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Synthesis, Characterization, and Optical Properties of Copolymers Containing Fluorine-Substituted Distyrylbenzene and Nonconjugated Spacers

Ananda M. Sarker, Bernd Strehmel, and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43403

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ABSTRACT: Copolymers containing fluorinated distyrylbenzenes as conjugated segments have been synthesized using the Horner−Emmons reaction of dialdehydes and diphosphonates. The presence of well-defined conjugated fluorinated systems gives rise to strong blue emissions in solution. Quantum yields and emission maxima in solution depend on the substituents on the chromophore and the nature of the nonconjugated segments. Construction of conjugated segments containing a central perfluorophenyl ring and aromatic groups substituted with electron-donating groups at the terminae, as evidenced by strong solvatochromic behavior, allow an induced intramolecular charge transfer state. Face-to-face π stacking has been observed in thin films formed from each of the polymers and causes large red shifts in the emission as compared to those in solution. The low quantum yield of emission in thin films is a result of self-quenching due to stacking.

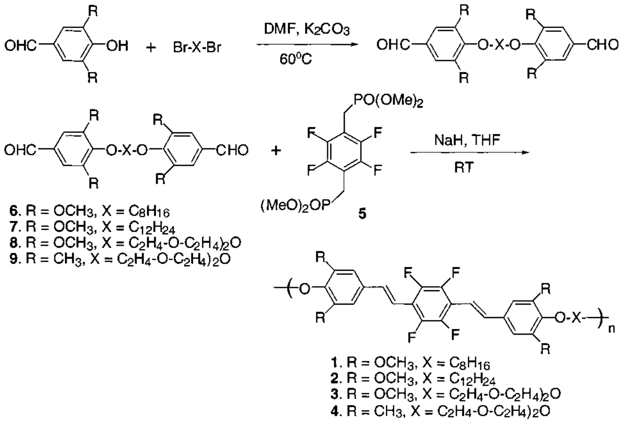
Introduction

Poly(phenylenevinylene), PPV, and derivatives with well-defined chemical structures are among the most extensively studied organic electroluminescent materials.[2] The optoelectronic properties of conjugated polymeric examples vary significantly depending not only on the extent of π-conjugation but also on the substituents attached to the main chain. Substitution of the PPV backbone by electron-donating or electron-withdrawing groups allows chemical control of the HOMO−LUMO band gap and changes the electronic and optical properties in the desired direction.[3] While modest success has been achieved in using such materials, the search for optimum materials for light-emitting devices (LED), especially in the blue region, continues. Obtaining highly efficient blue light emission from conjugated polymers[4] that also cannot be made easily from inorganic materials remains a challenge.

Recently, we have synthesized fluorinated oligophenylenevinylenes with various alkyl or alkoxy groups on the aryl ring. As expected, a dramatic blue emission of high quantum yield was observed in solution.[5] In an effort to build similar emission properties into polymeric systems, we now report the synthesis of copolymers consisting of conjugated fluorinated distyrylbenzene as the oligophenylenevinylene moiety and aromatic groups substituted with long alkoxy groups. Fluorinated PPVs appear promising because fluorine is a small atom with a strong electron-withdrawing effect, and it is expected that this will stabilize the PPV backbone to photooxidation[6] without perturbing the system's planarity. On the other hand, fluorine incorporation has also been found to bring about desirable changes in optical properties[7] and also increases the thermal stability.[8]

In this contribution, we describe the synthesis and report photoluminescence studies of a series of fluorinated polymers in which the backbone consists of oligomeric PPV fragments and flexible chains (Scheme 1). We have concentrated on the specific effects of fluorine and other donor substituents, such as methoxy and methyl, on the optical properties of PPVs. Thus, the same configuration length for the oligophenylenevinylene moiety was maintained in the all polymers. The solubility of the conjugated system is conferred by the presence of long alkoxy and long ether chains on the substituted distyrylbenzene units.

Scheme 1



Experimental Section

General Methods. All new compounds were characterized by NMR, FTIR, GC-MS, and elemental analysis (Atlantic Microlab, Inc.). Nuclear magnetic resonance (NMR) spectra were taken on a Gemini GEM-200 (200 MHz). Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Infrared (IR) spectra were recorded using a 6020 Galaxy FTIR spectrometer either as neat films, neat liquids, or sodium chloride (NaCl) pellets. The absorption peaks are reported in cm^{-1}. Ultraviolet−visible (UV−vis) spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Emission spectra were measured using a SPEX Fluorolog 2 spectrophotometer. The corresponding emission quantum yields were determined using 9,10-diphenylanthracene in cyclohexane as standard ($\Phi_f = 0.90$).[9] Cuvettes (1.0 cm) were used for all absorption and emission measurements in solution in the rectangular geometry. The emission spectra of films were measured in front face geometry. Compounds **6** and **7** were synthesized according to published procedures.[10] Melting point determinations were made using a Thomas-

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Hoover capillary melting point apparatus; all temperatures are uncorrected. Chemicals were obtained from Aldrich Chemical Co. unless otherwise noted. Gel permeation chromatography (GPC) experiments were carried out on a Waters GPC consisting of a model 590 pump. Tetrahydrofuran (THF) was used as the eluent solvent with 0.1% solution of polymers, and calibrated samples of polystyrene used as standards. The films were made by spin coatings of 5 wt % solution of polymer (dissolved in chloroform for **1**−**3** and 1,4-dioxane for **4**) on a glass plate with an area 4.84 cm^2. The volume of the spin-coated polymer solution was 0.5 mL.

1,11-Bis(4-formyl-2,6-dimethoxyphenoxy)-3,6,9-trioxaundecane (8). A mixture of 3,5-dimethoxy-4-hydroxybenzaldehyde (2.93 g, 16.08 mmol), 1,11-dibromide-3,6,9-trioxaundecane (2.56 g, 8.0 mmol), and potassium carbonate (3.00 g, 28.30 mmol) in *N*,*N*-dimethylformamide (10 mL) was heated to 60−65 °C for 16 h. The mixture was cooled to room temperature and poured into ice−water (300 mL). The aqueous mixture was extracted with chloroform. The chloroform layer was washed with brine and dried over magnesium sulfate. After evaporation of chloroform, the oily product was obtained. Finally, it was purified by silica gel column (ethyl acetate: hexanes = 1:1). ^{1}H NMR ($CDCl_3$, δ): 9.85 (s, 2H), 7.01 (s, 4H), 4.23 (t, J = 5.8 Hz, 4H), 3.89 (s, 12H), 3.79 (t, J = 5.8 Hz, 4H), 3.66 (m, 8H). Anal. Calcd for $C_{26}H_{34}O_{11}$: C, 59.79; H, 6.51. Found: C, 59.70; H, 6.48.

1,11-Bis(4-formyl-2,6-dimethylphenoxy)-3,6,9-trioxaundecane (9). Prepared as described above. After chromatography on silica gel (ethyl acetate:hexanes = 1:1), an oily product was obtained (46% yield). ^{1}H NMR ($CDCl_3$, δ): 9.87 (s, 2H), 7.54 (s, 4H), 4.01 (t, J = 4.6 Hz, 4H), 3.84 (t, J = 4.6 Hz, 4H), 3.73 (m, 8H), 2.35 (s, 12H). Anal. Calcd for $C_{26}H_{34}O_{17}$: C, 68.26; H, 7.42. Found: C, 68.20; H, 7.38.

1,4-Bis(tetrafluorobenzalphosphonate) (**5**). In a 100 mL round-bottom flask, 1,4-bis(bromomethyl) tetrafluorobenzene[11] (2.0 g, 5.95 mmol) in trimethyl phosphite (2.22 g, 17.85 mmol) was heated overnight at 90 °C. Hexanes (50 mL) was added to the reaction mixture which was allowed to solidify at 0 °C and filtered, and the solid was recrystallized from ethanol. White needles of **5** were obtained (1.10 g, 47% yield); mp 95−96 °C. ^{1}H NMR ($CDCl_3$, δ): 3.81 (s, 6H), 3.75 (s, 6H), 3.28 (d, J = 20.2 Hz, 4H). Mass spectrum *m*/*e* calcd for $C_{12}H_{16}F_4O_6P_2$: 394.06. Found: 394.05. Other fragments: 374, 285, 253, 176, 109 (100%), 93, 44.

Polymer 1. To a 50 mL oven-dried round-bottom flask was placed sodium hydride (0.23 g, 60% in oil) under argon. The reaction flask was flushed with argon and anhydrous THF (20 mL) added. Diphosphonate **5** (0.39 g, 1.00 mmol) in THF (4 mL) was added by syringe, and the reaction mixture was stirred at room temperature for 20 min. Dialdehyde **6** (0.47 g, 1.00 mmol) in THF (2 mL) was then added, and the mixture was stirred for 48 h at room temperature. The reaction was quenched with water (3 mL) and extracted with chloroform (100 × 2 mL). The chloroform solution was concentrated (3.0 mL) and added dropwise into methanol (300 mL). Yellow polymer **1** that precipitated was filtered and dried under vacuum (63% yield). ^{1}H NMR ($CDCl_3$, δ): 7.43 (d, J = 16.8 Hz, 2H), 6.97 (d, J = 16.4 Hz, 2H), 6.76 (s, 4H), 4.00 (t, J = 6.6 Hz, 4H), 3.91 (s, 12H), 1.77 (m, 4H), 1.40 (m, 8H). ^{13}C NMR ($CDCl_3$, δ): 155.74, 140.35, 138.97, 134.14, 117.01, 115.20, 108.72, 106.14, 75.66, 58.23, 32.13, 31.42, 27.82. FTIR (film, cm^{-1}): 3064, 2996, 2928, 2854, 1629, 1580, 1504, 1467, 1419, 1343, 1242, 1128, 1013, 964. Anal. Calcd for $C_{34}H_{36}F_4O_5$: C, 68.02; H, 6.00. Found: C, 67.19; H, 6.02.

Polymer 2. Synthesized as described above (68% yield). ^{1}H NMR ($CDCl_3$, δ): 7.42 (d, J = 16.4 Hz, 2H), 6.96 (d, J = 16.4 Hz, 2H), 6.76 (s, 4H), 4.00 (m. 4H), 3.91 (s, 12H), 1.75 (m, 4H), 1.29 (m, 16H). ^{13}C NMR ($CDCl_3$, δ): 155.74, 140.39, 138.95, 134.11, 116.99, 115.15, 108.74, 106.17, 75.69, 58.23, 32.13, 31.66, 31.47, 27.87. FTIR (film, cm^{-1}): 3066, 2997, 2928, 2853, 1630, 1581, 1504, 1467, 1481, 1420, 1344, 1242, 1129, 1043, 1009, 965, 816, 730. Anal. Calcd for $C_{38}H_{44}F_4O_6$: C, 67.87; H, 6.54. Found: C, 67.23; H, 6.49.

Table 1. Molecular Weight of Polymers 1−4[a]

polymer	yield (%)	$M_w \times 10^3$	M_w/M_n[b]
1	63	10.5	3.5
2	68	17.2	3.0
3	73	12.0	3.2
4	53	8.4	3.8

[a] GPC based on a standard polystyrene calibration curve. [b] Polydispersity.

Polymer 3. This polymer was synthesized by a procedure identical to that for polymer **1** (73% yield). ^{1}H NMR ($CDCl_3$, δ): 7.41 (d, J = 16.4 Hz, 2H), 6.95 (d, J = 16.4 Hz, 2H), 6.74 (s, 4H), 4.12 (m, 4H), 3.90 (s, 12H), 3.77 (m, 4H), 3.64 (m, 8H). ^{13}C NMR ($CDCl_3$, δ): 155.60, 139.99, 138.88, 134.38, 116.93, 115.26, 108.61, 106.01, 74.35, 72.66, 72.40, 58.19. FTIR (film, cm^{-1}): 3012, 2924, 2869, 1690, 1584, 1504, 1467, 1420, 1343, 1244, 1128, 1040, 966, 732. Anal. Calcd for $C_{34}H_{36}F_4O_9$: C, 61.47; H, 5.42. Found: C, 60.29; H, 5.49.

Polymer 4. Synthesized according to the procedure described for polymer **1** except polymerization was performed in dioxane, instead of THF. After quenching with water, polymer was extracted into chloroform and the solution concentrated by a rotary evaporator. Finally, it was purified by precipitation in methanol (53% yield). ^{1}H NMR ($CDCl_3$, δ): 7.36 (dd, J = 17.0 Hz, J = 4.0 Hz, 2H), 7.19 (s, 4H), 6.93 (dd, J = 17.0 Hz, J = 4.0 Hz, 2H), 3.97 (m, 4H), 3.85 (m, 4H), 3.75 (m, 8H), 2.31 (s, 12H). FTIR (film, cm^{-1}): 2917, 2869, 1621, 1597, 1482, 1301, 1218, 1133, 1054, 968, 885, 602. Anal. Calcd for $C_{34}H_{36}F_4O_5$: C, 68.02; H, 6.00. Found: C, 66.96; H, 6.08.

Results and Discussion

Synthesis and Characterization. Horner−Emmons coupling was employed between dialdehyde **6**−**9** and phosphonate **5** to afford the "blue" copolymers **1**−**4** having trans configurations (Scheme 1). Conventional Wittig or Heck reactions, had they been used in this synthesis, would create a mixture of trans and cis isomers and produce polymers having inferior properties. Dialdehydes **6**−**9** were synthesized by a Williamson reaction between methoxy- or methyl-substituted 4-hydroxybenzaldehyde and the necessary dibromides in DMF. Polymers **1**−**4** were purified by precipitation from chloroform into methanol. Each polymer was soluble in THF, dioxane, chloroform, and halogenated solvents. Good quality transparent films can easily be cast. Polymer **4**, which contains the methyl-substituted chromophore and flexible long ether linkage, is less soluble in organic solvents when compared to methoxy-substituted polymers **1**−**3**. An initial attempt to make polymer **4** using 1,12-dibromododecane resulted in formation of an insoluble product. None of the polymers were found to exhibit phase separation in the above solvents, even after a week at room temperature.

The ^{1}H NMR spectra of polymers **1**−**4** showed the coupling constants of the vinylic protons to be more than 16 Hz, confirming the configurations to be trans. The infrared spectra show a band around 964 cm^{-1} due to the C−H stretch of the vinylic units also supporting trans configurations. Moreover, peaks due to the aldehyde group were absent in both ^{1}H and ^{13}C NMR spectra and suggest that no monomeric residues remain in the polymers. The FTIR absorption around 1700−1740 cm^{-1} was also absent, suggesting that no undesired carbonyl moieties are formed during synthesis.[12]

Gel permeation chromatography (GPC) shows the molecular weight (M_w) distributions of the polymers (Table 1) are broad, which is typical for Wittig type reactions.[10] The low molecular weight of polymer **4** is due to early precipitation in the polymerizing solvents and could be accounted for by the steric bulkiness of the methyl substitution on the chromophore. All poly-

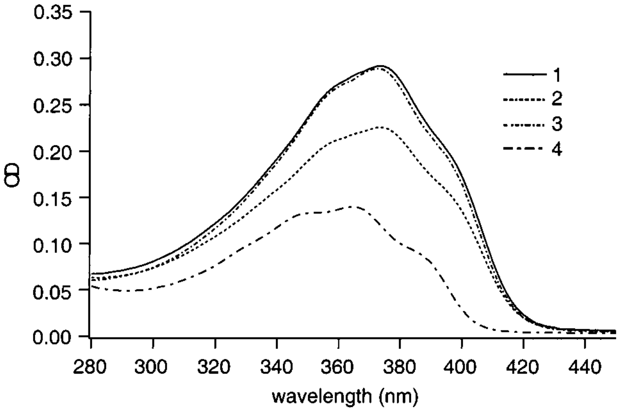

Figure 1. Absorption spectrum of polymers **1**–**4** in chloroform (10^{-5} M) at room temperature.

Table 2. Optical Properties of Polymers 1–4 in Chloroform (10^{-5} M)

polymer	λ_{max} (nm) absorption	λ_{max} (nm)[a] emission	$\epsilon_{max} \times 10^4$ ($M^{-1} cm^{-1}$)	Φ_f
1	373	465	2.90	0.50
2	372	465	2.86	0.52
3	373	463	2.90	0.53
4	363	426	1.60	0.21

[a] Excited at absorption maximum.

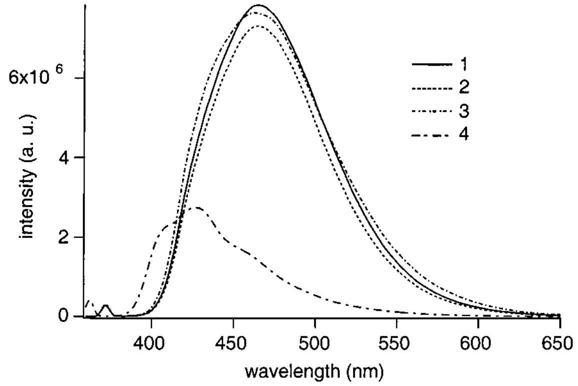

Figure 2. Emission spectrum of polymers **1**–**4** in chloroform (10^{-5} M) at room temperature.

mers except polymer **4** possess intense color in the solid state. In solution, they fluoresce strongly, and this can be visualized with the naked eye.

Optical Properties in Solution. The absorption spectra of polymers **1**–**4** in chloroform (1×10^{-5} M) are shown in Figure 1. Spectral maxima and extinction coefficients in chloroform are summarized in Table 2. The large molar absorption coefficients indicate the dominance of strongly allowed π–π^* transitions from the phenylenevinylene segments. The absorption spectra have a strong dependence on the nature of the substituents on the aryl ring. Polymers **1**–**3**, which are methoxy-substituted, show similar broad peaks around 373 nm with a similar pattern. The spectrum of the methyl-substituted polymer **4** is blue-shifted likely because the methyl group causes the conjugated system to be less planar, decreasing overall π-delocalization.[13] It appears that the UV–vis spectra of **1**–**4** are independent of either the structure or the conformation of the nonconjugated chain.

Figure 2 shows the fluorescence spectra of polymers **1**–**4** in chloroform. Polymers with long flexible chains were selected in order to observe quenching effects on fluorescence quantum yields. The quantum yields of fluorescence of **1**, **2**, and **3** are identical within experimental error (Table 2). It appears that the flexible chain in the polymer backbone is inert and leads to no enhanced fluorescence quenching. The emission spectra of all of the polymers are independent of the excitation wavelength but highly dependent on the structure of the polymers.

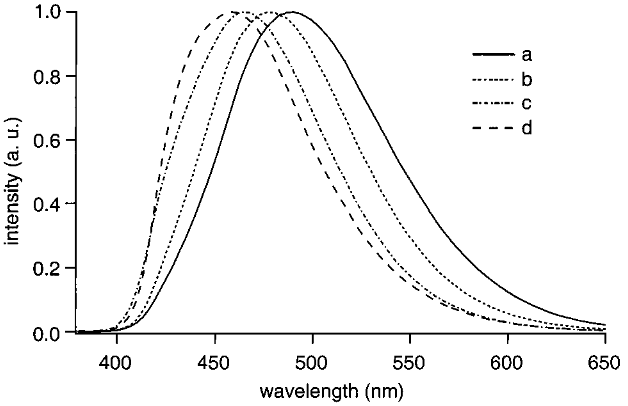

Figure 3. Emission spectrum of polymer **1** in solvents of different polarity at room temperature: (a) butanone, (b) chloroform, (c) tetrahydrofuran, (d) toluene.

Polymers **1**–**3** show emission maxima at approximately 465 nm with similar spectral slopes. On the other hand, the emission of polymer **4** is blue-shifted by approximately 30 nm, and the quantum yield emission of **4** in chloroform (10^{-5} M) is considerably lower than that of polymers **1**–**3**. We believe this not due to the flexible nonconjugated units, but to the methyl substituent. As mentioned before, the methyl group induces a torsional angle in the polymer main chain, resulting in less planarity and less π-delocalization of the entire conjugated system and, hence, a decrease in the luminescence efficiency.

It is well-known that both solvent polarity and polarizability affect the energy levels of excited states in the trans isomers of such polymers.[5] Therefore, both the spectral shape and the position of fluorescence of the polymers should, in principle, be affected. Figure 3 shows the fluorescence spectrum of polymer **1** at room temperature in solvents of differing polarity. A substantial red shift is observed with an increase in solvent polarity. A similar result was found for polymer **2**. The red-shifted emission maximum in nonpolar solvents and broad featureless emission spectra in polar solvents indicate the intramolecular charge transfer nature of the excited state.[14] The emission in toluene is less symmetrical than is the emission spectrum in more polar solvents. The spectrum has an emission maximum at approximately 458 nm with a shoulder at 437 nm, indicating the fluorescence has a dual nature. Dual fluorescence and strong solvatochromaticity suggest the existence of two excited states, such as a locally excited (LE) and an intramolecular charge transfer state (ICT).[5] The absorption maximum is less sensitive to the solvent polarity, indicating that solute–solvent interactions are of minor importance in the ground state. Therefore, this ICT state is believed to be populated through relaxation of the initially formed Franck–Condon excited state (locally excited state, LE).[15] This is also supported by a large Stokes shift as solvent polarity is increased. The Stokes shift increases from 82 to 117 nm on changing the solvent from toluene to butanone. This behavior is

Table 3. Optical Properties of Polymers 1–4 in Thin Films

polymer	λ_{max} (nm) absorption	λ_{max} (nm)[a] emission	Stokes shift (nm)	ΔE (cm^{-1})
1	365	487	122	6863
2	365	502	137	7477
3	362	501	139	7664
4	332	421	89	6368

[a] Excited at absorption maximum.

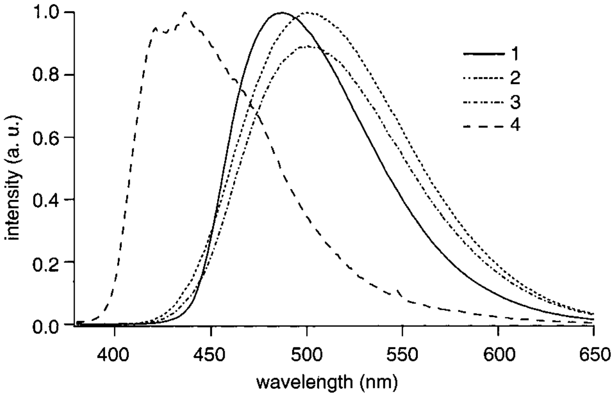

Figure 4. Emission spectrum of polymers **1**–**4** in thin films at room temperature.

well-known and is due to the charge transfer character of the solvent relaxed emissive state in the more polar solvents.

The emission spectra of polymers **3** and **4** are less sensitive to solvent polarity. This indicates that the nature of the relatively long, nonconjugated chain has a significant effect on the interaction between the solvent dipole and the lowest excited states of the polymers. Polymers **3** and **4** contain nonconjugated segments that are more flexible than those of polymers **1** and **2**. Because of this flexibility, this chain can coil around the conjugated rigid segment and thus prevent the interaction between solvents and excited states of the trans configuration. Since polymer **4** is a methyl-substituted phenylenevinylene, this is also a reason that it shows no effect of solvent polarity on the emission maximum. Similar results were previously observed for methyl-substituted oligophenylenevinylenes.[5]

Optical Properties in Thin Films. The ground-state absorption spectra for thin films of each of the polymers showed small blue shifts compared to those of the solution spectra (Table 3). This may be the result of solid-state aggregation.[16] The fluorescence spectra of thin films of polymers **1**–**4** spin-coated onto glass slides are shown in Figure 4. In contrast to the absorption spectra, the emission spectra were dramatically red-shifted in thin films relative to solution. These are characterized by broad, structureless emissions that are red-shifted from the spectra in dilute solution (Figure 2). The large bathochromic shifts of the emission maxima in films (Table 3) are likely due to the highly ordered structure in the solid-state films. This ordered structure in the solid state arises from both intra- or intermolecular $\pi-\pi$ interactions of the chromophores. These, in turn, are responsible for the unique optical properties.[17] It is well-known that a face-to-face stacking interaction between the phenyl and perfluorophenyl group takes place in the solid state.[18] However, $\pi-\pi$ interactions or stacking depends on the molecular architecture of the polymers (both the chromophore and the nonconjugated flexible chain).

Although polymer **1** contains similar conjugated segments to polymers **2** and **3**, its emission maximum is about 15 nm blue-shifted, demonstrating that intermolecular stacking may take place in polymer **1** due to the short nonconjugated spacer. In contrast, polymers **2** and **3** have flexible spacers long enough to stack in an intramolecular, as well as intermolecular, fashion. As a consequence, these polymers exhibit longer wavelength, red-shifted emissions. The emission for polymer **4** being more toward the blue indicates that the planarity of the conjugated segments controls the stacking morphology as well. Therefore, it can be concluded that, in planar polymers where a maximization of the extended π stacking occurs, this results in red-shifted emission. This is consistent with the results obtained with similar oligophenylenevinylenes.[5]

Conclusions

The optical properties found in the present work give important information about the effect of fluorinated, planar, conjugated systems on excited-state properties of PPVs. Fluorine atom substitution in the conjugated segment allows the polymers to become planar and, in turn, exhibit an efficient “blue” emission in solution. Since these compounds form stacked structures in the solid state, they are unattractive as light-emitting devices. Formation of π-stacks in the solid state is, on the other hand, an important physical criterion for the formation of discotic liquid crystals,[19] and oligophenylenvinylenes are well-known mesogenic groups.[20] The attachment of a flexible chain with these fluorinated conjugated segments will allow the alignment of the polymers in a disklike shape and cause them to exhibit liquid crystal texture. Consequently, the observation of π-stacking in PPVs opens up new vistas for theoretical and experimental understanding of such materials and for developing them for liquid crystal devices.

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