Enhanced Emission Efficiency and Excited State Lifetime Due to Restricted Intramolecular Motion in Silole Aggregates

Yan Ren,^{†,‡} Jacky W. Y. Lam,[§] Yongqiang Dong,[§] Ben Zhong Tang,[§] and Kam Sing Wong^{*,†}

Departments of Physics and Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China, and State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, People's Republic of China

Received: July 27, 2004; In Final Form: October 30, 2004

The aggregation-induced emission (AIE) properties of 1,1,2,3,4,5-hexaphenylsilole (HPS) and poly{11-[(1,2,3,4,5-pentaphenylsilolyl)oxy]-1-phenyl-1-undecyne} (PS9PA) were studied by time-resolved fluorescence technique. The enhanced fluorescence and long fluorescent lifetime were obtained for the sample in an aggregate state as compared to the sample in solution. The time-decay of fluorescence of HPS and PS9PA in high viscosity solvents and low-temperature glasses has also been measured in detail to further investigate the possible mechanism for AIE. Enhanced light emission and long fluorescence lifetime were detected for both HPS and PS9PA in the solution-thickening and -cooling experiments. These results provided direct evidence that the enhanced photoluminescence (PL) efficiency is due to restricted intramolecular motion, which ascribes AIE to the deactivation of nonradiative decay caused by restricted torsional motions of the molecules in the solid state or aggregate form.

Introduction

The emission efficiency is a key factor to evaluate the performance of an organic electroluminescent device.^{1,2} In these devices, the luminescent materials are normally used in a form of thin film prepared by spin coating its solution onto the glass substrate or by the vacuum vapor deposition technique. But frequently, we find that highly fluorescent organic materials in solution become nonluminescent or weakly luminescent in the solid state. Therefore, how to mitigate the aggregation quenching has always been an attractive issue.^{3,4} Recently, silole-based organic light-emitting materials have attracted much attention because of their unusual highly luminescent properties in the aggregate state.^{5–9} An intriguing phenomenon was found in that a spot of HPS solution just dropped on the TLC plate was nonluminescent under the UV lamp, while it became highly luminescent after the solvent evaporated. Thereafter, the enhanced PL and high fluorescence quantum yield of this kind of silole-based material was found in the ethanol solution after the addition of excessive water, a poor solvent of this material. Nanoparticles of aggregate siloles were detected in the mixed solvents with the size of a few tens to 100 nm.⁶ Recently, a number of other compounds were also found to show strong aggregation-induced emission.^{10,11} Measurements showed that PL efficiency of the silole-based compounds increases several orders of magnitude in the solid or aggregate form as compared to the solution state.⁵ It is suggested that the possible mechanism of the AIE is the nonradiative channel via the vibrational/ torsional energy relaxation processes which is blocked in the aggregate state, thus populating the radiative state of excitons, and turns on the emission for this kind of compound.⁶ Since vibrational, rotational, and torsional motions of a molecule

strongly depend on temperature and viscosity of the solvent, we expect strong modification of PL efficiency and emission lifetime as a function of these parameters.

The fluorescence lifetime and quantum yield are perhaps the most important characteristics of light-emitting materials. The lifetime determines the time available for the fluorophore to interact with its environment, and the information can be available from its emission. Since the steady-state fluorescence is an average of the time-resolved phenomena over the intensity decay of the sample, much of the molecular information available from fluorescence is lost during the time-averaging process. By contrast, time-resolved fluorescence can provide valuable information about the interaction of molecule in the excited state with its environment.^{12,13} In this paper, to further investigate the possible mechanism for AIE, we studied the PL enhancement behaviors of siloles in detail by using a timeresolved fluorescence technique with a Ti:sapphire femtosecond pulse as the excitation source. Solution-thickening and -cooling experiments were performed for HPS and PS9PA. The evidence obtained from these experiments strongly supported the restricted intramolecular rotation model for the AIE.

Experimental Procedures

Materials.

HPS was synthesized by first reacting diphenylacetylene with an appropriate amount of lithium metal and then reacting the resultant 1,4-dilithiotetraphenylbutadiene with dichlorodiphenylsilane. Monomer of PS9PA was prepared by nucleophilic substitution of 1-chloro-1,2,3,4,5-pentaphenylsilole with 11phenyl-10-undecyn-1-ol. Polymerization of the monomer was effected by the WCl₆-Ph₄Sn catalyst in toluene at 60 °C, which gave PS9PA in ~60% yield. Detailed procedures for the synthesis of HPS and PS9PA can be found in our previous publications.^{6,7,14} The polymeric PS9PA in addition to monomeric HPS is studied because PS9PA can be spin-coated into

^{*} Corresponding author. E-mail: phkswong@ust.hk. Tel: (852) 2358 7475. Fax: (852) 2358 1652.

[†] Department of Physics, The Hong Kong University of Science.

[‡] Shandong University.

[§] Department of Chemistry, The Hong Kong University of Science.



Figure 1. SEM photomicrograph of HPS particles in solution containing 90% volume fraction of water and 10% DMF imaged two weeks after preparation. The scale shown in the figure is 1 μ m under the magnification of 8500.

smooth thin solid films so that the polymer-based light-emitting diode can be fabricated. The development of PS9PA thus will extend the silole-based compounds for organic optoelectronic applications using both evaporation and spin-coating techniques.

Three groups of samples were prepared for the PL lifetime measurements. The mixed solutions of HPS were prepared by different volume ratios of water into the HPS/DMF solution being added. The final solutions obtained by this method have the identical concentration of 1.3×10^{-5} mol/L. DMF was used as the solvent because of its good miscibility with water. The solution with 30% water was clear when mixing was finished, while those containing 70 and 90% water became slightly milky. This indicates that some particles with large sizes are formed after excessive water is added into the DMF solution, and the scattering of the visible light by these particles makes the solutions misty. Despite all this, all the solutions prepared were homogeneous without visible deposits observed after mixing. Moreover, the solution with 90% water was very stable even after it was kept for more than two months. There was no trace of visible deposits of HPS in the solution. The SEM image of HPS particles obtained from the mixed solution (two weeks after preparation) containing 90% volume fractions of water are shown in Figure 1. This shows that HPS forms particles of a few hundred nanometers in size.

1,2-Dichloroethane, ethylene glycol monoethyl ether, and benzyl alcohol were used for preparing the other group of samples for the solution-thickening experiment. We selected these solvents because they possess different viscosities but similar polarity to avoid the possible effect of polarity on the PL of the materials. The samples used in the solution-cooling measurement are 2 wt % HPS and PS9PA/DMF solutions.

Instrumentation.

Before the PL lifetime measurement, the UV-vis absorption and time-integrated PL spectra were measured for HPS and PS9PA by using a UV-2401 (Shimadzu) spectrophotometer and fiber spectrometer (Ocean Optics Inc.), respectively, to select the optimal excited laser source and wavelength for the PL signal collection. Benzene solution (0.002 wt %) was used in the UVvis absorption measurement, and 2 wt % benzene solution was used in the time-integrated PL spectrum measurement.

The absorption and fluorescence spectra are shown in Figure 2. The maximum absorption and fluorescence of HPS is located at \sim 366 and \sim 500 nm, respectively. For PS9PA, the absorption



Figure 2. UV-vis absorption (0.002 wt %) and fluorescence (2 wt %) spectra of benzene solutions of HPS and PS9PA.

and fluorescence peaks are a little red-shifted as compared to those of HPS. Laser pulses at 267 nm were used as the excitation laser source for the PL measurements. This was produced by the frequency summation of 800 nm with its 400 nm frequencydoubling from a Ti:sapphire regenerative amplifier (200 fs pulse width and 1 kHz repetition rate). For time-resolved fluorescence measurements, the fluorescence signals were collimated and focused onto the entrance slit of a monochromator with the output plane connected to a synchroscan streak camera (Hamamatsu Model C4334, 20 ps resolution). The PL signals were measured near the emission peak at \sim 500 nm. In the optical setup, a flip mirror was inserted before the monochromatorstreak camera system to reflect the fluorescence to a fiber spectrometer (Ocean Optics Inc.) to record the time-integrated PL spectra before each run of the lifetime measurement. The laser energy level for excitation is $\sim 400 \,\mu$ W. In the experiment, all samples used were freshly prepared.

Results and Discussion

In the previous measurements,⁵ the fluorescence quantum yields (Φ_F) of silole aggregates were dramatically enhanced by up to several hundred times of those in pure solutions with identical concentrations. In our experiment, HPS in pure solution was also weakly emissive even though it was excited with a relatively high peak power focused laser. By contrast, very bright fluorescence was observed in the sample containing a 70 and 90% volume fraction of water.

The strongly enhanced fluorescence of HPS in solution with an increased water volume fraction also showed corresponding dramatic changes in emission lifetime as illustrated by the timeresolved fluorescence curves in Figure 3. It can be shown that $\Phi_{\rm F} = \tau/\tau_{\rm r}$, where PL lifetime τ is related to radiative $(\tau_{\rm r})$ and nonradiative (τ_{nr}) lifetimes by the expression $1/\tau = 1/\tau_r + 1/\tau_{nr}$. $\tau_{\rm r}$ is the intrinsic property of the molecule; therefore, it is a constant. The low $\Phi_{\rm F}$ and the PL lifetime τ are essentially limited in system resolution for HPS in pure DMF solvent and in mixtures with low volume fractions of water (few tens of picoseconds), indicative of strong nonradiative recombination process. Increasing the water fraction caused an enhanced emission and increased the PL lifetime to nanoseconds. The lifetime data are shown in Table 1. The fluorescence decay behavior of HPS in pure DMF solvent with the same concentration as that of the DMF/H₂O mixture is well-fitted by the singleexponential function. It shows that the excited state relaxation of HPS in pure solvent is actually a single-exponential decay (i.e., all the excited molecules of HPS decay through the same



Figure 3. Time-resolved fluorescence of HPS in solution with different volume fractions of water and DMF. The identical concentration for the mixtures is 1.3×10^{-5} mol/L.

TABLE 1: PL Lifetime of HPS in DMF/H_2O Mixtures with Identical Concentrations of 1.3×10^{-5} mol/L

H ₂ O (%)	A_1/A_2	$ au_1$ (ns)	τ_2 (ns)
0	1/0	0.04	
30	0.80/0.20	0.10	3.75
70	0.50/0.50	0.82	4.98
90	0.43/0.57	1.27	7.16

pathway). Its fluorescence lifetime is only as short as 40 ps, which is close to the resolution limit of the streak camera system (\sim 25 ps). The fluorescence lifetime data for HPS in the mixture are also given in Table 1, which were obtained by fitting the time-resolved fluorescence curves based on the following double-exponential function:

$$y = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

Fitting based on this function gave better fitting results than that on the single-exponential function for the sample with water. It indicates that the molecules in the mixed solvent may exist in two different environments, or they decay through two relaxation pathways. The values of A_1 and A_2 represent the fractional amount of molecules in each environment. The decay in one pathway is short, and that in another is relatively long. For HPS in 30% water mixture, 80% of the molecules decay through the fast pathway. The lifetime is only 0.1 ns for the fast decay component. With the volume fraction of water in the mixture getting higher, the decay time of molecules through the fast pathway is over 20 times longer than that in pure solvent. In the mixture containing 90% water, the molecular radiative decay is mainly through the slow pathway. The fluorescence lifetime of the slow decay rises to \sim 7 ns. Although measurement on PL quantum yield as a function of volume fraction of water shows a threshold at \sim 50% water fraction,^{5,6} the time-resolved measurement is able to separate short- and long-lived components and observation of small slow PL decay component at <50% water fraction, indicating that there are already some aggregates formed in the solutions with low water fractions. The amount of aggregates is small at the low water volume fractions, so that it has a small contribution to the overall quantum yields as compared to the large water volume fraction case.

Restricted intramolecular motion has been suggested as the possible mechanism of AIE previously described,^{6,7} considering that vibrational/torsional motion of the molecule can affect



Figure 4. (A) Fluorescence peak intensities of DMF solution of HPS (2 wt %) at different temperatures and (B) its PL spectra at 295, 135, and 30 K.

drastically the radiative/nonradiative recombination processes of the excited state.¹⁵⁻¹⁹ For HPS in dilute solution, since its peripheral benzene rings rotate actively around the single bonds linked to the central silole ring, the excitons are believed to be effectively annihilated by this kind of intramolecular torsional motion. Therefore, siloles are nonluminescent or weakly luminescent in solution. While in aggregate state, the intramolecular motion is restricted. According to the previous mechanism, the nonradiative decay channel is blocked, which populates the radiative decay and makes the siloles luminescent. We then performed the time-resolved fluorescence measurements of HPS and PS9PA in viscous solution and at low temperature because both approaches are expected to effectively hamper the intramolecular motion.⁶ Through the previous two experiments, we try to investigate the real role of restricted intramolecular motion on the PL properties of siloles.

In the low-temperature experiment, the fluorescence became stronger when the sample temperature was decreased. This was especially apparent when the sample was cooled to a temperature below the melting point of DMF (mp = $-60.4 \,^{\circ}C$;²⁰ however, the melting point of the siloles/DMF solution could be much lower than that of pure DMF), and the fluorescence signal was so strong that we had to use an attenuator to decrease the intensity to avoid saturation of the signal in the streak camera. Figure 4A shows the fluorescence peak intensity of HPS/DMF solution at different temperatures. The emission intensity peaks at about 135 K, and at this temperature, the emission intensity is over 2 orders of magnitude stronger than that at room temperature. Further cooling of the sample below 135 K caused it to decrease in emission intensity. The decrease in intensity at



Figure 5. Time-resolved fluorescence of HPS solutions (0.2 wt %) with different solvent viscosities at room temperature.



Figure 6. Time-resolved fluorescence of DMF solution of HPS (2 wt %) at different temperatures. The inset is the PL decay at 30 K at 5 ns time scale, showing the slow decay component of PL at the low temperature.

low temperature below the melting point of the solution was caused by the scattering loss because when the solution freezes into solid, it is highly scattered. This is further confirmed by lifetime measurements where the PL decay time continues to increase from 150 to 30 K as shown in the next section. The PL spectra at three different temperatures are shown in Figure 4B. One can see that the spectra shape and peak positions of the PL spectra are not shifted with sample cooling. Similar to the cooling experiment, an enhancement in fluorescence efficiency was also observed from the samples with higher solvent viscosity.

The time-resolved fluorescence spectra of HPS in solutions with different viscosities and at different temperatures are shown in Figures 5 and 6, respectively. The fitted decay lifetimes from the time-resolved PL data are summarized in Tables 2 and 3. One can see that their fluorescence decay behavior in solutionthickening and -cooling experiments can be well-interpreted by the restricted intramolecular motion model, which deactivates the nonradiative pathways and hence enhances the fluorescence of siloles for high viscosity solvents or at low temperatures. For HPS in low viscosity solvent and at room temperature, since the molecules are basically in a completely free state and little restriction imposed on intramolecular motion, A_1 is close to 1. Almost all molecules are in the same environment and decay through the same pathway (i.e., A_1 is close to 1 so that excitedstate relaxation is a single-exponential decay), and the decay is very fast due to efficient nonradiative process via vibrational/ torsional molecular motion. Their lifetimes are as short as about 40 ps for HPS in 1,2-dichloroethane and DMF solvents as shown in Figures 5 and 6, respectively. As the viscosities of the solvents become high and the sample temperature decreased, the intramolecular motion was restricted to some degree due to a change in the environment. The time-decay process of HPS is characterized by radiative/nonradiative depopulation of the excited state through two pathways. Moreover, more than 50% of silole molecules recombined through the slow pathway as shown in Table 2. In a high viscosity solution, the decay time of HPS through the fast pathway rises to 10 times of that in the low viscosity solution. The time-decay behaviors of HPS are distinctive with the solution cooling, especially when the temperature was decreased to below the melting point of DMF where the intramolecular motion of HPS is effectively restricted. For example, at 150 K, the fast decay of HPS takes 1.23 ns, and its slow decay takes 7.19 ns, which is up to \sim 30-fold of that at room temperature (Table 3). The lifetime of HPS becomes longer at even lower temperature. As shown in the inset of Figure 6, the excited state decay at 30 K is well over 10 ns, indicating that this is the intrinsic radiative recombination lifetime of the HPS excited state. The fluorescence enhancement in restricted intramolecular vibrational/torisional state can be obtained not only from the small silole molecule but also from the silole-based polymer. It is unavoidable that the inherent structural difference between PS9PA and HPS will have an effect on recombination dynamics; hence, the measured lifetime and temperature effect are slightly different from each other. However, as shown in Tables 2 and 3, the general behaviors are essentially the same (i.e., the PS9PA solution exhibits a substantial increase in PL decay time at low temperatures and in high viscosity solvents).

It has been suggested that planarization of the molecule upon formation of aggregate state²¹ may have caused this enhanced emission.⁵ However, in this case, we would expect to see red shifts and well-resolved vibronic features in the emission spectra in the aggregate or solid samples as compared to the solution case. In our case, both silole solution and aggregate emissions are broad and featureless, and there are essentially no shifts in the emission peak positions. Furthermore, recent X-ray measurement showed that the ground state structure of the silole crystal is actually also nonplanar.⁶ The silole crystal structure is shown in Figure 7, which clearly indicates that the silole molecule is highly nonplanar; thus, this model of planarization in the aggregation state giving rise to high fluorescence yield can be ruled out. However, planarization may take place at the excited state since there is large red-shift in the emission with respect to absorption. This cannot explain the large enhancement in the PL yield in aggregate as compared to solution. The PL spectra are sharp, and peak positions are the same for the silole solution and aggregate, which indicates that the degree of excited-state planarization is about the same for both cases. We also note that planar conformation of the excited state will normally emit fluorescence with well-resolved vibronic features,²² which is in contrast to our case where the fluorescence is featureless. Furthermore, interaction with the solvent molecules is expected to progressively reduce for growing thermal activation so that planarization becomes more effective at higher temperatures.²² This would yield stronger PL at higher temperatures; however, our temperature-dependent measurements in Figure 4 show an opposite trend.

TABLE 2: Room Temperature PL Lifetime of 0.2 wt % HPS and 0.17 wt % PS9PA in Solvents with Different Viscosities

solvent ^a		HPS		PS9PA				
	η^b	ϵ^{c}	A_1/A_2	τ_1 (ns)	τ_2 (ns)	A_1/A_2	τ_1 (ns)	ϕ_2 (ns)
DMF ^d DCE EGME BA	0.794 0.799 1.85 5.47	$\begin{array}{c} 38.25^{20} \\ 10.42^{20} \\ 13.38^{25} \\ 11.92^{30} \end{array}$	1/0 0.96/0.04 0.63/0.37 0.60/0.40	0.04 0.05 0.09 0.24	2.17 1.38 3.40	0.86/0.14 0.79/0.21 0.53/0.47 0.49/0.51	0.16 0.08 0.13 0.42	0.58 0.84 1.53 2.47

^{*a*} Abbreviations: DMF = dimethylformamide, DCE = 1,2-dichloroethane, EGME = ethylene glycol monoethyl ether, and BA = benzyl alcohol. ^{*b*} Viscosity at 25 °C. ^{*c*} Dielectric constant at given temperature. ^{*d*} Concentration: 2 wt %.

 TABLE 3: PL Lifetime of DMF Solutions of HPS and

 PS9PA (2 wt %) at Different Temperatures

		HPS			PS9PA		
$T(\mathbf{K})$	A_1/A_2	τ_1 (ns)	τ_2 (ns)	A_1/A_2	τ_1 (ns)	τ_2 (ns)	
295	1/0	0.04		0.86/0.14	0.16	0.58	
250	1/0	0.11		0.72/0.38	0.69	3.43	
200	0.51/0.49	0.31	2.89	0.58/0.42	0.79	9.24	
150	0.43/0.57	1.23	7.19	0.44/0.56	0.80	8.26	
30	0.34/0.66	2.49	10.39	0.26/0.74	1.18	7.44	

The previous results provide strong evidence that the enhanced PL efficiency of siloles is due to restricted intramolecular motion. The phenomenon observed was also consistent with the previous report about the enhancement of time-integrated fluorescence in a restricted intramolecular rotation state of siloles.^{6,7} Therefore, we can understand the AIE of HPS in the following way by analyzing the packing state of HPS molecules in nanoparticles in the DMF/water mixture: we consider that HPS molecules existed in different aggregate morphologies in the system as different volume fractions of water were added. In the dilute solution without water added, molecules exist completely in a free state without a restriction imposed on the intramolecular torsional motions. Therefore, molecules of HPS are nonluminescent or weakly luminescent due to depopulation of the excited state mainly by nonradiative decay; after a small fraction of water was added in the DMF solution, because water is a poor solvent of HPS, some molecules began to pack in the aggregate state. However, most of the molecules are still in the free state, and aggregate particles formed are small in size. In one particle, there may be only a few molecules to aggregate. In addition, the molecules in the aggregate state are less in quantity as compared to that of the molecules in the free state. Consequently, the fluorescence enhancement effect caused by restricted intramolecular motion is not distinct. However, after a large volume fraction of water was added in the system, for example, in a mixture containing 70 or 90% water, the aggregate particles with large sizes predominated in morphology of HPS molecules in the mixture. The particle size is large enough to be easily observed under SEM. From Figure 1, one can see that the size of particles formed in the mixture containing 90% water is at the range of few tens to few hundreds of nanometers in diameter. Obviously, in one particle, there are approximately a few hundreds of packed molecules. In this situation, HPS is characterized by the enhanced emission because of the intramolecular vibrational/torsional motions restricted in these packed nanoparticles. Although it is well-known that well-packed aggregates with $\pi - \pi$ stacking such as in an H-aggregate tend to prevent radiative recombination, the silole molecule has distinct nonplanar structure in the solid state with an interplane molecular distance of ~10 Å and virtually no $\pi - \pi$ stacking as shown in Figure 7. This suppresses the intermolecular interaction that tends to induce nonradiative recombination as seen in H-aggregates. The interplane and intermolecular distances indicated in Figure 7 are the separation between the silicon atoms in the molecules; however, the neighboring phenyl rings



Figure 7. Crystal structure of silole clearly shows that the silole molecule is nonplanar. The interplane distance is 10.04 Å, and intermolecular distance within the unit cell is 7.61 Å.

are very close to each other, and this will restrict the torsional/ vibrational motions of these molecules in the solid state due to steric hindrances.

It has been proposed that the enhanced emission in the film or solid state is a result of arresting the geometry relaxation of the excited fluorescent state to a nonfluorescent state located between HOMO and LUMO levels.¹¹ This model is entirely consistent with our result that the torsional motion is restricted in the aggregate so that this prevents or at least partially restricts geometry relaxation in the excited state. Currently, there is no experimental evidence for this nonfluorescent state in silole compounds. However, photoinduced absorption experiments are now underway to verify the existence of this nonfluorescent state (i.e., triplet state). Nevertheless, our temperature dependence and solvent viscosity measurements, irrespective of whether this dark state model is correct, indicate clearly that restricted motion of the phenyl rings of the silole molecules enhances the radiative recombination.

Conclusions

We studied the PL enhancement behaviors of siloles in the aggregate state in detail by using a time-resolved fluorescence technique. The time-decay behaviors of siloles in solution-thickening and -cooling experiments provide direct evidence for the restricted intramolecular motion model. Our conclusion is that the AIE of silole is attributed to the deactivation of nonradiative decay by restricted intramolecular vibrational and torsional motions.

Acknowledgment. This research was supported in part by the Research Grant Council of Hong Kong under Grants N_HKUST610/02 and HKUST6085/02P. The optical experiment was performed in the Joyce M. Kuok Laser and Photonics Laboratory at The Hong Kong University of Science and Technology.

References and Notes

- (1) Hung, L. S.; Chen, C. H. Mater. Sci. Eng., A 2002, 39, 143-222.
- (2) Salbeck, J. Ber. Bunsen-Ges. Phys. Chem. 1996, 100, 1667-1677. (3) Friend, R. H.; Gymer, R. W.; Holms, A. B.; Burroughes, J. H.;
- Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J.
- L.; Lögdlund, M.; Salaneck, W. R. Nature 1999, 397, 121-128. (4) Tang, B. Z. Chem. Innov. 2001, 31, 8.
- (5) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. Chem. Commun. 2001, 1740-1741.
- (6) Chen, J.; Law, C. C. W.; Lam, J. W. Y.; Dong, Y.; Lo, S. M. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535–1546.
- (7) Chen, J.; Xie, Z.; Lam, J. W. Y.; Law, C. C. W.; Tang, B. Z. Macromolecules 2003, 36, 1108-1117.
- (8) Chen, H.; Lam, J. W. Y.; Luo, J.; Ho, Y.; Tang, B. Z.; Zhu, D.;
- Wong, M.; Kwok, H. S. *Appl. Phys. Lett.* **2002**, *81*, 574–576. (9) Chen, J.; Peng, H.; Law, C. C. W.; Dong, Y.; Lam, J. W. Y.; Williams, I. D.; Tang, B. Z. Macromolecules 2003, 36, 4319-4327.
- (10) An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. J. Am Chem. Soc. 2002, 124, 14410-14415.
- (11) Jayanty, S.; Radhakrishnan, T. P. Chem.-Eur. J. 2004, 10, 791-797.

- (13) Slavík, J. Fluorescence Microscopy and Fluorescent Probes; Plenum Press: New York, 1996.
- (14) Tang, B. Z.; Zhan, X.; Yu, G.; Lee, P. P. S.; Liu, Y.; Zhu, D. J. Mater. Chem. 2001, 11, 2974-2978.
- (15) Malkin, J. Photophysical and Photochemical Properties of Aromatic Compounds; CRC Press: Boca Raton, FL, 1992.
- (16) Wise, D. L.; Wnek, G. E.; Trantolo, D. J.; Cooper, T. M.; Gresser, J. D. Photonic Polymer Systems; Marcel Dekker: New York, 1998.
- (17) Wong, K. S.; Wang, H.; Lanzani, G. Chem. Phys. Lett. 1998, 288, 59-64.
- (18) Li, Y.; Vamvounis, G.; Holdcroft, S. Macromolecules 2002, 35, 6900-6906.
- (19) Kanemitsu, Y.; Suzuki, K.; Masumoto, Y. Phys. Rev. B 1994, 50, 2301 - 2305.
- (20) Lide, D. R. Handbook of Organic Solvents; CRC Press: Boca Raton, FL, 1995.
- (21) Levitus, M.; Schmieder, K.; Ricks, H.; Schimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. J. Am. Chem. Soc. 2001, 123, 4259-4265.
- (22) Bongiovanni, G.; Botta, C.; Brédas, J. L.; Cornil, J.; Ferro, D. R.; Mura, A.; Piaggi, A.; Tubino R. Chem. Phys. Lett. 1997, 278, 146-153.