Photophysical Properties of 9,10-Disubstituted Anthracene Derivatives in Solution and Films
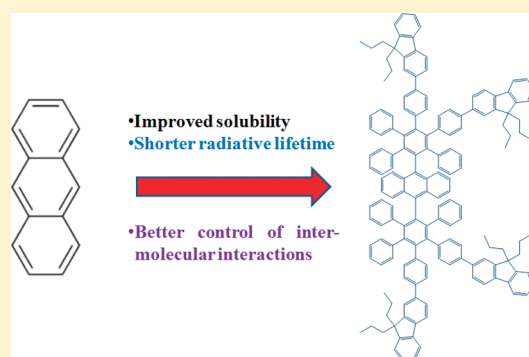
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ABSTRACT: We have carried out absorption, time-resolved fluorescence, and fluorescence quantum yield measurements of four new soluble anthracene derivatives. They show natural radiative lifetimes in the range of 2.5−4.4 ns, which is 5−10 times shorter than those reported for unsubstituted anthracene. The 9,10-bis(phenylethynyl)anthracene (BPEA) derivatives show the largest fluorescence transition dipoles, which is attributed to extended π-conjugation between anthracene and phenyls through acetylene linkages. Spin-cast films of the BPEA derivatives show strong fluorescence quenching by weakly emitting low energy excitations, which is attributed to excimer-like traps. Quenching is significantly reduced when bulky dendrons are attached so that they give maximum coverage of the emitting chromophore and prevent their aggregation. The results show that anthracene derivatives can be developed into efficient solution-processable fluorescent emitters for the blue and green spectral regions.

•Improved solubility
•Shorter radiative lifetime

•Better control of inter-molecular interactions

1. INTRODUCTION

Light-emitting conjugated organic molecules have been the subject of intensive studies[1−7] due to their potential for a range of applications, including large-area flat panel displays and solid-state organic lasers. Small organic molecules are generally deposited by thermal evaporation under high vacuum to form thin films. On the other hand, conjugated polymers and dendrimers present the advantages of being solution-processable and can be integrated into highly efficient device structures simply by spin-coating or inkjet printing techniques. In particular, conjugated dendrimers[7−11] have been used in phosphorescent organic light-emitting diodes (OLEDs)[12−14] showing external quantum efficiencies as high as 16% as well as being successfully employed in one- and two-photon pumped solid-state organic lasers[15,16] and, more recently, sensors.[17,18] These dendritic conjugated compounds are typically composed of a light-emitting core, dendrons, and surface groups that control the solution-processing properties. Their well-defined chemical structure is extremely convenient to investigate the semiconducting properties of organic conjugated materials.[19−21]

Anthracene derivatives present attractive photophysical and charge transport properties and are very promising candidates for high efficiency OLEDs, organic field-effect transistors (OFETs) and other optoelectronic devices.[22−30] The first report on organic electroluminescence was based on the use of anthracene single crystals.[31] Since this discovery, the anthracene moiety has been widely used as a building block for conjugated small molecules, polymers, oligomers, and dendrimers with good optoelectronic properties. Anthracene derivatives have been successfully used either as emitters in deep-blue OLEDs[32] or as host materials for electroluminescent blends.[33] They have also been employed in high performance p-type OFETs with hole field-effect mobilities as high as 0.5 cm^2 V$^{−1}$ s$^{−1}$ and are attractive candidates for flexible organic electronic circuits.[34] Because of their high potential for blue light-emitting devices, the design and synthesis of new anthracene derivatives with improved color purity, luminescence efficiency and stability is still of strong interest. Apart from OLED applications they also have been used to develop materials with a large cross-section of two-photon absorption,[35] liquid crystalline behavior,[36] and new fluorescent probes for detection and structural studies of nucleic acids.[37]

In this article, we report on the photophysical properties of four new solution-processable anthracene derivatives. Short radiative lifetimes of 9,10-bis(phenylethynyl)anthracene (BPEA) derivatives indicate their potential as efficient green emitters. It is found that further chemical engineering is required to prevent concentration quenching in spin-cast films, which could be achieved by attaching bulky dendrons to the fluorescent core.
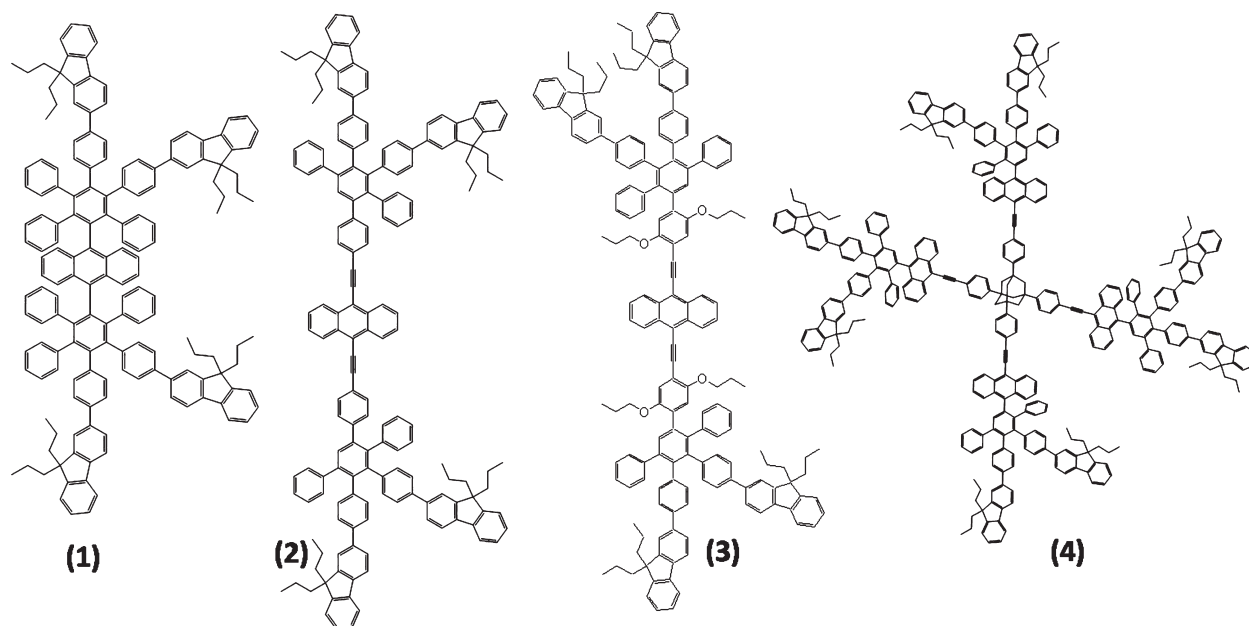
2. EXPERIMENTAL SECTION

The molecular structures of the four anthracene-based dendrimers used in this study are shown in Figure 1. Dendrimer **1** has

Figure 1. Chemical structures of the anthracene-based dendrimers used in this work.

bulky polyphenyl dendrons with 9,9-di-*n*-propylfluorenyl surface groups attached directly to the anthracene core. Dendrimers **2** and **3** have the same dendrons, but with an extended BPEA core, with **3** also having two alkoxy groups attached to each of the phenyl groups of the BPEA chromophore. Finally, dendrimer **4** has four phenyacetylenylanthracene units spaced in a tetrahedral arrangement around an adamantyl center. Dilute solutions for fluorescence measurements were prepared in toluene and held in a quartz cuvette with 1 cm path length at ambient temperature. Films were spin-coated onto precleaned fused silica substrates from a toluene solution at 20 mg/mL under clean room conditions. UV−vis absorption spectra were recorded on a Cary Varian model 300 absorption spectrophotometer. Absorption coefficient measurements were performed on dilute solutions in dichloromethane. Steady-state photoluminescence (PL) spectra were obtained using a Jobin Yvon Fluoromax 2 fluorimeter. The photoluminescence quantum yield (PLQY) in solution was measured using quinine sulfate in 0.5 M sulfuric acid with a PLQY of 54.6% as reference. In this experiment, the excitation wavelength was 360 nm where the absorption of the solutions was close to 0.1. The film PLQYs were measured in an integrating sphere under a flowing nitrogen atmosphere using a previously reported method[38] and a helium−cadmium laser emitting at 325 nm as excitation light source. In time-resolved fluorescence measurements the samples were excited with 100 fs pulses at a repetition rate of 80 MHz at 390 nm for the solution and 375 nm for the neat films using a frequency doubled Ti:sapphire oscillator. For this experiment, the neat films were placed in a vacuum of less than 5×10^{-4} mbar, and the excitation pulse energy was attenuated to the level at which the fluorescence decays showed no dependence on the pulse energy. These precautions were taken to prevent film oxidation and fluorescence quenching by exciton−exciton annihilation and by accumulated long-lived excitations, such as triplets. Time-resolved fluorescence intensity was recorded on a synchroscan streak camera with an instrumental response function of 2 ps after dispersing it in a spectrograph.
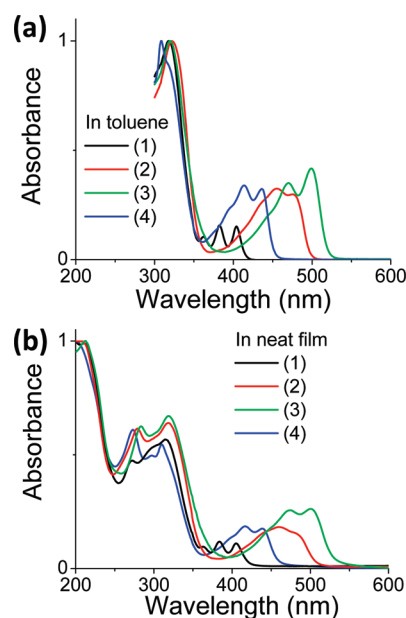

Figure 2. Normalized absorption spectra of the anthracene-based dendrimers in dilute toluene solution (top) and in neat films (bottom).

3. RESULTS AND DISCUSSION

Figure 2 displays the absorption spectra of the anthracene derivatives in both solution and neat film. Dendrimer **1** has low energy absorption peaks at 404, 382, and 362 nm with $\sim$1400 cm^{-1} separation between them, which are attributed to 0−0, 0−1, and 0−2 vibronic peaks of the electronic transition between singlet states, respectively. The peak positions are red-shifted by about 20 nm as compared to the unsubstituted anthracene chromophore,[39] which can be explained by changes in electronic structure caused by the dendron. BPEA derivatives (compounds **2** and **3**) also show vibronic progressions with similar separations between peaks but red-shifted by 70 and

Table 1. Solution data: Molar Absorption Coefficient ε_A at the 0−0 Vibronic Peak in Dichloromethane Solution, Position of the PL 0−0 Vibronic Peak λ_{0-0}, PL Quantum Yield (PLQY), Fluorescence Lifetime τ, Radiative Lifetime τ_R, and Nonradiative Lifetime τ_{NR} Measured in Toluene Solution, and Fluorescence Transition Dipole $|d_f|$ in Debye Obtained from eq 2
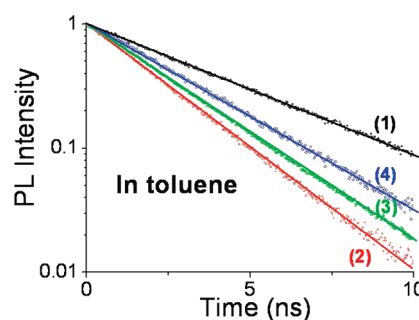
compound	ε_A ($\times 10^4$ M^{-1} cm^{-1})	λ_{0-0} (nm)	PLQY (%)	τ (ns)	τ_R (ns)	τ_{NR} (ns)	$|d_f|$ (D)
1	2.5 (at 404 nm)	416	93	4.1	4.4	60	6.3
2	5.8 (at 478 nm)	493	88	2.2	2.5	18	10.6
3	10 (at 499 nm)	515	98	2.5	2.6	65	11.5
4	12.5 (at 437 nm)	450	93	2.9	3.2	31	8.4
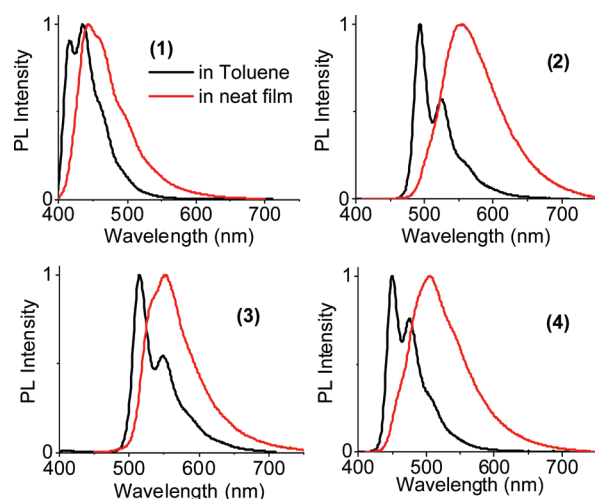
Figure 3. PL spectra of the anthracene-based dendrimers in dilute solution and in neat films. For measurements in solution, the excitation wavelength was 360 nm. In neat films, the excitation wavelength was 375 nm for **1** and 400 nm for the others.

Figure 4. Fluorescence decays of the anthracene-based dendrimers in dilute toluene solution. Fluorescence intensity is integrated over the spectral window of 120 nm, which covers almost the entire PL spectra. The solid lines are the fits with a single exponential decay function. The excitation wavelength was 390 nm.

90 nm relative to **1**, which indicates extended π-conjugation between anthracene and the phenyls through acetylene linkages. The red shift of the absorption of **3** relative to **2** is due to the electron donating ability of the *n*-propyloxy groups attached to the phenyl rings. The absorption of dendrimer **4** lies between **1** and **3**, and this is due to the fact that the anthracene in **4** is attached to one phenylacetylene and that each of the four chromophores of **4** are not in conjugation due to the adamantyl center. The molar absorption coefficient for dendrimer **1** $\varepsilon_A = 2.5 \times 10^4$ M^{-1} cm^{-1} at the 0−0 vibronic peak of the anthracene core absorption is two times higher than that of the unsubstituted anthracene, which has been reported to be about 1×10^4 M^{-1} cm^{-1} at 356 nm in cyclohexane solution.[40] This can be explained by the increase of the transition dipole moment caused by the dendrons. The other anthracene derivatives show even higher ε_A values, which are given in Table 1. Dendrimer **3** has the highest ε_A value per anthracene chromophore as dendrimer **4** has four anthracene chromophores in its chemical structure. Absorption in all four compounds at wavelengths below 350 nm is essentially dominated by the absorption of the dendrons and the fluorenyl surface groups. The absorption spectra in thin films are very similar to those measured in solution.

Figure 3 shows the steady-state PL spectra of these four compounds in dilute solutions in toluene and in neat film. Solution spectra show well-defined vibronic peaks at 416 and 435 nm for **1**, 493 and 525 nm for **2**, 515 and 550 nm for **3**, and 450 and 476 nm for **4**. The separation of vibronic peaks

is 1100−1200 cm^{-1} and consistent with previous reports on similar compounds.[41,42] All solutions show very high PLQYs (Table 1), and hence, the dendrimers could be used as effective fluorescent markers. The PL spectra of spin-cast films are redshifted and broader as compared to solutions, which is consistent with previous reports[43−45] and indicates contributions from more than one emitting species.

Figure 4 shows the PL kinetics of four compounds measured in dilute solution. The kinetics were independent of the detection wavelength and can be fitted with a monoexponential decay function with a characteristic time constant τ. From the measured values of PLQY and decay time constants, the radiative and nonradiative lifetimes, denoted τ_R and τ_{NR} respectively, are determined using the following equations:

$$\text{PLQY} = \tau/\tau_R \quad \text{and} \quad 1/\tau = 1/\tau_R + 1/\tau_{NR} \qquad (1)$$

The data are summarized in Table 1. The radiative lifetimes measured in the four dendrimers in this study are much shorter than the reported values of unsubstituted anthracene in solution in the range between 17 and 23 ns.[46] Shorter radiative lifetimes favor the radiative deactivation channel and are advantageous for applications in light-emitting devices. For the strength comparison of the electronic transition, it is better to compare the fluorescence transition dipoles $|d_f|$, which are determined using the Strickler−Berg equation[47]

$$|d_f|^2 = \frac{3\pi\varepsilon_0\hbar^4 c^3\langle E^{-3}\rangle}{n_0\tau_R} \qquad (2)$$

where $\langle E^{-3}\rangle = \int E^{-3}I(E)\mathrm{d}E / \int I(E)\mathrm{d}E$ is calculated from the fluorescence spectrum intensity $I(E)$ at the photon energy E, $\hbar = h/2\pi$ is Planck's constant, c is the speed of light, ε_0 is the vacuum dielectric constant, and n_0 is the refractive index of the medium. The measured values of $|d_f|$ are listed in Table 1.
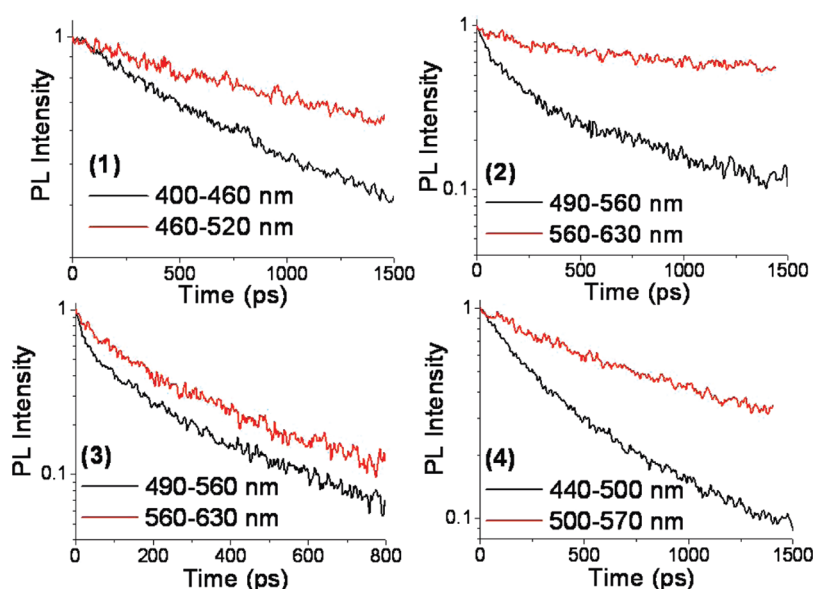
Figure 5. Fluorescence decays of the anthracene-based dendrimers in neat films integrated over different spectral windows. The excitation wavelength was 375 nm.

Table 2. Film PL Data: Position of the Peak λ_{max}, Quantum Yield (PLQY), Average Fluorescence Lifetime $\langle\tau\rangle$ Detected in Different Spectral Windows, and a Radiative Lifetime τ_R Calculated Using eq 1 and $\langle\tau\rangle$ Values from the Shorter Wavelength Spectral Window

compound	λ_{max} (nm)	PLQY (%)	$\langle\tau\rangle$ (ns)	τ_R (ns)
1	443	43	1.9 (400−460 nm)	4.4
			3.3 (460−520 nm)	
2	553	23	0.55 (490−560 nm)	2.4
			2.8 (560−630 nm)	
3	554	8	0.2 (490−560 nm)	2.6
4	504	16	0.53 (440−500 nm)	3.3
			1.2 (500−570 nm)	

Compounds **2** and **3** show the highest $|d_f|$ values, which can be explained by increased conjugation between anthracene and the phenyls through the acetylene linkages. This is consistent with the highest molar absorption coefficient per anthracene chromophore observed in these compounds as the low energy absorption and fluorescence both occur from the same electronic transition. The intermediate value of the transition dipole of **4** is consistent with the extension of the conjugation by an acetylene group only on one side of the anthracene chromophore.

Figure 5 shows the PL decays in neat films integrated over the spectral windows of short and long wavelength. For all compounds, the decays are substantially slower in the long wavelength window, which can be explained by downhill exciton diffusion and emission from low energy traps. Some of the PL kinetics cannot be described by a single exponential decay function; therefore, we have fitted them by a sum of two exponential functions: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ and then calculated the average PL lifetime using $\langle\tau\rangle = \Sigma_i(A_i\tau_i)/\Sigma_i A_i$. The $\langle\tau\rangle$ and PLQY values obtained in neat films are listed in Table 2. For each of the dendrimers, both are substantially lower than in solution, indicating strong concentration quenching. Using eq 1 and the $\langle\tau\rangle$ values of the shorter wavelength PL

window, where the solution luminescence occurs, we get essentially the same τ_R values as in solution. This indicates that predominant emitting excitations in films are intramolecular in nature. The species that emit at long wavelengths and show a slower decay appear to contribute very little to the PLQY, which implies that these low energy excitations have much longer radiative lifetimes. As there is no observable ground state absorption in the low energy region where long-lived emission is observed, we attribute the low energy emission to the excimer-like trap states, in agreement with a previous report in anthracene.[48] Excimers have low oscillator strength and thus act as fluorescence quenchers. Concentration quenching is the smallest for dendrimer **1**, which suggests a reduction in the excimer concentration. This is an important result because dendrimer **1** differs from the other dendrimers in that the emissive chromophore (the anthracene moiety) is directly attached to and protected by the bulky dendrons, which are twisted out of plane with respect to the emitting chromophore. The steric encumbrance increases the distance between the cores of neighboring dendrimers and reduce the possibility of excimer formation. It is also interesting to note that having chromophores rigidly held in three dimensions, as in **4**, does not necessarily stop intermolecular interactions and excimer formation that leads to PL quenching. These results provide important design criteria for light-emitting dendrimers and suggest that the dendritic approach is very promising for the prevention of concentration quenching of fluorescence in neat films of anthracene derivatives.

4. CONCLUSION

We have presented a steady-state and time-resolved photophysical study of four new solution-processable fluorescent anthracene derivatives emitting in blue and green spectral regions. For all these compounds, very high PLQY values exceeding 90% are observed in solution. They show natural radiative lifetimes in the range of 2.5−4.4 ns, which is 5−10 times shorter than those reported for unsubstituted anthracene and can be explained by the increase of the transition dipole

moment caused by the substituents. The shortest radiative lifetime and the most red-shifted absorption and PL spectra are observed in 9,10-bis(phenylethynyl)anthracene derivatives and are attributed to extended π-conjugation through acetylene linkages. Concentration quenching is observed in spin-cast films. However, when bulky dendrons are attached directly to the core in such a way that they can protect the emissive chromophore from intermolecular interactions, then the PLQY is increased. These results show that when designing a dendrimer it is necessary to take into account the size and shape of the chromophore as well as the dendron type and generation. They support the desirability of using dendritic structures for improving the PL efficiency and the performance of organic light-emitting devices.

■ REFERENCES

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

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

(3) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151.

(4) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4.

(5) McGehee, M. D.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 1655.

(6) Samuel, I. D. W.; Turnbull, G. A. *Chem. Rev.* **2007**, *107*, 1272.

(7) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *Adv. Mater.* **2007**, *19*, 1675.

(8) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371.

(9) Freeman, A. W.; Shannon, C. K.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12385.

(10) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1993**, *65*, 807.

(11) Hermann, A.; Weil, T.; Sinigersky, V.; Wiesler, U. M.; Vosh, T.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *Chem.—Eur. J.* **2001**, *7*, 4844.

(12) Lo, S.-C.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, I. D. W. *Adv. Mater.* **2002**, *14*, 975.

(13) Lo, S. C.; Anthopoulos, T. D.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2005**, *17*, 1945.

(14) Ribierre, J. C.; Stevenson, S. G.; Samuel, I. D. W.; Staton, S. V.; Burn, P. L. *J. Disp. Technol.* **2007**, *3*, 233.

(15) Ribierre, J. C.; Tsiminis, G.; Richardson, S.; Turnbull, G. A.; Samuel, I. D. W.; Barcena, H. S.; Burn, P. L. *Appl. Phys. Lett.* **2007**, *91*, 081108.

(16) Tsiminis, G.; Ribierre, J. C.; Ruseckas, A.; Barcena, H. S.; Richards, G. J.; Turnbull, G. A.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2008**, *20*, 1940.

(17) Cavaye, H.; Smith, A. R. G.; James, M.; Nelson, A.; Burn, P. L.; Gentle, I. R.; Lo, S.-C.; Meredith, P. *Langmuir* **2009**, *25*, 12800.

(18) Cavaye, H.; Shaw, P. E.; Wang, X.; Burn, P. L.; Lo, S.-C.; Meredith, P. *Macromolecules* **2010**, *43*, 10253.

(19) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bässler, H. *Adv. Mater.* **2001**, *13*, 258.

(20) Köse, M. E.; Mitchell, W. J.; Kopidakis, N.; Chang, C. H.; Shaheen, S. E.; Kim, K.; Rumbles, G. *J. Am. Chem. Soc.* **2007**, *129*, 14257.

(21) Ribierre, J. C.; Ruseckas, A.; Knights, K.; Staton, S. V.; Cumpstey, N.; Burn, P. L.; Samuel, I. D. W. *Phys. Rev. Lett.* **2008**, *100*, 017402.

(22) Kim, Y. H.; Shin, D.-C.; Kim, S. H.; Ko, C. H.; Yu, H. S.; Chae, Y. S.; Kwon, S. K. *Adv. Mater.* **2001**, *13*, 1690.

(23) Li, Y.; Fung, M. K.; Xie, Z.; Lee, S. T.; Hung, L. S.; Shi, J. *Adv. Mater.* **2002**, *14*, 1317.

(24) Danel, K.; Huang, T. H.; Lin, J. T.; Tao, Y. T.; Chuen, C. H. *Chem. Mater.* **2002**, *14*, 3860.

(25) Shen, W. J.; Dodda, R.; Wu, C. C.; Wu, F. I.; Liu, T. S.; Chen, H. H.; Chen, C. H.; Shu, C. F. *Chem. Mater.* **2004**, *16*, 930.

(26) Adachi, C.; Takito, S.; Tsutsui, T.; Satto, S. *Jpn. J. Appl. Phys.* **1988**, *27*, L269.

(27) Garay, R. O.; Naarman, H.; Müllen, K. *Macromolecules* **1994**, *27*, 1922.

(28) Benzman, R.; Faulkner, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 6317.

(29) Aleshin, A. N.; Lee, J. Y.; Chu, S. W.; Kim, J. S.; Park, Y. W. *Appl. Phys. Lett.* **2004**, *84*, 5383.

(30) Ando, S.; Nishida, J. I.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamshita, Y. *Chem. Mater.* **2005**, *17*, 1261.

(31) Sano, M.; Pope, M.; Kallmann, H. *J. Chem. Phys.* **1965**, *43*, 2920.

(32) Kim, Y. H.; Jeong, H. C.; Kim, S. H.; Yang, K.; Kwon, S. K. *Adv. Funct. Mater.* **2005**, *15*, 1799.

(33) Gao, Z. Q.; Mi, B. X.; Chen, C. H.; Cheah, K. Z.; Cheng, Y. K.; Wen, W. S. *Appl. Phys. Lett.* **2007**, *90*, 123506.

(34) Meng, H.; Sun, F.; Goldfinger, M. B.; Jaycox, G. D.; Li, Z.; Marshall, W. J.; Blackman, G. S. *J. Am. Chem. Soc.* **2005**, *127*, 2406.

(35) Yang, W. J.; Seo, M. S.; Wang, X. Q.; Jeon, S.-J.; Cho, B. R. *J. Fluoresc.* **2008**, *18*, 403.

(36) Giménez, R.; Pinol, M.; Serrano, J. L. *Chem. Mater.* **2004**, *16*, 1377.

(37) Malakhov, A. D.; Skorobogatyi, M. V.; Prokhorenko, I. A.; Gontarev, S. V.; Kozhich, D. T.; Stetsenko, D. A.; Stepanova, I. A.; Shenkarev, Z. O.; Berlin, Y. A.; Korshun, V. A. *Eur. J. Org. Chem.* **2004**, 1298.

(38) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Philips, R. T.; Kessener, R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.

(39) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 235.

(40) *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Berlman, I. B., Ed.; Academic Press, Inc.: New York, 1971.

(41) Levitus, M.; Garcia-Garibay, M. A. *J. Phys. Chem. A* **2000**, *104*, 8632.

(42) Boens, N.; Qin, W.; Basaric, N.; Hofkens, J.; Ameloot, M.; Pouget, J.; Lefevre, J. P.; Valeur, B.; Gratton, E.; van de Ven, M.; Silva, N. D.; Engelborghs, Y.; Willaert, K.; Sillen, A.; Rumbles, G.; Phillips, D.; Visser, A. J. W. G.; van Hoek, A.; Lakowicz, J. R.; Malak, H.; Gryczynski, I.; Szabo, A. G.; Krajcarski, D. T.; Tamai, N.; Miura, A. *Anal. Chem.* **2007**, *79*, 2137.

(43) Helfrich, W.; Lipsett, F. R. *J. Chem. Phys.* **1965**, *43*, 4368.

(44) Dreger, Z. A.; Lucas, H.; Gupta, Y. M. *J. Phys. Chem. B* **2003**, *107*, 9268.

(45) Seko, T.; Ogura, K.; Kawamaki, Y.; Sugino, H.; Toyotama, H.; Tanaka, J. *Chem. Phys. Lett.* **1998**, *291*, 438.

(46) *Handbook of Photochemistry*, 3rd ed.; Montalti, M., Credi, A., Prodi, L., Teresa Gandolfi, M., Eds.; Taylor and Francis: New York, 2006.

(47) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

(48) Mc Vey, J. K.; Shold, D. M.; Yang, N. C. *J. Chem. Phys.* **1976**, *65*, 3375.