($M_w / M_n = 2.24$) relative to polystyrene standard. Thus, the number-average molecular weights of PES-Acid, PES-E and NLO polymers should be close to 1.41×10^5 .

4. 4. Synthesis and characterization of crosslinkable NLO polyethersulfone

As previously discussed, introducing softer alkyl side chain lowers the T_g of a PES polymer (≤ 160 °C), while covalently linking zwitterionic chromophore PeQDM as a pendant group will largely increase the polarity of the polymer. Since an NLO polymer should be poled at a temperature near its T_g without causing any decomposition, the target NLO polymers should be partially grafted with PeQDM chromophore, so that the product will have reasonable low T_g . A preliminary study on the T_g of NLO polymer with different contents of pendent groups was carried out in order to identify an appropriate composition for NLO polymer.

Two NLO polymers (NLO-P1 and NLO-P2) grafted with PeQDM-C2OH and 1-hexanol were prepared using the same procedure as for the synthesis of PES-E. Their

structures are shown in Figure 4.8. The term of “chromophore core content” is applied to replace the conventional “chromophore content” herein, where the “core” refers to the moiety that only contains the donor and acceptor (Figure 4.8), rather than the whole molecule of a given chromophore. The composition and properties of the two NLO polymers are summarized in Table 4.2.

Figure 4.8. Chemical structures of NLO-P1 and NLO-P2

Table 4.2. Composition and properties of NLO-P1 and NLO-P2

polymer	X:Y ^a	Core content (wt%) ^b	T _g (°C)	T _d (°C)	λ _{max} (nm) ^c
NLO-P1	1:1	21.4	No	205	684
NLO-P2	1:2	15.1	No	255	684

^a X and Y are the molar ratio of PeQDM-C2OH and 1-hexanol in feed. ^b The actual core content of the polymer was determined by ¹H NMR analysis. ^c Absorption in DMF.

NLO-P1 and NLO-P2 have apparently lower thermostability compared to PES-E, which is governed by the stability of PeQDM-C2OH (T_d = 215 °C). No glass transition temperature was observed for both polymers before decomposition, implying the presence of strong interchain interaction. It was visibly observed that the cast film of

NLO-P2 polymer was phase separated, implying incompatibility between the side chain and the polar chromophore. This problem may be solved by replacing the longer hexyl chain with a shorter one such as the methyl group. Therefore, to design a suitable NLO polymer in this case, a balance between the chain flexibility and local polarity must be considered. In addition, a cross-linking group should be introduced onto the NLO polymer in order to enhance the temporal stability of EO activity.

Accordingly, a crosslinkable NLO polymer (C-NLO-P) was designed and synthesized (Scheme 4.3) by grafting PeQDM-C3OH, 5-aminobenzocyclobutenone (Amino-BCBO) and methanol consecutively onto PES-Acid (see experimental section).

Scheme 4.3. Synthetic route to C-NLO-P

A small amount of Amino-BCBO (5 mol%) was introduced onto the NLO polymer as a crosslinker. BCBO is known to undergo thermolysis at 250 °C to form a reactive

vinylketene intermediate by ring-opening followed by self [4+2] cycloaddition and a 1,5-hydrogen shift to form a dimer (Scheme 4.4).⁸ For a BCBO-containing polymer, such a dimerization can lead to formation of a polymer network and crosslinking usually takes place above 200 °C.^{5c}

Scheme 4.4. Thermolysis of benzocyclobutenone (BCBO)

The chromophore core content was controlled by adjusting the feed ratios (X: Y: Z) of the grafting agents, and the actual content in C-NLO-P1 and C-NLO-P2 was determined by UV-Vis analysis to be 4.8 wt% and 6.6 wt%, respectively (Table 4.3). The chromophore loading in C-NLO-P is higher than the guest-host system, in which the highest chromophore core content is 3.8 wt% (see chapter 5: the highest doping level of PeQDM-Ben in a commercial PES is 5 wt%). A free standing film can be prepared by casting the polymer solution onto the ITO coated glass.

Table 4.3. Physical properties of C-NLO-P1 and C-NLO-P2

NLO polymer	X: Y: Z	Core content (wt%) ^a	T _g (°C)	T _d (°C)	λ _{max} (nm) ^b
C-NLO-P1	3: 1: 16	4.8	158	293	685
C-NLO-P2	6: 1: 13	6.6	174	232	683

^a The actual core content of the polymer was determined by UV-Vis analysis by plotting the curve of PeQDM-C3OH in DMF solution. ^b Absorption in DMF.

The crosslinkable polymers were characterized by ¹H NMR, IR and UV-Vis methods. The ¹H NMR spectrum of C-NLO-P1 shows the proton resonances corresponding to the

PeQDM and BCBO moieties and the unlabeled peaks are for the polymer mainchain and the methyl group (Figure 4.9). While the peaks marked with a star attributed to impurities are most probably from the coupling reagent EDC and the by-product.⁹ The IR spectrum of C-NLO-P1 gave $\nu_{\text{C}\equiv\text{N}}$ at 2219 and 2162 cm^{-1} . The red-shift absorption of C-NLO-P ($\lambda_{\text{max}} = 685, 683 \text{ nm}$) in DMF solution compared to PeQDM-C3OH ($\lambda_{\text{max}} = 671 \text{ nm}$) is due to less polar environment imparted by the polymer. Although C-NLO-P1 and C-NLO-P2 gives very similar UV-Vis spectra in DMF solution, the spectra of their corresponding films are apparently different (Figure 4.10). The CT band of C-NLO-P1 is much broader than that of C-NLO-P2. The broad peak is due to some J-aggregation of chromophores in less polar C-NLO-P1. The effect of aggregation on the EO activity of NLO materials will be discussed in chapter 5.

Figure 4.9. ^1H NMR spectrum (300 MHz, DMSO-d_6) of C-NLO-P1

Figure 4.10. UV-Vis spectra of a solution of C-NLO-P1 in DMF (1), film of C-NLO-P1 (2) and film of C-NLO-P2 (3)

The two NLO polymers show high thermal stability and glass transition temperatures (Table 4.3). The higher T_d of C-NLO-P1 (293 °C) compared to C-NLO-P2 (232 °C) is attributed to a lower chromophore content. Since T_d was determined according to 5 wt% loss of the polymer, the actual decomposition temperature of C-NLO-P1 should be around 232 °C, which is closer to the T_d of PeQDM-C3OH ($T_d = 238$ °C). The higher T_g of C-NLO-P2 (174 °C) compared to C-NLO-P1 (158 °C) is due to a higher chromophore content.

As shown in the DSC trace of C-NLO-P1 (Figure 4.11), after the glass transition, the heat flow continues to decrease until 179 °C and then increases to a maximum at 203 °C. The exothermic process after the glass transition is due to the ring-opening of the BCBO group.⁹ Actually, the BCBO crosslinking can take place at a lower temperature (e.g., 180 °C). By heating C-NLO-P polymers at 180 °C for ten minutes, the polymers became insoluble in organic solvents such as DMAC, DMSO, NMP and DMF.

Figure 4.11. DSC trace of C-NLO-P1

4. 5. Conclusions

Two crosslinkable polyethersulfones based on PeQDM-C3OH chromophore have been synthesized and characterized. Covalently grafting PeQDM onto a polymer can increase the chromophore loading level to a certain extent with a tradeoff between the chromophore content and the overall chain mobility.

4. 6. Experimental

Materials. All reagents and solvents were purchased from Aldrich and used as received unless otherwise stated. Anhydrous N,N-dimethylacetamide (DMAC) and N-methylpyrrolidinone (NMP) were dried over calcium hydride, vacuum distilled and then stored over 4 Å molecular sieves.

Methods. The ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Bruker AMX 400 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 or a Bomen Michelson 120 FTIR spectrometer. UV-Vis absorption spectra were

recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in nitrogen on a TA DSC Q100 and Hi-Res TGA 2950 thermogravimetric analyzer with a heating rate of 5 °C min⁻¹.

Preparation of PES-Acid

4,4'-Bis(4-hydroxyphenyl)valeric acid (5.726 g, 20 mmol), 4-chlorophenyl sulfone (5.744 g, 20 mmol), anhydrous potassium carbonate (8.280 g, 60 mmol), 60 mL of DMAC and 120 mL of toluene were charged into a 250 mL, three necked flask. After being purged with nitrogen for half an hour at room temperature, the reaction mixture was heated to reflux with stirring while the water was removed by azeotropic distillation. The mixture was kept at 190 °C overnight and a minimum amount of DMAC was added to completely dissolve the mixture. After the mixture was cooled to room temperature, it was acidified with concentrated HCl with caution and then added dropwise into a large amount of water with vigorous stirring to precipitate the polymer. The polymer was re-dissolved in hot DMAC and precipitated into water and methanol twice. The final product obtained as white fibrous solids in 70% yield (6.96 g). ¹H NMR (300 MHz, DMSO-d₆): δ 12.08 (s, 1H), 7.89 (d, J = 8.7 Hz, 4H), 7.23 (d, J = 8.7 Hz, 4H), 7.01-7.10 (m, 8H), 2.34 (t, J = 6.9 Hz, 2H), 2.00 (t, J = 6.9 Hz, 2H), 1.58 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆): δ 174.9, 161.8, 152.9, 145.6, 135.6, 130.3, 129.4, 120.2, 118.3, 45.2, 36.5, 30.3, 27.4; IR (KBr, cm⁻¹): 1717 (ν_{C=O}).

Preparation of PES-E (with an example of PES-E-1)

PES-E-1. A mixture of PES-Acid (200 mg, 0.40 mmol), 4-(dimethylamino)pyridine (DMAP) (81 mg, 0.66 mmol), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (114 mg, 0.60 mmol), 0.05 mL of anhydrous methanol and 4 mL of NMP was stirred at room temperature for 2 days and then the mixture was added slowly into a plenty of methanol to precipitate the crude product. After the crude product was purified by redissolving in hot DMAC and precipitated from methanol twice, 0.19 g (92% yield) of final product as white fibers was collected. ^1H NMR (300 MHz, CDCl_3): δ 7.87 (d, J = 9.0 Hz, 4H), 7.23 (d, J = 8.7 Hz, 4H), 6.95-7.04 (m, 8H), 3.65 (s, 3H), 2.48 (t, J = 7.5 Hz, 2H), 2.16 (t, J = 7.2 Hz, 2H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 173.9, 161.8, 153.1, 145.1, 135.5, 129.7, 128.9, 119.9, 117.8, 51.7, 45.2, 36.5, 30.0, 27.7; IR (Neat, cm^{-1}): 1735 ($\nu_{\text{C=O}}$).

PES-E-2. Yield: 74%. ^1H NMR (300 MHz, CDCl_3): δ 7.88 (d, J = 8.7 Hz, 4H), 7.23 (d, J = 8.7 Hz, 4H), 6.96-7.05 (m, 8H), 4.04 (t, J = 6.9 Hz, 2H), 2.47 (t, J = 7.2 Hz, 2H), 2.14 (t, J = 7.2 Hz, 2H), 1.58-1.61 (m, 5H), 1.30 (s, 6H), 0.89 (t, J = 6.6 Hz, 3H); IR (Neat, cm^{-1}): 1731 ($\nu_{\text{C=O}}$).

PES-E-3. Yield: 88%. ^1H NMR (300 MHz, CDCl_3): δ 7.87 (d, J = 8.7 Hz, 4H), 6.97-7.39 (m, 17H), 3.65 (s, 3H), 2.60 (t, J = 7.8 Hz, 2H), 2.42 (t, J = 7.8 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 172.0, 161.8, 153.2, 150.6, 144.9, 135.6, 129.8, 129.4, 129.0, 125.9, 121.4, 120.0, 117.8, 45.3, 36.3, 30.4, 27.8; IR (Neat, cm^{-1}): 1757 ($\nu_{\text{C=O}}$).

PES-E-4. Yield: 87%. ^1H NMR (300 MHz, CDCl_3): δ 7.87 (d, J = 8.7 Hz, 4H), δ 7.38 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.5 Hz, 4H), 6.96-7.05 (m, 10H), 2.59 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 1.71 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 172.2, 161.8, 153.2, 148.7, 148.2, 145.0, 135.6, 129.8, 129.0, 126.3, 120.7, 119.9, 117.9, 45.3, 36.3, 34.5, 31.4, 30.4, 27.8; IR (Neat, cm^{-1}): 1754 ($\nu_{\text{C=O}}$).

Preparation of C-NLO-P (with an example of C-NLO-P1)

C-NLO-P1. A mixture of PES-Acid (250 mg, 0.50 mmol), PeQDM-C3OH (27 mg, 0.075 mmol), DMAP (15 mg, 0.12 mmol), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (21 mg, 0.11 mmol) and 5 mL of anhydrous NMP was stirred for 1 day at room temperature. Then, 5-aminobenzocyclobutenone (7 mg, 0.025 mmol), DMAP (5 mg, 0.041 mmol) and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (7 mg, 0.03 mmol) were added. After the mixture was stirred for another day at room temperature, 0.08 mL of methanol (excess), DMAP (80 mg, 0.66 mmol) and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (112 mg, 0.59 mmol) were added to the mixture and the reaction continued for another day. The reaction mixture was added dropwise into 100 mL of methanol to precipitate the polymer. After the product was dried in vacuum at 50 °C overnight, 0.27 g (95% yield) of blue polymer was obtained. ^1H NMR (300 MHz, DMSO-d_6): δ 10.04 (br, s), 8.92 (br, m), 8.26 (br, s), 7.86 (br, m), 7.68 (br, m), 7.52 (br, m), 7.20 (br, s), 7.03 (br, m), 4.56 (br, s), 4.06 (br, s), 3.86 (br, s), 3.49 (br, s), 2.33 (br, s), 2.01 (br, m), 1.55 (br, s); IR (KBr, cm^{-1}): 2219 and 2161 ($\nu_{\text{C=N}}$); UV-Vis: λ_{max} = 685 nm (DMF).

C-NLO-P2. Yield: 80%. ^1H NMR (300 MHz, DMSO- d_6): δ 10.03 (br, s), 8.91 (br, m), 8.25 (br, s), 7.86 (br, m), 7.69 (br, m), 7.52 (br, m), 7.20 (br, s), 7.04 (br, m), 4.56 (br, s), 4.07 (br, s), 3.86 (br, s), 3.50 (br, s), 2.33 (br, s), 2.04 (br, m), 1.56 (br, s); IR (KBr, cm^{-1}): 2215 and 2163 ($\nu_{\text{C}\equiv\text{N}}$); UV-Vis: $\lambda_{\text{max}} = 683$ nm (DMF).

4. 7. References

- (1) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2002**, *12*, 565
- (2) (a) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science*, **2000**, *288*, 119. (b) Cheng, Y.-J.; Luo, J.; Hau, S.; Bale, D. H.; Kim, T.-D.; Shi, Z.; Lao, D. B.; Tucker, N. M.; Tian, Y.; Dalton, L. R.; Reid, P. J.; Jen, A. K.-Y. *Chem. Mater.* **2007**, *19*, 1154.
- (3) Zhang, C.; Wang, C.; Dalton, L. R.; Zhang, H.; Steier, W. H. *Macromolecules* **2001**, *34*, 253.
- (4) (a) Liang, Z.; Dalton, L. R.; Garner, S. M.; Kalluri, S.; Chen, A.; Steier, W. H. *Chem. Mater.* **1995**, *7*, 941. (b) Song, N.; Men, L.; Gao, J. P.; Bai, Y.; Beaudin, A. M. R.; Yu, G.; Wang, Z. Y. *Chem. Mater.* **2004**, *16*, 3708.
- (5) (a) Garner, S. M.; Cites, J. S.; He, M.; Wang, J. *Appl. Phys. Lett.* **2004**, *84*, 1049. (b) Lu, Z.; Li, J.; Hua, J.; Li, X.; Qin, J.; Qin, A.; Ye, C. *Syn. Met.* **2005**, *152*, 217. (c) Bai, Y.; Song, N.; Gao, J. P.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. Y. *J. Am. Chem. Soc.* **2005**, *127*, 2060.
- (6) Kalluri, S.; Shi, Y.; Steier, W. H; Yang, Z.; Xu, C.; Wu, B.; Dalton, L. R. *Appl. Phys. Lett.* **1994**, *65*, 2651.
- (7) Esser, I. C. H. M.; Parsons, I. M. *Polymer* **1993**, *34*, 2836.
- (8) Wang, Z. Y. ; Suzzarini, L.; Gao, J. P. *Tetrahedron Lett.* **1997**, *38*, 5745.
- (9) Song, N. Ph. D. Thesis, Carleton University, Canada, **2004**.

Chapter 5 Electro-Optic Properties of NLO Materials

5. 1. Introduction

The EO properties of NLO materials rely on a noncentrosymmetric ordering of chromophore molecules. A common method aimed to achieve this ordering is an electric poling. Thin films of the polymers are typically poled near their T_g temperatures under an applied electric field with a voltage in the range of 50-100 V per μm thickness of film. However, many materials based on well-designed chromophores with a very large figure of merit ($\mu\beta$ value)¹ failed to exhibit the expected large EO activities. This discrepancy was ambiguously attributed to dye aggregations, which was indirectly supported and thought to be the reason for the loss of EO activity of NLO materials due to the competition between the electrostatic interaction of the dipoles and the electric-field force.²

Dye aggregation includes H- and J-aggregations and is well explained according to the molecular exciton models.^{3a} H-aggregation refers to a face-to-face orientation of dipolar dyes and its excitonic splitting results in a high-energy allowed transition and a low-energy forbidden transition (Figure 5.1).^{3b} Thus, the UV-Vis absorption of the H-aggregates is blue-shifted with respect to that of the monomer. Furthermore, the two monomers of an H-aggregate anti-parallel to each other with a large slip angle ($\theta = 54.7^\circ - 90^\circ$).^{3a} Conversely, the high-energy transition of J-aggregation is forbidden and the low-energy one is allowed, which leads to a red shift in absorption. The J-aggregate has a head-to tail orientation with a small slip angle ($\theta = 0^\circ - 54.7^\circ$).

Figure 5.1. Explanation of the blue-shifted UV-Vis absorption of H-aggregates of dipolar dyes according to molecular exciton models

Clear evidence has shown that dimerization of dipolar dyes to form H-aggregates in less polar solvents and in the solid state are due to the strong electrostatic interactions between the dipoles.² It is generally believed that the face-to-face anti-parallel H-aggregation is responsible for the loss of EO activity of NLO materials. Although both H- and J-aggregations of polar dyes are frequently observed in solution,⁴ direct observation of dipolar dye aggregation in a polymer matrix and study its influence on EO activity is seldom reported.

Therefore, this chapter describes: 1) direct experimental observation of the formation of both H- and J-aggregations in polymer hosts doped with PeQDM chromophores, and investigation of the effect of H- and J-aggregates and their thermodynamics on the poling efficiency and thus EO activity; 2) EO property of ES-PeQDM-1b doped polyethersulfone; 3) EO properties of ES-PeQDM-2 and ES-PeQDM-3; 4) EO properties of the crosslinkable polyethersulfones containing PeQDM chromophores.

5. 2. Electro-optic properties of zwitterionic chromophores

5. 2. 1. Molecular organizations of zwitterionic chromophores in polymers

It was found that PeQDM chromophores could form various molecular organizations in polymers, as evident by very different UV-Vis spectra. In order to identify these different organizations, PeQDM-Ben was selected as a representative for detailed studies. As discussed in chapter 2, PeQDM-Ben crystal cell contains a complete dimer and the two monomers anti-parallel to each other with a large slip angle ($\theta = 64.5^\circ$) or an H-aggregate. In order to identify the corresponding UV-Vis absorption of the H-aggregates, the crystalline powder of PeQDM-Ben was finely ground with KBr powder and suspended in glycerin for UV-Vis measurement. The crystalline powder exhibits two charge-transfer (CT) bands at 635 and 519 nm (Figure 5.2). The peak at 635 nm is assigned to the absorption of the monomers due to partly well dispersed chromophores in glycerin since the polarity of glycerin is very close to that of methanol (see chapter 2: the λ_{max} of PeQDM-Ben in methanol is 630 nm). The blue-shifted band at 519 nm is attributed to the absorption of the H-aggregates. Although PeQDM chromophores are soluble in some polar solvents such as DMF, NMP and DMSO and easily aggregate in less polar solvents, no aggregation was observed in solution by UV-Vis analysis. Meanwhile, concentration-dependent UV-Vis spectra in the polar solvents didn't show any signs for chromophore aggregation.

Figure 5.2. UV-Vis spectrum of PeQDM-Ben crystalline powder

In a polymer matrix, both H- and J-aggregations were observed by UV-Vis analysis. PeQDM-Ben was doped into the following polymers (Figure 5.3) with the increasing polarity and dielectric constant (ϵ): amorphous polycarbonate (APC, $\epsilon = 3.0$), polyethersulfones including PES-U (commercial trade name: Ultrason E, $\epsilon = 3.5$), PES-Met and PES-Hex, and poly(4-vinylphenol) (PVPh, $\epsilon = 4.5$). PES-U, APC and PVPh were purchased from BASF, Aldrich and Hoechst, respectively. PES-Met and PES-Hex were synthesized (see chapter 4). The polarity of these polymers should increase in the following order: APC < PES-Hex $\leq$ PES-Met < PES-U < PVPh. PeQDM-Ben can be doped up to 5 wt% (3.8 wt% core content) into all these polymers and uniform thin films in a thickness of 2-3 μm can be prepared by direct casting the chromophore-polymer solutions onto an ITO glass (see experimental section). Their corresponding UV-Vis spectra are shown in Figure 5.4.

Figure 5.3. Chemical structures of polymer matrices

Figure 5.4. UV-Vis spectra of 5 wt% PeQDM-Ben (3.8 wt% core content) in polymer matrices: a) PES-U, b) APC, c) PES-Met, d) PVPh, e) PES-Hex

In relatively more polar polymers such as PES-U and PVPh (Figure 5.4), chromophores are well dispersed as monomers, as only one CT band appears at 755 nm for the doped PES-U film and 606 nm for the PVPh film. The large difference in the CT band positions ($\Delta\lambda = 606 - 755 = -149$ nm) for the two polymers is relevant to the

observed negative solvatochromism in solution, demonstrating the strong stabilization effect of the polar polymer on the zwitterionic ground-state of the chromophore.

In less polar APC and PES-Hex (Figure 5.4), two different molecular organizations were found. In the doped APC, three CT bands were observed at 679, 780 and 848 nm, in which the two red-shifted bands (780 and 848 nm) are attributed to the J-aggregates. In the doped PES-Hex film, a mixture of monomers, H- and J-aggregates are present, as indicated by the peaks at 645 nm, 481 nm and 826 nm assigned to the monomers, H-aggregates and J-aggregates, respectively. For PES-Met having a polarity between those of PES-Hex and PES-U, a mixture of monomers and J-aggregates exist, as evident by a very broad peak between 500-950 nm without a shoulder on the left side. Therefore, the local structure or functional groups in the polymer can play a key role in controlling the formation of H- or/and J-aggregates.

5. 2. 2. EO properties of PeQDM-Ben doped polymers

EO properties of PeQDM-Ben in the above polymers were studied in order to probe the effect of the different molecular organizations on EO activity. Chromophore-doped thin films, except for PVPh (due to its film brittleness for contact poling), were poled near T_g of the materials (Table 5.1). In a routine contact poling process, the PeQDM-Ben doped films were treated by gradually applying a voltage of 70 V/ μm across the film for 5 min after reaching the final poling temperatures. The poling temperature is typically 4-5 °C below the T_g of the polymer film. The EO coefficients are measured by the Teng-Man reflection method.⁵ It was found that PES-U film without any aggregation exhibited the largest EO activity ($r_{33} = 110$ pm/V), while other films with dye aggregates gave much smaller EO coefficients ($r_{33} < 10$ pm/V) due to the strong electrostatic interactions

between the dipoles. The observed smaller EO coefficients should result from some free monomers in the polymer matrices.

Table 5.1. Glass transition (T_g), poling temperatures (T_p) and EO coefficients (r_{33} , 1550 nm) of 5 wt% PeQDM-Ben doped polymers.

Thin film	PES-U	PES-Met	PES-Hex	APC
T_g (°C)	205	144	98	172
T_p (°C)	190	140	94	167
r_{33} (pm/V)	110	9	8	6 (38 ^a)

^a The voltage was first applied before heating to the poling temperature.

Considering that different molecular organizations of chromophores in the polymer films may behave quite differently during the poling process, investigation into their thermodynamics (e.g., annealing) should give insight into the poling efficiency. Therefore, the polymer films were further thermally treated in order to probe any possible chromophore re-orientation or re-packing under the poling conditions. The UV-Vis spectra of the doped films of PES-U, PES-Met, and PES-Hex did not show any apparent changes when being heated for 30 min at their corresponding poling temperatures: 190 °C, 140 °C and 94 °C, indicating stable molecular organizations in these polymers. Reorientation of individual chromophores in PES-Met and PES-Hex under the electric field is more difficult due to additional dissociation of the stable aggregates to monomers. Thus, the doped PES-U film exhibited a higher poling efficiency because of well dissolved monomers presented in the polymer matrix.

For the doped APC film, with increase of the heating time at the poling temperature, the intensity of the three peaks at 679, 780 and 848 nm decreased, the monomer peak at 679 nm broadened and a new blue-shifted peak appeared at 480 nm (Figure 5.5, left). This

clearly indicates that some of the J-aggregates are transformed to H-aggregates. This transformation is fast (maybe less than a few minutes) when the film is heated above T_g at 180 °C, demonstrating that H-aggregates are more thermally stable in this polymeric environment. Therefore, by heating first during the routine poling process, J-aggregates in APC will be transferred into more stable H-aggregates, leading to very low EO activity ($r_{33} = 6$ pm/V). However, it was found that the poling efficiency of APC film can be greatly improved by applying a different poling profile. When applying a voltage of 70 V/ μ m first and then heating up to the poling temperature, the poling efficiency of the doped APC film was improved more than six fold ($r_{33} = 38$ pm/V). This finding strongly suggests that the transformation of J-aggregation to H-aggregation proceeds through a dissociated monomer intermediate and that by capturing and in-situ aligning this monomer intermediate, J-aggregates can still be re-oriented to a noncentrosymmetric structure and contribute to EO activity (Scheme 5.1).

Figure 5.5. Left: UV-Vis spectra of 5 wt% PeQDM-Ben doped APC: a) before heating, and heating at 167 °C for b) 2 min, c) 12 min, d) 42 min; Right: UV-Vis spectra of 5 wt% PeQDM- Ben doped PES-Hex: a) before heating, b) after heating at 120 °C for 30 min.

Scheme 5.1. Proposed model for the thermodynamics of H- and J-aggregations during poling process

Compared to thermodynamics of the J-aggregates of chromophore in APC film, the J-aggregates (826 nm) in PES-Hex film could be completely transferred to H-aggregates (481 nm) when the film was heated above T_g at 120 °C for 30 min (Figure 5.5, right). The UV-Vis spectrum of the thermally treated PES-Hex film became very similar to that of PeQDM-Ben crystalline powder (Figure 5.2), indicating the formation of a more stable and ordered molecular organization. Further evidence comes from the X-ray analysis of the thermally treated film (Figure 5.6). The broad peak at 18° corresponds to the polymer matrix (polyethersulfone) and those at 9° and 14° are attributed to (002) and (100) of PeQDM-Ben. After heating, the peaks at 9° and 14° became noticeably more intense, indicating an increase in order for chromophores in the polymer host. Thus, J-aggregates of chromophores readily transform to more stable, ordered H-aggregates in less polar APC and PES-Hex during the poling process.

Figure 5.6. X-ray diffraction pattern of PES-Hex film: A) before heating; B) after heating at 120 °C for 30 min.

5. 2. 3. Temporal EO stability of the poled PES-U film

The doped PES-U film without H- and J-aggregates exhibited not only the largest EO activity, but also an excellent temporal EO stability. The temporal stability of the poled film with 5 wt% PeQDM-Ben was tested at 80 °C in nitrogen in dark (Figure 5.7). In the first 80 h, the r_{33} value decreased about 5% of its initial value, and then diminished slowly to 90% until 1000 h. The results suggest that the initial relaxing of the poled order of chromophores is mainly responsible for the loss of some EO activity, and the T_g of the doped PES-U films is high enough to hold the oriented chromophores in place for a long time.

Figure 5.7. Temporal stability of the poled thin film of PES-U with 5 wt% (3.8 wt% core content) PeQDM-Ben at 80 °C in nitrogen

5. 3. Electro-optic properties of dendronized chromophores

For EO study, homogeneous thin films can be fabricated by doping the first series of ethersulfone dendron modified chromophores (see chapter 3) into PES-U. The chromophore core content can be up to 10 wt%, which is more than twice of PeQDM-Ben (3.8 wt%) in the same polymer. Moreover, the chromophore core content increases up to 14.9 and 16.9 wt% by using ES-PeQDM-2 and ES-PeQDM-3, respectively (Figure 5.8). Since the EO coefficient (r_{33} value) is proportional to the number density of NLO chromophore,⁶ these dendronized chromophores are expected to show even higher EO activity than PeQDM-Ben doped PES-U ($r_{33} = 110$ pm/V). However, these NLO materials exhibited much less EO activities than expected.

Figure 5.8. Chemical structures of ES-PeQDM-2 and ES-PeQDM-3

5. 3. 1. Electro-optic property of ES-PeQDM-1b doped polyethersulfone (PES-U)

Among the first series of dendronized chromophores (see chapter 4), ES-PeQDM-1b has the highest thermostability and a flexible spacer between the ES-dendron and PeQDM chromophore, which should facilitate chromophore reorientation under electric field. Thus, ES-PeQDM-1b was doped into PES-U for EO study. The chromophore core content of ES-PeQDM-1b doped PES-U film is 8.1wt%. The UV-Vis spectrum of the film ($\lambda_{\text{max}} = 724 \text{ nm}$) is shown in Figure 5.9, together with that of PeQDM-Ben doped PES-U film. A broader CT-band absorption with a shoulder at about 500 nm in ES-PeQDM-1b doped film compared to that of PeQDM-Ben indicates that some J- and H-aggregates are present in the ES-PeQDM-1b doped PES-U.

Figure 5.9. UV-Vis spectra of (1) PeQDM-Ben (3.8 wt% core content) and (2) ES-PeQDM-1b (8.1 wt% core content) doped PES-U films

The T_g of ES-PeQDM-1b doped film is 162 °C, as determined by DSC analysis. When the film was heated at 162 °C for 30 min, there was no apparent change in its UV-Vis spectrum, indicating stable molecular organizations of chromophores in the polymer matrix. The doped PES-U film was poled at 155 °C in a routine contact poling process with a voltage of 70 V/ μm across the film (2-3 μm) for 5 min. The EO coefficient as determined by the Teng-Man reflection method is 41 pm/V, which is less than that of PES-Ben doped PES-U film ($r_{33} = 110$ pm/V). This low EO activity is mainly due to chromophore aggregation. These results indicated that even a small amount of dye aggregates can greatly affect EO activity of NLO materials. Another possible cause for the low EO activity may come from the larger size of the dendritic structure itself, which may limit the mobility of chromophores during the poling process.

5. 3. 2. Electro-optic properties of ES-PeQDM-2 and ES-PeQDM-3

As discussed in chapter 3, good-quality films of ES-PeQDM-2 and ES-PeQDM-3 can be prepared by spin-coating (1,2-dichloroethane solutions). The corresponding chromophore core contents are calculated to be 14.9 and 16.9 wt%, respectively. However, significantly different molecular organizations were observed in ES-PeQDM-2 and ES-PeQDM-3 films (see the UV-Vis spectra in chapter 3). ES-PeQDM-2 formed almost completely H-aggregates, while ES-PeQDM-3 was amorphous except for a small amount of J-aggregates. These two different molecular organizations were further supported by x-ray analysis (Figure 5.10). In the X-ray pattern of ES-PeQDM-2 (Figure 5.10: left), the broad peak at 18° is attributed to ES-dendron and those at 14° and 26° peaks correspond to (100) and (105) of PeQDM-Ben. However, the ES-PeQDM-3 (Figure 5.10: right) does not show any other peaks besides the broad peak at 18° , indicating the absence of chromophore aggregation.

Figure 5.10. X-ray diffraction pattern of ES-PeQDM-2 (left) and ES-PeQDM-3 (right) films

When the spin-coated films were heated at their T_g temperatures (see chapter 3), their UV-Vis spectra didn't show any apparent changes, indicating thermally stable molecular

organizations under the poling conditions. The films (1-2 μm) of ES-PeQDM-2 and ES-PeQDM-3 were poled at the temperature of 5 $^{\circ}\text{C}$ lower than their glass transition temperatures. As expected, ES-PeQDM-2 was completely EO inactive ($r_{33} = 0 \text{ pm/V}$). ES-PeQDM-3 exhibited a larger EO coefficient ($r_{33} = 63 \text{ pm/V}$), still being lower than that of PeQDM-Ben doped PES-U. Except for the presence of a small amount of aggregates, the flexibility of the spacer between chromophore and dendrons may also affect the poling efficiency of the dendronized chromophore.

5. 4. Electro-optic properties of crosslinkable NLO polyethersulfones

By attaching zwitterionic chromophores to polyethersulfone, the chromophore core content increased to 4.8 wt% and 6.6 wt% in C-NLO-P1 and C-NLO-P2 (see chapter 4), respectively, compared to that of the PeQDM-Ben doped PES-U (3.8 wt% core content). Films (2-3 μm) of C-NLO-P1 and C-NLO-P2 were cast from DMF solution and had a T_g of 158 $^{\circ}\text{C}$ and 174 $^{\circ}\text{C}$, respectively. The poling was first done at 155 $^{\circ}\text{C}$ (for C-NLO-P1) or 170 $^{\circ}\text{C}$ (for C-NLO-P2) for 5 min with an applied 70 V/ μm voltage. The films were then heated up to 180 $^{\circ}\text{C}$ for 10 min while keeping the same voltage to complete crosslinking. The EO coefficients of C-NLO-P1 and C-NLO-P2 were determined by the Teng-Man reflection method to be 37 pm/V and 13 pm/V, respectively. The lower EO activity of C-NLO-P1 and C-NLO-P2 compared to PeQDM-Ben doped PES-U ($r_{33} = 110 \text{ pm/V}$) is mainly caused by chromophore aggregations, as evident by their broader absorptions (see chapter 4). As discussed in chapter 4, the CT band of C-NLO-P1 is even broader than that of C-NLO-P2, indicating more aggregation in C-NLO-P1. The observed higher EO activity of C-NLO-P1 is probably due to a lower T_g or higher chain

mobility. Since the poling temperature of C-NLO-P2 is close to the onset of the crosslinking temperature (see chapter 4), partial crosslinking may have taken place already after 5 min. Indeed, when the film was heated at 170 °C for 5 min, it couldn't be completely dissolved in DMF or was partially crosslinked. If the polymer composition could be further adjusted for a suitable polarity and glass transition temperature (T_g), it would be still possible to make a NLO polymer with large EO activity and excellent temporal stability.

5. 5. Conclusions

EO properties of zwitterionic PeQDM chromophores, dendronized PeQDM chromophores and crosslinkable NLO polyethersulfones have been studied. The results suggest that dipolar dye aggregation is the major cause for the loss of EO activity. The use of a polymer host with a large dielectric constant clearly favors the dispersion of monmeric chromophores, as evident by a guest-host system (5 wt% PeQDM-Ben in PES-U) showing the largest EO coefficient of 110 pm/V at 1550 nm. The J-aggregates formed in a less polar polymer host could still contribute to EO activity, if monomers dissociated during the J-H aggregate transformation could be oriented under the poling conditions.

An approach to increasing the chromophore number density and minimizing chromophore aggregation involves the functionalization of PeQDM with a large dendritic molecule. Site-isolation of both negative and positive centers of zwitterionic chromophores through dendrons can prevent intermolecular electrostatic interactions to a certain extent. As for crosslinkable NLO polymers, the poling should be done before the curing takes place. By further modification of the dendronized chromophores through

the types of dendrons and the spacers, it is possible to achieve even larger EO activity and excellent temporal stability for these zwitterionic chromophores.

5. 6. Experimental

Materials. PES-U (trade name: Ultrason E), APC [Bisphenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene) diphenol carbonate] and PVPh (Polyvinylphenol) were purchased from BASF, Aldrich and Hoechst, respectively. PES-Met and PES-Hex were synthesized (see chapter 4).

Methods. The UV-Vis, DSC and TGA methods refer to chapter 4. Refractive indices were measured using a Metricon 2010 prism coupler. Thickness of films was measured by an alpha-step 200 surface profiles. For the X-ray diffraction (XRD) studies of the films, a Bruker D8 Discover diffractometer equipped with a copper target ($K\alpha 1$ line, with wavelength $\lambda = 1.5406 \text{ \AA}$) was used under a step-scan rate of 0.05° per 10s in the scattering range of $5^\circ \sim 30^\circ$. The measurement was carried out in grazing incident mode with an incident angle at 0.2° in order to eliminate the effect of glass background. The EO coefficients (r_{33} value) of the poled polymer materials were measured by the Teng-Man setup, which was calibrated with a commercial LiNbO_3 crystals ($r_{33} = 31 \text{ pm/V}$ at 1550 nm) before use.

A typical procedure for the fabrication of thin films for EO study

For the cast films, a 2 wt% DMF solution containing chromophore doped polymer or NLO polymer was first stirred overnight at room temperature in dark. After the solution was filtered with Nylon 0.45 μm syringe filter, 85 μL of the filtered solution was cast

onto a 17 mm $\times$ 17 mm indium-tin oxide (ITO) glass slide and baked at 45 °C overnight under the protection of nitrogen in dark. Then, the film was baked in a vacuum oven at 80 °C for 24 h. The film thickness measured with an alpha-step 200 surface profiler is in the range of 2-3 μm . While for the spin-coated dendrimer film, 15 wt% 1,2-dichloroethane solution of the dendrimer was first placed onto the 17 mm $\times$ 17 mm ITO-coated glass to completely cover the ITO surface, and then the glass was spun at 1500 Hz for 20s. The spin-coated film was dried in a vacuum at room temperature for 24h and its thickness is in the range of 1-2 μm . Refractive indices were measured by a metricon 2010 prism coupler. Glass transition temperature (T_g) of the thin film was measured by DSC. In the end, a thin layer of gold (100 nm) was sputtered or evaporated onto the film as the top electrode.

Typical poling procedure

The film was poled in a homemade thermo-electric poling station under the protection of nitrogen in dark. The film was first heated from room temperature to the poling temperature at a heating rate of 5 °C min⁻¹ and then a voltage (70V/ μm) was gradually applied across the film. The poling temperature is typically 4-5 °C below the T_g of the polymer film. After the film was held at the poling temperature for 5 min, the heating was turned off while keeping the final voltage. After reaching room temperature, the voltage was taken off and the film was ready for EO measurement.

5. 7. References

- (1) (a) Szablewski, M.; Thomas, P. R.; Thornton, A.; Bloor, D.; Cross, G. H.; Cole, J. M.; Howard, J. A. K.; Malagoli, M.; Meyers, F.; Brédas, J.; Wenseleers, W.; Goovaerts, E. *J. Am. Chem. Soc.* **1997**, *119*, 3144. (b) Metzger, R. M.; Heimer, N. E.; Aswell, G. *J. Mol. Cryst. Liq. Cryst.* **1984**, *107*, 133. (c) Weir, C. A. M.; Hadizad, T.; Beaudin, A. M. R.; Wang, Z. Y. *Tetrahedron Lett.* **2003**, *44*, 4697. (d) Song, N.; Men, L.; Gao, J. P.; Bai, Y.; Beaudin, A. M. R.; Yu, G.; Wang, Z. Y. *Chem. Mater.* **2004**, *16*, 3708. (e) Beaudin, A. M. R.; Song, N.; Men, L.; Gao, J. P.; Wang, Z. Y.; Szablewski, M.; Cross, G.; Wenseleers, W.; Campo, J.; Goovaerts, E. *Chem. Mater.* **2006**, *18*, 1079.
- (2) (a) Würther, F; Yao, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 1978. (b) Würther, F; Yao, S; Debaerdemaeker, T; Wortmann, R. *J. Am. Chem. Soc.* **2002**, *124*, 9431.
- (3) (a) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371. (b) Wang, Y.; Ma, J.; Cheon, H.; Kishi, Y. *Angew. Chem. Int. Ed.* **2007**, *46*, 1333.
- (4) Mishra, M.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. P. *Chem. Rev.* **2000**, *100*, 1973.
- (5) Teng, C; Man, H. *Appl. Phys. Lett.* **1990**, *56*, 1734.
- (6) Dalton, L. R. *J. Phys.: Condens. Matter* **2003**, *15*, R897.

Contribution to Knowledge

1. A new series of zwitterionic NLO chromophores (PeQDM) are designed, showing large first hyperpolarizability, good thermostability, and can be further modified with large dendrons for the purpose of site isolation and improvement of poling efficiency or incorporated into polymers.
2. The EO coefficient of 110 pm/V for 5 wt% PeQDM-Ben doped PES-U has been obtained.
3. The chromophore J-aggregates can still contribute to EO activity, if a dissociated monomer during its transition to the H-aggregates can be effectively captured and poled under a high electric field.

Appendix A: X-ray data of PeQDM-Ben

Table 1. Crystal data and structure refinement for PeQDM-Ben

Identification code	cu414		
Empirical formula	C25 H19 N3 O2		
Formula weight	393.43		
Temperature	209(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 6.9438(9) Å		$\alpha = 79.690(2)^\circ$.
	b = 8.2773(10) Å		$\beta = 80.961(2)^\circ$.
	c = 19.208(2) Å		$\gamma = 68.408(2)^\circ$.
Volume	1004.9(2) Å ³		
Z	2		
Density (calculated)	1.300 Mg/m ³		
Absorption coefficient	0.084 mm ⁻¹		

F(000)	412
Crystal size	0.40 x 0.20 x 0.08 mm ³
Theta range for data collection	2.17 to 26.37°.
Index ranges	-8<= <i>h</i> <=8, -10<= <i>k</i> <=10, -23<= <i>l</i> <=23
Reflections collected	8111
Independent reflections	4060 [R(int) = 0.0274]
Completeness to theta = 26.37°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9933 and 0.9671
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4060 / 1 / 303
Goodness-of-fit on F ²	0.975
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1222
R indices (all data)	R1 = 0.1045, wR2 = 0.1387
Largest diff. peak and hole	0.165 and -0.234 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for PeQDM-Ben. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	7253(4)	3147(4)	1323(1)	52(1)
O(2)	8742(2)	3164(2)	1756(1)	43(1)
C(3)	9256(4)	1812(3)	2296(1)	38(1)
O(4)	8396(3)	721(2)	2396(1)	63(1)
C(5)	10802(3)	1866(3)	2684(1)	33(1)
C(6)	11652(3)	3197(3)	2438(1)	36(1)
N(7)	12322(3)	4311(3)	2253(1)	54(1)
C(8)	11538(3)	644(3)	3312(1)	31(1)
C(9)	13406(3)	467(3)	3570(1)	34(1)
C(10)	14096(3)	-643(3)	4174(1)	33(1)
C(11)	12953(3)	-1640(3)	4574(1)	30(1)
C(12)	11106(3)	-1498(3)	4317(1)	35(1)
C(13)	10429(3)	-408(3)	3709(1)	35(1)
C(14)	13665(3)	-2804(3)	5228(1)	30(1)

C(15)	15840(3)	-3257(3)	5323(1)	31(1)
N(16)	17568(3)	-3612(3)	5377(1)	42(1)
C(17)	12450(3)	-3513(3)	5709(1)	32(1)
C(18)	12995(3)	-4780(3)	6341(1)	31(1)
C(19)	14624(3)	-5038(3)	6742(1)	38(1)
C(20)	15030(4)	-6320(3)	7310(1)	39(1)
N(21)	13907(3)	-7381(2)	7495(1)	33(1)
C(22)	12291(4)	-7139(3)	7137(1)	37(1)
C(23)	11802(3)	-5852(3)	6570(1)	35(1)
C(24)	14507(4)	-8846(3)	8089(1)	41(1)
C(25)	14080(20)	-8230(20)	8807(4)	39(4)
C(26)	15800(20)	-8270(19)	9103(7)	67(3)
C(27)	15560(30)	-7752(14)	9770(7)	89(4)
C(28)	13600(40)	-7198(11)	10142(3)	74(5)
C(29)	11880(30)	-7163(12)	9847(5)	68(5)
C(30)	12120(20)	-7682(16)	9179(6)	58(3)
C(25B)	13818(18)	-8200(20)	8801(4)	42(4)
C(26B)	15180(20)	-8175(18)	9253(6)	56(2)
C(27B)	14430(30)	-7647(13)	9921(5)	65(4)
C(28B)	12310(30)	-7146(12)	10137(3)	75(4)
C(29B)	10940(20)	-7173(14)	9685(7)	87(3)
C(30B)	11698(18)	-7700(20)	9018(6)	67(3)

Table 3. Bond lengths [Å] and angles [°] for PeQDM-Ben

C(1)-O(2)	1.431(3)
O(2)-C(3)	1.364(3)
C(3)-O(4)	1.228(3)
C(3)-C(5)	1.417(3)
C(5)-C(6)	1.411(3)
C(5)-C(8)	1.455(3)
C(6)-N(7)	1.157(3)
C(8)-C(9)	1.409(3)
C(8)-C(13)	1.415(3)
C(9)-C(10)	1.375(3)

C(10)-C(11)	1.402(3)
C(11)-C(12)	1.403(3)
C(11)-C(14)	1.471(3)
C(12)-C(13)	1.371(3)
C(14)-C(17)	1.354(3)
C(14)-C(15)	1.449(3)
C(15)-N(16)	1.142(3)
C(17)-C(18)	1.455(3)
C(18)-C(23)	1.397(3)
C(18)-C(19)	1.399(3)
C(19)-C(20)	1.363(3)
C(20)-N(21)	1.345(3)
N(21)-C(22)	1.341(3)
N(21)-C(24)	1.493(3)
C(22)-C(23)	1.369(3)
C(24)-C(25B)	1.501(5)
C(24)-C(25)	1.503(5)
C(25)-C(26)	1.3900
C(25)-C(30)	1.3900
C(26)-C(27)	1.3900
C(27)-C(28)	1.3900
C(28)-C(29)	1.3900
C(29)-C(30)	1.3900
C(25B)-C(26B)	1.3900
C(25B)-C(30B)	1.3900
C(26B)-C(27B)	1.3900
C(27B)-C(28B)	1.3900
C(28B)-C(29B)	1.3900
C(29B)-C(30B)	1.3900
C(3)-O(2)-C(1)	115.64(18)
O(4)-C(3)-O(2)	119.8(2)
O(4)-C(3)-C(5)	127.5(2)
O(2)-C(3)-C(5)	112.68(19)
C(6)-C(5)-C(3)	117.1(2)
C(6)-C(5)-C(8)	119.0(2)

C(3)-C(5)-C(8)	123.9(2)
N(7)-C(6)-C(5)	178.2(3)
C(9)-C(8)-C(13)	115.8(2)
C(9)-C(8)-C(5)	121.3(2)
C(13)-C(8)-C(5)	122.9(2)
C(10)-C(9)-C(8)	122.1(2)
C(9)-C(10)-C(11)	121.5(2)
C(10)-C(11)-C(12)	117.0(2)
C(10)-C(11)-C(14)	121.68(19)
C(12)-C(11)-C(14)	121.3(2)
C(13)-C(12)-C(11)	121.5(2)
C(12)-C(13)-C(8)	122.1(2)
C(17)-C(14)-C(15)	120.0(2)
C(17)-C(14)-C(11)	124.0(2)
C(15)-C(14)-C(11)	115.88(19)
N(16)-C(15)-C(14)	178.0(2)
C(14)-C(17)-C(18)	129.5(2)
C(23)-C(18)-C(19)	116.6(2)
C(23)-C(18)-C(17)	117.5(2)
C(19)-C(18)-C(17)	125.9(2)
C(20)-C(19)-C(18)	120.3(2)
N(21)-C(20)-C(19)	121.4(2)
C(22)-N(21)-C(20)	120.0(2)
C(22)-N(21)-C(24)	120.55(19)
C(20)-N(21)-C(24)	119.40(19)
N(21)-C(22)-C(23)	120.7(2)
C(22)-C(23)-C(18)	120.9(2)
N(21)-C(24)-C(25B)	111.6(7)
N(21)-C(24)-C(25)	113.3(6)
C(25B)-C(24)-C(25)	6.8(9)
C(26)-C(25)-C(30)	120.0
C(26)-C(25)-C(24)	116.1(7)
C(30)-C(25)-C(24)	123.8(7)
C(27)-C(26)-C(25)	120.0
C(26)-C(27)-C(28)	120.0
C(29)-C(28)-C(27)	120.0

C(28)-C(29)-C(30)	120.0
C(29)-C(30)-C(25)	120.0
C(26B)-C(25B)-C(30B)	120.0
C(26B)-C(25B)-C(24)	123.6(7)
C(30B)-C(25B)-C(24)	116.3(7)
C(25B)-C(26B)-C(27B)	120.0
C(26B)-C(27B)-C(28B)	120.0
C(29B)-C(28B)-C(27B)	120.0
C(28B)-C(29B)-C(30B)	120.0
C(29B)-C(30B)-C(25B)	120.0

Symmetry transformations used to generate equivalent atoms

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for PeQDM-Ben. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	56(2)	60(2)	43(2)	9(1)	-18(1)	-27(1)
O(2)	48(1)	42(1)	44(1)	8(1)	-15(1)	-23(1)
C(3)	46(2)	30(1)	38(1)	-1(1)	-7(1)	-16(1)
O(4)	93(2)	55(1)	65(1)	22(1)	-45(1)	-53(1)
C(5)	34(1)	31(1)	36(1)	-6(1)	-1(1)	-15(1)
C(6)	31(1)	42(1)	36(1)	-5(1)	-2(1)	-14(1)
N(7)	53(1)	57(2)	61(2)	5(1)	-11(1)	-35(1)
C(8)	32(1)	29(1)	34(1)	-10(1)	-1(1)	-11(1)
C(9)	35(1)	36(1)	35(1)	-8(1)	1(1)	-18(1)
C(10)	29(1)	39(1)	35(1)	-9(1)	-2(1)	-16(1)
C(11)	29(1)	30(1)	32(1)	-11(1)	-1(1)	-10(1)
C(12)	33(1)	38(1)	39(1)	-4(1)	-2(1)	-19(1)
C(13)	30(1)	37(1)	41(1)	-3(1)	-9(1)	-15(1)
C(14)	29(1)	30(1)	35(1)	-9(1)	-2(1)	-11(1)
C(15)	32(1)	33(1)	32(1)	-7(1)	-2(1)	-16(1)
N(16)	34(1)	49(1)	49(1)	-8(1)	-5(1)	-19(1)
C(17)	28(1)	34(1)	36(1)	-8(1)	-5(1)	-9(1)

C(18)	28(1)	30(1)	34(1)	-11(1)	2(1)	-9(1)
C(19)	40(1)	45(2)	38(1)	-4(1)	-4(1)	-26(1)
C(20)	39(1)	47(2)	35(1)	-5(1)	-9(1)	-20(1)
N(21)	38(1)	31(1)	33(1)	-7(1)	-3(1)	-14(1)
C(22)	37(1)	39(1)	41(1)	-7(1)	-4(1)	-20(1)
C(23)	30(1)	41(1)	39(1)	-7(1)	-5(1)	-15(1)
C(24)	50(2)	30(1)	41(1)	-2(1)	-8(1)	-11(1)
C(25)	50(5)	20(7)	37(9)	7(6)	-7(5)	-6(4)
C(26)	83(6)	78(6)	45(5)	-9(5)	-25(4)	-26(6)
C(27)	112(10)	101(7)	58(6)	-17(5)	-32(7)	-29(7)
C(28)	123(15)	48(5)	36(5)	-4(4)	-10(6)	-13(6)
C(29)	92(10)	48(5)	50(6)	-13(4)	18(6)	-15(5)
C(30)	66(6)	51(5)	55(6)	-5(4)	-5(5)	-19(4)
C(25B)	51(6)	37(8)	39(10)	-3(7)	-6(5)	-16(6)
C(26B)	62(6)	48(5)	45(5)	8(4)	-19(4)	-7(4)
C(27B)	98(10)	51(6)	41(5)	-8(4)	-21(6)	-16(6)
C(28B)	100(12)	75(6)	43(6)	-9(4)	-6(5)	-21(6)
C(29B)	76(6)	120(8)	58(6)	-21(5)	18(5)	-31(6)
C(30B)	64(6)	91(7)	41(5)	-13(5)	12(4)	-26(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for PeQDM-Ben

	x	y	z	U(eq)
H(1A)	7776	2064	1114	78
H(1B)	7023	4134	947	78
H(1C)	5951	3234	1612	78
H(9)	14205	1128	3321	41
H(10)	15364	-735	4323	40
H(12)	10313	-2164	4567	42
H(13)	9191	-357	3552	42
H(17)	11047	-3129	5620	39
H(19)	15443	-4324	6619	45

H(20)	16118	-6466	7578	46
H(22)	11486	-7861	7278	45
H(23)	10649	-5687	6330	42
H(24A)	15994	-9523	8005	50
H(24B)	13738	-9629	8089	50
H(26A)	17133	-8644	8851	80
H(27A)	16723	-7775	9970	107
H(28A)	13430	-6848	10594	88
H(29A)	10547	-6789	10098	82
H(30A)	10956	-7658	8979	70
H(26B)	16617	-8514	9106	67
H(27B)	15352	-7629	10226	77
H(28B)	11798	-6789	10589	90
H(29B)	9509	-6835	9832	105
H(30B)	10775	-7720	8712	80

Table 6. Torsion angles [°] for PeQDM-Ben

C(1)-O(2)-C(3)-O(4)	-2.5(3)
C(1)-O(2)-C(3)-C(5)	177.4(2)
O(4)-C(3)-C(5)-C(6)	176.1(2)
O(2)-C(3)-C(5)-C(6)	-3.7(3)
O(4)-C(3)-C(5)-C(8)	-4.1(4)
O(2)-C(3)-C(5)-C(8)	176.08(19)
C(3)-C(5)-C(6)-N(7)	109(9)
C(8)-C(5)-C(6)-N(7)	-70(9)
C(6)-C(5)-C(8)-C(9)	-16.4(3)
C(3)-C(5)-C(8)-C(9)	163.8(2)
C(6)-C(5)-C(8)-C(13)	162.3(2)
C(3)-C(5)-C(8)-C(13)	-17.5(3)
C(13)-C(8)-C(9)-C(10)	-0.7(3)
C(5)-C(8)-C(9)-C(10)	178.1(2)
C(8)-C(9)-C(10)-C(11)	-1.1(3)
C(9)-C(10)-C(11)-C(12)	2.0(3)
C(9)-C(10)-C(11)-C(14)	-178.8(2)

C(10)-C(11)-C(12)-C(13)	-1.1(3)
C(14)-C(11)-C(12)-C(13)	179.6(2)
C(11)-C(12)-C(13)-C(8)	-0.7(3)
C(9)-C(8)-C(13)-C(12)	1.6(3)
C(5)-C(8)-C(13)-C(12)	-177.2(2)
C(10)-C(11)-C(14)-C(17)	165.9(2)
C(12)-C(11)-C(14)-C(17)	-14.9(3)
C(10)-C(11)-C(14)-C(15)	-17.4(3)
C(12)-C(11)-C(14)-C(15)	161.76(19)
C(17)-C(14)-C(15)-N(16)	143(7)
C(11)-C(14)-C(15)-N(16)	-34(7)
C(15)-C(14)-C(17)-C(18)	-2.0(4)
C(11)-C(14)-C(17)-C(18)	174.5(2)
C(14)-C(17)-C(18)-C(23)	-152.8(2)
C(14)-C(17)-C(18)-C(19)	26.7(4)
C(23)-C(18)-C(19)-C(20)	2.1(3)
C(17)-C(18)-C(19)-C(20)	-177.4(2)
C(18)-C(19)-C(20)-N(21)	0.9(4)
C(19)-C(20)-N(21)-C(22)	-3.0(3)
C(19)-C(20)-N(21)-C(24)	175.7(2)
C(20)-N(21)-C(22)-C(23)	2.0(3)
C(24)-N(21)-C(22)-C(23)	-176.7(2)
N(21)-C(22)-C(23)-C(18)	1.1(3)
C(19)-C(18)-C(23)-C(22)	-3.1(3)
C(17)-C(18)-C(23)-C(22)	176.4(2)
C(22)-N(21)-C(24)-C(25B)	-103.6(6)
C(20)-N(21)-C(24)-C(25B)	77.7(6)
C(22)-N(21)-C(24)-C(25)	-110.8(6)
C(20)-N(21)-C(24)-C(25)	70.5(6)
N(21)-C(24)-C(25)-C(26)	-103.6(7)
C(25B)-C(24)-C(25)-C(26)	179(12)
N(21)-C(24)-C(25)-C(30)	77.4(9)
C(25B)-C(24)-C(25)-C(30)	0(10)
C(30)-C(25)-C(26)-C(27)	0.0
C(24)-C(25)-C(26)-C(27)	-179.0(12)
C(25)-C(26)-C(27)-C(28)	0.0

C(26)-C(27)-C(28)-C(29)	0.0
C(27)-C(28)-C(29)-C(30)	0.0
C(28)-C(29)-C(30)-C(25)	0.0
C(26)-C(25)-C(30)-C(29)	0.0
C(24)-C(25)-C(30)-C(29)	179.0(13)
N(21)-C(24)-C(25B)-C(26B)	-110.3(9)
C(25)-C(24)-C(25B)-C(26B)	-5(10)
N(21)-C(24)-C(25B)-C(30B)	73.1(8)
C(25)-C(24)-C(25B)-C(30B)	179(12)
C(30B)-C(25B)-C(26B)-C(27B)	0.0
C(24)-C(25B)-C(26B)-C(27B)	-176.5(14)
C(25B)-C(26B)-C(27B)-C(28B)	0.0
C(26B)-C(27B)-C(28B)-C(29B)	0.0
C(27B)-C(28B)-C(29B)-C(30B)	0.0
C(28B)-C(29B)-C(30B)-C(25B)	0.0
C(26B)-C(25B)-C(30B)-C(29B)	0.0
C(24)-C(25B)-C(30B)-C(29B)	176.8(13)

Symmetry transformations used to generate equivalent atoms

Appendix B: Spectra of Synthesized Reactants and Products

^1H NMR (400MHz, CDCl_3) of H_2DMCQ

^{13}C NMR (100MHz, CDCl_3) of H_2DMCQ

MS (EI, M/Z) of H₂DMCQ: 272 (M⁺)

1g3501 Scan 23 RT=0:38 100%=475130 mv 10-Mar-2004 09:26
LRP +EI

¹H NMR (400MHz, DMSO-d₆) of 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyano-p-xylene

^{13}C NMR (100MHz, DMSO- d_6) of 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyano-p-xylene

IR (Neat, cm^{-1}) of 7,8-di(hydroxyethoxycarbonyl)-7,8-dicyano-p-xylene

MS (EI, M/Z) of **D(E-OH)CQ**: 330 (M^+)

1g2133 Scan 40 RT=1:07 100%=275066 mv 26-Jun-2003 09:45
LRP +EI

^1H NMR (400MHz, DMSO- d_6) of N-hexyl-4-methylpyridinium bromide

^{13}C NMR (100MHz, DMSO- d_6) of N-hexyl-4-methylpyridinium bromide

^1H NMR (400MHz, DMSO- d_6) of N-hydroxyethyl-4-methylpyridinium bromide

^{13}C NMR (100MHz, DMSO- d_6) of N-hydroxyethyl-4-methylpyridinium bromide

^1H NMR (300MHz, DMSO- d_6) of N-hydroxypropyl-4-methylpyridinium bromide

^{13}C NMR (75MHz, DMSO- d_6) of N-hydroxypropyl-4-methylpyridinium bromide

^1H NMR (400MHz, DMSO- d_6) of N-benzyl-4-methylpyridinium chloride

^{13}C NMR (100MHz, DMSO-d_6) of N-benzyl-4-methylpyridinium chloride

^1H NMR (300MHz, DMSO-d_6) of N-(4-hydroxymethyl)benzyl-4-methylpyridinium chloride

^{13}C NMR (75MHz, DMSO- d_6) of N-(4-hydroxymethyl)benzyl-4-methylpyridinium chloride

^1H NMR (300MHz, DMSO- d_6) of 1-2OH-4-methylpyridinium bromide

^{13}C NMR (75MHz, DMSO- d_6) of 1-2OH-4-methylpyridinium bromide

^1H NMR (400MHz, DMSO- d_6) of PeQDM-Hex

^{13}C NMR (100MHz, DMSO-d_6) of PeQDM-Hex

IR (KBr, cm^{-1}) of PeQDM-Hex

MS (ESI, CH₃CN, M/Z) of PeQDM-Hex

¹H NMR (400MHz, DMSO-d₆) of PeQDM-C2OH

^{13}C NMR (100MHz, DMSO- d_6) of PeQDM-C2OH

MS (ESI, $\text{CH}_3\text{CN}/\text{DMF}$: v/v = 8/1, M/Z) of PeQDM-C2OH: 348 ($\text{M}+\text{H}^+$)

^1H NMR (300MHz, DMSO- d_6) of PeQDM-C3OH

^{13}C NMR (75Hz, DMSO- d_6) of PeQDM-C3OH

IR (KBr, cm^{-1}) of PeQDM-C3OH

MS (ESI, $\text{CH}_3\text{CN}/\text{DMF}$: v/v = 8/1, M/Z) of PeQDM-C3OH: 362 ($\text{M}+\text{H}^+$)

^1H NMR (300MHz, DMSO-d_6) of PeQDM-BenOH

^{13}C NMR (75MHz, DMSO-d_6) of PeQDM-BenOH

IR (KBr, cm^{-1}) of PeQDM-BenOH

MS (ESI, $\text{CH}_3\text{CN}/\text{DMF}$: v/v = 1/1, M/Z) of PeQDM-BenOH: 424 ($\text{M}+\text{H}^+$)

^1H NMR (400MHz, DMSO-d_6) of PeQDM-2OH

^{13}C NMR (100MHz, DMSO-d_6) of PeQDM-2OH

IR (KBr, cm^{-1}) of PeQDM-2OH

MS (ESI, CH_3CN , M/Z) of PeQDM-2OH: 630 ($M+H^+$)

^1H NMR (300 MHz, DMSO- D_6) of PeQDM-C3OH-E-OH

^{13}C NMR (75 MHz, DMSO- D_6) of PeQDM-C3OH-E-OH

MS (ESI, Methanol/DMF: v/v = 1/1, M/Z) of PeQDM-C3OH-E-OH: 392 (M+H⁺)

¹³C NMR (75 MHz, DMSO-D₆) of ES-dendron

^{13}C NMR (100 MHz, DMSO- D_6) of ES-PeQDM-1a

^1H NMR (300 MHz, DMSO- D_6) of ES-PeQDM-1b

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) of ES-PeQDM-1b

IR (KBr, cm^{-1}) of ES-PeQDM-1b

MS (ESI, DMF/Methanol: v/v = 1/1, M/Z) of ES-PeQDM-1b: 1062 (M+H⁺)

¹H NMR (300 MHz, DMSO-D₆) of ES-PeQDM-1c

^{13}C NMR (75 MHz, DMSO- D_6) of ES-PeQDM-1c

IR (KBr, cm^{-1}) of ES-PeQDM-1c

MS (ESI, Acetonitrile, M/Z) ES-PeQDM-1c: 1124 (M+H⁺)

IR (Neat, cm⁻¹) of ES-PeQDM-2

IR (KBr, cm^{-1}) of PES-Acid

IR (Neat, cm^{-1}) of PES-E-1

^1H NMR (300MHz, CDCl_3) of PES-E-2

IR (Neat, cm^{-1}) of PES-E-2

^1H NMR (300MHz, CDCl_3) of PES-E-3

^{13}C NMR (75 MHz, CDCl_3) of PES-E-3

IR (Neat, cm^{-1}) of PES-E-3

^1H NMR (300 MHz, CDCl_3) of PES-E-4

^{13}H NMR (75 MHz, CDCl_3) of PES-E-4

IR (Neat, cm^{-1}) of PES-E-4