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A Photoluminescent, Segmented Oligo-Polyphenylenevinylene Copolymer with Hydrogen-Bonding Pendant Chains

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The syntheses and electronic spectroscopy of *E*,*E*-2,5-bis[2-hydroxyethoxy]-1,4-bis[2-(3,4,5-trimethoxyphenyl-1,2-ethenediyl]benzene, **3**, and alternating block copolymer analogue *alt*-poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-(*E*)-ethenediyl-2,5-(2-hydroxyethoxy)-1,4-phenylene-1,2-(*E*)-ethenediyl-3,5-dimethoxy-1,4-phenylene], **2,** are described. Polymer **2** has UV−vis absorbances at 320 nm (shoulder) and 389 nm (maximum), with fluorescence emission at 449 nm (maximum) and 480 nm (shoulder) upon excitation at various wavelengths. Model compound **3** shows virtually identical spectral behavior. Neat solid films of polymer **2** show UV−vis absorbance in the 400−450-nm region (broad) and fluorescence at about 490 nm. The 40-nm shift from solution to neat film emission for **2** is attributed to hydrogen-bond-assisted interactions between chromophores in the solid state. The fluorescence quantum yields in chloroform at room temperature (365-nm excitation) for **2** and **3** are 0.36 and 0.74, respectively, relative to quinine sulfate standards. There is no evidence of excimer formation, although crystallographic studies of model system **3** show hydrogen-bonded chains involving the hydroxyethoxy pendant chain. The model system also has a highly planar crystal structure, consistent with its high emission quantum yield; the planarity may be favored by interactions between the pendant hydroxyethoxy groups and the ethenediyl groups of the chromophore.

Introduction

There has been much activity in the development of organic-based photoluminescent polymers for uses in electronic and sensor materials.[1] Segmented block copolymers have been one particular area of activity because they allow precise synthetic control of chromophore length and nature.[2,3] A number of such systems have shown much promise as light-emitting materials, such as the work of Karasz and co-workers[2] with blue light-emitting segmented block copolymer **1**, an oligo-polyphenylenevinylene (PPV) segmented with polyethylene. Optimization of the practical light-emitting aspects of these and other organic systems requires understanding and control of various parameters, including chromophore conjugation through conformational control, interchain contact formation, and local crystallization effects. With control of these parameters, it will be far easier to control emission band gaps and bandwidths in solid state as well as solution, to avoid emission-quenching mechanisms, and generally to increase the efficiency and lifetime of devices based on such materials.

As part of our work in this area, we functionalized polymer **1** to add a hydrogen-bonding pendant group to make **2**. This was done partly to attempt to rigidify the planarity of the chromophoric portion of **2** by interactions between the vinylene groups and the pendant chains, and partly to investigate the effect upon emission of introducing a group that would tend to favor association of chromophore chains. As part of the study, we made model chromophore **3** and compared its properties to that of the polymer. Both **2** and **3** turn out to be strongly fluorescent systems, as we shall detail below.

Experimental Section

General Methods. All commercially available materials were used as received. Ether and THF were dried first over calcium hydride and then at reflux over sodium/benzophenone ketyl. Melting point determinations were made using a Melt-Temp melting-point apparatus and are uncorrected. UV−vis absorbance spectra were recorded on a Shimadzu UV-2401PC. Solution photoluminescence measurements were carried out on a Perkin-Elmer LS50B spectrometer. FTIR spectra were obtained on a Midac M2000 spectrometer. GPC was carried

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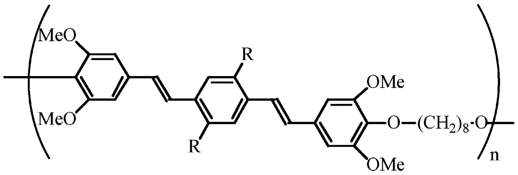
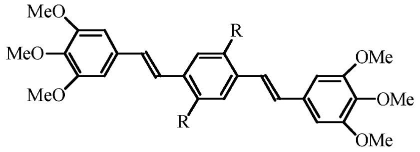
10.1021/cm034708z CCC: $27.50



1 R = H
2 R = OCH$_2$CH$_2$OH



3 R = OCH$_2$CH$_2$OH

out on a Polymer Labs LC 1120 system with a Millipore Waters differential refractometer detector, using polystyrene standards. 1,8-Bis[2,6-dimethoxy-4-formylphenoxy]octane[4] and 1,8-bis[2,6-dimethoxy-4-vinylphenoxy]octane (**8**)[5] were synthesized according to literature procedures.

1,4-Diiodo-2,5-dimethoxybenzene (5). This compound was synthesized according to a literature[6] procedure from 10 g (72.5 mmol) of 1,4-dimethoxybenzene (Avocado Research Chemicals), 7.75 g (36.3 mmol) of KIO_3, 19.5 g (76.77 mmol) of I_2, and a solution of 200:2.5:7.5 acetic acid:H_2SO_4:H_2O. Recrystallization from ethanol yielded 58% of **5** as white crystals with mp 174−176 °C [lit.[7] mp 171 °C]. ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 6H), 7.18 (s, 2H).

2,5-Diiodo-1,4-hydroquinol (6). This compound was synthesized according to the literature[7] from 5 g (12.8 mmol) of **5** and 25 mL (25 mmol) of BBr_3 (1 M in CH_2Cl_2), to yield 89% of light brown crystals of **6** after crystallization from benzene with mp 197−199 °C [lit. mp 195−197 °C]. ^{1}H NMR (acetone-d_6): δ 7.29 (s, 2H), 8.82 (s, 2H).^{13}C NMR (acetone -d_6): δ 83.15, 123.65, 150.43.

1,4-Bis[2-hydroxyethoxy]-2,5-diiodobenzene (4). Into a three-necked flask equipped with a magnetic stirrer, a condenser with an argon inlet and two addition funnels was placed 1.9 g (13.7 mmol) of K_2CO_3 in 10 mL of dry DMF. After flushing with argon, a solution of **6** (2.0 g, 5.5 mmol) in dry DMF was added slowly. After 30 min, 1.3 mL (19.3 mmol) of 2-chloroethanol (Alfa Aesar) was added dropwise, and the temperature was adjusted to 80 °C. After 48 h, the reaction mixture was allowed to cool to room temperature and then filtered, and the residue was washed with DMF. The organic filtrate was evaporated with a stream of air, and then the black residue was dissolved in hot acetone and refluxed with activated carbon for 10 min. After hot filtration, the filtrate was cooled to give **4** as light brown crystals (80%); mp 169−170 °C. ^{1}H NMR (DMSO-d_6): δ 3.67 (m, 4H), 3.97 (t, 4H, J = 5 Hz), 4.83 (t, 2H, J = 5 Hz), 7.36 (s, 2H). ^{13}C NMR (DMSO-d_6): 60.55, 72.80, 88.00, 123.99, 153.60. MS (m/z, relative intensity): 450 (M^+, 100%), 406, 362, 257, 234. HRMS calcd for $C_{10}H_{12}O_4I_2$ ($M^+ + H$) 450.0119, found 450.0123.

3,4,5-Trimethoxyethenylbenzene (7). Under an atmosphere of argon at 0 °C, 7.14 mL (15 mmol) of n-butyllithium (2.1 M in hexanes) was added dropwise to a suspension of 4.73 g (13.2 mmol) of methyl triphenylphosphonium bromide (Avocado Research Chemicals), in 50 mL of dry THF. After the reaction mixture was warmed to room temperature, 2 g (10 mmol) of 3,4,5-trimethoxybenzaldehyde (Avocado Research Chemicals) was added. The resulting orange solution was stirred overnight and then poured into 100 mL of water, extracted with ether, dried over $MgSO_4$, filtered, evaporated, and purified by column chromatography (silica, 4:1 hexanes: ethyl acetate) to yield a yellowish oily product (65%). This was sufficiently pure to use in the next synthetic step. ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H), 3.82 (s, 6H), 5.17 (dd, 1H, J = 10.8 Hz, J′ = 0.6 Hz, 1H), 5.62 (dd, 1H, J = 18 Hz, J′ = 0.6 Hz, 1H), 6.58 (dd, 1H, J = 10.8 Hz, J′ = 18 Hz), 6.59 (s, 2H).

***E,E*-2,5-Bis(2-hydroxyethoxy)-1,4-bis(3,4,5-trimethoxyphenyl-1,2-ethenediyl)benzene (3).** Into a 50-mL round-bottom flask fitted with a condenser flushed with argon was placed 0.27 g (1.4 mmol) of **7**, 0.313 g (0.7 mmol) of compound **4**, 84.6 mg of tri(o-tolyl)phosphine, and 12.5 mg of Pd(OAc)$_2$. Next, 10 mL of dry DMF was added. The reaction was heated to 80−85 °C, and 0.5 mL of triethylamine was added. After 2 days of heating, the reaction was cooled to room temperature, diluted with 20 mL of CH_2Cl_2, washed with water, and filtered, and the organic phase was dried over $MgSO_4$. Vacuum concentration produced a dark-yellow solid, which was recrystallized from $CHCl_3$/hexanes several times to yield 0.142 g (35%) of UV-fluorescent yellow crystals of **3** with mp 245−247 °C. ^{1}H NMR (DMSO-d_6): δ 3.67 (s, 6 H), 3.82 (singlet plus overlaid multiplet, 16 H), 4.08 (t, J = 4 Hz, 4 H), 6.89 (s, 4 H), 7.28 (d, J = 16 Hz, 2 H), 7.30 (s, 2H), 7.44 (d, J = 16 Hz, 2 H). FTIR (KBr pellet, cm^{-1}): 3490 (broad, OH str), 1581 (C=C str), 963 (trans =CH). MS (m/z): 582 (M^+, 100%), 567, 516, 494, 418, 368, 291, 236, 181, 105, 91. HRMS calcd for $C_{32}H_{38}O_{10}$ ($M^+ + H$) 582.6417, found 582.6493. UV−vis (chloroform, λ_{max}): 390 nm, $\epsilon = 27090$. Photoluminescence (chloroform, $\lambda_{exc} = 365$ nm): $\lambda_{max} = 447$ nm.

X-ray Crystallography of 3. Single crystals of **3** were obtained by slow crystallization from DMSO in the air. Analysis calculated for $C_{32}H_{38}O_{10}$: C, 65.98; H, 6.53; O, 27.49. Found: C, 64.09; H, 6.34. The low carbon percentage is consistent with the presence of DMSO in the crystal lattice. Single-crystal X-ray diffraction analysis was carried out at the UMass-Amherst X-ray Structural Characterization Facility on a Nonius (Bruker) KappaCCD P4 instrument at ambient temperature with graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.157 mm^{-1}. Yellow needle 0.10 × 0.15 × 0.75 mm, monoclinic, $P2_1/n$, molecular weight = 660.75, a = 5.3009(2) Å, b = 24.0823(10) Å, c = 13.0444(6) Å, β = 90.3582(16)°, Z = 2, V = 1665.19(12) Å^3, D_{calc} = 1.318 g/cm^3. Analysis was carried out using direct methods and difference Fourier techniques using the programs SHELXS-86 for solution and SHELXL-97 for refinement.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were included in the refinement as isotropic scatterers riding in ideal positions, except for the hydroxyl hydrogen atom, which was done with torsional refinement on the bonded atom. N = 2995 unique reflections were measured using ω scans for 4.14° < θ < 22.01°. For 1697 unique reflections with intensity greater than 2σ, $F(000) = 704$, R1($I > 2\sigma$) = 0.0498, R1(all) = 0.0600, wR2($I > 2\sigma$) = 0.1126, wR2(all) = 0.1183, $\Delta\rho_{max}$ = 0.160, $\Delta\rho_{min}$ (e·Å^{-3}) = 0.201. Table 1 shows selected crystallographic data for **3**. Crystallographic coordinates and other data are found in the Supporting Information.

Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-(*E*)-ethenediyl-2,5-(2-hydroxyethoxy)-1,4-phenylene-1,2-(*E*)-ethenediyl-3,5-dimethoxy-1,4-phenylene] (2). 4 (0.23 g, 0.5 mmol), 1,8-bis(2,6-dimethoxy-4-vinylphenoxy)octane (**8**) (0.24 g, 0.5 mmol), tri(o-tolyl)phosphine (46 mg), and Pd(OAc)$_2$ (6.8 mg) in a 50-mL round-bottom flask fitted with a condenser were flushed with argon, and 10 mL of dry DMF was added. The solution was heated to 80−85 °C, and 0.27 mL of triethylamine was added. After 24 h the reaction mixture was cooled to room temperature and then poured into 100 mL of water. The resulting solid was filtered out and dissolved in chloroform; slow addition of hexanes precipitates a fibrous yellow polymer. This procedure was repeated and the polymer

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Table 1. Crystallographic Parameters, Selected Bonding Parameters for 3[a]

chemical formula	$C_{32}H_{38}O_{10}\cdot C_2H_6SO$
chemical formula weight	660.75
temperature	293
cell setting, space group	monoclinic, $P2_1/n$
a, b, c (Å)	5.3009(2), 24.0823(10), 13.0444(6)
α, β, γ (deg)	90, 90.3582(16), 90
V (Å^3)	1665.19(12)
crystal dimensions (mm)	0.75 × 0.15 × 0.10
Z	2
D_x (Mg/m^3)	1.318
radiation type	Mo Kα
θ range (degrees)	4.14−22.01
F(000)	704
μ (mm^{-1})	0.157
crystal color	yellow needle
data collection method	$\omega-2\theta$ scans
collected/unique reflections	2995/1697
criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0. 0272
range of h,k,l	$-5 \rightarrow h \rightarrow 5$ $-25 \rightarrow k \rightarrow 23$ $-13 \rightarrow l \rightarrow 13$
completeness to 2θ	0.96
reflections, restraints, parameters	1967/0/227
H-atom treatment	mixed
goodness of fit on F^2	1.181
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.160, −0.201
R1, wR2 ($I > 2\sigma(I)$)	0.0498, 0.1126
R1, wR2 (all)	0.0600, 0.1183
program used	SHELXL97

C(1)−C(2)	1.372(4)	C(11)−C(9)#1	1.400(4)
O(1)−C(14)	1.429(4)	C(12)−C(13)	1.485(4)
O(2)−C(3)	1.373(3)		
O(2)−C(15)	1.437(4)	O(4)#1·····H(8)−C(8)	2.39[b]
O(3)−C(4)	1.374(3)	O(4)#1·····C(8)	2.748(4)
O(3)−C(16)	1.424(4)		
O(4)−C(11)	1.378(3)	C(1)−C(6)−C(7)	117.7(3)
O(4)−C(12)	1.430(4)	C(5)−C(6)−C(7)	122.9(3)
O(5)−C(13)	1.427(4)	C(8)−C(7)−C(6)	128.6(3)
C(1)−C(2)	1.378(4)	C(7)−C(8)−C(9)	126.3(3)
C(1)−C(6)	1.388(4)	C(11)−O(4)−C(12)	117.7(2)
C(2)−C(3)	1.398(4)	C(10)−C(11)−O(4)	123.1(3)
C(3)−C(4)	1.395(4)		
C(4)−C(5)	1.382(4)	C(1)−C(2)−O(1)−C(14)	4.5(4)
C(5)−C(6)	1.401(4)	C(5)−C(4)−O(3)−C(16)	−0.3(4)
C(6)−C(7)	1.467(4)	C(2)−C(3)−O(3)−C(15)	−70.2(4)
C(7)−C(8)	1.326(4)	C(1)−C(6)−O(7)−C(8)	178.9(3)
C(8)−C(9)	1.465(4)	C(7)−C(8)−C(9)−C(10)	3.5(5)
C(9)−C(11)#1	1.400(4)	C(10)−C(11)−O(4)−C(12)	16.0(4)
C(9)−C(10)	1.407(4)	C(11)−O(4)−C(12)−C(13)	170.2(2)
C(10)−C(11)	1.374(4)	O(4)−C(12)−C(13)−O(5)	74.9(3)

[a] All distances in angstroms; all angles and torsions in degrees. [b] Distance estimated based on generated hydrogen atom position; H(8) is the vinyl hydrogen attached to C(8), position estimated as described in the Experimental Section.

dried under vacuum overnight to yield 0.11 g (35%) of **2**. Analysis calculated for $C_{38}H_{48}O_{10}$: C, 68.67; H, 7.23; O, 24.10. Found: C, 67.49; H, 7.28. ^{1}H NMR ($CDCl_3$): δ 1.2−1.8 (m, 18H), 3.88 (s, 12H), 3.8−4.0 (m, 10 H), 4.15 (m, 4H), 6.74 (s, 4H), 7.0−7.4 (m, 6H). FTIR (neat film on NaCl plate, cm^{-1}): 3500 (broad, OH str), 964 (trans =CH), 754 (poly-CH_2−). GPC (THF) $M_w = 8068$, $M_n = 3453$. UV−vis (chloroform, $\lambda_{\max}$): 386 nm, $\epsilon = 59760$. Photoluminescence (chloroform, $\lambda_{\mathrm{exc}} = 365$ nm): $\lambda_{\max} = 449$ nm.

Electronic Spectroscopy. All spectra were obtained in spectrograde chloroform that was degassed with argon. The concentrations of solutions were adjusted to yield an absorptivity of $A \cong 0.05$ in the absorption spectrum for any fluorescence experiments, which corresponded to the micromolar concentration range for both **2** and **3**. Relative quantum yields (ϕ_{fl}) were measured using quinine sulfate in 0.10 M H_2SO_4 as a standard ($\Phi_{\mathrm{FL}} = 0.546$ at 365-nm excitation), according to the procedure[7] of Chen and Huang.

Results

Synthesis. Figure 1 shows the syntheses of both **2** and **3**. The general strategy follows the Heck methodology reported by Pasco et al.[5] earlier. Core molecule **4** was made by iodination of 1,4-dimethyoxybenzene to make **5**, demethylation to hydroquinol **6**, and Williamson etherification. With use of palladium-catalyzed methodology, compound **4** could then be coupled either with trimethoxystyrene **7** to make **3** or with previously reported[5] flexible block monomer unit **8** to make polymer **2.**

Polymer **2** was precipitated from chloroform with hexanes to give a fibrous, yellow solid. GPC analysis relative to polystyrene showed $M_n \sim 3500$ (degree of polymerization 4−5), with a polydispersity index of 2.3. Proton NMR and FTIR spectroscopy showed no evidence of cis vinylene linkages. The trans out-of-plane (oop) =

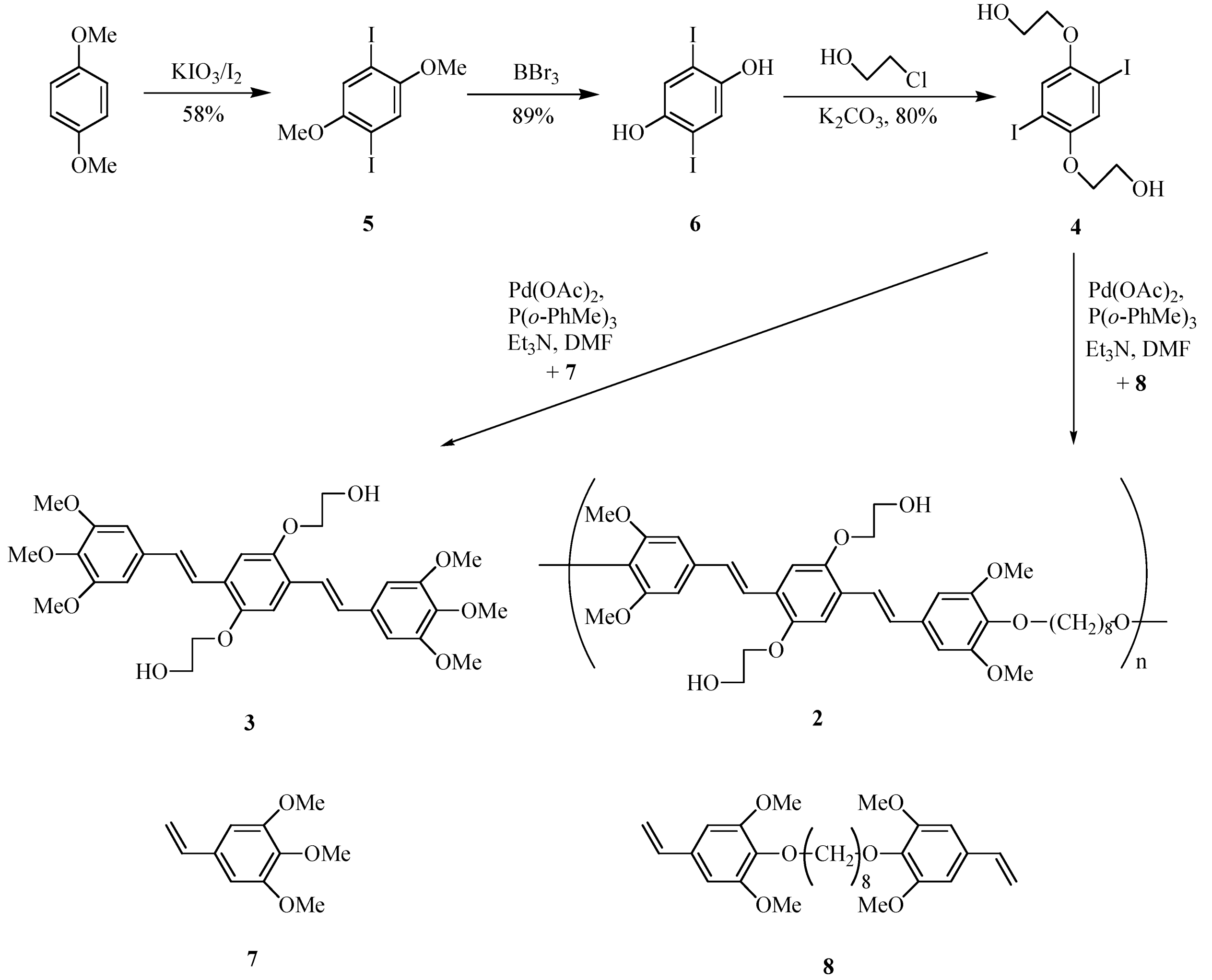


Figure 1. Synthesis of **2** and **3**.

C−H bend is readily apparent at 963−964 cm^{-1} in the FTIR spectrum in both **2** and **3**, while the NMR spectrum of **3** shows a well resolved *trans*-ethenyl coupling of 16 Hz at 7.30−7.44 ppm. The spectrum of polymer **2** is broadened and does not show the aromatic region in so well-resolved a manner). The polymer dissolves well in organic solvents and forms films when cast on glass.

Model compound **3**, like **2**, shows no cis vinylene linkages by spectroscopy: the trans =C−H oop bend is found in the FTIR at 963 cm^{-1}. In other respects, the FTIR of **3** looks very similar to that of **2**, as expected due to the similarity of structure. The NMR spectra are also quite similar, save that the polymer exhibits polyethylene resonances in the δ 1−2 region and additional −O−CH$_2$− units at about δ 4.2. It is a highly fluorescent solid that must be protected from air when dissolved, presumably because of oxidative reactivity to vinylene cleavage. In other respects it is quite stable. Although **3** readily crystallizes from chloroform/hexanes with sufficient purity for most of our uses, we needed to use DMSO to obtain crystals of sufficient quality for X-ray analysis (see Figure 2).

Photophysical Studies. Both **2** and **3** were studied by UV−vis and fluorescence (FL) spectroscopy in chloroform solutions and as dilute solid films in poly(methyl methacrylate). Polymer **2** was also examined as a neat film that was film cast from a 1 mM chloroform solution at 1000 rpm onto a microscope cover slide. The solution spectra for both are compared in Figure 3. The PMMA film spectra for **2** and **3** were qualitatively the same as the solution phase spectra, so they are not shown separately. The solid-state spectrum for **2** is shown in Figure 4. Neither the UV−vis nor the FL spectra for **2** and **3** change qualitatively upon increasing the concentration to 10^{-4} M. The 10^{-6} M concentration FL spectra do not change qualitatively when excited at other wavelengths. The FL excitation spectra for both **2** and **3** overlay the UV−vis spectra (Supporting Information).

We also carried out room-temperature solution phase quantum yield studies for **2** and **3** in argon degassed chloroform solutions, using the method of Chen and Huang[7] with quinine sulfate as a standard (Φ_{FL}[365 nm] = 0.546). Table 2 summarizes the electronic spectral results.

Discussion

A major goal for this study was to compare the photophysical properties of the oligo-PPV model molecular system to its segmented copolymeric analogue, with incorporation of a hydrogen-bonding pendant chain. We hoped that the behavior of the model system would correlate well with the polymer behavior, allowing the model molecule to be a useful benchmark. We also hoped that we could derive structural insight to the polymer

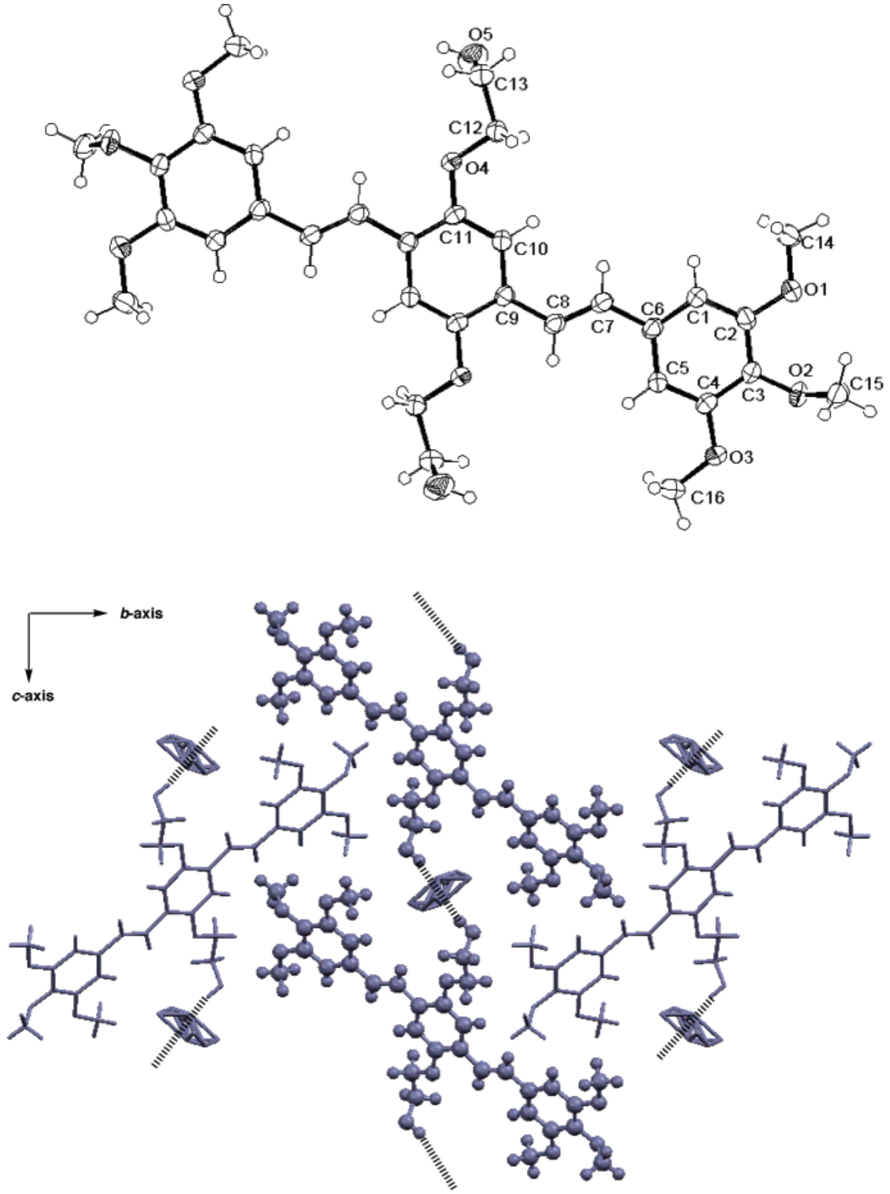
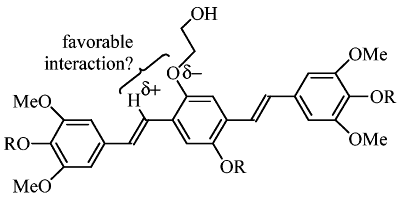


Figure 2. Crystallography for **3**. The upper picture shows an ORTEP representation of the crystal structure of **3**. A solvent molecule (DMSO) has been removed for simplicity of viewing. The inset shows hydrogen-bonded chains of **3** in the lattice; the disorder "pinwheels" are DMSO molecules that lie between pendant OH groups from different molecules. Thermal ellipsoid picture prepared using ORTEP-III for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565. Hydrogen-bonding picture prepared using (in part) program Mercury 1.1.2 for Windows from the Cambridge Crystallographic Data Centre, Cambridge, UK, 2003.

by studying the molecular model. Fortunately, **3** forms good crystals when crystallized from DMSO, although the solvent is incorporated into the lattice. The X-ray crystallographic study of model **3** shows that it is highly planar, with relative torsions between phenylene and vinylene units of a degree or less. While it is not clear whether the crystallographic conformation of **3** is the sole or even the most favored conformation in solution, this structure is consistent with a favorable dipolar interaction between the vinylene C−H group and the aryl−O−R functionality. As we shall see below, the fluorescence quantum efficiency of **3** is quite high, which we feel is consistent with a time-average planarized geometry as suggested by the crystallographic and computational results. If this is so, then the pendant alkoxy groups may help to planarize the *p*-phenylenevinylene chromophore. Similar conformational considerations should enhance planarity in the chromophoric portion of polymer **2**.



The high degree of planarity of **3** allows it to crystallize from DMSO with offset π-stacks along the *a*-axis with an interplanar distance of about 4.1 Å. These stacks also form hydrogen-bonded chains between the hydroxyethoxy pendant chains, incorporating DMSO solvent molecules. Figure 2 shows examples of such chains in the *bc*-plane, with the dashed lines showing $-CH_2OH$ ·····DMSO·····$HOCH_2-$ interactions. The DMSO molecules are disordered in the lattice, but serve an important role by assisting the hydrogen-bonded interactions that give chains of **3**. These results show

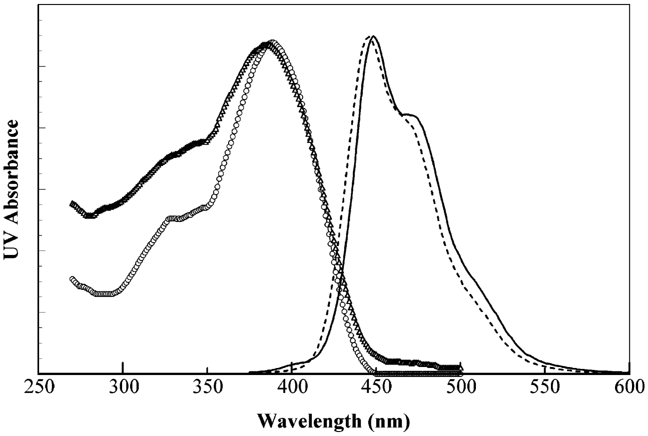


Figure 3. Electronic spectra for **2** and **3**, 10^{-6} M in chloroform at room temperature, arbitrarily scaled to a similar ordinate. UV−vis for **2** (△), UV−vis for **3** (○), FL for **2** (−), and FL for **3** (- - -). FL spectra shown for excitation wavelength of 365 nm.

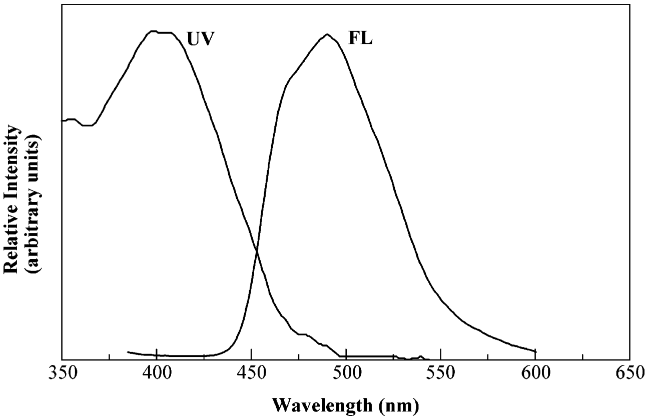


Figure 4. Neat film electronic spectra for **2** at room temperature, arbitrarily scaled to a similar ordinate. FL spectrum shown for excitation wavelength of 365 nm.

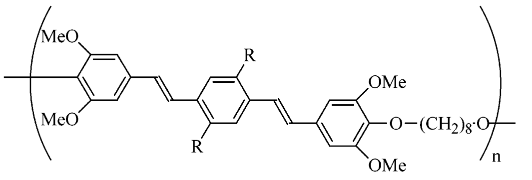
Table 2. Comparison of UV−Vis and FL Spectra for 1−3

	UV (max, nm)	FL (max,nm)	FL quantum yield (Φ_{FL})	solid-state FL (max,nm)
1[a]	365	440	0.40	470
2[b]	389	449 (480 sh)	0.36	492
3[b]	385	446 (480 sh)	0.74	

[a] See ref 5 and its cited references for details. [b] Experiments at 10^{-6} M in chloroform at 365-nm excitation. "sh" denotes a shoulder absorbance.

that hydrogen-bonding interactions can give some degree of aggregation of **3**. By analogy, we assume that similar interactions and aggregation can occur to some extent among the chromophores in polymer **2**. However, as we shall see below, such interactions do not occur to a sufficient extent in chloroform solution to affect the UV−vis or FL spectra.

Both the UV−vis and solution FL spectra of **2** and **3** virtually overlap (Figure 3): there is no significant solution phase perturbation of the electronic nature of the chromophoric group upon incorporation into the polymer. Both UV−vis spectra show a shoulder at about 320 nm, with dominant absorption at 380−390 nm. The FL spectra show an analogous appearance, with the maximum emission at about 450 nm (blue-white) and an overlapping, tailing shoulder with a plateau at about 480 nm. The FL spectra do not change qualitatively at different excitation wavelengths, and the excitation spectra of both **2** and **3** overlay the absorption UV−vis spectra. The evidence indicates that the UV−vis and FL features arise from a single absorbing/emitting chromophore, with no significant impurity spectra. Both absorption and emission characteristics of **2** and **3** are similar to those of polymer **1** (Table 1), with both spectra red-shifted by about 10−15 nm (roughly 0.1 eV in these wavelength ranges). This is presumably due to the alkoxy substitution on the central ring, the only structural change relative to **1**. Judging by the effect of alkoxy substituents on other oligo-PPVs, the red shift is due to electronic effects,[9] although the crystallographic planarity of **3** suggests that there may be some planarizing effect of the hydroxyethoxy group in **2** and **3** that should favor longer wavelength absorbances. By comparison, in earlier work by Pasco et al.[5] substitution with *n*-hexyl in polymer **9** gave very little UV−vis shift relative to parent polymer **1**, while substitution with a bulkier isopropyl group in **10** gave about a 20-nm blue-shift attributed to torsion of the oligo-PPV chromophore. Both **9** and **10** showed blue-shifted solution FL spectra relative to **1**, again attributed to torsion from the functional group.[5]



9 R = $(CH_2)_5CH_3$
10 R = $CH(CH_3)_2$

As mentioned earlier, there is no qualitative change or peak maximum shift in the UV−vis or FL spectra upon 100-fold increase of the concentrations of **2** and **3**, up to 100 μM. Under no conditions did we see any evidence of new peaks. Therefore, the hydroxyethoxy groups in **2** and **3** do not seem to enhance aggregation of chromophores in chloroform at room temperature to an extent that excimers can form. In addition, since we found that solid solutions of **2** and **3** in PMMA gave UV−vis and FL spectra that were virtually the same as the chloroform solutions, there seems to have been little aggregation in PMMA either. Since hydrogen bonding in **3** takes place in the neat crystalline state, we examined the electronic spectra of polymer **2** as a solid film to look for possible solid-state chromophore interaction effects (Figure 4).[10] Under these conditions, the UV−vis spectrum showed a broad absorbance in the 400−450-nm region. For the same films, the FL spectrum showed one peak with an emission maximum at 492 nm (blue to blue-green).

Pasco et al. found that polymers **9** and **10** exhibited a 10−15-nm red shift of their neat solid film FL spectra relative to solution FL spectra, while polymer **1** exhib-

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(9) For the effect of alkoxy substituents, see for example Brédas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *217*, 507.

(10) For some examples, see (a) Samuel, I. D. W.; Rumbles, G.; Collison, C. *J. Phys. Rev. B* **1995**, *52*, R11573. (b) Harrison, N. T.; Baigent, D. R.; Samuel, I. D. W.; Friend, R. H.; Grimsdale, A. C.; Moratti, S. C.; Holmes, A. B. *Phys. Rev. B* **1996**, *53*, 15815. (c) Blatchford, J. W.; Jessen, S. W.; Lin, L.-B.; Gustafson, T. L.; Fu, D.-K.; Wang, H.-L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1996**, *54*, 9180.

ited a 30-nm shift.[5] The smaller shift in **9** and **10** was attributed to a decrease in solid-state interchromophore interactions (relative to **1**) due to the steric bulk of the pendant alkyl side chains. Extrapolating this argument, the 40-nm red shift of the FL spectrum of **2** going from solution to neat film suggests that there is *increased* interchromophore interaction relative to **1**. Overall, **2** shows the largest solution to solid-state shift of FL emission maximum. We tentatively attribute the shift to increased association[10] between chromophores in **2**, assisted by hydrogen-bonding interactions. Although we cannot be sure that this is occurring with the present data, the solid film spectral shift is consistent with greater interchromophore interactions in the solid state of **2**, and this is consistent with the hydrogen bonding observed for model **3** in the solid state. The shift is not consistent with a simple change to a solid-state sample since we saw no significant shift in the PMMA film spectra of **2** and **3** relative to solution-phase spectra.

The quantum yield experiments (Table 1) show model compound **3** to have quite a good quantum yield, $\Phi_{FL} = 0.74$. We attribute this to a high degree of time-average planarity in solution for **3**, in accordance with the crystal structure analysis. Polymer **2** has about half this emission quantum yield under the same conditions. Polymer **1** has $\Phi_{FL} = 0.42$ in chloroform,[11] so chromophoric self-quenching in **2** is not significantly enhanced relative to **1**. This further supports our belief that the pendant hydroxyethoxy groups do not have a large aggregation effect on **2** *in solution* by comparison to **1**. However, the lower quantum yield in the polymers suggests some degree of increased interchromophore interaction and self-quenching in solution for both **1** and **2**. Further work is required to resolve details of this point.

Summary

Comparison of the electronic spectroscopy of model compound **3** to that of polymers **1** and **2** shows that there is little effect of a side chain hydroxyl-bearing unit upon the individual chromophore UV−vis or FL spectra. The quantum yield of the model molecule is twice that of the two polymers, suggesting that some degree of self-quenching occurs in the latter, possibly due to some degree of chromophore aggregation. If the lower quantum yield is due to time-averaged closer approaches between chromophores in the polymer than in the dilute solutions of the model, the effect is not large enough for excimers to form. The high quantum yield of model **3** shows inherently effective emission, which we attribute to a high degree of planarity in the chromophore that may be enhanced by interactions between its ethenediyl units and the alkoxy pendant chains. The crystal structure of model **3** shows the chromophoric unit to be highly planar, and the similarity of UV−vis and FL spectra for **2** and **3** suggests that polymer **2** does not undergo significant torsion of its chromophore relative to **3**. Since the hydroxyethoxy pendant groups allow for a variety of pendant functionalization of these chromophores, the present study serves as a benchmark for the behavior of these oligo-PPV materials.

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Supporting Information Available: General experimental methodology and tables of crystallographic data for **3** (including a CIF format summary). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Zheng, M.; Ding, L. M.; Gürel, E. E.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **2001**, *34*, 4124.