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Changing the Behavior of Chromophores from Aggregation-Caused Quenching to Aggregation-Induced Emission: Development of Highly Efficient Light Emitters in the Solid State

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The development of efficient luminescent materials in the solid state is of both scientific and technological interest. An obstacle to their development is the notorious aggregation-caused quenching (ACQ) effect: the emission of conventional luminophores is often weakened in the solid state in comparison to in solution, due to aggregate formation in the condensed phase.[1–3] The ACQ problem must be properly tackled, because the luminophores are commonly used as solid films in their practical applications. Various chemical, physical, and engineering approaches have been taken to frustrate luminophore aggregation.[4,5] The attachment of bulky alicyclics, encapsulation by amphiphilic surfactants, and blending with transparent polymers are widely used methods to impede aggregate formation. These processes, however, are often accompanied by severe side effects. The steric effects of bulky alicyclics, for example, can twist the conformations of the chromophoric units and jeopardize the electronic conjugation in the luminophores, and the electronic effects of the saturated surfactants and nonconjugated polymers can dilute the luminophore density and obstruct the charge transport in electroluminescence (EL) devices.

The current approaches to the problem are thus far from ideal, because the ACQ effect is alleviated at the expense of other useful properties of the luminophores. A win–win strategy would be the elimination of the ACQ effect without sacrificing other functional properties of the luminophores. In the work reported here, we have developed such a new approach. Triphenylamine (TPA) and its derivatives are luminescent when dissolved in good solvents[6] for them but become less emissive when aggregated in the solid state, and are therefore typical ACQ luminophores.[7] For example, $N^4,N^4,N^{4'},N^{4'}$-tetraphenylbiphenyl-4,4'-diamine, a TPA dimer (DTPA), shows a high fluorescence quantum yield in terahydrofuran (THF) solution ($\Phi_{F,s} = 75.6\%$) but a 5.5-fold lower efficiency in the film state ($\Phi_{F,f} = 13.7\%$; Fig. 1). TPA is well-known for its high hole mobility and has been widely used as a building block in the construction of hole-transport molecules.[8] In this Communication, we use DTPA and TPA as examples to demonstrate how our approach works. Through judicious structural design, we have succeeded in creating new (D)TPA-based luminogens that are completely free of the ACQ effect and whose $\Phi_{F,f}$ values are up to 100%, while retaining the excellent hole-transport properties of the (D)TPA chromophores.

The new luminogens are composed of (D)TPA and tetraphenylethene (TPE) components, with 3TPETPA and 4TPEDTPA being the adducts of TPA and DTPA cores with three and four TPE peripheral moieties, respectively (Fig. 1). TPE is chosen as the pendent because of its unique luminescence behavior. It is nonemissive when dissolved but becomes luminescent when aggregated, exhibiting aggregation-induced emission (AIE), exactly the opposite behavior to the ACQ effect.[9–11] The alicyclics, surfactants, and polymers employed in the traditional approaches discussed above are saturated and nonluminescent and exert antagonistic effects on the electronic and optical properties of the conventional luminophores. In contrast, the TPE unit is nonsaturated and luminogenic. It is hoped that it will work with the (D)TPA unit synergistically and cooperatively and that their melts at the molecular level will afford adducts with the combined advantages of the two components, that is, both AIE-active and hole-transporting.

The 3TPETPA and 4TPEDTPA luminogens were prepared according to the synthetic routes shown in Scheme 1. The detailed procedures for the syntheses of the reaction intermediates and final products are described in the Supporting Information and Experimental section. Briefly, **2** was prepared as a key intermediate in high yield by lithiation of **4**,[12] followed by treatment with trimethyl borate and hydrolysis catalyzed by acid.

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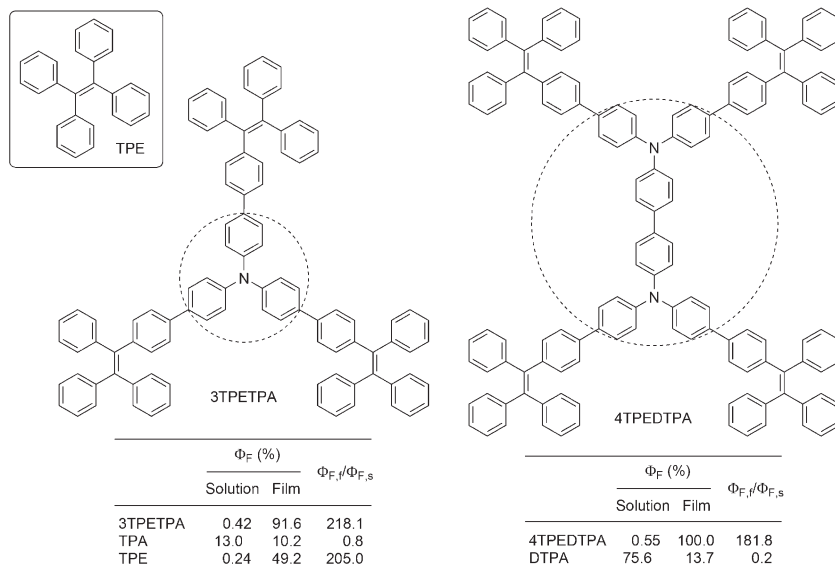Jilin University, Changchun 130023 (P. R. China)

Figure 1. Chemical structures of 3TPETPA and 4TPEDTPA and fluorescence quantum yields of their dilute solutions ($\Phi_{F,s}$) and amorphous films ($\Phi_{F,f}$). Data for their building blocks of TPE, TPA, and DTPA are shown for comparison. The TPA and DTPA units are marked with dotted circles.

	Φ_F (%)		$\Phi_{F,f}/\Phi_{F,s}$
	Solution	Film	
3TPETPA	0.42	91.6	218.1
TPA	13.0	10.2	0.8
TPE	0.24	49.2	205.0

	Φ_F (%)		$\Phi_{F,f}/\Phi_{F,s}$
	Solution	Film	
4TPEDTPA	0.55	100.0	181.8
DTPA	75.6	13.7	0.2

resolution mass spectrometry (HRMS) spectra (Figs. S1 and S2 in the Supporting Information), confirming the formation of the expected adducts.

3TPETPA and 4TPEDTPA show absorption peaks at 370 and 375 nm, respectively (Fig. S3), suggesting that the latter is more conjugated than the former. When illuminated with a UV lamp, neither of their THF solutions emitted any observable light but light was emitted strongly from their solid films, indicating that aggregate formation has turned on their light emission processes. To verify the visual observations, we measured the photoluminescence (PL) spectra of 3TPETPA in THF/water mixtures. Water was used because it is a nonsolvent of 3TPETPA: the luminogen molecules must aggregate in the aqueous mixtures with high water fractions (f_w). As shown in Figure 2, weak PL signals are recorded at $f_w \leq 40\%$ because the 3TPETPA molecules are genuinely dissolved in these mixtures. The PL intensity starts to rise for $f_w > 40\%$, where the solvating power of the mixture is worsened to such an extent that the luminogen molecules begin to aggregate. From the molecular solution in THF to the aggregate suspension in 90% aqueous mixture, the PL peak intensity of 3TPETPA at 484 nm increases ca. 97-fold. Similar behavior was observed for 4TPEDTPA (Fig. S4). Evidently, both the luminogens are AIE active.

Coupling reactions of **2** with **1** and **3** were catalyzed by Pd(PPh₃)₄, giving 3TPETPA and 4TPEDTPA, respectively, in good yields (ca. 56%–63%). The solubilities of the products are good in THF, chloroform, and dichloromethane (DCM) but poor in hexane and dimethyl sulfoxide (DMSO). All the reaction intermediates and final products were characterized spectroscopically, with satisfactory data obtained.[13] The reaction products, for example, gave M⁺ peaks at m/z 1236.6827 (calcd for 3TPETPA, 1236.5464) and 1810.0371 (calcd for 4TPEDTPA, 1809.7920) in their high-

Comparison of the Φ_F values of 3TPETPA and 4TPEDTPA in the solution and solid states further validates their AIE activity. While the $\Phi_{F,s}$ values of 3TPETPA and 4TPEDTPA in THF are as
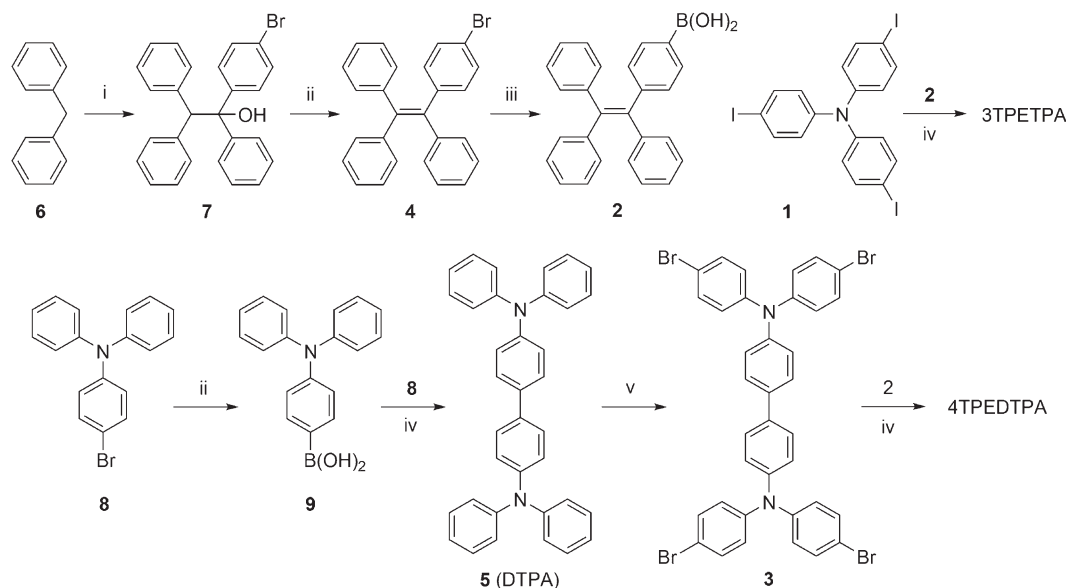
Scheme 1. Synthetic routes to 3TPETPA and 4TPEDTPA. Reagents and conditions: i) a) *n*-BuLi, THF, 0 °C, 30 min; b) 4-bromobenzophenone, room temperature (RT), 6 h; ii) *p*-toluenesulfonic acid, toluene, reflux, 4 h; iii) a) *n*-BuLi, THF, −78 °C, 3 h; b) B(OCH₃)₃, −78 °C, 2 h; c) HCl/H₂O, RT, 3 h; iv) Pd(PPh₃)₄, Na₂CO₃, THF, reflux, overnight; v) *N*-bromosuccinimide, DMF, 0 °C, overnight, then RT, 3 h.
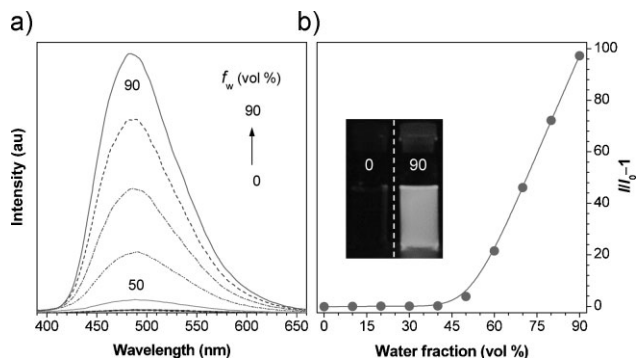
a)   b)

Figure 2. a) PL spectra of 3TPETPA in THF and THF/water mixtures. b) Plot of PL peak intensity at 484 nm vs. water fraction (f_w) of the aqueous mixture. Luminogen concentration: 74 μM; excitation wavelength: 360 nm. Inset: Solution of 3TPETPA in THF ($f_w = 0\%$) and its suspension in a THF/water mixture with $f_w = 90\%$; photographs taken under UV illumination.

low as 0.42% and 0.55%, those of their solid films are boosted to 91.6% and 100% by aggregate formation, resulting in AIE factors ($\alpha_{AIE} = \Phi_{F,f}/\Phi_{F,s}$) as high as 218.1 and 181.8, respectively. Since the PL intensities of the (D)TPA luminophores are weakened when they are fabricated into solid films (see Fig. 1) and when large amounts of water ($f_w > 60\%$) are added to their THF solutions (Figs. S5 and S6), it becomes clear that our design strategy of attaching the TPE peripheral groups to the (D)TPA cores has worked well. It has only not totally suppressed the detrimental ACQ effect of the (D)TPA luminophores but also conferred novel AIE attributes on the resultant 3TPETPA and 4TPEDTPA luminogens.

Although it varies in different molecules, the N_{sp3}–C_{Ph} bond is generally 1.394 Å in length, which is much shorter than the C_{sp3}–C_{Ph} bond (1.513 Å) and also shorter than the C_{sp2}–C_{Ph} bond (1.483 Å),[14] probably due to the n–π conjugation between the lone pairs of the nitrogen atom and the π electrons of the phenyl ring. The shorter bond distance implies stronger electronic interaction and smaller space for the phenyl ring to rotate, which rigidifies the conformations of the (D)TPA luminophores and makes them emissive in solution. In the aggregates, the luminophores experience strong intermolecular interactions, which weakens their emission intensities and red-shifts their emission colors (Figs. S5 and S6). In contrast, the multiple phenyl rings in the TPE units undergo active intramolecular rotations in the solutions,[9,10] which effectively quenches the light emissions of the 3TPETPA and 4TPEDTPA luminogens. In the aggregates, the propeller-shaped TPE units prevent the luminogens from packing in a π–π stacking process, while their intramolecular rotations are physically constrained in the condensed phase. The lack of intermolecular interactions and the restriction of intramolecular rotations account for the experimental observations that there is little shift in the PL spectra of the luminogens but that a remarkable increase in their PL intensities

accompanies the solution-to-aggregate transition (Fig. 2 and Fig. S4).

3TPETPA undergoes a glass transition at 143 °C (T_g) and loses 5% of its weight at 359 °C (T_d; Fig. S7). 4TPEDTPA gives similarly high T_g (134 °C) and T_d (470 °C) values. The high thermal stabilities and efficient film emissions of the luminogens prompted us to study their EL properties. We fabricated an organic light-emitting diode (LED; device I) according to the "standard recipe" used in our laboratories for screening tests: ITO/NPB (60 nm)/LEL/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/ Al (100 nm), where ITO is indium tin oxide; TPBi is 1,3,5-tris(N-phenylbenzimidazol- 2-yl)benzene (hole-blocking layer); Alq$_3$ is tris(8-hydroxyquinolinato)aluminum (electron-transport layer); NPB is 1,4-bis[(1-naphthylphenyl)amino]biphenyl (hole-transport layer); and the LEL (light-emitting layer) is 3TPETPA (20 nm). The EL spectrum of the device peaks at 492 nm (Fig. 3), which is slightly red-shifted from the PL peak (484 nm) of the thin film of 3TPETPA (Fig. S8) but far from the EL peak (ca. 524 nm) of Alq$_3$, verifying that the EL is from the 3TPETPA layer in device I. The device performance is moderate (Table 1 and Fig. S9), with maximum luminance (L_{max}) and current efficiency (CE_{max}) being 1662 cd m^{-2} and 3.1 cd A^{-1}, respectively.

As mentioned above, TPA is a well-known hole-transport material.[8] If 3TPETPA retains the hole-transport property of its TPA core, the use of NPB as an additional hole-transport layer is not necessary and could even be harmful, because it may break the charge balance in the EL device. With this in mind, we fabricated device II, in which the NPB layer was eliminated. Compared to device I, device II is turned on by a lower voltage ($V_{on} = 4.5$ V) and emits more intensely ($L_{max} = 6935$ cd cm^{-2}) and efficiently ($CE_{max} = 4.0$ cd A^{-1}; Fig. 3 and Table 1). Evidently, 3TPETPA is serving as a light emitter as well as a hole-transport material in the EL device. This helps to simplify the device structure, shorten the fabrication process, and lower production costs. The device fabricated from 4TPEDTPA without a NPB layer (device III) also shows good performance. It starts to emit at a low bias (4.1 V) and its L_{max} and CE_{max} reach 10723 cd m^{-2} and 8.0 cd A^{-1}, respectively. The data once again attest that the AIE luminogens are excellent hole-transport materials, in addition to being highly emissive in the solid state.
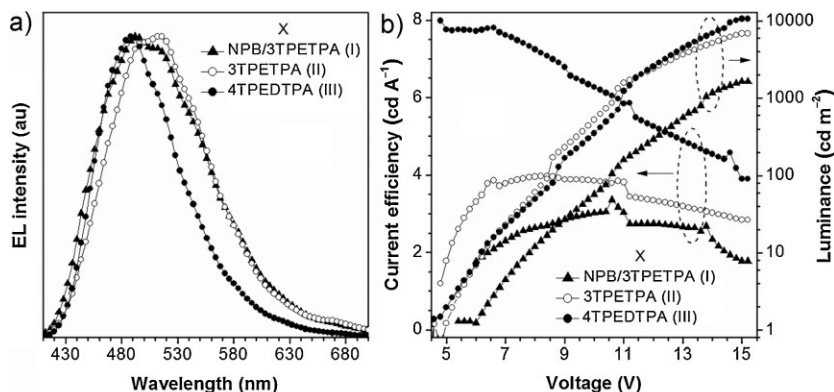
a)   b)

Figure 3. a) EL spectra of 3TPETPA and 4TPEDTPA and b) current efficiency–voltage and luminance–voltage plots of their multilayer LEDs with general device configuration ITO/X/TPBi/Alq$_3$/LiF/Al.

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Table 1. Performance of EL devices of 3TPETPA and 4TPEDTPA [a].

Device	λ_{max} [nm]	V_{on} [V]	L_{max} [cd m^{-2}]	PE_{max} [lm W^{-1}]	CE_{max} [cd A^{-1}]	EQE [%]
I	493, 511	5.4	1662	1.1	3.1	1.2
II	499, 513	4.5	6935	1.9	4.0	1.5
III	488	4.1	10723	5.2	8.0	3.7

[a] Device configuration: ITO/X/TPBi (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (100 nm); for device I: X = NPB (60 nm)/3TPETPA (20 nm); for device II: X = 3TPETPA (80 nm); for device III: X = 4TPEDTPA (30 nm). Abbreviations: λ_{max} = EL peak, V_{on} = turn on voltage, L_{max} = maximum luminance, PE_{max} = maximum power efficiency, CE_{max} = maximum current efficiency, and EQE = maximum quantum efficiency.

In summary, a new approach to efficient solid emitters by surmounting the notorious ACQ problem is developed in this work. Our approach is distinctly different from the conventional ones. The traditional processes mitigate the ACQ effect but generate new problems, whereas our new strategy solves the ACQ problem without causing adverse effects. Almost all the old approaches attempt to prevent luminophores from forming aggregates. However, because the luminophores have an inherent tendency to aggregate in the condensed phase, the old approaches are basically working against a very natural process and have thus ended up with only limited success and partial control. In sharp contrast, our new approach takes advantage of the intrinsic aggregation process and thus does not suffer from temporal and spatial instabilities. The success of our approach is manifested by the development of new luminogens with $\Phi_{F,f}$ up to 100% in the solid state. The AIE nature and hole-transport capability of the luminogens have enabled the fabrication of EL devices with simple structures but good performances. We are now working on expanding the applicability of our new structural design strategy: it is working so well that even such infamous ACQ luminophores as pyrene and anthracene are readily transformed to AIE luminogens with $\Phi_{F,f}$ of unity in the aggregate state.

Experimental

General Information: Tris(4-iodophenyl)amine (**1**) was prepared following our previously published procedures [15]. Intermediates **2** and **3** were prepared according to the synthetic routes shown in Scheme 1 (see also the Supporting Information). ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer. Thermogravimetric analyses and differential scanning calorimetry studies were conducted on TA TGA Q5500 and DSC Q1000 under nitrogen at heating rates of 20 and 10 °C min^{-1}, respectively. HRMS spectra were measured on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF (matrix-assisted laser desorption/ionization–time-of-flight) mode. The $\Phi_{F,s}$ values in THF solutions were estimated using 9,10-diphenylanthracene (Φ_F = 90% in cyclohexane) or quinine sulfate (Φ_F = 54% in 0.1 M H$_2$SO$_4$) as standards, while the $\Phi_{F,f}$ values of the solid films were determined using an integrating sphere.

EL devices were fabricated on an ITO-coated glass substrate with a sheet resistance of 25 Ω/□. The substrate was ultrasonically cleaned with detergent and deionized water, followed by CF$_4$ plasma treatment. Thermal evaporation of organic materials was carried out at a chamber pressure of 7×10^{-7} Torr. Light-emitting area was 4 mm^2. $I - V$ curves of EL devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were recorded by a calibrated UDT PIN-25D silicon photodiode. The L and EQE parameters of

the devices were inferred from photocurrents of the photodiode. EL spectra were obtained on a PR650 spectrophotometer.

Synthesis of 3TPETPA: To a 100 mL, two-necked, round-bottom flask were added **1** (187 mg, 0.3 mmol), **2** (376 mg, 1.0 mmol), and Pd(PPh$_3$)$_4$ (20 mg). The flask was evacuated under vacuum and then flushed with dry nitrogen three times. THF (50 mL) and sodium carbonate solution (2 M, 3 mL) were injected into the flask and the mixture was refluxed overnight and then slowly cooled to room temperature. The solution was poured into water (50 mL) and extracted with DCM. The collected organic layer was filtered, washed with water and brine twice, and then dried over anhydrous sodium sulfate (3 g). After solvent evaporation, the crude product was purified by silica-gel column chromatography using chloroform/hexane (1:5 by volume) as eluent. A yellow solid was obtained in 63.2% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.45 (d, 6H), 7.32 (d, 6H), 7.02−7.14 (aromatic protons of TPE moieties). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 146.66, 143.79, 142.40, 141.02, 140.58, 138.16, 131.79, 131.41, 131.35, 127.74, 127.66, 127.62, 126.45, 125.67, 124.31. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for C$_{96}$H$_{69}$N, 1236.5464; found, 1236.6827.

Synthesis of 4TPEDTPA: The experimental procedure for this luminogen is similar to that for the synthesis of 3TPETPA described above. A yellow solid was obtained in 55.9% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.46 (d, 12H), 7.33 (d, 8H), 7.02−7.17 (m). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 146.72, 143.77, 143.74, 142.40, 141.02, 140.58, 138.18, 135.00, 132.72, 131.79, 131.41, 131.35, 130.99, 127.74, 127.66, 127.62, 127.39, 126.45, 126.25, 125.68, 124.32. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for C$_{140}$H$_{100}$N$_2$, 1809.7920; found, 1810.0371.

[1] a) S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339. b) P.-I. Shih, C.-L. Chiang, A. K. Dixit, C.-K. Chen, M.-C. Yuan, R.-Y. Lee, C.-T. Chen, E. W.-G. Diau, C.-F. Shu, *Org. Lett.* **2006**, *8*, 2799. c) Z. Ning, Z. Chen, Q. Zhang, Y. Yan, S. Qian, Y. Cao, H. Tian, *Adv. Funct. Mater.* **2007**, *17*, 3799.

[2] a) C.-T. Chen, *Chem. Mater.* **2004**, *16*, 4389. b) G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, Z. Y. Wang, D. Ma, *Adv. Mater.* **2009**, *21*, 111. c) S.-J. Chung, K.-Y. Kwon, S.-W. Lee, J.-I. Jin, C. H. Lee, C. E. Lee, Y. Park, *Adv. Mater.* **1998**, *10*, 1112.

[3] J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London **1970**.

[4] a) C.-L. Chiang, S.-M. Tseng, C.-T. Chen, C.-P. Hsu, C.-F. Shu, *Adv. Funct. Mater.* **2008**, *18*, 248. b) J.-S. Yang, J.-L. Yan, *Chem. Commun.* **2008**, 1501. c) J. Wang, Y. C. Dou Zhao, H. Sun, P. Xu, K. Ye, J. Zhang, S. Jiang, F. Li, Y. Wang, *J. Phys. Chem. B* **2007**, *111*, 5082. d) S.-F. Lim, R. H. Friend, I. D. Rees, J. Li, Y. Ma, K. Robinson, A. B. Holms, E. Hennebicq, D. Beljonne, F. Cacialli, *Adv. Funct. Mater.* **2005**, *15*, 981. e) C. Fan, S. Wang, J. W. Hong, G. C. Bazan, K. W. Plaxco, A. J. Heeger, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 6297. f) S. Hecht, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **2001**, *40*, 74. g) J. N. Moorthy, P. Natarajan, P. Venkatakrishnan, D.-F. Huang, T. J. Chow, *Org. Lett.* **2007**, *9*, 5215.

[5] a) B. S. Gaylord, S. Wang, A. J. Heeger, G. C. Bazan, *J. Am. Chem. Soc.* **2001**, *123*, 6417. b) C. W. Tang, S. A. Vanslyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*,

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3610. c) V. Bulovic, A. Shoustikov, M. A. Baldo, E. Bose, V. G. Kozlov, M. E. Thompson, S. R. Forrest, *Chem. Phys. Lett.* **1998**, *287*, 455.

[6] a) Z. Ge, T. Hayakawa, S. Ando, M. Ueda, T. Akiike, H. Miyamoto, T. Kajita, M. Kakimoto, *Adv. Funct. Mater.* **2008**, *18*, 584. b) V. Promarak, M. Ichikawa, D. Meunmart, T. Sudyoadsuk, S. Saengsuwan, T. Keawin, *Tertrahedron Lett.* **2006**, *47*, 8949. c) H.-C. Yeh, S.-J. Yeh, C.-T. Chen, *Chem. Commun.* **2003**, 2632.

[7] T. Förster, K. Kasper, *Z. Phys. Chem. (Muenchen, Ger.)* **1954**, *1*, 275.

[8] P. J. Low, M. A. J. Paterson, D. S. Yufit, J. A. K. Howard, J. C. Cherryman, D. R. Tackley, R. Brook, B. Brown, *J. Mater. Chem.* **2005**, *15*, 2304.

[9] a) H. Tong, Y. Hong, Y. Q. Dong, M. Häußler, J. W. Y. Lam, Z. Li, Z. F. Guo, Z. H. Guo, B. Z. Tang, *Chem. Commun.* **2006**, 3705. b) Y. Q. Dong, J. W. Y. Lam, A. Qin, J. Sun, J. Liu, Z. Li, S. Zhang, J. Z. Sun, H. S. Kwok, B. Z. Tang, *Appl. Phys. Lett.* **2007**, *91*, 011111. c) Y. Hong, M. Häußler, J. W. Y. Lam, Z. Li, K. Sin, Y. Q. Dong, H. Tong, J. Liu, A. Qin, R. Renneberg, B. Z. Tang, *Chem. Eur. J.* **2008**, *14*, 6428.

[10] For reviews, see: a) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* **2009**, 4332. b) J. Liu, J. W. Y. Lam, B. Z. Tang, *J. Inorg. Organomet. Polym. Mater.* **2009**, *19*, 249. c) J. Liu, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2009**, *109*, 5799.

[11] a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* **2001**, 1740. b) B. K. An, S. K. Kwon, S. D. Jung, S. Y. Park, *J. Am. Chem. Soc.* **2002**, *124*, 14410.

[12] M. Banerjee, S. J. Emond, S. V. Lindeman, R. Rathore, *J. Org. Chem.* **2007**, *72*, 8054.

[13] See Supporting Information for details.

[14] a) *CRC Handbook of Chemistry and Physics* (Ed: D. R. Lide), CRC Press, Boca Raton, FL **1994**, Sect. 9. b) For example, the lengths of the $C_{Ph}-N_{sp3}$ bond in TPA and the $C_{Ph}-C_{sp2}$ bond in TPE are 1.42 and 1.494 Å, respectively, the former being 0.074 Å shorter than the latter.

[15] R. Zheng, M. Häussler, H. Dong, J. W. Y. Lam, B. Z. Tang, Macromolecules **2006**, 39, 7973.

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