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Photophysical and Optoelectronic Properties of Green-Emitting Alkoxy-Substituted PE/PV Hybrid Conjugated Polymers

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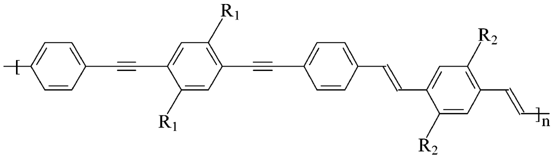
ABSTRACT: A series of phenyleneethynylene (PE)/phenylenevinylene (PV) hybrid conjugated polymers with alkoxy side chains were studied. It was found that longer alkoxy side chains improve EL efficiency through enhanced material solubility and film-forming properties. Polymers with longer side chains attached to the phenylenevinylene units exhibit higher EL efficiency. With increasing solvent polarity, both absorption and emission spectra of the polymer display bathochromic shifts. With increasing chromophore concentration, the solution PL spectra display red shifts and new bands, indicating intermolecular excimer formation. The relative intensity of the 0−0 band in the solution PL spectra increases with increase of the excitation energy. When the nonsolvent methanol is added to the homogeneous polymer/chloroform solution, the absorption and emission spectra display red shifts and new bands, clearly indicating aggregate and excimer formation in the solvent/nonsolvent systems.

Introduction

Since the first report of electroluminescence from poly(*p*-phenylenevinylene) (PPV) by the Cavendish group in 1990,[1] much effort has been expended in developing new conjugated polymers with balanced carrier injection/transport properties for LED devices.[2] PPV is an adequate hole-transporting material; thus, the modification of this polymer to improve its electron transport properties has been a challenging issue. It was discovered by Bunz et al.[3] and Egbe et al.[4] that incorporating electron-withdrawing acetylene ($-C\equiv C-$) bonds into the PPV backbone to obtain hybrid phenylenevinylene/phenyleneethynylene (PV/PE) materials confers several advantages. Materials with similar structures[5] which can be used in photovoltaic cells and LEDs have been subsequently reported. Pang et al.[5c] also developed green-emitting PE/PV hybrid polymers with phenyl rings linked alternately at meta and para positions, providing an efficient intramolecular energy transfer across *m*-phenylene. In this paper, we report the photophysical and optoelectronic studies of a series of PE/PV hybrid conjugated polymers bearing alkoxy side chains. The effects of side chain length and location, solvent polarity, concentration, and excitation wavelength on the photophysical properties of these materials and device performances are discussed with particular reference to aggregate and excimer formation in solvent/nonsolvent mixtures.

Experimental Section

Alkoxy-substituted phenyleneethynylene (PE)/phenylenevinylene (PV) hybrid conjugated polymers of basic backbone structure $(-Ph-C\equiv C-Ph-C\equiv C-Ph-CH=CH-Ph-CH=CH-)_n$ (**1ab**, **1ba**, **2ac**, **2ca**, **3aa**, **3dd**, and **3ad**) (Figure 1) were synthesized according to procedures described previously.[4c] In fabrication of LED devices, PEDOT/PSS (Bayer Co.) was spin-cast directly onto ITO glass, and polymer solutions (10 mg/mL in chloroform) filtered through 0.2 μm Millex-FGS Filters (Millipore Co.) were spin-cast onto the dried PEDOT/ITO substrates under a nitrogen atmosphere. Calcium electrodes of 400 nm thickness were evaporated onto the polymer films at about 10^{-7} Torr, followed by a protective coating of aluminum. The electroluminescent properties of these LEDs sealed in argon were characterized using a custom-made system described previously.[6] UV−vis spectra were recorded on a Hitachi U-3010 UV/vis spectrophotometer. PL spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer.



1ab: R_1=Octadecyloxy, R_2=Octyloxy
1ba: R_1=Octyloxy, R_2=Octadecyloxy

2ac: R_1=Octadecyloxy, R_2=2-Ethylhexyloxy
2ca: R_1=2-Ethylhexyloxy, R_2= Octadecyloxy

3aa: R_1=R_2=Octadecyloxy
3dd: R_1=R_2=Dodecyloxy
3ad: R_1=Octadecyloxy, R_2=Dodecyloxy

Figure 1. Polymer structures.

Results and Discussion

Effect of Side Chains on Electroluminescence. The absorption, PL, and EL spectra of films of polymers **1ab**, **1ba**, **2ac**, **2ca**, **3aa**, **3dd**, and **3ad** are shown in Figure 2. The current density−voltage−luminance characteristics for corresponding devices ITO/PEDOT/polymer/Ca are shown in Figure 3. Photophysical data and EL data are summarized in Table 1. The band gap for each polymer was obtained from measurement of the point at which the normalized absorption and emission spectra intersect.[7] The band gap values are in the range 2.40−2.46 eV and show no significant change with the change of length or location of the side chains. The obvious broadening of the EL spectra relative to the

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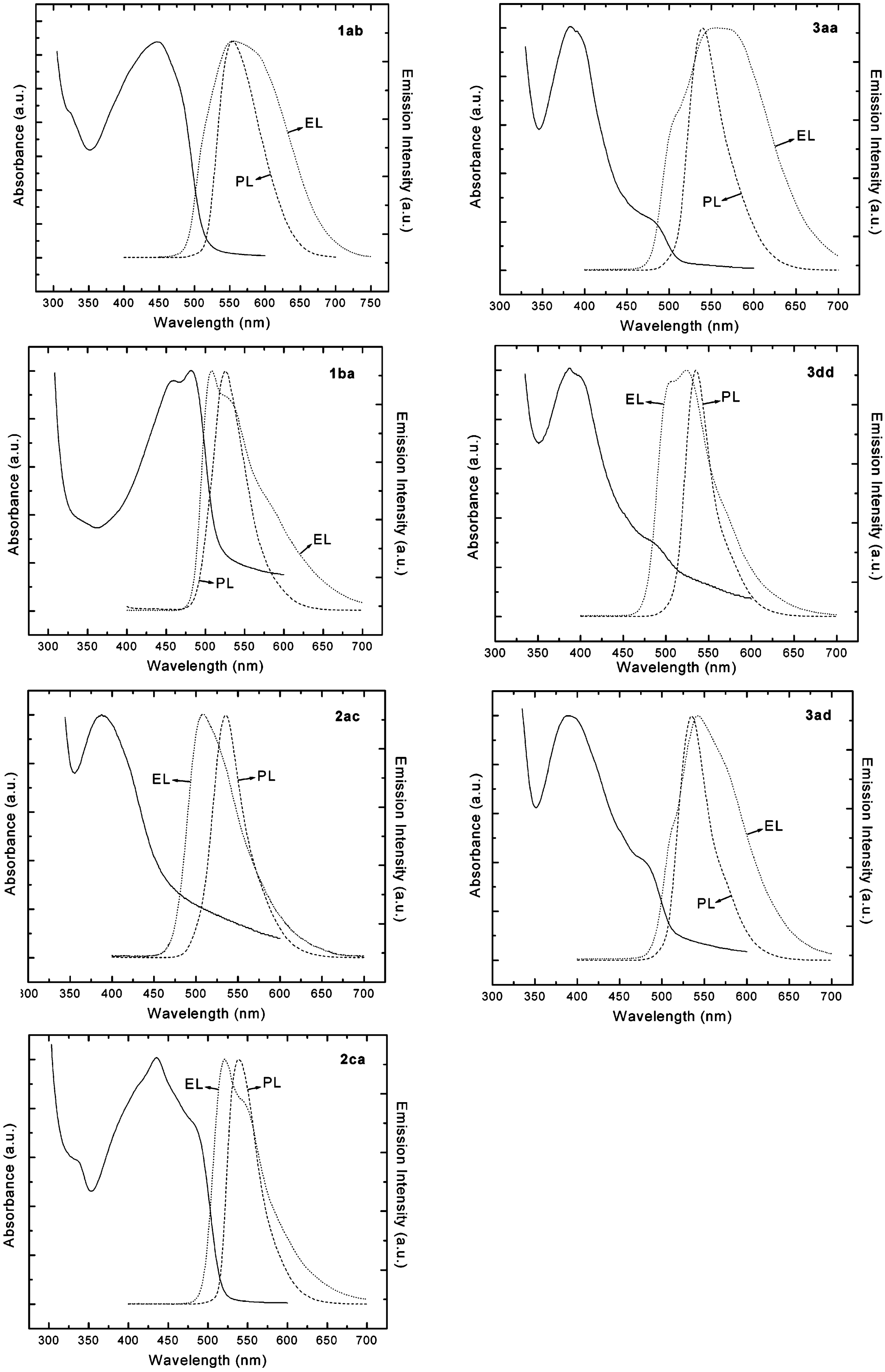

Figure 2. Absorption, PL, and EL spectra of **1ab**, **1ba**, **2ac**, **2ca**, **3aa**, **3dd**, and **3ad**.

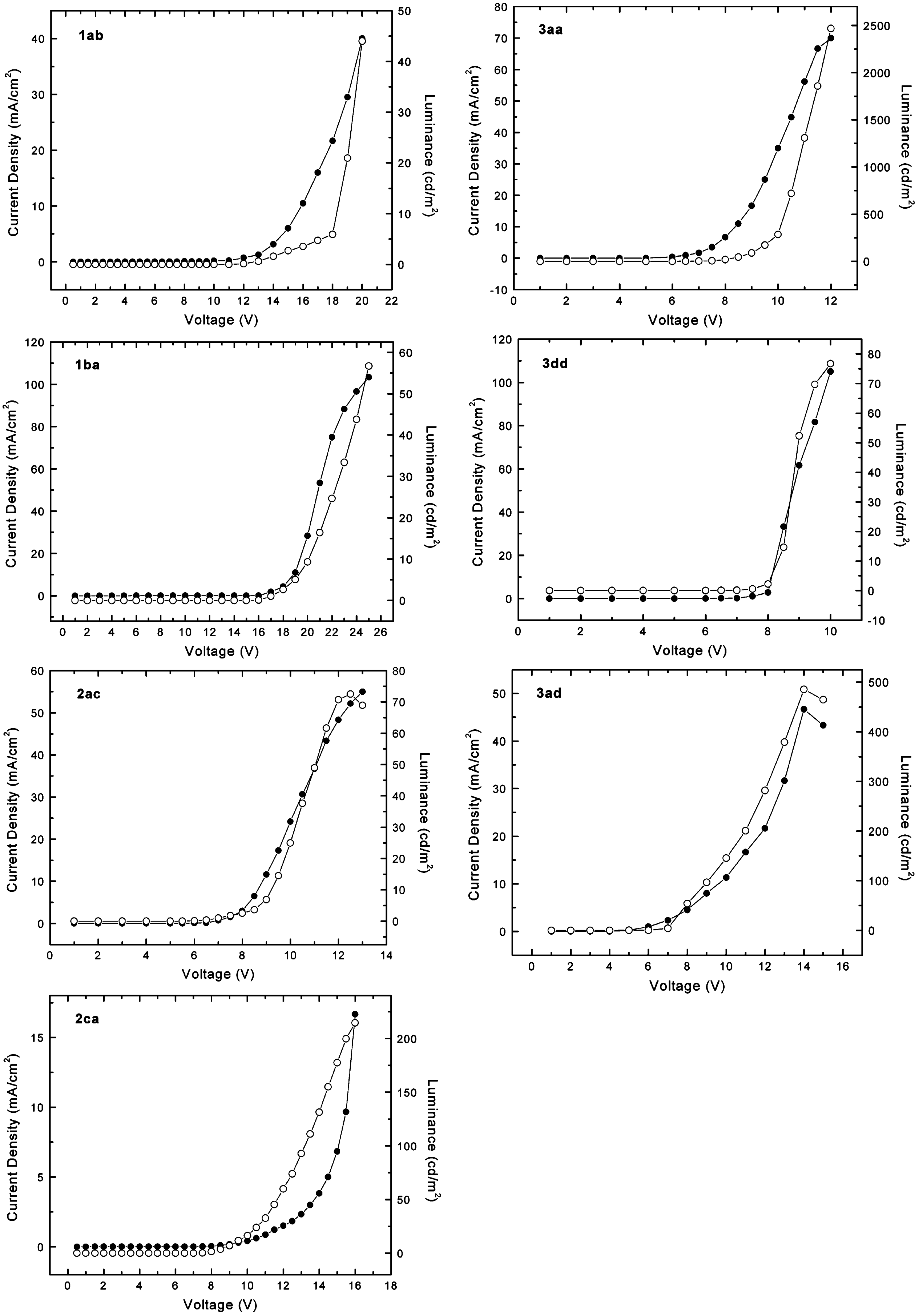

Figure 3. Current density (●)−voltage−luminance (○) characteristics for devices ITO/PEDOT/polymer/Ca.

Table 1. Photophysical Properties of the Polymer Films and LED Characteristics

polymer	λ_{max}^{Abs} (nm)	λ_{max}^{PL} (nm)[a]	band-gap (eV)[b]	λ_{max}^{EL} (nm)	turn-on voltage (V)[c]	LE (cd/A)[d]	QE_{ext} (%)[e]
1ab	446	554	2.40	554	12	0.11	0.028
1ba	482	525	2.45	508	16	0.12	0.028
2ac	388	535	2.45	508	8	0.20	0.047
2ca	436	538	2.41	521	8	4.0	0.95
3aa	383	540	2.46	555	8	3.5	0.89
3dd	387	535	2.42	524	8	0.085	0.02
3ad	389	535	2.44	542	7	1.3	0.32

[a] Excitation wavelength 380 nm. [b] The band-gap was obtained from the point at which the normalized absorption and emission spectra intersect. [c] The turn-on voltage was defined as the voltage at which the luminance starts to increase rapidly. [d] Maximum luminous efficiency. [e] Maximum external quantum efficiency.

corresponding PL spectra results from different exciton generation processes and heating of the LEDs during measurement.[8] Comparing the luminous efficiency (LE) of **3dd** with that of **3ad** and **3aa**, it may be seen that the LE increase as the side chain length increases. When dodecyloxy side chains are replaced by longer octadecyloxy groups, the material efficiency increases by a factor of 40. The longer alkoxy side chains improve material solubility and film-forming capability and promote changes in film morphology. The longer side chains also form small insulating domains which limit exciton interchain migration and enhance exciton confinement. All these factors favor improvement in LED performance and EL efficiency. The polymer **2ca** (or **1ba**) is more efficient than **2ac** (or **1ab**), indicating that grafting longer side chains onto the PV units substantially enhances the material EL efficiency. The optimal sample **2ca** displayed a maximum external quantum efficiency of 0.95%. It is not yet clear why the polymers **1ab** and **1ba** show much higher turn-on voltages compared to other five samples; this is under investigation. The voltage dependence of the EL spectra is shown in Figure 4. For the **2ac** LED, a 10 nm blue shift in EL occurs when the applied voltage is raised from 10 to 15 V. For the **2ca** LED, increasing the applied voltage from 15 to 21 V produces a 6 nm blue shift. With increasing applied voltage up to 30 V, the EL peak wavelength is unchanged at 515 nm, while the 542 nm shoulder almost disappears. The EL blue shift under higher electrical field is related to Joule heating in the LEDs, which results in a thermochromic effect.[8] Additionally, band-gap distributions in the polymers contribute to the effect; at higher applied voltages, emission from the higher band-gap segments contributes proportionally more to the total emission. From Figure 4, it is also concluded that in an electrical field LEDs using the polymers with longer side chains on the PV units are more stable.

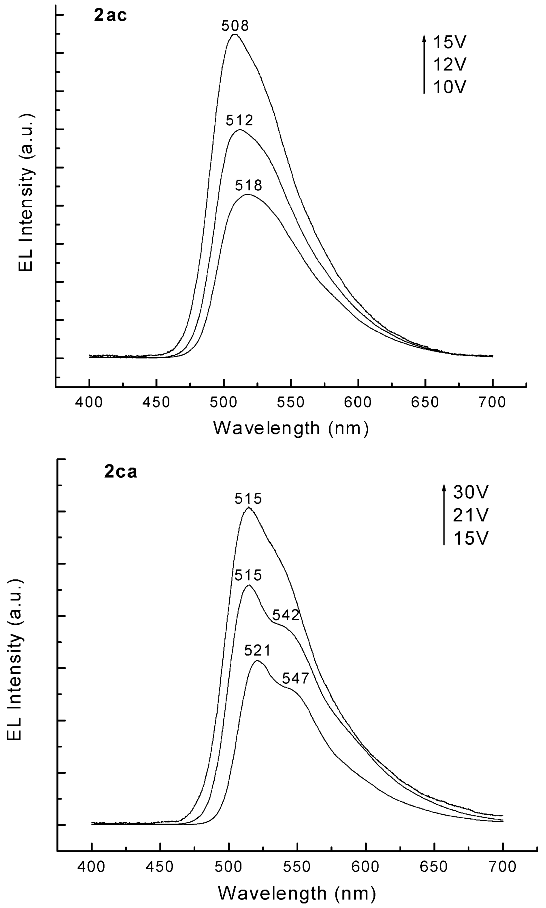

Figure 4. EL spectra for ITO/PEDOT/**2ac**/Ca and ITO/PEDOT/**2ca**/Ca at different voltages.

Effect of Solvent Polarity on Absorption and PL Spectra. To investigate the effect of solvent polarity on the absorption and emission spectra of conjugated polymers, the solvents propylbenzene, xylene, toluene, benzene, chlorobenzene, 1-chlorobutane, chloroform, dichloromethane, ethyl acetate, and methyl ethyl ketone were used to prepare polymer solutions (0.001 mg/mL) of **2ca**. The absorption and emission data for **2ca** in the different solvents are shown in Table 2. Reichardt[9] has shown that the chemical structure and physical properties of the chromophore and the solvent molecules determine the strength of the intermolecular solute/solvent interactions in the equilibrium ground state and in the Franck−Condon excited state and the observed solvatochromism. A bathochromic (or red) shift, with increasing solvent polarity, has been termed a "positive solvatochromism", and this might result from increased stabilization of the molecule in the excited state relative to that in the ground state. In this study, the polymer solutions using solvents of similar structures have been compared in three groups: xylene, toluene, benzene, and chlorobenzene; chloroform and dichloromethane; ethyl acetate and methyl ethyl ketone. With increasing solvent polarity, absorption within all groups show red shifts, indicating that the polymer **2ca** is more stable in the respective excited states than in the ground state. With increasing solvent polarity, PL spectra show similar bathochromic shifts though the shifts are smaller than that observed in absorption. This indicates that the excited-state energy levels are affected less than those in the electronic ground state. This result is opposite to a previous result on carbazole−quinoline oligomer in solvents of varying polarity.[10]

Concentration Dependence of PL Spectra. The emission spectra for polymer **2ca** in chloroform solution of different concentrations are shown in Figure 5. The peak wavelengths are listed in Table 3. With increasing

Table 2. Absorption and Emission Properties for Polymer 2ca in Different Solvents (0.001 mg/mL)

solvent	polarity[a] (kcal/mol)	λ_{max}^{Abs} (nm)	λ_{max}^{PL} (nm)[b]
propylbenzene		448	**488**, 517
xylene	33.1	448	**489**, 517
toluene	33.9	448	**489**, 517
benzene	34.3	448	**489**, 517
chlorobenzene	36.8	456	**494**, 523
1-chlorobutane		448	**487**, 517
chloroform	39.1	448	**490**, 519
dichloromethane	40.7	452	**492**, 521
ethyl acetate[c]	38.1	428	**483**, 513
methyl ethyl ketone[c]	41.3	434	**487**, 515

[a] Data from ref 9. High value corresponds to high solvent polarity. [b] Excitation wavelength 390 nm. [c] **2ca** solubilities in these solvents are poor, and the concentration for the saturated solutions are lower than 0.001 mg/mL.

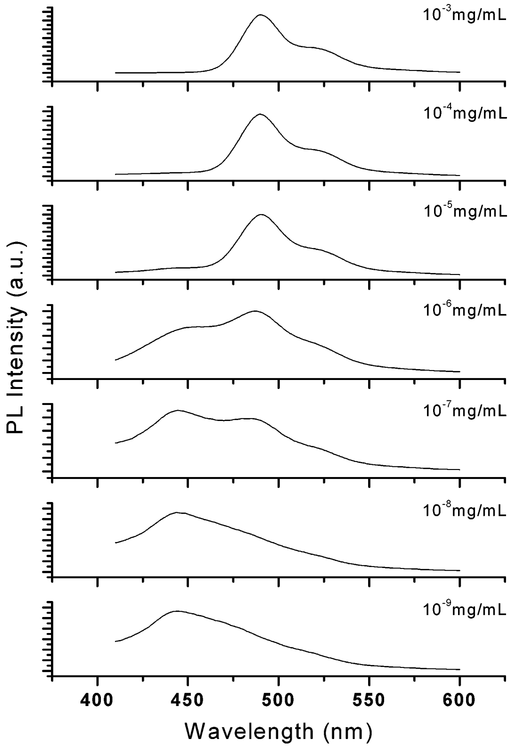

Figure 5. Concentration dependence of PL spectra for **2ca** in chloroform. Excitation wavelength 390 nm.

Table 3. Emission Properties of Polymer 2ca in Chloroform

concn (mg/mL)	λ_{max}^{PL} (nm)[a]		
10^{-9}	**444**		
10^{-8}	**444**		
10^{-7}	**444**	483	
10^{-6}	456	**487**	
10^{-5}		**490**	519
10^{-4}		**490**	519
10^{-3}		**490**	519

[a] Excitation wavelength 390 nm.

2ca concentration, the PL spectra display a red shift and also new bands. At the extreme dilutions of 10^{-9} and 10^{-8} mg/mL, only one peak at 444 nm is observed. At concentration higher than 10^{-8} mg/mL, two new bands appear: one at 483 nm and the other at 519 nm. With increased concentration, the major band at 444 nm decreases in intensity and finally disappears; the band at 490 nm continues to grow and finally dominates, while the 519 nm band develops as a strong shoulder. The new bands appearing in PL spectra are attributed to intermolecular excimer formation.[11] The excimer, a sandwich dimer, is formed by the interaction of a ground-state molecule with an excited molecule.[12] It is noted that in studies of the fluorescence spectra of poly((2,5-bis(*n*-dodecyloxy)-*p*-phenylene)ethynylene-*p*-phenyleneethynylene) in THF solution[12b] the major band in the spectra showed only an ~6 nm red shift, and the relative intensity of the second band increased with increasing solute concentration. It was suggested that the second band was due to excimer formation. In this study, with concentration increase, the PL spectra change substantially with new bands appearing. The structure of the PE component of polymer **2ca** is quite similar to that of the PPE polymer in ref 12b. The PV component increases the flexibility of the hybrid polymer backbone, thus improving the interchain entanglement, interactions, and excimer formation at higher concentration. This contributes to the strong excimer emission observed in **2ca**/chloroform solution at high concentration.

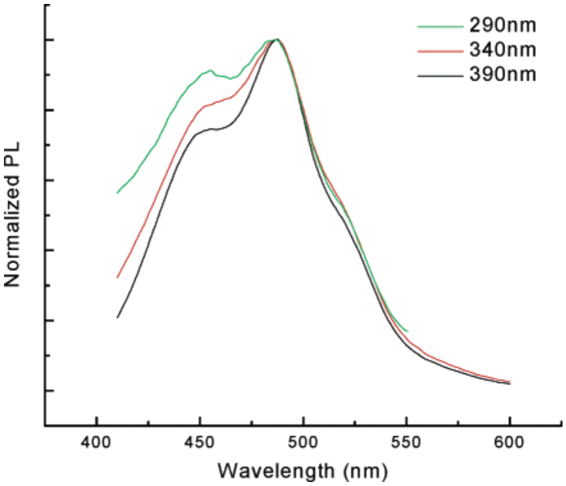

Figure 6. Excitation energy dependence of PL spectra for **2ca** in chloroform (10^{-6} mg/mL).

Effect of Excitation Wavelength on Solution PL Spectra. The normalized emission spectra for **2ca** in chloroform (10^{-6} mg/mL) under different excitation wavelengths (390, 340, and 290 nm) are shown in Figure 6. Under 390 nm excitation, the emission spectrum displays bands at 456, 487, and 519 nm, which correspond to the 0−0, 0−1, and 0−2 band, respectively. With increasing excitation energy, the relative intensity of the band at 456 nm increases, and finally this band becomes an obvious emission peak. This suggests that the 0−0 band is sensitive to excitation energy change and also that the solution PL spectra of these conjugated polymers depend on the excitation wavelength. A similar result was obtained for a violet-blue-emitting polymer in chloroform.[13] For poly[(1-hexyloxy-4-methyl-2,6-phenylenevinylene)-*alt*-(1,3-phenylenevinylene)] in chloroform (1 × 10^{-4} mg/mL), when decreasing excitation wavelength from 412 to 309 nm, the emission peak shifted from 451 to 412 nm and the spectral shape exhibited a large change with a 39 nm blue shift.[13] In this study, with a decrease of excitation wavelength, the shape of the PL spectra did not change significantly with the major band constant at ~487 nm; only the relative intensity of the 0−0 band increased. This indicates that the hybrid conjugated polymer with a lower band-gap is more stable under photoexcitation than the poly(*m*-phenylenevinylene) derivative with a higher band-gap.

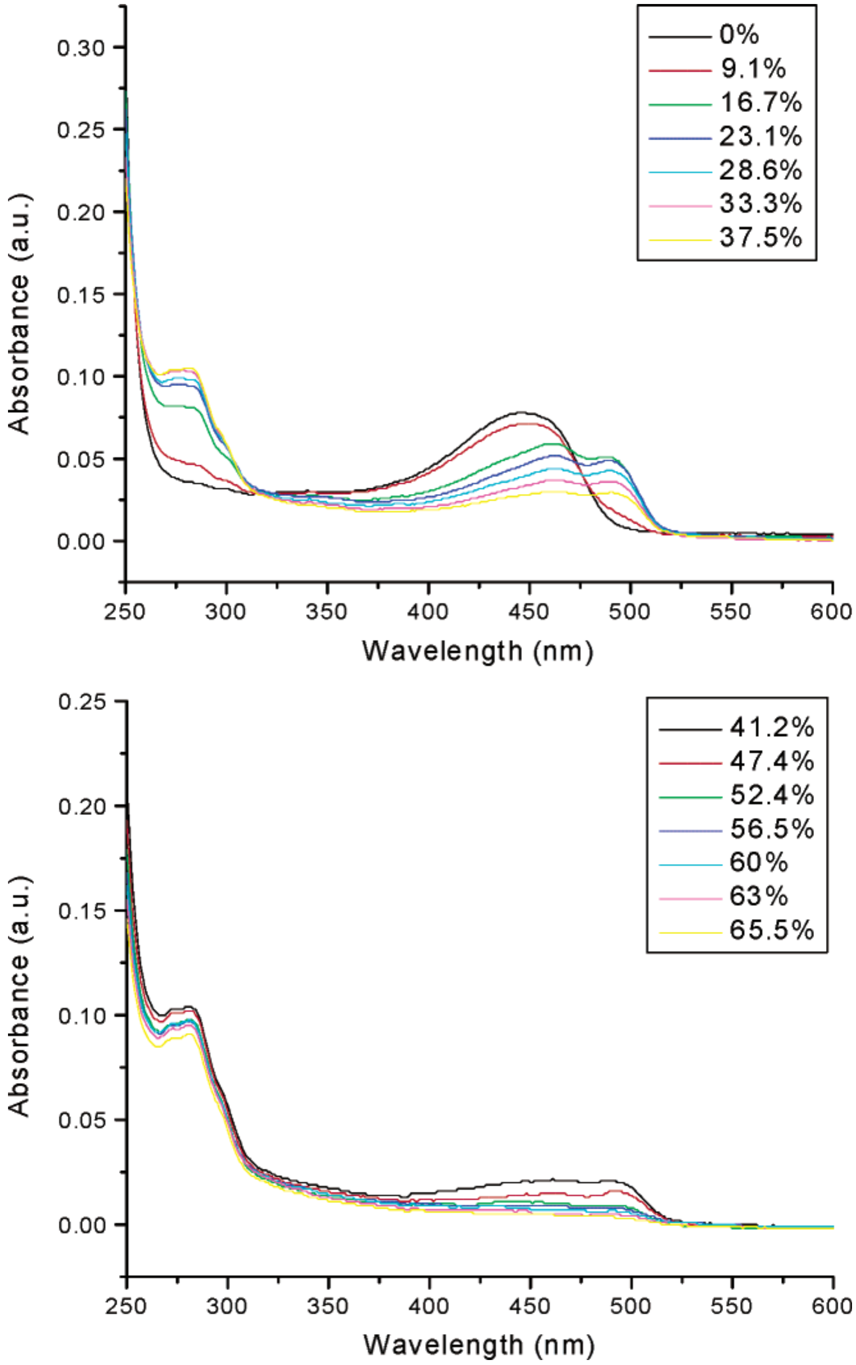

Figure 7. Absorption spectra of polymer **3aa** in chloroform on addition of methanol. Inset: % methanol (v/v).

Aggregate and Excimer Formation in Solvent/ Nonsolvent Solution. The absorption and emission spectra of polymer **3aa** in chloroform/methanol mixtures with different volume concentrations of methanol are shown in Figures 7 and 8, respectively. It should be noted here that in all cases the bulk solution maintains homogeneity. With an increase of methanol concentration, the maximum absorption of the polymer shifts from 446 nm observed in pure chloroform (1.2×10^{-3} mg/mL) to 462 nm, and a new band at 490 nm appears. When the methanol concentration reaches 47.4 vol %, the 490 nm band becomes stronger than the 462 nm band. The spectral red shift from 446 to 462 nm corresponds to a disorder-to-order transformation of the conjugated polymer chains.[14] Since polymer **3aa** is insoluble in methanol, the addition of methanol to the homogeneous chloroform solution leads to aggregate formation. In the aggregate the polymer possesses a more extended conjugated structure, so the new band at 490 nm can be assigned to the aggregate. Similar phenomena were found in chloroform/methanol solutions of 2,5-dialkylpoly(*p*-phenyleneethynylenes),[11b] poly(fluorenyleneethynylene)s,[15] and poly(*p*-phenyleneethynylene) copolymers[16] by Bunz et al. The aggregate bands here are not as distinct as those observed in refs 11b and 15, which might be due to the fact that polymer **3aa** contains two chromophores (PE and PV) while Bunz's polymers contain one chromophore. On the addition of methanol, the emission spectra of polymer **3aa** show a similar red shift. In pure chloroform, the emission spectrum of polymer **3aa** displays a peak at 490 nm and a shoulder at 520 nm. On adding methanol to 16.7 vol %, the emission peak shifts to 508 nm with a weak shoulder at ~540 nm, and the original major

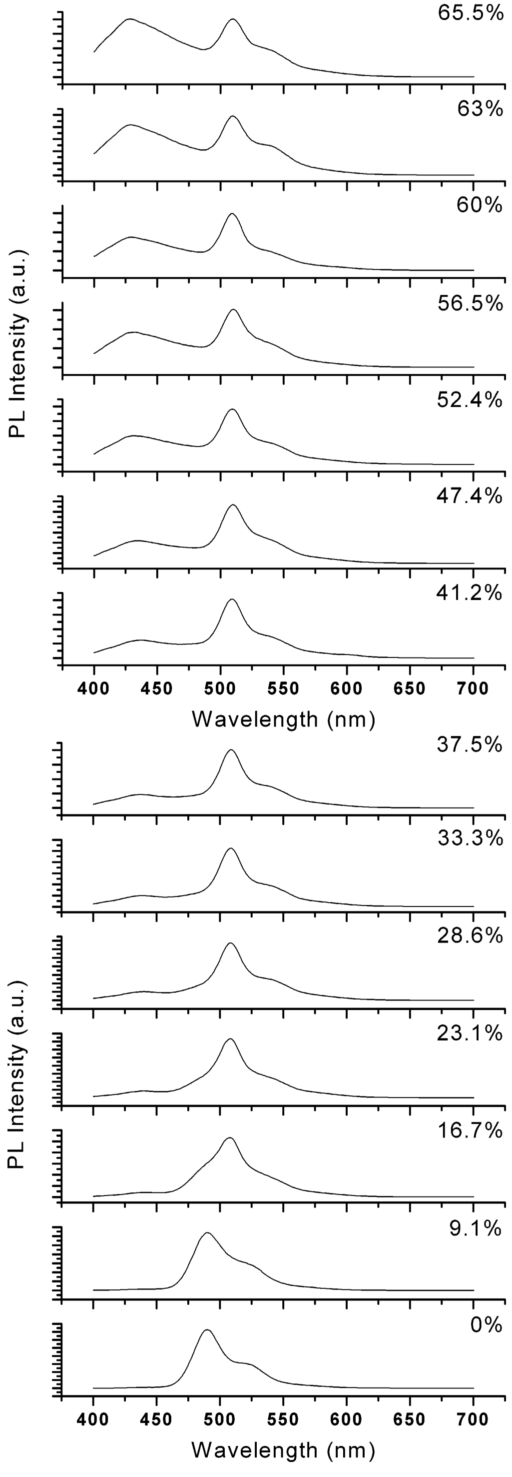

Figure 8. Emission spectra of polymer **3aa** in chloroform on addition of methanol. Inset: % methanol (v/v). Excitation wavelength 380 nm.

band at 490 nm is greatly suppressed. Additionally, a small band at ~441 nm was found. The latter band intensifies with a further increase of methanol concentration and also undergoes a blue shift. When the methanol concentration reaches 65.5 vol %, the 441 nm band shifts to 428 nm with a slightly stronger intensity than the main peak at 510 nm. The ~20 nm red shift in the PL spectrum of the solution with 16.7 vol % methanol originates from intermolecular excimer formation.[16] The new band at 441−428 nm results from aggregate formation. Similar results for an alkyne-bridged carbazole polymer have been reported,[17] in which a significant blue shift (~100 nm) in the solution fluorescence was found upon addition of methanol (50%) to a polymer/chloroform solution.

Conclusion

Optoelectronic studies of a series of alkoxy-substituted phenyleneethynylene (PE)/phenylenevinylene (PV) hybrid conjugated polymers showed that longer alkoxy side chains improve EL efficiency. In particular, polymers with longer side chains on the PV moiety show higher EL efficiency. With increasing solvent polarity, both the absorption and emission spectra of the polymer show bathochromic shifts. With increasing chromophore concentration, the solution PL spectra show red shifts and new bands, indicating intermolecular excimer formation at the higher concentrations. The 0−0 band of the solution PL spectra is sensitive to excitation energy. When adding nonsolvent methanol to the polymer/chloroform solution, both the absorption and emission spectra show red shifts and new bands, indicating aggregate and excimer formation, respectively. Specifically, the new band at 441−428 nm in the PL spectra of the polymer/chloroform/methanol solution indicates aggregate formation.

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References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.

(2) (a) Huang, W.; Meng, H.; Yu, W. L.; Gao, J.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 593. (b) Mikroyannidis, J. A.; Spiliopoulos, L. K.; Kasimis, T. S.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2003**, *36*, 9295. (c) Shu, C. F.; Dodda, R.; Wu, F. I.; Liu, M. S.; Jen, A. K. Y. *Macromolecules* **2003**, *36*, 6698. (d) Peng, Z. H.; Bao, Z. N.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086. (e) Peng, Z. H.; Zhang, J. H. *Chem. Mater.* **1999**, *11*, 1138.

(3) (a) Brizius, G.; Pschirer, N. G.; Steffen, W.; Stitzer, K.; zur Loye, H.-C.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2000**, *122*, 12435. (b) Wilson, J. N.; Windscheif, P. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 8681. (c) Wilson, J. N.; Josowicz, M.; Wang, Y.; Bunz, U. H. F. *Chem. Commun.* **2003**, 2962.

(4) (a) Egbe, D. A. M.; Tillmann, H.; Birckner, E.; Klemm, E. *Macromol. Chem. Phys.* **2001**, *202*, 2712. (b) Egbe, D. A. M.; Birckner, E.; Klemm, E. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 2670. (c) Egbe, D. A. M.; Roll, C. P.; Birckner, E.; Grummt, U.-W.; Stockmann, R.; Klemm, E. *Macromolecules* **2002**, *35*, 3825. (d) Egbe, D. A. M.; Roll, C. P.; Klemm, E. *Des. Monomers Polym.* **2002**, *5*, 245. (e) Egbe, D. A. M.; Bader, C.; Nowotny, J.; Günther, W.; Klemm, E. *Macromolecules* **2003**, *36*, 5459. (f) Egbe, D. A. M.; Bader, C.; Klemm, E.; Ding, L.; Karasz, F. E.; Grummt, U.-W.; Birckner, E. *Macromolecules* **2003**, *36*, 9303.

(5) (a) Ramos, A. M.; Rispens, M. T.; van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2001**, *123*, 6714. (b) Schenning, A. P. H. J.; Tsipis, A. C.; Meskers, S. C. J.; Beljonne, D.; Meijer, E. W.; Brédas, J. L. *Chem. Mater.* **2002**, *14*, 1362. (c) Chu, Q.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2003**, *36*, 3848.

(6) Hu, B.; Karasz, F. E. *Chem. Phys.* **1998**, *227*, 263.

(7) Boardman, F. H.; Grice, A. W.; Rüther, M. G.; Sheldon, T. J.; Bradley, D. D. C.; Burn, P. L. *Macromolecules* **1999**, *32*, 111.

(8) (a) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982. (b) Braun, D.; Moses, D.; Zhang, C.; Heeger, A. J. *Appl. Phys. Lett.* **1992**, *61*, 3092.

(9) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

(10) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315.

(11) (a) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765. (b) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. (c) Morisaki, Y.; Chujo, Y. *Macromolecules* **2002**, *35*, 587.

(12) (a) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586. (b) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52.

(13) Ding, L.; Karasz, F. E.; Lin, Y.; Pang, Y.; Liao, L. *Macromolecules* **2003**, *36*, 7301.

(14) Yu, W.; Meng, H.; Pei, J.; Huang, W.; Li, Y.; Heeger, A. J. *Macromolecules* **1998**, *31*, 4838.

(15) Pschirer, N. G.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 3961.

(16) Pschirer, N. G.; Miteva, T.; Evans, U.; Roberts, R. S.; Marshall, A. R.; Neher, D.; Myrick, M. L.; Bunz, U. H. F. *Chem. Mater.* **2001**, *13*, 2691.

(17) Brizius, G.; Kroth, S.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 5317.

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