Synthesis and Properties of Zwitterionic Nonlinear Optical Chromophores with Large Hyperpolarizability for Poled Polymer Applications

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The electric-field-dependent change in refractive index in nonlinear optical (NLO) materials can be utilized for electrical-to-optical signal conversion, such as fast electrooptic (EO) modulators needed in optical telecommunication.[1] Compared to inorganic NLO crystals (e.g., LiNbO$_3$), organic NLO materials offer advantages such as higher EO coefficients, lower dielectric constants, and good processibility.[2] To obtain a large EO response, chromophores with a high molecular nonlinearity (hyperpolarizability β) need to be oriented to form a macroscopically noncentrosymmetric material. For chromophores with a large dipole moment (μ), one way to achieve such a polar ordering is by electric-field poling of the chromophores in a polymer matrix. Consequently, the main figure of merit describing the performance of NLO chromophores in such EO polymer applications is the scalar product $\mu\beta$. Among many types of organic NLO chromophores, zwitterionic derivatives of 7,7,8,8-tetracyanoquinodimethane (TCNQ) such as (Z)-4-[1-cyano-3-(diethylamino)-2-propenylidene]-2,5-cyclohexadiene-1-ylidenepropanedinitrile (DEMI; Figure 1) are known to possess very high molecular hyperpolarizabilities and show the largest $\mu\beta$ values reported to date.[3]

To be useful for EO applications, the chromophores need to be either doped in a medium (e.g., polymer or sol−gel glass) or covalently linked to a polymer and oriented under an electric field. While the zwitterionic nature of the NLO chromophores is in favor of attaining a large $\mu\beta$ value, it can also present limitations for EO applications as a result of poor solubility and strong dipole−dipole interactions. For example, DEMI was reported to have a high $\mu\beta_0$ value of
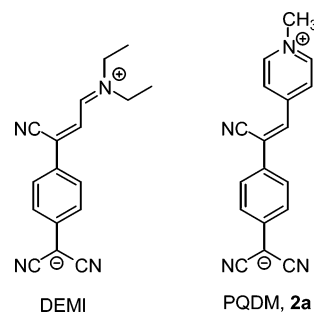

Figure 1. Zwitterionic NLO chromophores.

9500×10^{-48} esu (β_0 = static hyperpolarizability).[3] An analogue, picolinium quinodimethane (PQDM) **2a** (Figure 1), was calculated to have a static molecular hyperpolarizability of 1270×10^{-30} esu.[4] However, both chromophores are highly crystalline and have no functional groups (e.g., OH or NH$_2$), making it very difficult to either physically or chemically incorporate them into a host polymer.

A simple method to assess new chromophores for potential use as NLO materials is to measure the EO response of a chromophore-doped polymer after poling. However, the amount of chromophores that can be doped in a polymer is limited due to the tendency of phase separation. In comparison, functionalized chromophores are more desirable, because a relatively large amount of chromophores can be incorporated into a host polymer via covalent bonds to form a processable homogeneous polymer. To explore the potential of zwitterionic chromophores, it is necessary to obtain and evaluate the functionalized chromophores. We report herein the synthesis of a series of PQDM chromophores and studies on the molecular hyperpolarizability (β) and EO coefficients (r_{33} at 1550 nm) of the PQDM-doped poly(ether sulfone) (PES).

Chromophore Design and Synthesis. The synthesis of PQDM chromophores is based on the condensation reaction of a picolinium salt and TCNQ. Chromophore **2a** was previously prepared in a low yield (15 to 30%) over a long reaction time (5−14 days).[4] It was later found that by using 2 molar equiv of LiTCNQ (the adduct from TCNQ and LiI) and an amine base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the reaction yield for **2a** could be improved to 97%.[5] To introduce a functional group into PQDM chromophores, the picolinium moiety in PQDM was chosen as the site of modification. Thus, using the same strategy as that reported in ref 6, alkyl bromides readily reacted with 4-picoline in boiling anhydrous ethanol to produce the corresponding N-alkylated picolinium salts (**1a−i**). The subsequent reactions with TCNQ or LiTCNQ in the presence

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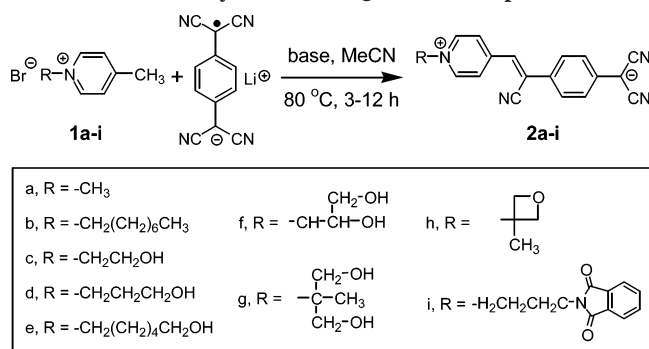‡ University of Durham.
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Scheme 1. Synthesis of PQDM Chromophores

a, R = -CH₃

b, R = -CH₂(CH₂)₆CH₃

c, R = -CH₂CH₂OH

d, R = -CH₂CH₂CH₂OH

e, R = -CH₂(CH₂)₄CH₂OH

f, R = -CH-CH-OH with CH₂-OH

g, R = -C-CH₃ with CH₂-OH and CH₂-OH

h, R = oxetane with CH₃

i, R = -H₂CH₂CH₂CH₂N-phthalimide

of *N*-(2-hydroxyethyl)piperidine or DBU afforded PQDM **2a**−**i** (Scheme 1). Chromophores containing the simple alkyl substituents (**2a,b**) were used as model compounds for optimizing the reaction conditions. The oxetane-containing PQDM **2h** is a precursor to the diol **2g** and can yield the polymers by the ring-opening polymerization of the oxetane moiety. Chromophore **2i** serves as a precursor to an amine-containing PQDM.

Hydroxy-containing PQDM chromophores were pursued so that they could be utilized in design and synthesis of a variety of NLO polymers by the grafting approach. The monohydroxy-containing chromophores **2c**−**e** contain alkyl chains with varying lengths. The chromophores containing the longer alkyl chains would presumably be ideal because this would allow for a higher mobility of the pendent chromophore in polymer during the poling process. The diol-containing chromophores (**2f,g**) are potential monomers for making linear and hyperbranched polyesters and polyurethanes.

Members of the PQDM series give similar absorption peaks in the UV−vis spectra with λ_{max} at 655 nm in DMF (Figure 2) and extinction coefficients (log ϵ) between 4.42 and 4.65 (Table 1). As evidence of the charge-separated nature of these chromophores, the PQDM zwitterions display a negative solvatochromic effect in solvents with different
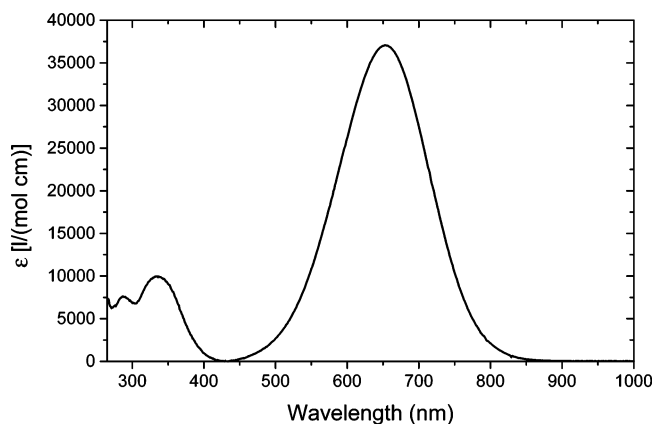

Figure 2. UV−vis spectrum of PQDM **2d** in DMF.

Table 1. Absorption Data of PQDM Chromophores in DMF

PQDM	λ_{max}, nm	log ϵ	PQDM	λ_{max}, nm	log ϵ
2a	658	4.42	**2f**	655	4.60
2b	654	4.45	**2g**	670	4.56
2c	653	4.48	**2h**	661	4.61
2d	653	4.57	**2i**	659	4.22
2e	654	4.58			

Table 2. Solvatochromic Effect on PQDM 2d

solvent	λ_{max}, nm	log ϵ	dielectric constant (ϵ)
1,4-dioxane	749	4.70	2.2
toluene	766	4.65	2.4
diethyl ether	737	4.54	4.3
chloroform	757	4.43	4.8
tetrahydrofuran	737	4.76	7.6
methanol	624	4.51	32.7
nitromethane	654	4.53	35.9
DMF	653	4.58	36.7
acetonitrile	650	4.55	37.5
dimethyl sulfoxide	638	4.53	46.7

polarities. As shown with PQDM **2d**, a blue shift was observed in solvents of increasing polarity (Table 2). It is known that other zwitterionic chromophores also display a negative solvatochromic shift with an increase in polarity of the solvents that can stabilize the zwitterions.[6,7] The infrared spectroscopic data also provide evidence of the zwitterionic structures, showing two C≡N stretches, rather than one conjugated C≡N similar to TCNQ at 2223 cm⁻¹, at approximately 2130 and 2175 cm⁻¹.

The ¹H NMR spectrum (see Supporting Information) of PQDM **2d** reveals further a zwitterionic character of the PQDM chromophores. The two protons on the pyridyl moiety experience the greatest deshielding and resonate at 8.8 and 8.3 ppm, respectively, and compared favorably with the published data.[6] The proton at 7.8 ppm is part of the olefinic bridge, while the two aromatic protons within close proximity to the acceptor moiety resonate at 6.8 and 7.5 ppm as a result of the developing negative charge at the dicyanomethanide group.[3] The ¹³C NMR spectrum (see Supporting Information) further supports the structure of the PQDM chromophore as shown for **2d**. There is a total of 15 lines in the spectrum, which is consistent with the number of nonequivalent carbons in **2d**. The methine carbons on the pyridyl ring show up in a relatively lower field (144.0 and 127.5 ppm) than those on the benzene ring (118.1 and 123.2 ppm). Two different nitrile carbons appear at 120.0 and 117.0 ppm, respectively. The three carbons in the alkyl tail appear at 58.0, 57.5, and 32.0 ppm.

The stability of the chromophores represents one of the important criteria in the design of EO devices. The chromophores should be thermally and chemically stable over the lifetime of the device. The PQDM chromophores are thermally stable up to 287 °C as assessed by thermogravimetry in nitrogen (see Supporting Information). When the chromophores are isolated from light and placed under an inert atmosphere at 25 °C, the UV−vis spectra indicate no degradation over a long time (e.g., > 1 year in the crystalline solid state). However, in the presence of oxygen and light, these chromophores in solution gradually decompose.[5]

Molecular Hyperpolarizability. To achieve a large EO coefficient, the active chromophores need to possess both a large molecular NLO response (hyperpolarizability β) and a high degree of co-alignment (determined by the dipole moment μ, as well as the material properties of the polymer matrix). To be able to investigate both aspects separately,

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the molecular hyperpolarizabilities of the model chromophore **2a** as well as the hydroxy derivative **2d** were determined from hyper-Rayleigh scattering (HRS) experiments.[8,9] This technique is based on the incoherent second harmonic generation obtained directly from the randomly oriented chromophores in a dilute liquid solution and, hence, is far more straightforward to interpret than electric-field-induced second harmonic generation or solid state (Kurtz powder) measurements. Both compounds yield extremely large hyperpolarizabilities of $\beta_{zzz}(-2\omega; \omega, \omega) = 1865 \times 10^{-30}$ esu for **2a** and 1930×10^{-30} esu for **2d**, at a fundamental wavelength of 1.07 μm, which is about twice as large as the closely related compound DEMI (780×10^{-30} esu in CHCl$_3$[3]; $\sim$1100 $\times 10^{-30}$ esu in DMF). Within the two-level model, these near resonant values correspond to static hyperpolarizabilities of 595 and 602 $\times 10^{-30}$ esu, respectively. The larger molecular hyperpolarizabilities are in line with theoretical predictions[4] and can be attributed to the slightly longer conjugated chain compared to DEMI, combined with the even stronger aromaticity stabilizing the charge-separated resonance form of this molecule, shifting it further rightward in the bond length alternation diagram.[10] Consequently, in reference to the dipole moment (38 D) of some PQDM analogues (in which the pyridinium moiety is replaced with a quinolinium unit) measured in a solid polymer matrix,[11] the present PQDM chromophores should also have a large dipole moment on the order of 40 D in a polymer matrix. Thus, this leads to the expectation of an extremely high figure of merit $\mu\beta$ for poled polymer applications, also demonstrating that the substitution on the pyridinium ring provides a versatile means of functionalizing the chromophores for improving solubility or covalent attachment to polymers, without affecting the strong molecular nonlinearity.

The measured β is near resonantly enhanced, owing to the long wavelength of absorption, between the fundamental wavelength of the laser and its second harmonic. Assuming that this strong low-energy charge-transfer transition gives the dominant contribution to the hyperpolarizability, the NLO response of the molecules can be described by a two-level model:[12]

$$\beta(-2\omega; \omega, \omega) = \beta_0 \frac{\omega_{eg}^4}{(\omega_{eg}^2 - \omega^2)(\omega_{eg}^2 - 4\omega^2)}$$

where β_0 is the static hyperpolarizability, ω_{eg} is the transition energy of the molecule, and ω is the laser frequency.

It should be noted that the second harmonic wavelength is probably too close to resonance for the two-level model to provide an accurate description of the dispersion of β in this wavelength range. However, it is still useful to provide

a rough estimate of the static hyperpolarizability or other frequency components of the hyperpolarizability, such as $\beta(-\omega; \omega, 0)$ relevant to EO applications:[13]

$$\beta(-\omega; \omega, 0) = \beta_0 \frac{\omega_{eg}^4 - (1/3)\omega^2\omega_{eg}^2}{(\omega_{eg}^2 - \omega^2)^2}$$

which yields β values for EO modulation at 1550 nm of 832 and 839 $\times 10^{-30}$ esu for compounds **2a** and **2d**, respectively.

Electrooptic Studies. To assess the potential of PQDM chromophores in EO applications, a doping study was carried out and the macroscopic EO activity of the poled NLO guest−host polymer was assessed. Although the chromophores **2c**−**i** were readily soluble in polar organic solvents such as *N,N*-dimethylformamide (DMF) and dimethylacetamide (DMAc), the strong intermolecular interactions of these chromophores, arising from their large dipole moments,[10] limited the doping level to about 2%. Levels higher than this led to phase separation. Thus, the guest−host NLO polymers were prepared using chromophore **2d** and commercial PES. PES was selected mainly because of its high glass transition temperature ($T_g = 225$ °C), which could prevent or minimize the chromophore relaxation after poling. The DMAc solution of PES containing 1 wt % PQDM (relative to PES) was cast onto indium tin oxide (ITO) glass substrates. After drying in the absence of oxygen and light for 24 h at ambient temperatures, the polymer films ($\sim$2 μm thickness) were further dried for 12 h at 100 °C under vacuum (5 mmHg) before sputtering a thin layer of gold (150 nm) as a top electrode onto the polymer films. During the contact poling, the sample cells were gradually heated to 200 °C and the voltage applied across the polymer films was maintained between 55 and 60 V/μm while keeping the current across the films below 10 μA. The EO coefficients of the poled films were then measured using a Teng−Man ellipsometric setup,[14] which was calibrated with a commercial LiNbO$_3$ crystal ($r_{33} = 31$ pm/V at 1550 nm).

Although the chromophore loading was low, the poled NLO polymer samples were found to have a high r_{33} value, typically around 21 pm/V at 1550 nm, as measured immediately after poling. The high quality of polymer films, for example, pinhole free and no phase separation, is important to ensure a successful poling without electrical breakdown and to obtain reproducible EO coefficients. The temporal stability of the EO response observed for this polymer was then evaluated. The sample cell was kept at 85 °C in the dark under a nitrogen atmosphere. The EO coefficients were determined at intervals of 168 h (1 week) while minimizing exposure to the atmosphere and light. The EO coefficients dropped significantly during the first 350 h but retained a good value of 16 pm/V at 750 h (Figure 3). The decrease of the EO signal is expected as a result of the relaxation of the ordered, polar chromophores within the non-cross-linked polymer matrix.

In conclusion, a series of PQDM chromophores were synthesized in good yields. The functionalized PQDM **2c**−**i**

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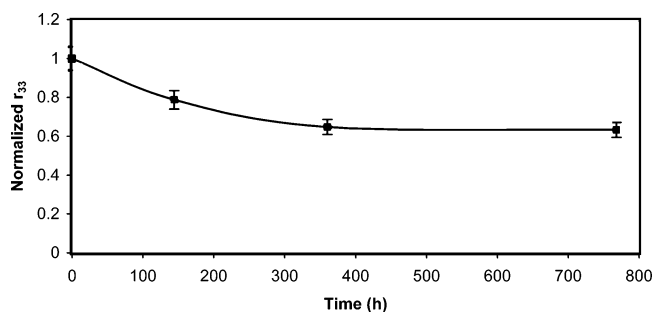(14) Teng, C.; Man, H. *Appl. Phys. Lett.* **1990**, *56*, 1734.

Figure 3. Temporal stability of the poled polymer (**2d** in PES) at 85 °C in nitrogen.

are thermally stable and soluble in polar organic solvents. A high β value of 1930×10^{-30} esu ($\beta_0 \sim -602 \times 10^{-30}$ esu) was obtained by HRS for chromophore **2d**. A guest−host polymer showed a high EO coefficient of 21 pm/V at 1550 nm and a good temporal stability over 700 h.

The experimental details are as follows. The reagents and solvents were obtained from Aldrich Canada, Ltd., and used without purification. Chromophores **2a** and **2b** and the adduct (LiTCNQ) from TCNQ and LiI were prepared according to the literature procedure.[5] PES (Ultrason, $T_g = 225$ °C) was obtained from BASF. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 400 MHz or a Gemini 200 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. UV−vis absorption spectra were recorded on Perkin-Elmer Lamda 900 and Varian Cary 5 UV−vis−NIR spectrophotometers. Thermogravimetric analysis was done on a Seiko TG/DTA 220 in nitrogen at a heating rate of 10 °C/min. The EO coefficients were recorded on a Teng−Man ellipsometric setup at 1550 nm. The LiNbO$_3$ wafer was purchased from Thorlabs, Inc., in New Jersey and used to calibrate the Teng−Man setup.

Synthesis of Picolinium Salts. 1c. In a three-necked, round-bottomed flask flushed with nitrogen, 2-bromo-1-ethanol (4.40 g, 40.0 mmol), 4-picoline (4.00 g, 43.5 mmol), and absolute ethanol (16 mL) were combined and heated for 3.5 h at 50 °C under nitrogen with stirring. The reaction was stopped, and the contents of the flask were transferred to a one-necked round-bottomed flask. The solvent was removed under vacuum, the residue was washed with diethyl ether (4 × 100 mL), and any remaining solvent was removed under vacuum. The product was obtained as a viscous orange liquid which crystallized on standing: 2.96 g (34%); ^{1}H NMR (200 MHz, CDCl$_3$) 8.9 (d, 2H), 8.0 (d, 2H), 2.6 (s, 3H), 4.6 (s, 2H), 3.8 (s, 2H), 5.2 (s, 1H); ^{13}C NMR (50 MHz, CDCl$_3$) 160.0, 142.0, 128.5, 59.1, 58.0, 32.3; IR (neat, cm^{-1}) 3303 (OH), 1640 (aromatic C=N), 1474 (aromatic C=C).

1d. In a three-necked, round-bottomed flask flushed with nitrogen, 3-bromo-1-propanol (60.0 g, 431 mmol), 4-picoline (43.8 g, 470 mmol), and absolute ethanol (250 mL) were combined and heated at 60 °C for 24 h. The reaction was cooled to room temperature, and the solvent was removed under vacuum to afford the product as a viscous liquid. The crude product was triturated with diethyl ether (4 × 100 mL), and the resulting solid was collected by filtration: 96.0 g (96%); ^{1}H NMR (400 MHz, CDCl$_3$) 8.98 (d, 2H), 8.00 (d, 2H), 4.64 (t, 2H), 3.44 (t, 2H), 2.62 (s, 3H), 2.06 (p, 2H);

^{13}C NMR (50 MHz, DMSO-d_6) 159.0, 143.0, 128.2, 59.0, 58.8, 32.5, 21.6; IR (neat, cm^{-1}) 3332, 1642, 1518.

1e. The procedure for **1d** was repeated using 6-bromo-1-hexanol (5.00 g, 27.6 mmol), 4-picoline (2.80 g, 30.1 mmol), and absolute ethanol (16 mL). The reaction was stopped after 36 h, and the solvent was removed under vacuum. The crude residue was washed with diethyl ether (4 × 100 mL) to remove unreacted 6-bromo-1-hexanol to afford the product as a viscous oil: 6.80 g (90%); ^{1}H NMR (400 MHz, DMSO-d_6) 9.01 (d, 2H), 8.02 (d, 2H), 4.57 (t, 2H), 4.01 (s, 1H), 3.37 (t, 2H), 2.26 (s, 3H), 1.89 (p, 2H), 1.21−1.49 (6H, m); ^{13}C NMR (50 MHz DMSO-d_6) 160.5, 143.4, 128.0, 61.0, 59.1, 32.2, 30.0, 25.0, 24.7, 22.0; IR (neat, cm^{-1}) 3285, 1610.

1g. To a round-bottomed flask equipped with a calcium chloride drying tube were added 4-picoline (5.00 g 54.0 mmol) and 2-bromomethyl-2-methyl-1,3-propanediol (9.85 g, 54.0 mmol). The solution was heated at 100 °C under nitrogen for 48 h. The reaction was then cooled to room temperature, and the solvent was removed under vacuum to afford the product as a viscous oil which crystallized on cooling: 12.8 g (85%); ^{1}H NMR (200 MHz, DMSO-d_6) 8.80 (d, 2H), 8.00 (d, 2H), 4.50 (s, 2H), 3.20 (dd, 4H), 2.50 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) 158.5, 143.0, 130.0, 70.0, 56.5, 32.1, 15.0; IR (KBr, cm^{-1}) 3400, 1625.

1f. A mixture of freshly distilled 4-picoline (10.0 g, 108 mmol) and 2,3-dihydroxy-1-chloropropane (10.0 g, 91 mmol) was heated at 80−100 °C for 24 h while being protected from moisture by a calcium chloride drying tube. After cooling, the resulting solid was broken up with the aid of a spatula, and then 20 mL of ethyl acetate was added. The solid mass was collected by filtration and washed with ethyl acetate to give N-(2,3-dihydroxypropyl)-4-picolinium chloride as a moisture-sensitive pale-brown solid: 3.0 g (16.4%); recrystallization from ethanol gave off white crystals; mp 157−158 °C. Anal. Calcd for C$_9$H$_{14}$ClNO$_2$: C, 53.08; H, 6.93; N, 6.88%. Found: C, 52.21; H, 6.91; N, 6.74%. ^{1}H NMR (200 MHz, DMSO-d_6) 8.88 (d, 2H), 7.97 (d, 2H), 5.66 (s, 1H), 4.77 (dd, 1H), 4.47 (dd, $J = 1$ Hz), 3.89 (m, 1H), 3.47−3.53 (m, 1H), 3.27−3.33 (m, 1H), 2.60 (s, 3H); IR (KBr, cm^{-1}) 3280, 1623.

1h. The procedure for **1d** was repeated using 3-bromomethyl-3-methyloxetane (5.00 g, 30.0 mmol), 4-picoline (2.82 g, 30.0 mmol), and absolute ethanol (20 mL). The reaction was cooled after 24 h, and the precipitate was filtered by suction. The filtrate was washed with 20 mL of diethyl ether to give the product as a white amorphous solid: 6.95 g (90%); ^{1}H NMR (200 MHz, DMSO-d_6) 9.00 (d, 2H), 8.10 (d, 2H), 4.75 (s, 2H), 4.55−4.25 (dd, 4H), 2.60 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) 160.0, 142.3, 129.0, 84.5, 62.0, 32.5, 20.0; IR (KBr, cm^{-1}) 2170, 2135, 1630.

1i. In a three-necked, round-bottomed flask flushed with nitrogen, a solution of N-(3-bromopropyl)phthalimide (1.00 g, 3.7 mmol) and 4-picoline (0.36 g, 3.7 mmol) in acetonitrile (50 mL) was refluxed for 12 h. The reaction mixture was cooled to room temperature, and diethyl ether (20 mL) was added to the reaction mixture. The product was observed as a fine white precipitate. The precipitate was filtered by suction and dried in vacuo as a fine white powder: 1.01 g

(76%); ^{1}H NMR (400 MHz, CDCl$_3$) 9.40 (d, 2H), 7.86 (d, 2H), 7.60 (m, 4 H), 4.92 (t, 2H), 3.67 (t, 2H), 2.58 (s, 3H), 2.39 (t, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) 168, 159, 144, 134, 132, 129, 123, 58, 34, 30, 22; IR (KBr, cm^{-1}) 1769, 1713.

Chromophore Synthesis. *PQDM 2c*. To 100 mL of acetonitrile in a round-bottomed flask were added LiTCNQ (1.500 g, 7.100 mmol) and picolinium salt **1c** (1.080 g, 7.100 mmol). While at reflux, 1.5 mL of *N*-(2-hydroxyethyl)-piperidine was added, and the resulting green solution was allowed to continue at reflux while monitoring using the UV−vis spectrophotometer. After 20 h, the reaction was allowed to cool to room temperature. The dark blue to black precipitate was filtered by suction and was recrystallized from acetonitrile to give a blue solid: 0.700 g (30%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.80 (d, 2H), 8.30 (d, 2H), 7.80 (s, 1H), 7.50 (d, 2H), 6.80 (d, 2H), 4.50 (t, 2H), 3.50 (t, 2H), 2.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) 148.6, 147.3, 144.1, 127.5, 125.0, 124.1, 123.2, 121.6, 119.7, 118.2, 116.0, 61.1, 59.3; UV−vis λ_{max} 650 nm (DMF); IR (KBr, cm^{-1}) 3403, 2174, 2132, 1633, 1565.

PQDM 2d. Chromophore **2d** was synthesized in the same manner as **2c** using compound **1d** (0.55 g, 2.35 mmol), LiTCNQ (1.00 g, 4.70 mmol), and 1.54 molar equiv of DBU. The reaction was stopped after 30 h. The precipitate was recovered by filtration, dissolved in methanol, and then precipitated by addition to a volume of diethyl ether: 0.52 g (68%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.8 (d, 2H), 8.3 (d, 2H), 7.8 (s, 1H), 8.0 (d, 2H), 7.5 (d, 2H), 6.8 (d, 2H), 4.5 (m, 2H), 3.5 (m, 2H), 2.1 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) 148.0, 147.1, 144.2, 130.0, 127.5, 125.1, 124.5, 123.2, 120.5, 119.8, 118.1, 116.1, 60.0, 59.0, 32.2; UV−vis λ_{max} 653 nm (DMF); IR (KBr, cm^{-1}) 3403, 2174, 2132, 1633, 1565.

PQDM 2e. The procedure for compound **2c** was repeated, using picolinium salt **1e**. After 3 h the product precipitated from the reaction solution upon cooling. The product was collected by filtration as a dark blue powder: 0.48 g (45%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.90 (d, 2H), 8.30 (d, 2H), 7.80 (s, 1H), 7.60 (d, 2H), 6.80 (d, 2H), 4.50 (m, 2H), 3.40 (m, 2H), 1.92 (m, 2H), 1.32−1.42 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) 148.0, 147.0, 144.3, 126.9, 125.0, 124.9, 123.0, 120.2, 119.6, 118.0, 117.0, 60.0, 59.0, 32.2, 30.0, 25.5, 25.0; UV−vis λ_{max} 655 nm (DMF); IR (KBr, cm^{-1}) 3403, 2174, 2132, 1633, 1565, 1547, 1505.

PQDM 2f. To acetonitrile (100 mL) in a round-bottomed flask were added LiTCNQ (1.00 g, 4.70 mmol) and picolinium salt **1f** (0.965 g, 4.70 mmol). The resulting green solution was allowed to continue at reflux while monitoring the formation of the desired chromophore by UV−vis spectrophotometry. After 120 h the reaction mixture was blue, the heating was stopped, and the reaction vessel was allowed to cool to room temperature. The reaction mixture was reduced to dryness under vacuum. The crude dark product was recrystallized from acetonitrile to give a fine black powder: 0.300 g (18.3%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.88 (d, 2H), 8.30 (d, 2H), 7.88 (s, 1H), 7.60 (d, 2H), 6.87 (d, 2H), 5.50 (s, 1H), 4.70 (d, 2H), 4.38 (t, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) 149.5, 146.9, 144.9, 128.2,

125.6, 124.6, 123.7, 120.9, 119.4, 118.3, 116.7, 70.3, 70.2, 62.9; UV−vis λ_{max} 653 nm (DMF); IR (KBr, cm^{-1}) 3430, 2179, 2129, 1638, 1580.

PQDM 2g. Chromophore **2g** was synthesized in the same manner as **2c.** The reaction was stopped after 24 h. The product was collected by filtration and recrystallized from acetonitrile: 0.24 g (37%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.80 (d, 2H), 8.30 (d, 2H), 7.85 (s, 1H), 7.58 (d, 2H), 6.80 (d, 2H), 5.00 (t, 2H), 4.5 (t, 2H), 3.20 (dd, 4H), 0.95 (s, 3H); ^{13}C NMR (100 MHz DMSO-d_6) 149.0, 147.0, 145.5, 127.5, 125.0, 124.0, 123.3, 121.1, 119.0, 118.0, 116.5, 63.8, 62.2, 42.1, 17.5; UV−vis λ_{max} 670 nm (DMF); IR (KBr, cm^{-1}) 3450, 2175, 2134, 1630.

PQDM 2h. Chromophore **2h** was synthesized in the same manner as **2c.** The reaction was stopped after 12 h. The crude product was collected by filtration and recrystallized from acetonitrile to give green gold crystals: 0.24 g (35%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.90 (d, 2H), 8.33 (d, 2H), 7.85 (s, 1H), 7.60 (d, 2H), 6.85 (d, 2H), 4.78 (s, 2H), 4.50 (dd, 4H), 1.26 (s, 3H); ^{13}C NMR (100 MHz DMSO-d_6) 149.0, 147.1, 144.3, 127.5, 125.0, 124.2, 122.2, 121.0, 118.5, 116.4, 78.5, 64.5, 20.5; UV−vis λ_{max} 661 nm (DMF); IR (KBr, cm^{-1}) 2170, 2135, 1633.

PQDM 2i. To acetonitrile (100 mL) in a round-bottomed flask were added LiTCNQ (0.50 g, 2.37 mmol) and picolinium salt **1i** (0.855 g, 2.37 mmol). The resulting green solution was allowed to continue at reflux while monitoring by UV−vis spectrophotometry. After 120 h, the heating was stopped, and the reaction vessel was allowed to cool to room temperature. The dark precipitate was filtered by suction and was recrystallized from acetonitrile to give a blue/black powder: 0.240 g (22%); ^{1}H NMR (400 MHz, DMSO-d_6) 8.97 (d, 2H), 8.30 (d, 2H), 7.90, (m, 4 H), 7.82 (s, 1H), 7.57 (d, 2H), 6.85 (d, 2H), 4.58 (t, 2H), 3.7 (t, 4H), 2.27 (m, 2H); ^{13}C NMR (100 MHz DMSO-d_6) 149.4, 144.2, 134.2, 131.7, 127.4, 125.4, 124.9, 122.9, 120.9, 118.4, 117.2, 116.7, 57.6, 34.3, 29.7; UV−vis λ_{max} 649 nm (MeCN); IR (KBr, cm^{-1}) 2167, 2125, 1766, 1718.

Preparation and Measurement of NLO Guest−Host Polymers. A solution of PES containing 1 wt % of PQDM **2d** in DMAc (2.5 mL for 100 mg of sample) was stirred in a vial for 1 h and then filtered through a 0.2-μm mesh syringe filter. The filtered solution was cast onto an ITO glass substrate, and the solvent was allowed to evaporate overnight at 40 °C. The films were then dried in a vacuum oven at 80 °C for 24 h to remove residual DMAc. A thin layer of gold (150 nm) was sputtered onto the polymer surface to act as a top electrode. The poling voltage remained constant between 55 and 60 V/μm, and the current was kept below 10 μA. After reaching 180 °C, the samples were poled at 180 °C (10 min), 185 °C (10 min), 190 °C (5 min), and 195 °C (5 min) and then gradually cooled to room temperature while maintaining the final voltage. A Teng−Man ellisometry setup was first calibrated with a commercial LiNbO$_3$ crystal (r_{33} = 31 pm/V at 1550 nm) and then used to measure the EO coefficients of the poled polymer samples.

Hyper-Rayleigh Measurements. Molecular hyperpolarizabilities were determined by HRS measurements on dilute solutions (10^{-6} to 10^{-5} M) of the chromophores in DMF

(Acros, extra dry, water < 50 ppm). The beam ($\lambda = 1.07$ μm; 2 ps pulse width; $\sim$20 mJ pulse energy at the sample; 1.5 kHz) from an optical parametric amplifier (Spectra-Physics OPA-800CP, pumped by a Spectra-Physics Spitfire Ti:sapphire regenerative amplifier) was focused using cylindrical lenses onto the sample solution in a 10 mm path length square cell. The scattered second harmonic light was collected at 90° and analyzed using a spectrograph with parallel intensified charge-coupled device detection (Stanford Computer Optics 4 Quik E; with 20 ns time gating around the laser pulses). In this way, the spectral content of the scattered light is recorded over a narrow ($\sim$23 nm) wavelength range around the second harmonic, allowing a complete correction for any multiphoton induced fluorescence background present.[15,16] Then, the integrated HRS intensities from the solutions are used to derive the hyperpolarizability of the solute by calibration against the signal from pure DMF. The hyperpolarizability of DMF (effective $\beta_{zzz} = 0.70 \times 10^{-30}$ esu) was determined by external reference to chloroform, for which the effective value of 0.49×10^{-30} esu[17] was adopted, as discussed before.[16] The experimental error on the relative β values (not including the uncertainty on the reference standard) is estimated to be less than 5%. The β values reported are effective β_{zzz} values. This is based upon the assumption that only this component (z along the long axis of the conjugated molecule) is significant. For solvent and solute molecules, spherical Lorentz−Lorenz local field factors were assumed in this case.

Supporting Information Available: Thermogravimetry and ^{1}H and ^{13}C NMR spectra of PQDM **2d**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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