Dibenzosuberenylidene-Ended Fluorophores: Rapid and Efficient Synthesis, Characterization, and Aggregation-Induced Emissions

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A series of π-conjugated compounds ending with dibenzosuberenylidene were synthesized efficiently. Their luminescence efficiencies were well-tuned by structural modification. Moreover, relative emission intensities were strongly affected by their existing appearances and exhibited aggregation-induced emission (AIE) behavior. Thus, emissions from nanoparticles, films, or powders were found to be more efficient than those from solutions. It demonstrated that these synthesized compounds might be practically used as fluorescent materials for potential optoelectronic applications.

Introduction

During the past decade, many studies on organic light-emitting materials have been focused on developing efficient, stable, and high color purity materials since the first efficient molecule-based organic light-emitting diodes (OLEDs) fabricated by Tang and VanSlyke in 1987.[1] However, ordered regions resulted in strong interchain coupling and lowered emission quantum yields in the case of polymer LEDs.[2] To address the above problems, studies on light-emitting materials with tetra-hedral structure,[3] cross-linked oligofluorene network,[4] and Si-containing hyperbranched architecture[3f,5] have been completed. Nevertheless, there still existed a serious problem of photoluminescence (PL) in solid states, which mostly exhibited lower efficiency compared with its performance in solution and limited its real utility. Therefore, it would be ideal if a molecule could emit intense light in its solid state. Swager and co-workers elegantly observed this unusual phenomenon that the PL quantum yield (Φ_F) of an aggregated film of a poly(*p*-phenylenethynylene) (PPE) was 3.5 times that of its solution.[6] Similar phenomena about aggregation-induced emissions (AIE) were further reported.[7] AIE-active materials were thereby found to be promising emitters for fabrication of highly efficient LEDs.[8] Thus, it is necessary to create molecular structures with AIE-active features.

Here, we wish to report the simple and efficient synthesis of a series of compounds ending with dibenzosuberenylidene groups. It is based on our continued research on non-benzenoid aromatic systems with specific optoelectronic properties.[9] On the basis of optical studies of synthesized compounds, their PL efficiencies in thin films or in powders were strongly enhanced compared to those in solutions. AIE behavior was observed. By investigating solvent, temperature, and concentration effects individually, a conclusion has been made that AIE behavior may be attributed to *J*-type aggregation with restricted intramolecular rotation in solid states.

Results and Discussion

Synthesis. Synthetic routes to compounds ending with dibenzosuberenylidene groups were shown in Scheme 1. The

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SCHEME 1: Synthesis of Conjugated Compounds
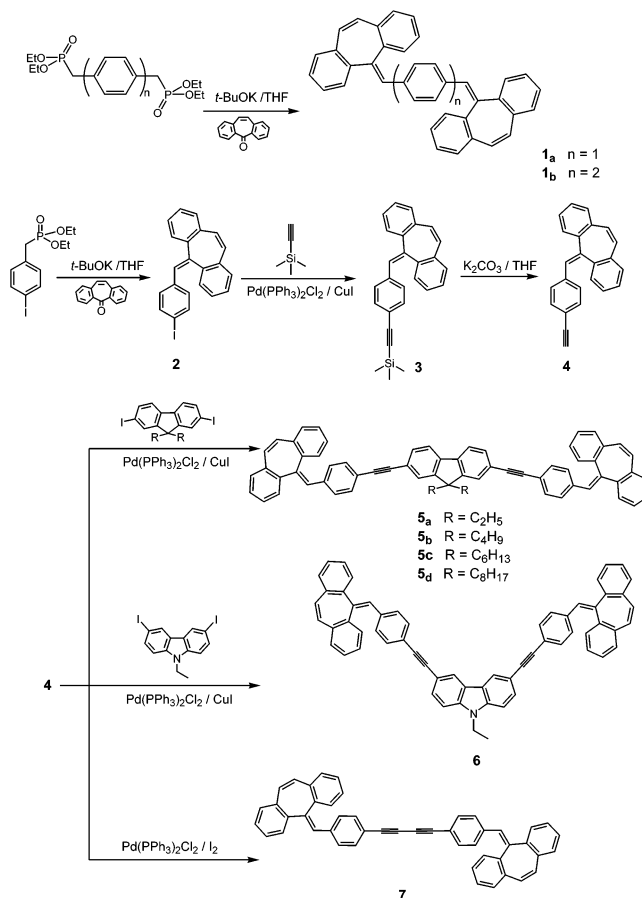
Wittig−Horner reaction was selected to synthesize **1_a** and **1_b** in 86% and 88% yields, respectively. Intermediate **2** was obtained in 82% yield by a similar procedure. Subsequent treatment of **2** with trimethylsilylacetylene, followed by desilylation, led to intermediate **4** in 91% yield.[10] The Sonagoshira reaction[11] provided an effective way to build π-systems with triple bonds. Thus, **4** was used as a substrate to react with 2,7-diiodo-9,9′-dialkylfluorene,[12] and 3,6-diiodo-9-alkyl carbazole[13] under Sonagoshira reaction conditions. A series of compounds (**5**, **6**) were synthesized in moderate yields. The Hay coupling

TABLE 1: Optical Properties of Compounds

compd	absorption λ_{max}^{abs} (nm)		photoluminescence λ_{max}^{PL} (nm)[c]				quantum yield Φ_F (%)[e]	
	solution[a]	nanosuspension[b]	solution[a]	film[d]	powder	nanosuspension[b]	solution[a]	film[c]
1a	333	337 (70%)	445 (371)	440	465	450 (70%)	0.0048	0.72
1b	339	378 (70%)	429 (358)	444	456	453 (70%)	0.012	0.71
5a	370	429 (70%)	409, 428 (361)	435	503	494 (70%)	0.065	0.67
5b	370	419 (50%)	408, 425 (361)	454	509	499 (50%)	0.084	0.73
5c	370	410 (50%)	412, 486 (361)	453	513	480 (50%)	0.083	2.1
5d	370	403 (50%)	409, 447 (361)	436	498	466 (50%)	0.073	1.2
6	358	396 (60%)	407, 431 (372)	428	448	439 (60%)	0.015	0.43
7	356	399 (70%)	415, 444 (378)	441	473	472 (70%)	0.023	0.99

[a] Measured in THF. [b] Water fractions are given in parentheses. [c] Excited wavelengths are given in parentheses. [d] Dispersed in PMMA films. [e] Quantum yields were calculated on the basis of 9,10-diphenylanthracene as standard ($\Phi = 0.95$ in hexane; $\Phi = 0.83$ in PMMA).

reaction[14] generated **7** in 85% yield. All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy (HRMS) matrix-assisted laser desorption ionization (MALDI).

Absorption and Emission Measurement. Compounds were soluble in common organic solvents, such as tetrahydrofuran (THF), toluene, chloroform, and so forth. Absorption and emission spectra in solution were measured in THF (5×10^{-6} M). Nanoparticles were formed by adding a large quantity of water into dilute 1,4-dioxane solution. Thin films were prepared by doping a certain amount of fluorophores in poly(methyl methacrylate) (PMMA) (concentration < 0.1 wt %). Absorption and emission properties in different appearances were summarized in Table 1. Normalized UV−vis absorption and fluorescence spectra for **1** and **5−7** in solutions, in thin films, and in powders are available in the Supporting Information.

Absorption Properties in Solutions. Maximum absorption wavelength of **1a** was found at 333 nm. In comparison to **1a**, maximum absorption wavelengths of **1b** and **5−7** were all bathochromically shifted as the conjugated length increased.

Maximum Emission Wavelengths vs Their Existing Appearances. Maximum emission wavelength of **1a** was found to be 445 nm in dilute solution and 440 nm in thin film when both were excited at 371 nm. Emissions of **1b** and **5−7** were all blue-shifted compared to **1a**, except for **5c** and **5d** in solutions. Maximum emission wavelengths from thin films with low concentrations (<0.1 wt %) of fluorophores were similar to those in solutions. When powder samples were measured for emission properties, maximum emission wavelengths were all red-shifted, typically for those with fluorene cores (**5a**−**5d**). Furthermore, maximum emission wavelengths observed for nanoparticles were similar to those in powders. For example, **5a** emitted at 503 nm in powder (PL^P), which was 68 nm red-shifted to its emission wavelength in thin film (PL^F), and 75 nm red-shifted to its emission wavelength in solution (PL^S) (Figure 1).

Quantum Yields vs Molecular Structures. Quantum yields were calculated on the basis of 9,10-diphenyl anthracene ($\Phi = 0.95$ in hexane, $\Phi = 0.83$ in PMMA).[15] As we designed molecular structures for better optical performance, **5** showed the highest quantum yields in solutions. The quantum yield of **1b** was 2.5 times that of **1a** due to longer conjugation. The quantum yield of **7** was 1.9 times that of **1b** due to planarization of **7** by inserting diyne into two phenyl rings to release torsional strain. When a fluorene core was introduced between two triple bonds, longer conjugation was constructed. Thus, the quantum yield of **5b** was 3.7 times that of **7**. Luminescent efficiency was well-tuned by structural modification (Scheme 2).

Although **6** had a similar planar core as **5**, a relatively lower quantum yield was observed for **6**. The reason might be that the delocalization of the triplet wave function in **6** is not limited to the carbazole core (resembling *m*-biphenyl), but is limited
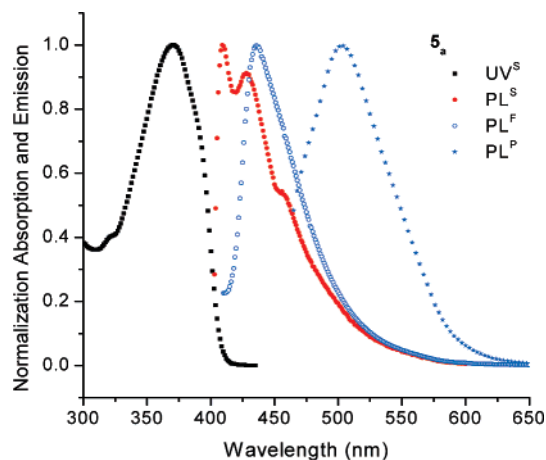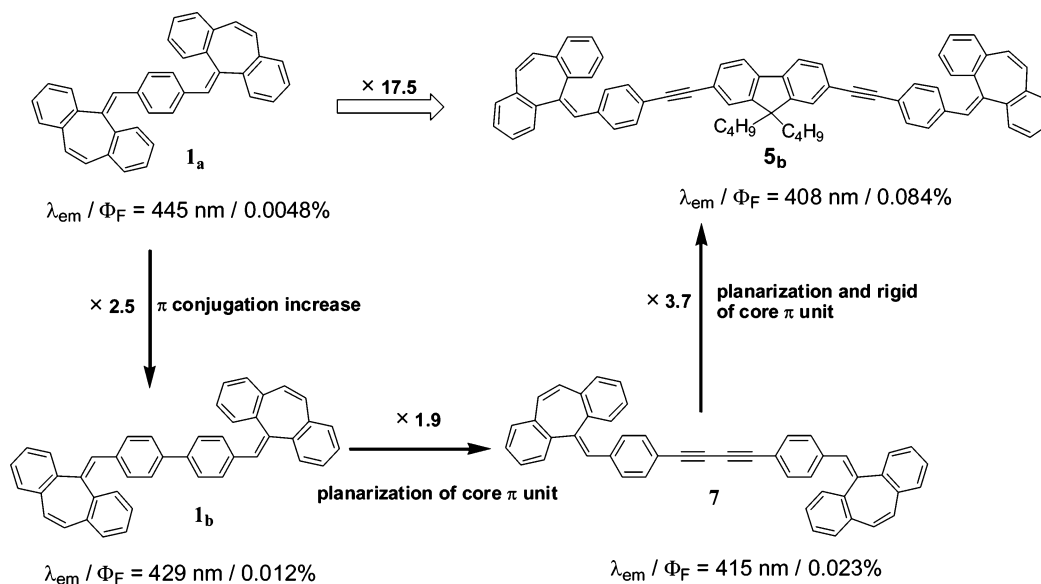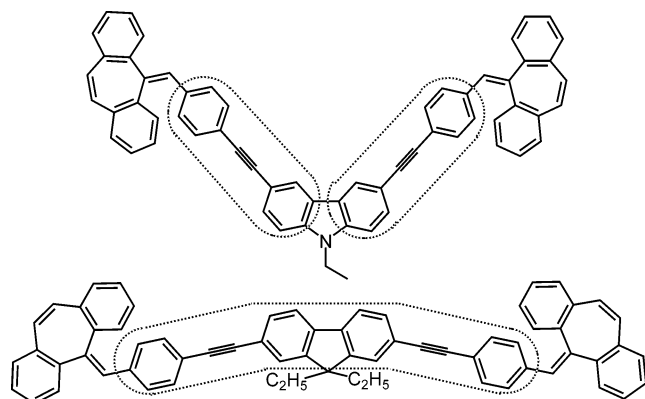

Figure 1. Absorption and emissions of **5a**.

in individual diphenylacetylene moieties. However, the delocalization of the triplet wave function in **5a** is well-extended through the fluorene core (resembling *p*-biphenyl).[16] This is also in accordance with studies on polyphenyl molecules. For *p*-polyphenyl molecules, the conjugated system is delocalized along the longest molecular axis, and for *m*-polyphenyl molecules, the triplet state is localized at every composing biphenyl structure (Scheme 3).[17]

Quantum Yields vs Their Existing Appearances. In comparison to emission in solution, emission from solid should be more attractive and practical, because the real state of the emitter fabricated in an optoelectronics device should be solid. It was observed that quantum yields of all synthesized compounds (**1, 5−7**) in films were higher than those in solutions (Table 1). For instance, the quantum yield of **1a** in film was 150 times that in solution.

The cause might be exciton diffusion and rotational deactivation in solution, which increased the number of nonradiative routes and decreased the luminescence efficiency[7b,8b] in solution. As to powder or film, intramolecular rotation was highly restricted because of molecular stacking. This result could also be clearly seen from Table 1. By structural analysis, **1a** → **1b** → **7** → **5b** (Scheme 2), **1a** has the smallest molecular size with the fastest movement in solution. To the solid state, molecular movement is restricted. Therefore, incremental increases of quantum yield for **1a** from solution to thin film is the largest. Experimental data supported this postulation. The quantum yield of **1a** in film was 150 times that in solution, while only 60, 43, and 9 orders of magnitude incremental increases were observed by changing the state from solution to thin film for **1b**, **7**, and **5b**, respectively.

Restricted Intramolecular Rotation vs Temperature. It is well-known that the rotational deactivation of an exciton was

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SCHEME 2: Emission Efficiency Tuned by Structural Modification

1a

λ_{em} / Φ_F = 445 nm / 0.0048%

× 17.5

5b

λ_{em} / Φ_F = 408 nm / 0.084%

× 2.5 | π conjugation increase

× 3.7 | planarization and rigid of core π unit

1b

λ_{em} / Φ_F = 429 nm / 0.012%

× 1.9

planarization of core π unit

7

λ_{em} / Φ_F = 415 nm / 0.023%

SCHEME 3: Chemical Structure of 6 (top) and 5a (bottom)^a

^{a} For compound **6**, the longest poly(*p*-phenylacetylene) chain is diphenylacetylene, while for compound **5a**, the chain is through biphenyl core.

highly dependent on solution temperature. Cooling-enhanced emissions as evidence for restricted intramolecular rotation were shown in Figure 2a. When dilute solutions of **1a**, **5a**, and **7** in 1,4-dioxane were cooled from 15 °C to −82 °C, solutions were gradually changed into a glassy solid. By recording emission spectra, it was found that emission efficiencies were increased as the temperature decreased. For instance, emission efficiency was amplified 13 times when the solution temperature changed from 15 °C to −82 °C (Figure 2b). It indicated that the rotation of heavy dibenzosuberenylidene groups was effectively limited when the temperature decreased. Restricted molecular rotation resulted in the enhanced emission efficiency.

Emission Efficiency vs Concentration. Emission efficiency was dependent not only on the temperature, but on the concentration also. As the concentration of **5a** in PMMA films increased, emission efficiency increased (Figure 3). That could be explained by aggregation-induced emission behavior. Except for this significant efficiency change, noticeable red-shifted emission were observed in this case. When the fluorophore concentration reached 15.5wt % in thin film, the maximum emission wavelength of **5a** reached 491 nm, and finally resembled its powder emission (λ_{max} = 503 nm). The reason
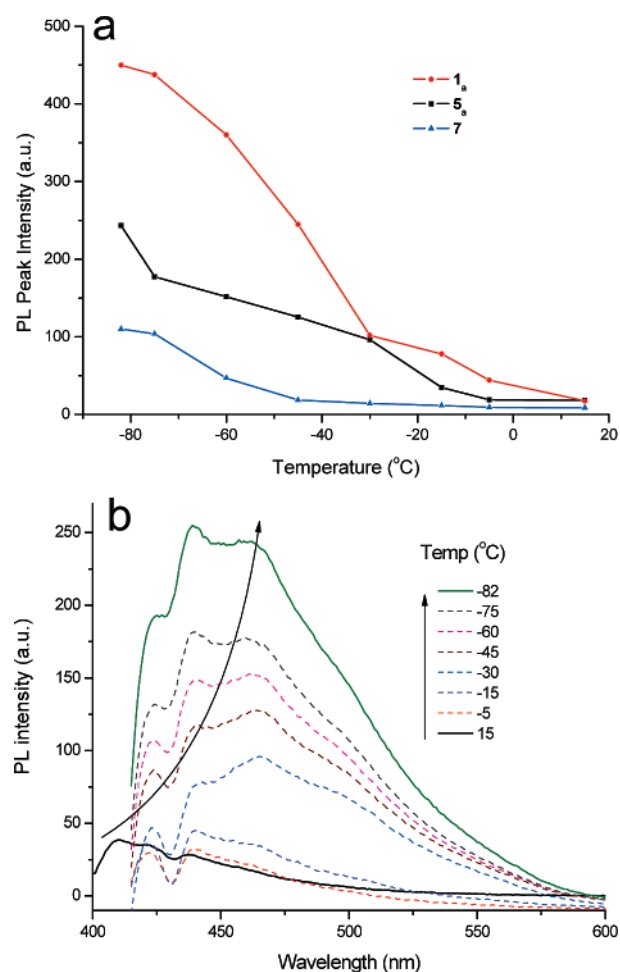

Figure 2. (a) Temperature effect on PL peak intensities of **1a**, **5a**, and **7** in 1,4-dioxane. (b) PL spectra of diluted solution of **5a** (30 μM) in 1,4-dioxane with changing temperature.

might be that **5a** dispersed in film might exist in its *J*-type aggregation state at high concentration.

Aggregation-Induced Emission. Emission enhancement resulting from fluorescent nanoparticle formation is the alternative way to prove AIE behavior.[7] Nanoparticles could be prepared by a simple reprecipitation without surfactants.[18] When
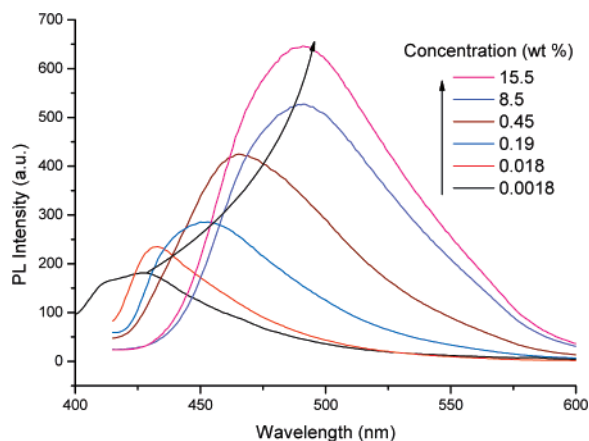
Figure 3. Emission spectra of 5_a in films with certain concentrations (wt %).
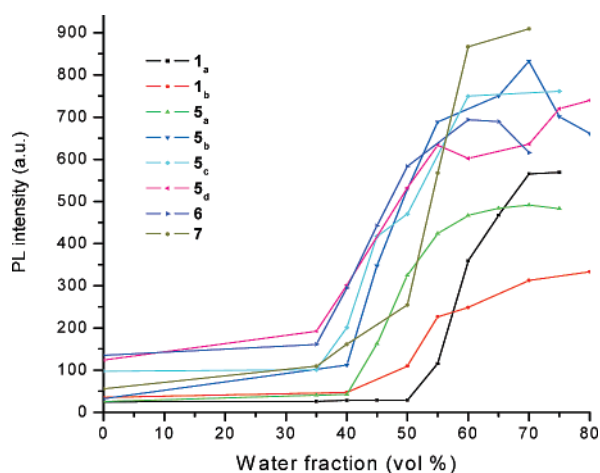

Figure 4. Changes of PL peak intensities of **1** and **5**−**7** vs solvent compositions of the water/1,4-dioxane mixtures.

a large quantity of water was added into a dilute 1,4-dioxane solution of fluorophore, emission spectra were recorded. As shown in Figure 4, turning points were observed in each case. Beyond these points, a dramatic increase in emission efficiency was observed.

A typical example of this scenario was shown in Figure 5. When dilute solution of 5_b was added with a large quantity of water, luminescence efficiency was increased 25 times when the water fraction reached 70%. As the water fraction reached 80%, the vessel was still visually clear and macroscopically homogeneous. Their aggregation must be nanodimensional. Transmission electron microscopy (TEM) showed nanoparticle size (80−200 nm) and distributions (Figure 6).

By recording UV absorption spectra of 5_b in water and 1,4-dioxane with different ratios, red-shifted absorption was seen in this case as the water fraction increased (Figure 5). The red-shifted absorption spectra indicated that *J*-type aggregation occurred in this case.[7a,19] Further, the ability to red-shift reflected the aggregation degree of the fluorophore. By investigation UV absorption spectra, only a 4-nm red-shift was observed for 1_a with the shortest conjugated linkage, while a 59-nm red-shift was found for 5_a with the longest conjugated linkage. Moreover, as for compounds **5** with different lengths of alkyl groups at nine positions, absorption spectra of 5_b, 5_c, and 5_d showed less red-shift ($\Delta\lambda = 49$, 40, and 33 nm, respectively) than that of 5_a because of decreasing stacking efficiencies resulting from increasing lengths of side chains.

In conclusion, a series of π-conjugated compounds ending with dibenzosuberenylidene groups were synthesized by general
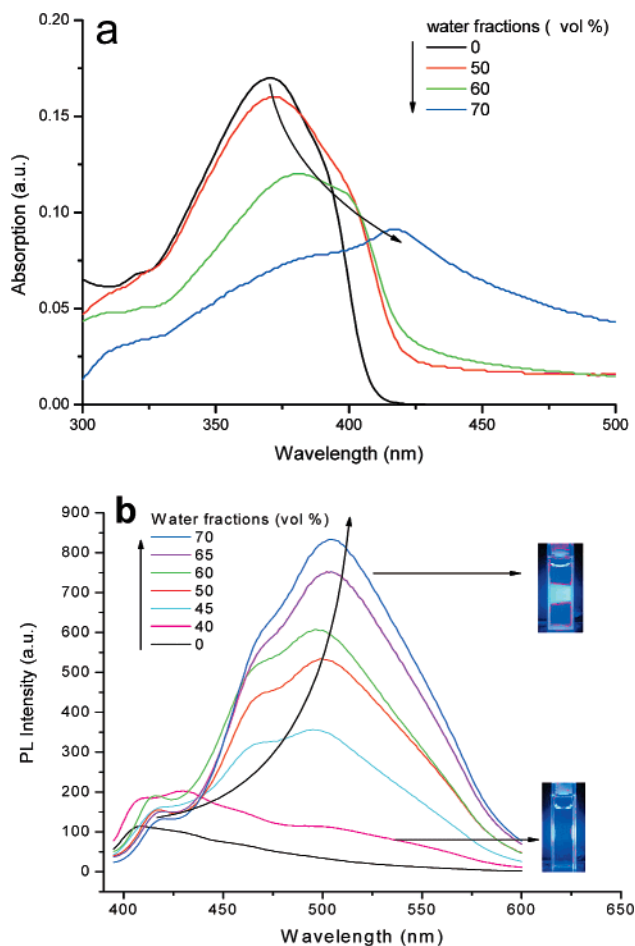

Figure 5. UV absorption spectra (a) and PL spectra (b) of 5_b in water/ 1,4-dioxane mixture with different volume fractions of water; concentration of 5_b, 20μM.

methods in good yields. Their luminescent efficiencies were well-tuned by structural modification. The synthesized compounds exhibited enhanced fluorescence emissions in solid states. Emission efficiencies could be enhanced by adding water to induce nanoparticle formation, by lowering temperature to form a glassy solid, or by doping in PMMA to restrict intramolecular rotation. Synthesis of these organic emitters systematically has proven to be an efficient way to produce excellent candidates for the potential utility in optoelectronics applications.

Experiment Section

General. Tetrahydrofuran and 1,4-dioxane for UV−vis and fluorescence spectroscopic measurements were redistilled. Distilled water was filtered through a membrane with 0.22-μm pore size. Commercially available reagents were used without further purification unless otherwise stated. Melting points were recorded on a BÜCHI 535. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer in CDCl$_3$ as solvent with tetramethylsilane (TMS) as internal standard. UV−vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. MALDI mass spectra were obtained on an Ionspec 4.7 T FTMS mass spectrometer and ESI mass spectra were obtained on a Bruker Esquire 3000 Plus with Bruker Daltonics DataAnalysis 3.0 instrument. TEM micrographs were obtained on a JEM-200CX transmission electron microscope. All reactions were
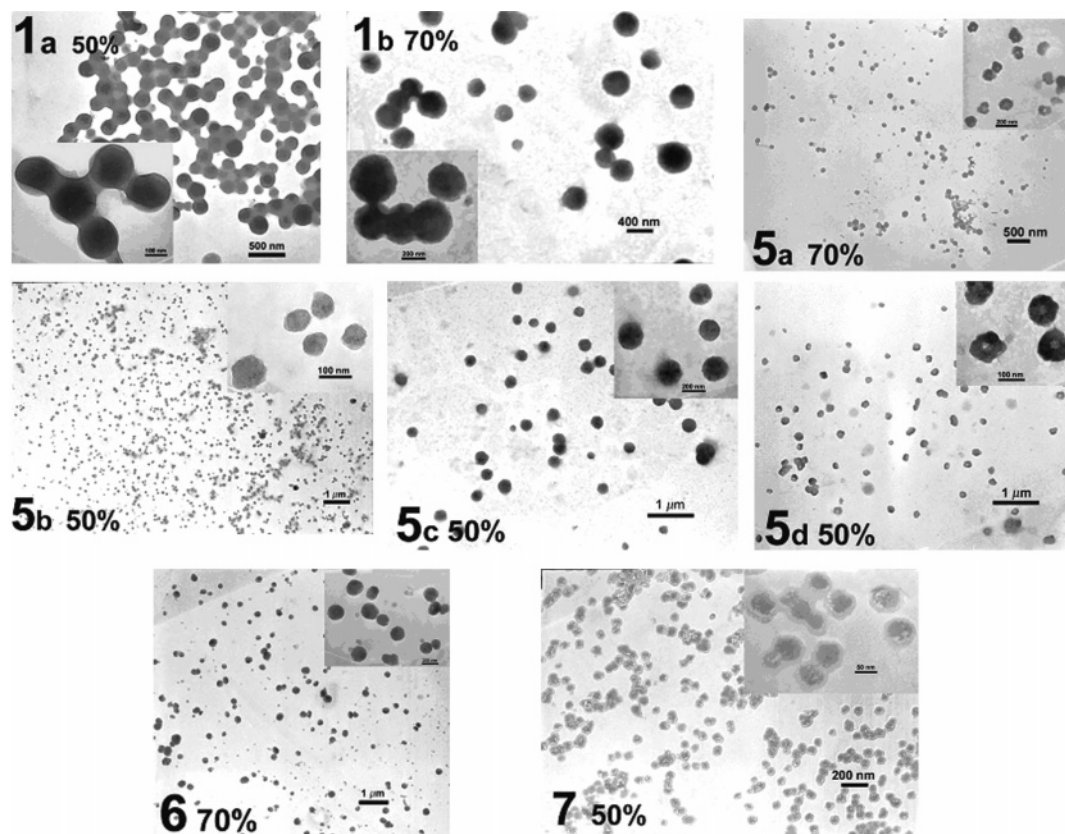
Figure 6. The TEM micrographs of **1**, **5**, **6**, and **7** nanoparticles obtained from nanoparticles' suspension with corresponding water fraction (vol %) in 1,4-dioxane.

carried out under N_2. All samples for UV−vis and fluorescence spectroscopic measurements were recrystallized from hexane/chloroform.

Synthesis. 2,7-Diiodo-9,9′-dialkylfluorene[12] and 3,6-diiodo-9-ethylcarbazole[13] were prepared by literature procedures.

General Procedures for Synthesis of 1,4-Bis(dibenzosuberenylidenemethyl)benzene (1ₐ) and 4,4′-Bis(dibenzosuberenylidenemethyl)biphenyl (1ᵦ). Diethyl bis(arylmethyl)phosphonate (1 mmol) and dibenzosuberenone (2 mmol) were dissolved in 40 mL anhydrous THF under nitrogen. The mixture was refluxed under stirring. To this solution, solid potassium *tert*-butoxide (3 mmol) was added in one portion. After refluxing for 3 h, solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexane/dichloromethane (6:1 by volume) as eluent. In this way, **1ₐ** and **1ᵦ** were obtained as a yellow solid, respectively.

1ₐ: yield 86%, mp 210.5−211.7 °C. ¹H NMR (CDCl₃): δ 6.38 (s, 0.84H), 6.39 (s, 1.16H), 6.64 (s, 1.70H), 6.67 (s, 2.25H), 6.87 (d, 2H, *J* = 12.0 Hz), 6.92 (d, 2H, *J* = 12.0 Hz), 7.06−7.16 (m, 4H), 7.21−7.28 (m, 6H), 7.33−7.38 (m, 4H), 7.45−7.47 (m, 2H) ppm. ¹³C NMR (CDCl₃): δ 127.14, 127.18, 127.21, 127.50, 128.54, 128.57, 128.89, 128.98, 129.01, 129.09, 129.12, 129.30, 129.45, 131.42, 131.45, 131.62, 132.26, 132.35, 134.54, 135.03, 135.03, 135.61, 137.68, 137.73, 142.32, 142.52, 142.75 ppm. HRMS (MALDI): calcd for $C_{38}H_{26}$, 482.2; found, 482.2 (M⁺).

1ᵦ: yield 88%, mp 262.9−264.4 °C. ¹H NMR (CDCl₃): δ 6.50 (s, 2H), 6.92−6.94 (m, 6H), 6.99 (d, 2H, *J* = 12.0 Hz), 7.14−7.30 (m, 4H), 7.27−7.20 (m, 10H), 7.39−7.43 (m, 4H), 7.53 (d, 2H, *J* = 7.5 Hz) ppm. ¹³C NMR (CDCl₃): δ 126.33, 126.36, 127.14, 127.21, 127.53, 128.56, 129.01, 129.05, 129.11, 129.35, 129.80, 131.40, 131.64, 132.07, 134.54, 135.13, 137.69, 138.85, 138.93, 142.61, 142.75 ppm. HRMS (MALDI): calcd for $C_{44}H_{30}$, 558.2; found, 558.2 (M⁺).

4-(Dibenzosuberenylidenemethyl)-iodobenzene (**2**) was prepared by a similar method as above except that the residue was purified by recrystallization from chloroform/ethanol. Yield 82%, mp 167−168.5 °C. ¹H NMR (CDCl₃): δ 6.4 (1H, s), 6.63 (2H, d, *J* = 8.0 Hz), 6.92 (1H, d, *J* = 12.0 Hz), 6.97 (1H, d, *J* = 12.0 Hz), 7.07 (1H, d, *J* = 7.5 Hz), 7.18 (1H, dd, *J* = 7.5 Hz), 7.27−7.30 (3H, m), 7.38−7.42 (4H, m), 7.50, (1H, d, *J* = 7.0 Hz). ¹³C NMR (CDCl₃): δ 92.43, 127.05, 127.40, 127.72, 128.62, 129.12, 129.17, 131.19, 131.32, 131.66, 134.42, 135.04, 136.67, 137.21, 142.33, 143.51. MS (ESI): *m/z* 406.8 ([M + H]⁺).

4-Trimethylsilylethynyl(dibenzosuberenylidenemethyl)-benzene (**3**) was prepared from **2** by literature procedure.[10] A mixture of **2** (406 mg, 1 mmol), trimethylsilylacetylene (150 mg, 1.5 mmol), CuI (20 mg, 0.1 mmol), PPh₃ (26.2 mg, 0.1 mmol), and Pd(PPh₃)₂Cl₂ (10 mg, 0.013 mmol) in Et₃N (40 mL) was refluxed for 40 h. After cooling to room temperature, the solvent was removed by evaporation. The residue was purified by column chromatography as above. In this way, 362 mg of **3** was obtained in 96% yield as a yellowish solid. Mp 122.9−124.1 °C. ¹H NMR (CDCl₃): δ 0.21 (s, 9H), 6.46 (s, 1H), 6.82 (d, 2H, *J* = 8.0 Hz), 6.90, (d, 1H, *J* = 12.0 Hz), 6.96 (d, 1H, *J* = 12.0 Hz), 7.04 (d, 1H, *J* = 7.5 Hz), 7.14 (dd, 1H, *J* = 7.5 Hz), 7.18−7.20 (m, 2H), 7.24−7.31 (m, 3H), 7.37−7.41 (m, 2H), 7.49, (d, 1H, *J* = 8.0 Hz) ppm. ¹³C NMR (CDCl₃): δ 0.22, 94.82, 105.48, 121.38, 127.12, 127.38, 127.68, 128.63, 129.06, 129.12, 129.17, 129.24, 129.31, 131.40, 131.64, 131.73, 131.89, 134.49, 135.08, 137.34, 137.54, 142.39, 143.58 ppm. MS (ESI): *m/z* 377.0 ([M + H]⁺).

4-(Dibenzosuberenylidenemethyl)phenylacetylene (**4**) was also prepared from **3** by literature procedure[17] in 95% yield. Mp 145.5−146.2 °C. ¹H NMR (CDCl₃): δ 3.04 (s, 1H) 6.47 (s, 1H), 6.85 (d, 2H, *J* = 8.5 Hz), 6.92 (d, 1H, *J* = 12.0 Hz), 6.97 (d, 1H, *J* = 12.0 Hz), 7.07 (d, 1H, *J* = 7.5 Hz), 7.17 (dd,

1H, J = 7.0 Hz), 7.21−7.24 (m, 2H), 7.26−7.32 (m, 3H), 7.38−7.42 (m, 2H), 7.50 (d, 1H, J = 7.5 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ 77.80, 84.06, 120.44, 127.17, 127.48, 127.81, 128.70, 129.16, 129.21, 129.25, 129.31, 129.38, 131.44, 131.72, 131.80, 131.97, 134.53, 135.13, 137.34, 137.89, 142.43, 143.81 ppm. MS (ESI): *m/z* 304.9 ([M + H]$^+$).

Synthesis of Compounds 5−6. *2,7-Bis(4-dibenzosuberenylidenemethylphenyl)ethynyl-9,9′-diethylfluorene (5$_a$)*. A mixture of 2,7-diiodo-9,9′-diethylfluorene (237 mg, 0.5 mmol), **4** (456 mg, 1.5 mmol), CuI (20 mg, 0.1 mmol), PPh$_3$ (26.2 mg, 0.1 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (10 mg, 0.013 mmol) in Et$_3$N/benzene (40/10 mL) was refluxed for 40 h. After cooling to room temperature, the solvent was removed by evaporation. The residue was purified by column chromatography as above. In this way, 330 mg of **5$_a$** was obtained in 80% yield as yellow solid. Mp 146.3−147.8 °C. ^{1}H NMR (CDCl$_3$): δ 0.32 (t, 6H, J = 6.5 Hz), 2.03 (q, 4H, J = 6.5 Hz), 6.52 (s, 2H), 6.91 (4H, d, J = 8.0 Hz), 6.94 (d, 2H, J = 12.0 Hz), 7.01 (d, 2H, J = 12.0 Hz), 7.13 (d, 2H, J = 7.5 Hz), 7.20 (dd, 2H, J = 7.5 Hz), 7.30−7.32 (m, 10H), 7.41−7.55 (m, 10H), 7.65 (d, 2H, J = 8.0 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ 8.59, 32.93, 56.48, 90.24, 91.13, 120.15, 121.64, 122.24, 126.25, 127.13, 127.39, 127.71, 128.64, 129.09, 129.16, 129.18, 129.33, 129.43, 130.99, 131.33, 131.41, 131.67, 131.92, 132.24, 134.45, 134.50, 134.56, 135.09, 137.25, 137.41, 141.27, 142.47, 143.52, 150.50 ppm, HRMS (MALDI): calcd for C$_{65}$H$_{46}$, 826.4; found, 826.4 (M$^{+·}$).

2,7-Bis(4-dibenzosuberenylidenemethylphenyl)ethynyl-9,9′-dibutylfluorene (5$_b$) was prepared by a similar method as **5$_a$** in 85% yield. Mp 133.8−135.2 °C. ^{1}H NMR (CDCl$_3$): δ 0.54−0.60 (m, 4H), 0.67 (t, 6H, J = 7.0 Hz), 1.07 (q, 4H, J = 7.0 Hz), 1.94−1.97 (m, 4H), 6.51 (s, 2H), 6.90 (4H, d, J = 8.0 Hz), 6.94 (d, 2H, J = 12.0 Hz), 7.00 (d, 2H, J = 12.0 Hz), 7.11 (d, 2H, J = 7.5 Hz), 7.18 (dd, 2H, J = 7.5 Hz), 7.28−7.32 (m, 10H), 7.41−7.48 (m, 8H), 7.53 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.0 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ 14.06, 23.28, 26.40, 40.44, 55.36, 90.20, 91.19, 120.17, 121.63, 122.20, 126.16, 127.13, 127.38, 127.70, 128.64, 129.08, 129.16, 129.19, 129.34, 129.43, 130.92, 131.33, 131.41, 131.68, 131.92, 134.51, 135.12, 137.28, 137.41, 140.88, 142.47, 143.53, 151.31 ppm. HRMS (MALDI): calcd for C$_{69}$H$_{54}$, 882.4; found, 882.4 (M$^{+·}$).

2,7-Bis(4-dibenzosuberenylidenemethylphenyl)ethynyl-9,9′-dihexanylfluorene (5$_c$) was prepared by a similar method as **5$_a$** in 83% yield. Mp 119.0−121.0 °C. ^{1}H NMR (CDCl$_3$): δ 0.54−0.60 (m, 4H), 0.76 (t, 6H, J = 7.0 Hz), 1.0−1.04 (m, 8H), 1.10 (m, 4H), 1.93−1.96 (m, 4H), 6.51 (s, 2H), 6.90 (4H, d, J = 8.0 Hz), 6.93 (d, 2H, J = 12.0 Hz), 6.99 (d, 2H, J = 12.0 Hz), 7.11 (d, 2H, J = 7.5 Hz), 7.18 (dd, 2H, J = 7.5 Hz), 7.28−7.33 (m, 10H), 7.40−7.47 (m, 8H), 7.52 (d, 2H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ 14.18, 22.80, 23.89, 29.89, 31.72, 40.58, 55.37, 90.13, 91.15, 120.11, 121.58, 122.12, 126.08, 127.07, 127.32, 127.65, 128.58, 129.02, 129.10, 129.12, 129.27, 129.37, 130.85, 131.27, 131.35, 131.61, 131.86, 134.44, 135.04, 137.19, 137.34, 140.81, 142.40, 143.47, 151.25 ppm. HRMS (MALDI): calcd for C$_{73}$H$_{62}$, 938.5; found, 938.5 (M$^{+·}$).

2,7-Bis(4-dibenzosuberenylidenemethylphenyl)ethynyl-9,9′-dioctanylfluorene (5$_d$) was prepared by a similar method as **5$_a$** in 87% yield. Mp 103.5−107.0 °C. ^{1}H NMR (CDCl$_3$): δ 0.53−0.61 (m, 4H), 0.81 (t, 6H, J = 7.0 Hz), 1.03−1.13 (m, 16H), 1.17−1.21 (m, 4H), 1.93−1.96 (m, 4H), 6.51 (s, 2H), 6.90 (d, 4H, J = 8.0 Hz), 6.93 (d, 2H, J = 11.5 Hz), 6.99 (d, 2H, J = 11.5 Hz), 7.11 (d, 2H, J = 7.5 Hz), 7.18 (dd, 2H, J = 7.5 Hz), 7.28−7.30 (m, 10H), 7.40−7.48 (m, 8H), 7.53 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.0 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ 14.32,

22.83, 23.93, 29.47, 30.23, 32.02, 40.58, 55.43, 90.18, 91.21, 120.15, 121.65, 122.19, 126.14, 127.13, 127.38, 127.70, 128.64, 129.07, 129.11, 129.18, 129.34, 129.42, 130.91, 131.32, 131.40, 131.67, 131.93, 134.51, 135.11, 137.26, 137.41, 140.87, 142.47, 143.52, 151.32 ppm. HRMS (MALDI): calcd for C$_{77}$H$_{70}$, 994.5; found, 994.5 (M$^{+·}$).

3,6-Bis(4-dibenzosuberenylidenemethylphenyl)ethynyl-9-ethylcarbazole (6) was prepared by a similar method as **5$_a$** in 78% yield. Mp 185.7−187.3 °C. ^{1}H NMR (CDCl$_3$): δ 1.42 (t, 3H, J = 7.0 Hz), 4.32 (q, 2H, J = 7.0 Hz), 6.51 (s, 2H), 6.90 (d, 4H, J = 8.5 Hz), 6.94 (d, 2H, J = 12 Hz), 7.00 (d, 2H, J = 12 Hz), 7.13 (d, 2H, J = 7.5 Hz), 7.20 (dd, 2H, J = 7.5 Hz), 7.29−7.34 (m, 12H), 7.40−7.44 (m, 4H), 7.53 (d, 4H, J = 7.5 Hz), 7.60 (d, 2H, J = 8.0 Hz), 8.21 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 14.08, 38.08, 88.26, 91.39, 108.98, 114.19, 122.15, 122.82, 124.37, 127.16, 127.35, 127.69, 128.63, 129.11, 129.15, 129.18, 129.37, 129.41, 129.96, 131.23, 131.44, 131.66, 132.05, 134.53, 135.11, 136.85, 137.49, 140.14, 142.56, 143.28. HRMS (MALDI): calcd for C$_{62}$H$_{41}$N, 799.3; found, 799.3 (M$^{+·}$).

1,4-Bis(4-dibenzosuberenylidenemethylphenyl)buta-1,3-diyne (7). To a mixture of **4** (304 mg, 1 mol), Pd(PPh$_3$)$_2$Cl$_2$ (10 mg, 0.01 mmol), CuI (10 mg, 0.05 mmol), I$_2$ (126 mg, 0.5 mmol), and Et$_3$N (20 mL) were added. The mixture was stirred at room temperature for 3 h and then poured into 50 mL of water with some sodium bisulfite. The mixture was extracted by dichloromethane (20 mL × 3). Solvent was removed by evaporation. The residue was purified by column chromatography using *n*-hexane/dichloromethane to give 256 mg of **7** (yield, 85%). Mp 249.3−250.2 °C. ^{1}H NMR (CDCl$_3$): δ 6.47 (s, 2H), 6.86 (d, 4H, J = 8.0 Hz), 6.93 (d, 2H, J = 12 Hz), 6.98 (d, 2H, J = 12 Hz), 7.09 (d, 2H, J = 7.5 Hz), 7.19 (dd, 2H, J = 7.5 Hz), 7.23 (d, 4H, J = 8.0 Hz), 7.28−7.33 (m, 6H), 7.40−7.43 (m, 4H), 7.52 (d, 2H, J = 7.5 Hz). ^{13}C NMR (CDCl$_3$): δ 74.49, 82.04, 119.80, 126.81, 127.18, 127.56, 128.38, 128.86, 128.93, 129.15, 131.10, 131.40, 131.99, 134.19, 134.77, 136.96, 137.99, 142.07, 143.84. HRMS (MALDI): calcd for C$_{48}$H$_{30}$, 606.2; found, 606.2 (M$^{+·}$).

Film Preparation. In a typical experiment, a certain amount of fluorophore was added into a certain volume of 10% PMMA in THF. Solids could be easily dissolved in this solution. The resulting mixture was pasted on the glass slide to produce a wet film. The wet film was dried under atmosphere. By this method, films could be fabricated, and the concentrations could be controlled by the amounts of fluorophores.

Nanoparticle Preparation. Distilled water filtered by membrance with 0.22 μm pore size was added dropwise into the dilute solution of fluorophore in 1,4-dioxane with vigorous stirring at room temperature. In all cases, the concentrations of fluorophores were constant after distilled water was completely added. For the TEM observations, sample solutions were kept for 10 days without stirring. Several drops of solution were place on a 200-mesh copper grid covered with a carbon film. Excess solutions were removed with filter paper. The resultant grid was air-dried for 5 h. The TEM micrographs were obtained on a JEM-200CX instrument.

Supporting Information Available: UV−vis absorption spectra and PL spectra of compounds in solutions, in thin films, and in powders are available. Full characterizations (^{1}H NMR,

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¹³C NMR, and HRMS spectra) of new compounds are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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