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Functionalized Picolinium Quinodimethane Chromophores for Electro-Optics: Synthesis, Aggregation Behavior, and Nonlinear Optical Properties

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A new series of functionalized and thermally stable zwitterionic picolinium (dicyano)esterquinodimethane (PeQDM) chromophores have been synthesized in one step from 7,8-di(methoxycarbonyl)-7,8-dicyanoquinodimethane (DMCQ) and various picolinium salts in methanol in nearly 50% overall yields. Hyper-Rayleigh scattering (HRS) measurements at 1.07 μm show very large near-resonant molecular first hyperpolarizabilities β up to 1800×10^{-30} esu, despite the fact that, compared to previously studied zwitterionic NLO chromophores, one of the strong CN acceptor groups is substituted by a weaker ester group to allow for further functionalization. The ester functionality can be further utilized for attachment of solubility-imparting groups, cross-linkers, and reactive groups for grafting the chromophore onto a polymer. To optimize the electro-optic (EO) activity in the polymer matrix, the aggregation behavior of the PeQDM chromophores is studied. X-ray crystallographic analysis confirms the charge-separated ground-state of PeQDM and reveals the formation of a face-to-face, antiparallel H-aggregation with a large slip angle ($\theta = 64.5^\circ$) between the chromophores. In a less polar polymer matrix, PeQDM chromophores can form H- and/or J-aggregates and only J-aggregates could contribute to the EO activity if the monomeric chromophores released during the thermally induced J–H transformation could be captured and effectively poled. In a more polar polymer host, chromophores are well dissolved as monomers and effectively poled. A large and stable EO activity ($r_{33} = 110$ pm/V) has been achieved with a polyethersulfone film doped with 5 wt % of *N*-benzyl picolinium (dicyano)esterquinodimethane (PeQDM-Ben).

1. Introduction

Over the past decades, much attention has been devoted to organic electro-optic (EO) materials due to their paramount advantages over their inorganic counterparts, such as structural versatility, ease of processing, lower dielectric constant, and the demonstrated large EO activity.¹ Highly polar zwitterionic chromophores are promising classes of nonlinear optical (NLO) chromophores for EO applications. Examples include (Z)-4-[1-cyano-3-(diethylamino)-2-propenylidene]-2,5-cyclohexadiene-1-ylidene-propane-dinitrile (DEMI, Figure 1),² picolinium quinodimethane (PQDM, Figure 1),³ merocyanines^{4a} and dicyanomethanides,^{4b,c} and the twisted π -electron chromophores.⁵ Zwitterionic chromophores are often referred to as right-hand-side (RHS) chromophores,

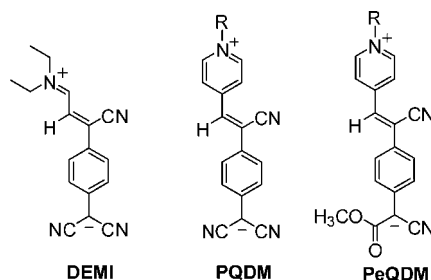


Figure 1. Chemical structures of zwitterionic NLO chromophores discussed herein: DEMI,² PQDM,³ and PeQDM (this work).

because they are positioned at the right side (i.e., to the right from the cyanine limit) in the bond-length alternation (BLA) diagram,⁶ meaning that their ground-state is dominated by the charge-separated, aromatic resonance structure, while the excited-state is dominated by the neutral, quinoidal structure. Indeed, DEMI was found to be at the right-hand-side already in moderately polar solvents² and PQDM is shifted even

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further to the right due to the additional stabilization of the charge-separated structure by a second aromatic ring.^{3d} Because of the stabilization of the charge-separated (zwitterionic) structure in the ground-state by a gain in aromaticity, these chromophores exhibit both a large molecular first hyperpolarizability (β) and a strong dipole moment (μ), leading to some of the largest figures of merit for poled polymer applications ($\mu\beta$ values) reported to date,^{2,3d} comparable to or even larger than the well-studied neutral ground-state or left-hand-side (LHS) chromophores⁷ (despite the often much larger molecular size of the latter). However, the strong electrostatic interactions between the dipoles result in chromophore aggregation or low chromophore loading level in the guest–host polymer system, thus giving rise to the limited EO activities. For example, in spite of a high $\mu\beta$ value for DEMI,² its highly crystalline nature hampers high-level doping in a polymer host and realization of high EO values. Furthermore, PQDM-grafted (10 wt %) linear and hyperbranched polymers had higher EO coefficients (45 and 65 pm/V, respectively)⁸ than that of the guest–host polymer with 1 wt % PQDM dopant (21 pm/V).^{3d} In all cases, a sharp decrease in EO activity was observed when the chromophore loading was further increased, due to strong chromophore aggregation.

It is generally believed that the formation of antiparallel H-aggregates is responsible for the loss of EO activity without direct experimental proof and systematic study. Aggregation behavior of polar merocyanine dyes in solution and in the solid state has been systematically investigated by Würthner and his co-workers.⁹ The formation of centrosymmetric dimers (H-aggregates) is due to strong electrostatic interactions between the dipoles and is characterized by a hypsochromically shifted band in the UV–vis spectrum and a large slip angle ($\sim 60^\circ$). The optical properties of H- and J-aggregates are well explained by the molecular exciton models.¹⁰ Contrary to H-aggregates, J-aggregates display a bathochromically shifted UV–vis absorption. Both H- and

J-aggregation of polar dyes are frequently observed in solution,¹¹ but to date it is still unclear how H- and J-aggregation affect the poling efficiency and EO activity of the NLO materials.

Since PQDM chromophores³ are readily synthesized from various picolinium salts and TCNQ, this synthetic route can be extended to the synthesis of a new series of zwitterionic chromophores simply by using TCNQ analogues. One possible TCNQ analogue is 7,8-di(methoxycarbonyl)-7,8-dicyanoquinodimethane (DMCQ), in which the two esters can be used for additional functionalization. In the resulting new zwitterionic chromophores, the ester group together with the R group on the pyridinium nitrogen allow for attachment of solubility-imparting groups, cross-linkers, and reactive groups for grafting chromophores onto a polymer. Since the ester is considered to be a weaker electron acceptor than the nitrile, the overall zwitterionic nature and thus also the hyperpolarizability of the resulting new chromophores may be affected. Therefore, structural and NLO characterizations of the new chromophores are necessary.

Hence, we report herein the one-step synthesis of a new series of functionalized picolinium (dicyano)esterquinodimethane (PeQDM, Figure 1) chromophores derived from DMCQ and various picolinium salts, experimental investigations into their NLO properties by hyper-Rayleigh scattering (HRS) measurements at the standard wavelength of 1.07 μm , and preliminary studies on the chromophore aggregation in relation to the poling process and EO response.

2. Experimental Section

Materials and Methods. 7,8-Di(methoxycarbonyl)-7,8-dicyanoquinodimethane (DMCQ) was synthesized according to the literature method.¹² PES-U (polyethersulfone-ultrason, commercial trade name: Ultrason E), APC (amorphous polycarbonate), and PVPh (polyvinylphenol) were purchased from BASF, Aldrich, and Hoechst, respectively. PES-Met (polyethersulfone-methyl ester) and PES-Hex (polyethersulfone-hexyl ester) were synthesized, as will be reported elsewhere. All other reagents and solvents were purchased from Aldrich and used as received. All the reactions were carried out under the protection of nitrogen atmosphere except for special statements. ¹H NMR and ¹³C 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 analyses (TGA) were carried out in nitrogen on a TA DSC Q100 and Hi-Res TGA 2950 thermogravimetric analyzer. The decomposition temperatures (T_d) were determined by 5% weight loss from the TGA curves at 5 $^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Refractive indices were measured by a Metricon 2010 prism coupler, and the film thickness was measured by means of an Alpha-Step 200 surface profiler. The EO coefficients (r_{33} values) of the poled polymers were measured using a Teng-Man setup at 1550 nm, which was calibrated with a commercial LiNbO₃ crystal ($r_{33} = 31$ pm/V) without taking into account the optical properties of

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the ITO layer.¹³ For the X-ray diffraction (XRD) studies of the polymer thin films, a Bruker D8 Discover diffractometer equipped with a copper target (K α 1 line, with wavelength $\lambda = 1.5406 \text{ \AA}$) was used under a step-scan rate of 0.05° per 10 s in the scattering range of $5\text{--}30^\circ$. The measurement was carried out in a grazing incidence mode with an incident angle of 0.2° to eliminate the effect of the glass background.

Synthesis of Picolinium Halides. *N*-Hexyl-4-methylpyridinium Bromide. A solution of 4.65 g of 4-picoline (50 mmol) and 9.90 g of 1-bromohexane (60 mmol) in 30 mL of acetonitrile was refluxed for 3 h and then cooled to room temperature. The cooled viscous mixture was slowly added to 100 mL of ethyl ether under vigorous stirring. After the mixture was kept standing for a while and the upper ether layer was decanted, the left 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 to remove residual starting materials. The resulting viscous liquid was dried under vacuum, and off-white waxy solids were 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). ¹³C 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.

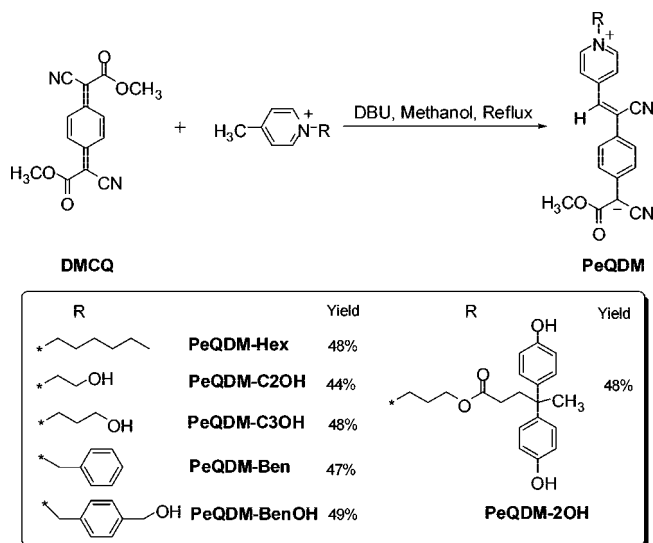
N-(2-Hydroxyethyl)-4-methylpyridinium Bromide. As for the synthesis of *N*-hexyl-4-methylpyridinium bromide, 12.66 g of 4-picoline (136 mmol), 17.00 g of 2-bromoethanol (136 mmol), and 60 mL of acetonitrile were refluxed for 3 h. The product (9.01 g, 98% yield) as off-white waxy solids was obtained. It is highly hygroscopic 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). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 158.7, 144.0, 127.8, 62.1, 59.9, 21.3.

N-(3-Hydroxypropyl)-4-methylpyridinium Bromide. As for the synthesis of *N*-hexyl-4-methylpyridinium bromide, 12.66 g of 4-picoline (136 mmol), 18.90 g of 3-bromopropanol (136 mmol), and 60 mL of acetonitrile were refluxed for 3 h. The product (30.00 g, 95% yield) as viscous liquid was obtained. This product is highly hygroscopic 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). ¹³C 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 2.53 g of benzyl chloride (20 mmol) and 1.86 g of 4-picoline (20 mmol) in 20 mL of acetonitrile was refluxed for 3 h and cooled to room temperature and then in a refrigerator. Pale pink crystals precipitated from the solution were filtered and washed with ethyl ether (3 \times 5 mL): 4.09 g (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). ¹³C 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 3.00 g of 4-(chloromethyl)benzyl alcohol (19.2 mmol) and 2.25 g of 4-picoline (24.1 mmol) in 20 mL of acetonitrile was refluxed for 3 h and then cooled to room temperature. After the upper colorless liquid was decanted, the residual pale pink solid was dissolved in 5 mL of methanol and dispersed into 50 mL of ethyl ether. The precipitated pale pink solids were collected and washed with ethyl ether (3 \times 5 mL): 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* =

Scheme 1. Synthesis of the Functionalized PeQDM Chromophores



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). ¹³C 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.

Picolinium Bromide for Making PeQDM-2OH. This compound was synthesized according to the reported method.^{8b} 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.

General Synthesis of PeQDM Chromophores (with PeQDM-Hex as an example). After 5 mL of a solution of 0.2812 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.85 mmol) in methanol was added dropwise (in 30 min) to a refluxed suspension of 0.5000 g of DMCQ (1.85 mmol), 0.2387 g of *N*-hexyl-4-methylpyridinium bromide (0.925 mmol), and 25 mL of anhydrous methanol (see Scheme 1), the reaction was monitored by UV–vis spectra of the reaction mixture in DMF and typically the reaction is finished within 4–5 h after adding the DBU solution. To do this, a small amount of reaction mixture was taken out and dissolved in DMF for a UV–vis measurement. The reaction was stopped when the charge-transfer band of the chromophore (at $\sim 670 \text{ nm}$) was much stronger than the characteristic peaks of the radical anion (at $\sim 430, 740$, and 830 nm). Then the reaction mixture was cooled to room temperature and the solid was collected by filtration. After the crude product was washed alternately with methanol and ethyl ether three times, 0.17 g of pure product was obtained (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). ¹³C 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, CH₃CN, *m/e*): 388 (*M* + *H*⁺). IR (KBr, cm^{−1}): 2227 and 2155 ($\nu_{\text{C}\equiv\text{N}}$), 1752 ($\nu_{\text{C}=\text{O}}$). TGA: *T*_d = 228 $^\circ\text{C}$.

PeQDM-C2OH. A total of 0.20 g of *N*-(2-hydroxyethyl)-4-methylpyridinium bromide was used (0.925 mmol) to yield 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

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(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, $\text{CH}_3\text{CN}/\text{DMF}$: $v/v = 8/1$, m/e): 348 ($\text{M} + \text{H}^+$). IR (KBr, cm^{-1}): 2226 and 2161 ($\nu_{\text{C}\equiv\text{N}}$), 1751 ($\nu_{\text{C}=\text{O}}$). TGA: $T_d = 215$ °C.

PeQDM-C3OH. A total of 0.22 g of *N*-(3-hydroxypropyl)-4-methylpyridinium bromide (0.925 mmol) was used to yield 0.16 g of product (48% yield). ^1H NMR (300 MHz, DMSO- d_6): 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). ^{13}C NMR (75 MHz, DMSO- d_6): 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, $\text{CH}_3\text{CN}/\text{DMF}$: $v/v = 8/1$, m/e): 362 ($\text{M} + \text{H}^+$). IR (KBr, cm^{-1}): 2229 and 2148 ($\nu_{\text{C}\equiv\text{N}}$), 1749 ($\nu_{\text{C}=\text{O}}$). TGA: $T_d = 238$ °C.

PeQDM-Ben. A total of 0.20 g of *N*-benzyl-4-methylpyridinium chloride (0.925 mmol) was used to yield 0.17 g of product (47% yield). ^1H NMR (400 MHz, DMSO- d_6): 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). ^{13}C NMR (100 MHz, DMSO- d_6): 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, CH_3CN , m/e): 394 ($\text{M} + \text{H}^+$); IR (KBr, cm^{-1}): 2226 and 2146 ($\nu_{\text{C}\equiv\text{N}}$), 1750 ($\nu_{\text{C}=\text{O}}$). TGA: $T_d = 250$ °C.

PeQDM-BenOH. A total of 0.23 g of *N*-(4-hydroxymethyl)benzyl-4-methylpyridinium chloride (0.925 mmol) was used to yield 0.19 g of product (49% yield). ^1H NMR (300 MHz, DMSO- d_6): 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/e): 424 ($\text{M} + \text{H}^+$). IR (KBr, cm^{-1}): 2219 and 2157 ($\nu_{\text{C}\equiv\text{N}}$). TGA: $T_d = 222$ °C.

PeQDM-2OH. A total of 0.46 g of the corresponding picolinium bromide (0.925 mmol) was used to yield 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/e): 630 ($\text{M} + \text{H}^+$). IR (KBr, cm^{-1}): 2226 and 2155 ($\nu_{\text{C}\equiv\text{N}}$), 1733 ($\nu_{\text{C}=\text{O}}$). TGA: $T_d = 234$ °C.

Preparation and Measurement of NLO Guest–Host Polymers. A mixture of 5 wt % PeQDM-Ben in a polymer was added to DMF at a concentration of 2 wt %, and this solution was stirred overnight at room temperature in the dark. After the solution was filtered with a Nylon 0.45- μm syringe filter, the filtrate (85 μL) was cast onto a 17 mm \times 17 mm indium tin oxide (ITO) coated glass slide and baked at 45 °C overnight under nitrogen atmosphere in the dark. The films were further baked in a vacuum oven at 80 °C for 24 h. The film thickness was measured to be in the range of 2–3 μm . A thin layer of gold (100 nm) was then sputtered onto the films as the top electrode.

The film was poled in a homemade thermo-electric poling station under nitrogen atmosphere in the dark. In a typical poling process, the film was first heated from room temperature to the final poling temperature at a heat rate of 5 °C/minute while the voltage was

gradually applied across the film with an average of 70 V/ μm . The poling temperature is typically 4–5 °C below the T_g of the polymer film, to prevent electrical breakdown. After the film was held at the final poling temperature for 5 min, the heating was turned off while keeping the final voltage on. The cooling of the film was controlled by blowing room temperature air and is generally slower than the heating process (about 1 h). Once room temperature was reached, the voltage was removed and the film was immediately used for EO measurement. A Teng-Man ellipsometry 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 Scattering Measurements. The molecular first hyperpolarizabilities (β) of the functionalized PeQDM chromophores were determined by hyper-Rayleigh scattering (HRS) measurements at the wavelength of 1.07 μm in dilute solutions (10^{-6} to 10^{-5} M) in DMF (Acros, extra dry, water < 50 ppm). The applied laser system is based on an optical parametric amplifier (Spectra-Physics OPA-800CP) producing 2 ps pulses at the high repetition rate of 1.5 kHz, pumped by a Ti:sapphire regenerative amplifier (Spectra-Physics Spitfire). Spectral analysis of the scattered light around the second harmonic wavelength is carried out in a parallel way by means of a spectrograph and an intensified charge coupled device, which allows for a complete correction of the measurements for any possible background of multiphoton fluorescence. All measurements are internally calibrated to pure DMF, for which the effective β value is determined to be 0.70×10^{-30} esu 3d from external calibration to the EFISHG value of 0.49×10^{-30} esu for chloroform. 14 More details about the setup, the data collection, and the dispersion modeling are given in our previous report. 3e The use of the standard wavelength of 1.07 μm leads for the present series of PeQDM chromophores to near-resonant enhanced β values, with the second-harmonic wavelength even at the blue side of the intense linear absorption band associated with donor–acceptor charge-transfer. For this reason, the commonly used undamped two-level model of Oudar and Chemla 15 is not appropriate to deduce off-resonant (static) values β_0 , since line-broadening mechanisms need to be taken into account. Therefore, in this work a lower and upper limit to the actual static value β_0 of the chromophores is obtained by means of two opposite extreme limiting cases of vibronic β dispersion models which were developed and evaluated in a previous publication 3e (see Results and Discussion).

3. Results and Discussion

Chromophore Design, Synthesis and Characterization. When using DMCQ in the chromophore synthesis, the structural variation on the chromophores only can come from another reactant or picolinium salts. Thus, the different functional groups should be introduced into picolinium salts prior to the reactions with DMCQ. Considering further incorporation of the resulting chromophores into a polymer, either by doping, grafting, or copolymerization, the picolinium salts should be functionalized with some simple alkyl, hydroxy, or dihydroxy groups. The functionalized picolinium salts are typically prepared by refluxing the corresponding alkyl halides with 4-picoline in acetonitrile.

The reaction of a picolinium salt and TCNQ was first reported to proceed in a long time (5–14 days) and with low yields (15–30%). 3a,b Later, it was found that with the

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Table 1. Physical Properties of the PeQDM Chromophores, in Comparison to the PQDM Chromophores Examined Earlier^{3d,a}

chromophore	λ_{\max} (nm)	$\log \varepsilon_{\max}$ (L mol ⁻¹ cm ⁻¹)	T_d (°C)	$ \beta_{zzz,1.07\mu\text{m}} $ (10 ⁻³⁰ esu)	$ \beta_{0,\text{lowerlimit}} ^b$ (10 ⁻³⁰ esu)	$ \beta_{0,\text{upperlimit}} ^c$ (10 ⁻³⁰ esu)
PeQDM-Hex	674	4.22	228	1700	322	476
PeQDM-C2OH	668	4.58	215	1730	321	486
PeQDM-C3OH	671	4.47	238			
PeQDM-2OH	677	4.48	234	1660	312	498
PeQDM-Ben	691	4.49	250	1800	416	546
PeQDM-BenOH	691	4.52	222			
PQDM-Me ^{3d}	647	4.42		1865	259	441 ^d
PQDM-C3OH ^{3d}	653	4.57	287	1930	295	472

^a λ_{\max} is the spectral position of the lowest energy transition in DMF, ε_{\max} is the corresponding extinction coefficient, and T_d is the decomposition temperature (i.e., the onset temperature for 5% of weight loss by thermogravimetric analysis at 5 °C min⁻¹ in nitrogen). The last three columns contain the experimental molecular first hyperpolarizabilities $|\beta|$ measured by HRS and the static values derived by two opposite limiting cases of vibronic β dispersion models.^{3e} ^b Static values derived by means of the single-mode vibronic model^{3e} (serving as a lower limit). ^c Static values obtained from the purely homogeneous vibronic-like model^{3e} (serving as an upper limit). ^d For PQDM-Me, narrower limits to β_0 (247 to 397 $\times 10^{-30}$ esu) have been determined previously from extensive tunable wavelength HRS measurements.^{3e}

Table 2. Solvatochromism of the PeQDM Chromophores

solvent (E _T 30) ^a	λ_{\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

^a The solvent polarities are given by the E_T30 parameters.¹⁶

use of 2 molar equiv of TCNQ or its lithium adduct and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) as a base, a higher yield (even up to 97%) within a shorter reaction time (14–30 h) could be achieved.^{3c} Attempts were made to improve the yields by using the Li-DMCQ adduct instead of DMCQ but failed because the desired adduct could not be obtained due to the polymerization of DMCQ under the reaction conditions. Thus, by refluxing 2 molar equiv of DMCQ and picolinium salts in methanol, a new series of picolinium (dicyano)esterquinodimethane (PeQDM) chromophores were readily obtained within 4–5 h in nearly 50% overall yield (Scheme 1). All the PeQDM chromophores were purified by simple filtration and washing. The synthesis can be scaled up, for example, 8 g of PeQDM-C2OH per batch, and still complete within 5 h, to yield the desired product in ~50% yield. Therefore, large-scale production of PeQDM chromophores over hundreds of grams is highly feasible owing to this simple, fast, reliable, and moderate-yield reaction. Chromophores containing the alkyl and benzyl groups are designed as model compounds for characterization of the molecular hyperpolarizability using hyper-Rayleigh scattering experiments and for doping studies. Hydroxy-containing PeQDM chromophores are particularly useful for grafting onto a polymer having the pendent acid groups. The diol-containing chromophores are potential monomers for making linear or hyperbranched NLO polyesters and polyurethanes.

All the chromophores have been characterized by ¹H NMR, ¹³C NMR, IR, and MS analyses (see Supporting Information) and are quite thermally stable, as assessed by thermogravimetric analysis ($T_d > 215$ °C, Table 1).

All the PeQDM chromophores display UV–vis spectra similar to those of the PQDM chromophores in DMF solution. These new chromophores also exhibit very clearly the expected negative solvatochromism (Table 2, and also

see Supporting Information), which is typical for a zwitterionic chromophore situated at the right-hand-side in the BLA-diagram,⁶ as it shows the stronger stabilization effect of the polar solvent on the charge-separated ground-state.

The zwitterionic nature of the PeQDM chromophores is further confirmed by the X-ray crystallographic analysis of one of the chromophores, PeQDM-Ben (Figure 2A). Single crystals of PeQDM-Ben were grown by slow diffusion of methanol into a concentrated DMF solution of PeQDM-Ben at room temperature. From the selected bond lengths of the crystals (Table 3), the zwitterionic (aromatic) structure of the chromophore is clearly revealed by the central double bond between C14 and C17 (1.354 Å) and the single bonds between C5 and C8 (1.455 Å), between C11 and C14 (1.471 Å), and between C17 and C18 (1.455 Å). The bond distance between C5 and C8 (1.455 Å) as well as the accompanying shortened C–CN (1.411 Å) and CH₃OOC–C (1.417 Å) bonds and the elongated C≡N (1.157 Å) bond compared with the central C≡N bond (1.142 Å) indicates that the negative charge is localized on the (CH₃OOC)–C–(CN) part. The localization of the negative charge is also supported by the lower wavenumber and higher intensity of the stretching frequency of C≡N (2146 cm⁻¹) of the (CH₃OOC)–C–(CN) moiety compared to that of the central C≡N bond (2226 cm⁻¹). Note also that the C3–C5 bond is shortened to almost the same extent as the C5–C6 bond, which indicates that apart from the cyano group also the ester group acts as a significant electron acceptor. As shown in Figure 2B, the crystal cell of the zwitterionic PeQDM-Ben contains two chromophore molecules and they overlap antiparallel to each other with a large slip angle ($\theta = 64.5^\circ$, Figure 2C).

Molecular Hyperpolarizability. To achieve a large EO coefficient, the chromophores must possess both a large molecular hyperpolarizability (β) and a high degree of coalignment (determined by the dipole moment μ , as well as the material properties of the polymer matrix). The β values of the PeQDM chromophores were determined from hyper-Rayleigh scattering (HRS) experiments (in DMF at the wavelength of 1.07 μm). Very large nearly resonant hyperpolarizabilities $|\beta_{zzz}(-2\omega;\omega,\omega)|$ were obtained for all PeQDM chromophores (see Table 1), up to 1800×10^{-30} esu for PeQDM-Ben. The present values for the PeQDM

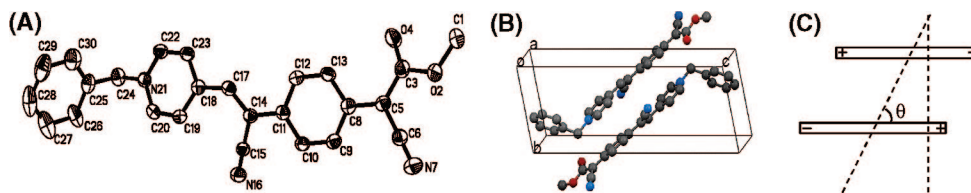


Figure 2. (A) ORTEP drawing of PeQDM-Ben; (B) packing diagram of PeQDM-Ben in the unit cell; and (C) slip angle of the dimer (the hydrogen atoms are omitted for clarity).

Table 3. Selected Bond Lengths from the Crystallographic Data of PeQDM-Ben

Cn–Cm	Å	Cn–Cm	Å	Cn–Cm	Å	Cn–Cm	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)				

derivatives are comparable to the ones for the PQDM chromophores studied before.^{3c} Because the PQDM and PeQDM chromophores listed in Table 1 are comparably resonant, this already means that one of the strongly electron-accepting cyano groups at the acceptor side of the PQDM chromophore can be replaced by a weaker ester group (for additional functionalizability) without significantly disturbing the NLO properties of the push–pull system. This observation is in line with the X-ray analysis of PeQDM-Ben (see above), which already indicated that the ester group exhibits a comparable electron-withdrawing ability to that of the cyano group. With this in mind, it can be assumed that the PeQDM chromophores have a dipole moment μ in the same order as the PQDM chromophores, which results in an extremely high (near-resonant) figure of merit $\mu\beta$ of about $70\,000 \times 10^{-48}$ esu for PeQDM-Ben (using an estimated dipole moment of 40 D, based on the value of 38 D for some PQDM analogues measured in a solid polymer matrix.¹⁷ Furthermore, the consistently high β values for the different PeQDM chromophores show very clearly that several functional groups can be bound to the nitrogen of the pyridinium ring, without destroying the favorable molecular NLO properties. This opens the interesting possibility to increase the solubility of the chromophores and to enable covalent binding of the chromophores to the polymer chain, which both reduce the tendency for aggregation and also to enable cross-linking after alignment for a higher orientational stability.

It is also useful to convert the measured, near-resonant hyperpolarizabilities to static hyperpolarizabilities (β_0), both from a fundamental point of view, to compare the intrinsic nonlinear response of different chromophores separate from resonance effects, and from a practical point of view, to assess their potential for applications (e.g., EO) at longer wavelengths, away from resonance. The undamped two-level model of Oudar and Chemla,¹⁵ although used almost universally in literature for the derivation of static hyperpolarizabilities, is not applicable for this purpose. Indeed, from the extensive wavelength dependent HRS study of the analogous PQDM chromophore,^{3c} it was shown that all three

types of line-broadening mechanisms (homogeneous damping and inhomogeneous broadening as well as vibrational structure) need to be considered to obtain a correct description of the β dispersion in this wavelength range and that the deduced static hyperpolarizability depends very critically on the exact modeling of these mechanisms. With the more reliable, more physically realistic models, the static values obtained still depend on the amount of homogeneous or inhomogeneous broadening contributing to the observed absorption bandwidth: more inhomogeneous broadening leads to lower tails of the hyperpolarizability resonance curve and thus to lower static values β_0 . A lower and upper bound to the actual static β_0 is therefore derived from the two opposite extreme cases of vibronic β dispersion models developed in ref 3e, that is, the so-called single-mode vibronic model (with maximal amount of inhomogeneous broadening) and the purely homogeneous vibronic-like model (see Table 1). Note that if the undamped two-level model was applied (inappropriately), much higher static values β_0 would be obtained in the range of $542 - 697 \times 10^{-30}$ esu (for PQDM-Met and PeQDM-Ben, respectively), in each case far outside of the range predicted by the more physically realistic vibronic models.

Interestingly, the static hyperpolarizabilities obtained for the PeQDM chromophores are even (slightly) larger than those of the PQDM chromophores, despite the weaker acceptor end group of the PeQDM chromophores. This suggests that the dicyanomethine group of the PQDM chromophores is actually a too strong acceptor group to obtain an optimal hyperpolarizability, that is, in the BLA diagram PQDM not only resides at the right side of the cyanine limit, it is even shifted rightward beyond the second (negative) extreme of β_0 . PeQDM, with its slightly weaker acceptor (as is also confirmed by its larger λ_{\max}), then resides slightly more to the left in the BLA diagram, bringing it closer to the (negative) extreme of β_0 . Thus, the substitution with the ester group not only adds new possibilities for functionalization, it at the same time optimizes the molecular hyperpolarizability.

Chromophore Aggregation and Electro-optic Studies.

Due to their large dipole moments, the zwitterionic PeQDM chromophores only dissolve well in polar solvents such as

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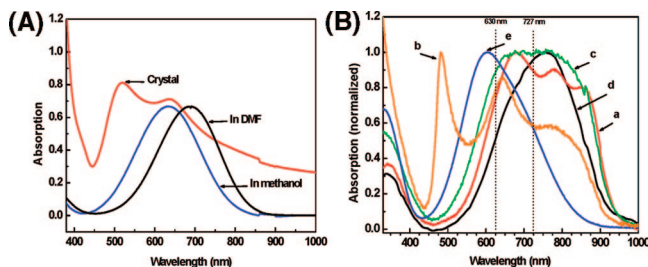


Figure 3. (A) UV-vis spectrum of PeQDM-Ben crystalline powders finely grinded together with KBr in glycerin (for comparison, the absorption spectra of PeQDM-Ben in methanol and DMF are also included). (B) UV-vis spectra of 5 wt % PeQDM-Ben in polymer matrices: (a) APC, (b) PES-Hex, (c) PES-Met, (d) PES-U, and (e) PVPh. Two vertical lines indicate the maximum absorption of PeQDM-Ben in methanol (630 nm) and in acetone (727 nm).

DMF, DMAC, DMSO, and NMP and are insoluble in less polar organic solvents such as THF and chloroform. In polar solutions no chromophore aggregation was observed by UV-vis analysis for concentrations in the range of 10^{-5} to 10^{-4} M. In comparison, the UV-vis spectrum of a sample prepared by finely grinding crystalline PeQDM-Ben together with KBr powder (to help in the grinding and dispersion of the chromophores) in glycerin displayed two charge-transfer (CT) bands at 635 and 519 nm (Figure 3A). The absorption peak at 635 nm is assigned to partially dissolved monomers in glycerin, as the polarity of glycerin is very close to that of methanol (Table 2: $\lambda_{\text{max}} = 630$ nm for PeQDM-Ben in methanol), while the blue-shifted band at 519 nm is attributed to crystalline powders containing the molecules that are head-to-tail (or antiparallel) overlapped.

To investigate the aggregation behavior of the chromophores in a polymer matrix, PeQDM-Ben was selected as a guest and doped into the following polymers (Figure 4) with different polarities or dielectric constants: amorphous polycarbonate (APC, $\epsilon = 3.0$), polyethersulfones including PES-Hex, PES-Met, and PES-U (commercial trade name: Ultrason E, $\epsilon = 3.5$), and poly(4-vinylphenol) (PVPh, $\epsilon = 4.5$). On the basis of the dielectric constants, the polarity of these polymers increases in the following order: APC < PES-Hex \leq PES-Met < PES-U < PVPh. PeQDM-Ben can be doped up to 5 wt % into all these polymers, and smooth thin films with a thickness of 2–3 μm can be prepared by directly casting the chromophore-polymer solutions onto glass or ITO glass. Their corresponding UV-vis spectra are shown in Figure 3B.

In relatively more polar PES-U and PVPh, the PeQDM-Ben chromophore molecules seem to be well dispersed, since one CT band appear at 755 nm for the doped PES-U film and at 606 nm for the doped PVPh film. In the less polar APC, three bands were observed at 679, 780, and 848 nm. One peak (679 nm) falls in the gap between the two the maximum absorptions of PeQDM-Ben in methanol (630 nm) and in acetone (727 nm), which implies the presence of monomeric chromophores. The two red-shifted bands at longer wavelengths (780 and 848 nm) are tentatively assigned to the absorption of J-aggregates. In the PES-Hex film, the sharp peak at 481 nm and a broad shoulder at 826 nm suggest the presence of H-aggregate and J-aggregate chromophores. For PES-Met having a polarity between that of PES-Hex

and PES-U, a very broad peak between 500 and 950 nm could suggest the presence of a mixture of monomers and J-aggregates and the absence of the H-aggregates like those shown in the PES-Hex film (at 481 nm, Figure 3B, trace b). Thus, in line with expectations, zwitterionic chromophores tend to aggregate in polymers having low dielectric constants due to strong electrostatic interactions. The local structure or functional groups in the polymer can play a key role in controlling the formation of H- and/or J-aggregates.

To probe the EO activity, chromophore-doped polymer films, except for PVPh (due to film brittleness), were poled near the T_g of the film materials (Table 4). In a routine electric poling process, the PeQDM-Ben doped films were subjected to 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 $^{\circ}\text{C}$ below the T_g of the polymer film to prevent the often occurred electrical breakdown of the soft polymer film at the T_g temperature. The EO response (r_{33} at 1550 nm) is measured by the Teng-Man reflection method.¹³ It was found that the PES-U film without any aggregation exhibited the largest EO activity ($r_{33} = 110$ pm/V), while other films containing chromophore aggregates afforded much lower values ($r_{33} < 10$ pm/V). The poled PeQDM-Ben doped PES-U film exhibited excellent temporal stability with retention of 90% of initial EO activity at 80 $^{\circ}\text{C}$ for 1000 h (see Supporting Information). This is a significant improvement over the previously examined PQDM chromophores, for which the doping level in PES was limited to only 1% leading to an initial r_{33} value of 21 pm/V, which decreased to the stable value of 16 pm/V after 750 h.^{3d}

Considering the thermodynamics of different molecular organizations of chromophores during the poling process, the polymer films were further thermally treated to probe any possible chromophore reorientation or repacking under the poling conditions. The UV-vis spectra of the PeQDM-Ben doped films of PES-U, PES-Met, and PES-Hex did not show any apparent changes when being heated for 30 min at the corresponding final poling temperatures of 190, 140, and 94 $^{\circ}\text{C}$, demonstrating stable molecular organizations in these polymers. Ordering of the chromophores in PES-Met and PES-Hex under the electric field is expected to be very difficult as this would also require the dissociation of the stable aggregates to monomers. In comparison, the chromophores in the PES-U film can be poled efficiently because they are well dissolved as monomers in the polymer matrix.

For the doped APC film, with the increase of the heating time at the poling temperature, the intensity of the three peaks at 679, 780, and 848 nm decreased, the peak at 679 nm broadened, and a new blue-shifted peak appeared at 480 nm (Figure 5A). This suggests that some of the less stable J-aggregates are readily transformed to more stable H-aggregates. It was found that this transformation was much faster (in just a few minutes) when the film was heated above the T_g (at 180 $^{\circ}\text{C}$). Therefore, with heating before applying the poling field (i.e., according to the routine poling process), the J-aggregates in APC can be transformed into more stable H-aggregates, making the poling much more difficult and thus leading to the observed very low EO activity ($r_{33} = 6$

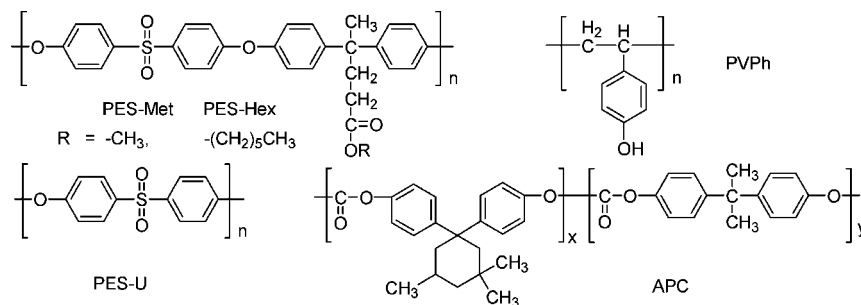


Figure 4. Chemical structures of host polymers.

Table 4. Glass Transition (T_g) and Poling Temperatures (T_p) and EO Coefficients (r_{33} , 1550 nm) of 5 wt % PeQDM-Ben Doped Polymers

host	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)

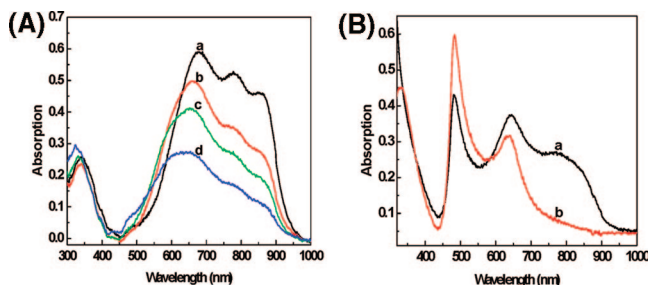
^a The voltage was applied before heating to the poling temperature.

Figure 5. (A) 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, and (d) 42 min. (B) UV-vis spectra of 5 wt % PeQDM-Ben doped PES-Hex (a) before heating and (b) after heating at 120 °C for 30 min.

pm/V). However, when first applying a voltage of 70 V/ μ m and then heating up to the final poling temperature, the poling efficiency was significantly improved and the EO coefficient increased more than sixfold ($r_{33} = 38$ pm/V). This finding strongly suggests that the transformation of J-aggregation to H-aggregation proceeds through an intermediate step of dissociated monomers and that, by capturing and in situ aligning of these monomers, J-aggregates can still be reoriented to a noncentrosymmetric structure and contribute to EO activity.

Compared to the thermodynamics of J-aggregates in the APC film, the J-aggregates (826 nm) in the PES-Hex film could be completely transformed to H-aggregates or even crystalline powders when the film was heated above the T_g at 120 °C for 30 min (Figure 5B). The UV-vis spectrum of the thermally treated PES-Hex film became very similar to that of the PeQDM-Ben crystalline powder (Figure 3A). Further evidence comes from the X-ray analysis of the thermally treated film (Figure 6). The broad peak at 18° corresponds to the polymer matrix, and those at 9°, 14°, and 26° are attributed to (002), (100), and (105) of PeQDM-Ben crystals (Figure 6A). After heating (Figure 6B), the peaks at 9° and 14° became noticeably more intense and a new peak appeared at 26°, clearly indicating an increase in the order of the chromophores in the polymer host. Thus, J-type chromophore aggregates readily transform to more

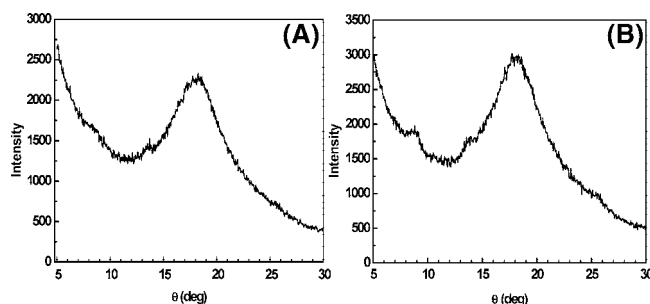


Figure 6. X-ray diffraction pattern of PES-Hex film (A) before heating and (B) after heating at 120 °C for 30 min.

stable H-aggregates in less polar APC and PES-Hex during the poling process.

4. Conclusions

A new series of zwitterionic PeQDM chromophores with large molecular first hyperpolarizabilities β has been synthesized. These chromophores allow for functionalization at two positions (for increasing solubility, for grafting, and/or for cross-linking), at the donor side as well as at the acceptor end of the molecule, without destroying the highly favorable nonlinear optical properties. Quite remarkably, the high molecular hyperpolarizability is maintained, or even further optimized, compared to the previously studied PQDM chromophores, despite the fact that the second position for functionalization is achieved by substituting one of the strong CN acceptor groups of the PQDM chromophore by a weaker ester group. This unexpected result can be explained in terms of the BLA model, if one considers that the PQDM chromophores form a too strong push-pull system shifting the BLA beyond the (negative) maximum of β_0 , while the PeQDM chromophores have a more optimally balanced donor-acceptor strength. The use of a more polar polymer host clearly favors the solubilization of monomeric chromophores, as evidenced by a guest-host polymer (5 wt % PeQDM-Ben in PES-U) showing a very large and highly stable EO coefficient (110 pm/V at 1550 nm). By heating to the poling temperature, the J-aggregates formed in a less polar polymer can be transformed to H-aggregates, passing through an intermediate step of dissociated monomers. It is demonstrated that by orienting these released monomers before they start to form the more stable H-aggregates (i.e., by applying the poling field from the beginning of the heating cycle), they can contribute to the EO response.

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Supporting Information Available: Crystallographic information (Cif) for PeQDM-Ben, negative solvatochromism, EO temporal stability of poled PES-U doped 5 wt % PeQDM-Ben at 80 °C in nitrogen, and ^1H , ^{13}C NMR and MS spectra of PeQDM-Ben (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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