New Carbazole-Based Fluorophores: Synthesis, Characterization, and Aggregation-Induced Emission Enhancement

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A series of new carbazole-based luminophores (**1**−**12**) were synthesized and well characterized, which demonstrated aggregation-induced emission enhancement (AIEE) properties. The obtained experimental results demonstrated that the attachment of aromatic rotors to luminophore moieties would lead to the decreased quantum yields (measured in diluted solutions); the more rotors attached, the smaller the quantum yields tested. This further confirmed that the AIEE phenomena were caused by the restriction of the intramolecular vibrational and rotational motions in an indirect manner.

Introduction

Conjugated molecules have attracted growing attention in recent years, due to their huge potential applications as bio- and chemosensors, molecular conducting wires, light-emitting diodes (LED), photovoltaic cells, and field-effect transistors.[1−3] Especially, many efforts were paid to the light-emitting diodes. Pushed by many big corporations, lots of good conjugated molecular LED materials with high efficiency have been reported to be becoming commercial. Moreover, to realize the practical utilization of them, some issues were still needed to be addressed. For example, the organic conjugated molecules generally exhibited strong luminescence in diluted solutions; however, in the solid state or in solutions with high concentrations, the formation of delocalized excitons or excimers, according to the aggregation of the luminophores, often quenched the emission of organic luminophores.[4] Thus, many efforts were attempted to suppress the aggregation of organic luminophores.[5] In contrast to the normal thought of hampering the aggregation of luminophores, the best approach to the above notorious problem might be to develop new luminophoric materials whose aggregates could emit more efficiently than their solutions.[6] Along this line of approach, two novel photoluminescence (PL) processes have been identified: one was the "aggregation-induced emission enhancement (AIEE)" and another was the "aggregation-induced emission (AIE)".[7−10] Siloles (TPS, Chart 1) were typical examples of AIE molecules, which were nonemissive in diluted solutions but highly emissive upon aggregation with the fluorescent quantum yields 2 orders of magnitude higher. Later, some other AIE molecules were developed. For example, tetraphenylethene (TPE, Chart 1) and 4-butoxybiphenyl (BBP) were designed and demonstrated AIE properties.[11]

As for the possible mechanism of AIE and AIEE phenomena, the theoretical calculations, the experimental results obtained by a time-resolved fluorescence technique, and the *internal* structural control of silole examples strongly supported that the AIE phenomena were due to the restrictions of the intramolecular phenyl vibrational and rotational motions.[12] According to this point, it was expected that if the emitting unit was the same, the quantum yields in diluted solutions would decrease when some aromatic moieties with rotational motions were linked to the emitting group, and the more aromatic rotors linked, the smaller the quantum yields tested. However, the corresponding experimental proofs were still very scarce.

On the other hand, it was well-known that carbazole was a good hole-transporting and electroluminescent unit, and many LED materials contained carbazole moieties as important construction blocks.[13] Considering this point, and with the aim to develop more AIE and AIEE molecules and get a more deep understanding of the AIE and AIEE phenomena, we wondered if it was possible to obtain some carbazole-based AIE or AIEE luminophores just with the structure shown in Chart 1, in which different aromatic rings were linked to the carbazole cores through single bonds. Thus, partially based on our previous work,[11,14] we have prepared totally 12 new carbazole-based luminophores (Chart 2), in which different aromatic rings were introduced to one or two of the 3- and 6-positions of the carbazole ring, and studied their photophysical properties. The obtained results demonstrated that they were AIEE molecules, and emitted in the UV or blue region, indicating that they might be good candidates for the practical photonic applications. Also, really, it was observed that when the linked aromatic rings were small, the more aromatic rings introduced, the smaller the tested quantum yields of the resultant luminophors in diluted solutions, confirming the above-mentioned thought according to the mechanism of AIE and AIEE phenomena. Herein, we would like to present their syntheses, characterization, and optical properties in detail.

Experimental Section

Materials and Instrumentation. Tetrahydrofuran (THF) was dried over and distilled from K−Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Benzeneboronic acid (**14**) and tetraphenylcyclopentadienone (**21**) were purchased from Alfa Aesar. All other reagents were used as received. The synthesis of **13**, **18**, **19**, **20**, and **22** are given in the Supporting Information. Boronic acid **15**, **16**, and **17** were synthesized according to the similar procedure reported in our previous work.[15]

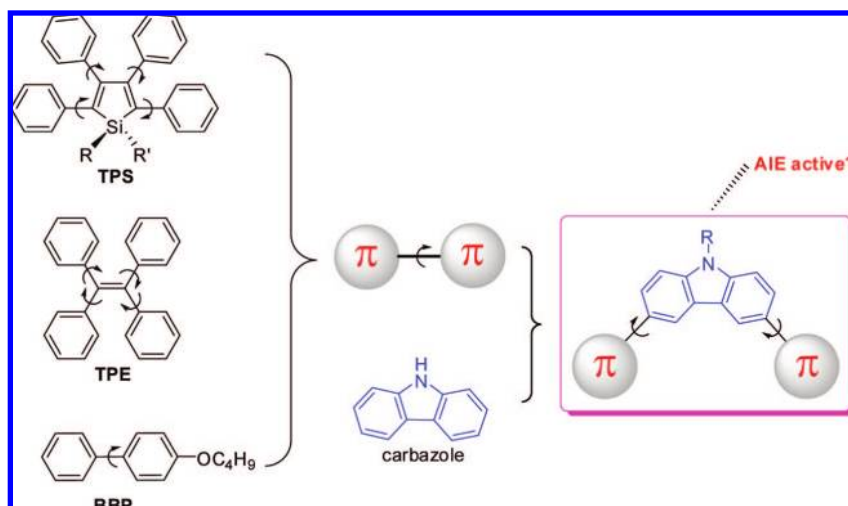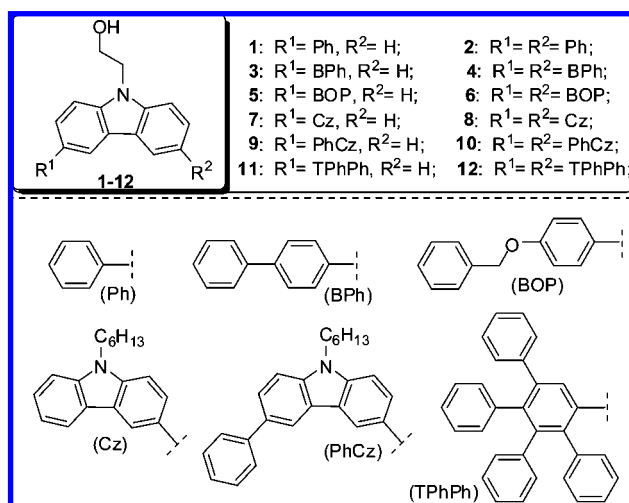* Corresponding author. Tel.: 86-27-62254108. Fax: 86-27-68756757. E-mail: lizhen@whu.edu.cn.

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CHART 1

CHART 2

^{1}H and ^{13}C NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum One spectrometer in the region of 3000−400 cm^{-1}. UV−visible spectra were obtained by using a Shimadzu UV-2550 spectrometer. Fluorescence spectra were obtained by using a Hitachi F-4500 fluorescence spectrophotometer. Elementary analysis was taken on a Vario EL III elementary analysis instrument. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. The thermometer for measurement of the melting point was uncorrected.

General Procedure for the Synthesis of Compounds 1 to 10. A mixture of compound **13** or **19** (1.00 equiv), the benzeneboronic acid (**14**), compound **15**, **16**, **17**, or **18** (1.50 equiv in the case of compound **13**, 3.00 equiv in the case of compound **19**), sodium carbonate (5.00 equiv), THF/water (3:1 in volume), tetrakis(triphenylphosphine)palladium (Pd(PPh$_3$)$_4$) (3−5 mol %) was degassed and charged with argon. The reaction was stirred at 60 °C for 24 h. After cooling to room temperature, the organic layer was separated, dried over sodium sulfate, filtered, and evaporated to remove the solvent. The crude product was purified by column chromatography.

Compound 1. Compound **13** (0.70 g, 2.41 mmol), benzeneboronic acid (**14**) (0.44 g, 3.62 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether

(1/3) as eluent to afford sticky colorless oil (0.56 g, 80.9%). ^{1}H (CDCl$_3$) δ (ppm): 4.11 (t, $J = 5.1$ Hz, 2H, −CH$_2$−OH), 4.53 (t, $J = 5.7$ Hz, 2H, N−CH$_2$−), 7.29 (m, 1H, ArH), 7.34 (d, $J = 6.9$ Hz, 1H, ArH), 7.48 (m, 4H, ArH), 7.55 (d, $J = 7.8$ Hz, 1H, ArH), 7.70 (d, $J = 6.9$ Hz, 3H, ArH), 8.14 (d, $J = 6.9$ Hz, 1H, ArH), 8.31 (s, 1H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 45.8, 61.8, 109.2, 109.3, 119.1, 119.6, 120.7, 123.4, 123.7, 125.6, 126.3, 126.7, 127.5, 129.0, 133.1, 140.5, 141.4, 142.2. IR (thin film), ν (cm^{-1}): 1600, 761 (Ar); 1049 (−C−O−). MS (EI), m/z [M$^+$]: 287.3, calcd: 287.1. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 286; $\epsilon_{max} = 2.47 \times 10^4$ mol^{-1} L cm^{-1}.

Compound 2. Compound **19** (0.50 g, 1.36 mmol), benzeneboronic acid (**14**) (0.50 g, 4.07 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/1) as eluent to afford white powder (0.40 g, 81.0%). Mp = 190−193 °C. ^{1}H (CDCl$_3$) δ (ppm): 4.14 (t, $J = 5.1$ Hz, 2H, −CH$_2$−OH), 4.55 (t, $J = 5.4$ Hz, 2H, N−CH$_2$−), 7.36 (t, $J = 7.5$ Hz, 2H, ArH), 7.49 (t, $J = 7.2$ Hz, 4H, ArH), 7.57 (d, $J = 8.1$ Hz, 2H, ArH), 7.72 (d, $J = 7.5$ Hz, 6H, ArH), 8.38 (s, 2H, ArH). ^{13}C NMR (acetone-d_6) δ (ppm): 46.0, 60.6, 110.1, 118.8, 123.8, 125.2, 126.6, 127.2, 129.0, 132.4, 134.3, 141.2, 142.2. IR (thin film), ν (cm^{-1}): 1600, 766 (Ar); 1047 (−C−O−). MS (EI), m/z [M$^+$]: 363.2, calcd: 363.2. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 295; $\epsilon_{max} = 4.42 \times 10^4$ mol^{-1} L cm^{-1}. C$_{26}$H$_{21}$NO (EA) (%, found/calcd): C, 86.38/85.92; H, 5.63/5.82; N, 3.71/3.85.

Compound 3. Compound **13** (1.00 g, 3.45 mmol), compound **15** (1.02 g, 5.18 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/2) as eluent to afford white powder (0.90 g, 71.9%). Mp = 183−186 °C. ^{1}H (CDCl$_3$) δ (ppm): 4.12 (t, $J = 5.1$ Hz, 2H, −CH$_2$−OH), 4.54 (t, $J = 5.1$ Hz, 2H, N−CH$_2$−), 7.28 (m, 1H, ArH), 7.37 (d, $J = 7.2$ Hz, 1H, ArH), 7.50 (m, 4H, ArH), 7.57 (d, $J = 9.0$ Hz, 1H, ArH), 7.66 (d, $J = 8.1$ Hz, 2H, ArH), 7.73 (d, $J = 8.7$ Hz, 2H, ArH), 7.79 (t, $J = 9.0$ Hz, 3H, ArH), 8.16 (d, $J = 7.2$ Hz, 1H, ArH), 8.37 (s, 1H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 45.9, 61.8, 109.2, 109.4, 119.0, 119.7, 120.7, 123.4, 123.8, 125.5, 126.3, 127.3, 127.5, 127.8, 127.9, 129.1, 132.4, 139.6, 140.5, 141.1, 141.2, 141.4. IR (thin film), ν (cm^{-1}): 1598, 763 (Ar); 1049 (−C−O−). MS (EI), m/z [M$^+$]: 363.0, calcd: 363.2. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 300; $\epsilon_{max} = 5.79 \times 10^4$ mol^{-1} L cm^{-1}. C$_{26}$H$_{21}$NO (EA) (%, found/calcd): C, 85.37/85.92; H, 5.71/5.82; N, 3.48/3.85.

Compound 4. Compound **19** (1.00 g, 2.71 mmol), compound **15** (1.61 g, 8.13 mmol). Purified by column chromatography

on silica gel using dichloromethane as eluent to afford white powder (0.60 g, 42.9%). Mp >300 °C. ^{1}H (CDCl$_3$) δ (ppm): 4.15 (t, J = 5.4 Hz, 2H, −CH$_2$−OH), 4.57 (t, J = 5.4 Hz, 2H, N−H$_2$−), 7.37 (t, J = 6.9 Hz, 2H, ArH), 7.48 (t, J = 7.2 Hz, 4H, ArH), 7.59 (d, J = 8.1 Hz, 2H, ArH), 7.67 (d, J = 7.5 Hz, 4H, ArH), 7.74 (d, J = 7.8 Hz, 4H, ArH), 7.81 (t, J = 6.0 Hz, 6H, ArH), 8.43 (s, 2H, ArH). IR (thin film), v (cm^{-1}): 1598, 766 (Ar); 1050 (−C-O-). MS (EI), m/z [M$^+$]: 515.6, calcd: 515.2. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 309; ϵ_{max} = 6.29 × 10^4 mol^{-1} L cm^{-1}. C$_{38}$H$_{29}$NO (EA) (%, found/calcd): C, 88.20/88.51; H, 5.75/5.67; N, 2.39/2.72.

Compound 5. Compound **13** (0.80 g, 2.76 mmol), compound **16** (0.94 g, 4.14 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/3) as eluent to afford white powder (0.85 g, 78.3%). Mp = 135−138 °C. ^{1}H (CDCl$_3$) δ (ppm): 4.11 (t, J = 5.1 Hz, 2H, −CH$_2$−OH), 4.52 (t, J = 5.1 Hz, 2H, N−CH$_2$−), 5.15 (s, 2H, −CH$_2$−O−Ar), 7.12 (d, J = 8.1 Hz, 2H, ArH), 7.28 (m, 1H, ArH), 7.38 (d, J = 7.2 Hz, 1H, ArH), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.48−7.53 (m, 5H, ArH), 7.62−7.69 (m, 4H, ArH), 8.13 (d, J = 8.1 Hz, 1H, ArH), 8.27 (s, 1H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 45.8, 61.8, 70.4, 109.2, 109.3, 115.4, 118.7, 119.5, 120.7, 123.4, 123.7, 125.4, 126.2, 127.8, 128.2, 128.5, 128.9, 132.7, 135.1, 137.3, 140.1, 141.3, 158.1. IR (thin film), v (cm^{-1}): 1605, 804, 747 (Ar); 1059 (−C−O−). MS (EI), m/z [M$^+$]: 393.2, calcd: 393.2. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 284; ϵ_{max} = 5.71 × 10^4 mol^{-1} L cm^{-1}. C$_{27}$H$_{23}$NO$_2$ (EA) (%, found/calcd): C, 82.16/82.42; H, 5.64/5.89; N, 3.34/3.56.

Compound 6. Compound **19** (0.50 g, 1.36 mmol), compound **16** (0.93 g, 4.07 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/2) as eluent to afford white powder (0.54 g, 69.0%). Mp = 245−249 °C. ^{1}H (CDCl$_3$) δ (ppm): 4.12 (t, J = 4.5 Hz, 2H, −CH$_2$−OH), 4.53 (t, J = 4.5 Hz, 2H, N−CH$_2$−), 5.14 (s, 4H, −CH$_2$−O−Ar), 7.11 (d, J = 8.7 Hz, 4H, ArH), 7.35 (m, 2H, ArH), 7.42 (t, J = 7.2 Hz, 4H, ArH), 7.50 (t, J = 7.2 Hz, 6H, ArH), 7.66 (m, 6H, ArH), 8.30 (s, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 45.9, 61.9, 70.4, 109.3, 115.4, 118.7, 123.9, 125.5, 127.7, 128.2, 128.5, 128.8, 132.8, 135.1, 140.5, 158.1. IR (thin film), v (cm^{-1}): 1606, 801, 734 (Ar); 1045 (−C−O−). MS (EI), m/z [M$^+$]: 575.4, calcd: 575.3. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 294; ϵ_{max} = 6.10 × 10^4 mol^{-1} L cm^{-1}. C$_{40}$H$_{33}$NO$_3$ (EA) (%, found/calcd): C, 83.62/83.45; H, 5.52/5.78; N, 2.18/2.43.

Compound 7. Compound **13** (0.80 g, 2.76 mmol), compound **17** (1.22 g, 4.14 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/3) as eluent to afford light yellow solid (1.11 g, 87.2%). Mp = 67−70 °C. ^{1}H (CDCl$_3$) δ (ppm): 0.89 (t, J = 7.5 Hz, 3H, −CH$_3$), 1.27−1.44 (m, 6H, −CH$_2$−CH$_2$−CH$_2$−CH$_3$), 1.92 (m, 2H, −CH$_2$−C$_4$H$_9$), 4.13 (t, J = 5.7 Hz, 2H, −CH$_2$−OH), 4.35 (t, J = 7.2 Hz, 2H, −N−CH$_2$−C$_5$H$_{11}$), 4.55 (t, J = 5.7 Hz, 2H, -N-CH$_2$-), 7.23−7.31 (m, 2H, ArH), 7.47−7.42 (m, 2H, ArH), 7.49−7.52 (m, 3H, ArH), 7.59 (d, J = 8.1 Hz, 1H, ArH), 7.84 (t, J = 5.7, 2H, ArH), 8.18 (d, J = 8.1 Hz, 2H, ArH), 8.41 (s, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.4, 22.9, 27.3, 29.3, 31.9, 43.4, 45.8, 61.7, 109.1, 109.2, 109.4, 119.1, 119.2, 119.5, 120.8, 123.3, 123.5, 123.7, 123.8, 125.8, 126.0, 126.2, 133.4, 134.1, 139.9, 140.0, 141.2, 141.4. IR (thin film), v (cm^{-1}): 1601, 799, 746 (Ar); 1063 (−C-O-). MS (EI), m/z [M$^+$]: 460.3, calcd: 460.3. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 300; ϵ_{max} = 4.36 × 10^4 mol^{-1} L cm^{-1}. C$_{32}$H$_{32}$N$_2$O (EA) (%, found/calcd): C, 82.97/83.44; H, 6.75/7.00; N, 5.62/6.08.

Compound 8. Compound **19** (0.70 g, 1.90 mmol), compound **17** (1.68 g, 5.70 mmol). Purified by column chromatography

on silica gel using ethyl acetate/petroleum ether (1/2) as eluent to afford light yellow solid (0.90 g, 66.7%). Mp = 95−98 °C. ^{1}H (CDCl$_3$) δ (ppm): 0.88 (t, J = 7.2 Hz, 6H, −CH$_3$), 1.32−1.44 (m, 12H, −CH$_2$−CH$_2$−CH$_2$−CH$_3$), 1.92 (m, 4H, −CH$_2$−C$_4$H$_9$), 4.17 (t, J = 5.1 Hz, 2H, −CH$_2$−OH), 4.35 (t, J = 6.6 Hz, 4H, −N−CH$_2$−C$_5$H$_{11}$), 4.59 (t, J = 5.1 Hz, 2H, −N−CH$_2$−), 7.23−7.28 (m, 2H, ArH), 7.42−7.53 (m, 6H, ArH), 7.61 (d, J = 8.1 Hz, 2H, ArH), 7.85 (m, 4H, ArH), 8.19 (d, J = 7.5 Hz, 2H, ArH), 8.44 (s, 2H, ArH), 8.51 (s, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.3, 22.8, 27.3, 29.3, 31.9, 43.5, 46.0, 61.9, 109.0, 109.2, 109.4, 119.0, 119.2, 119.3, 120.7, 123.3, 123.7, 124.1, 125.7, 125.9, 126.1, 133.3, 134.1, 139.8, 140.5, 141.1. IR (thin film), v (cm^{-1}): 1601, 800, 747 (Ar); 1066 (−C−O−). MS (EI), m/z [M$^+$]: 709.9, calcd: 709.4. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 306; ϵ_{max} = 7.04 × 10^4 mol^{-1} L cm^{-1}. C$_{50}$H$_{51}$N$_3$O (EA) (%, found/calcd): C, 84.53/84.59; H, 7.32/7.24; N, 5.78/5.92.
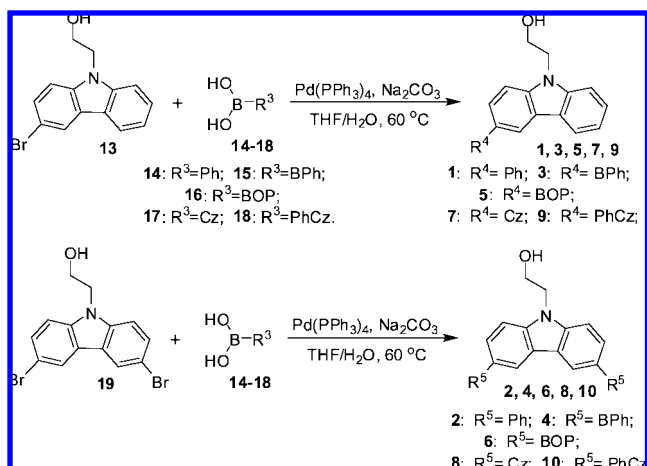
Compound 9. Compound **13** (0.50 g, 1.72 mmol), compound **18** (0.96 g, 2.59 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/3) as eluent to afford white solid (0.70 g, 76.0%). Mp = 107−110 °C. ^{1}H (CDCl$_3$) δ (ppm): 0.90 (t, J = 6.6 Hz, 3H, −CH$_3$), 1.34−1.44 (m, 6H, −CH$_2$−CH$_2$−CH$_2$−CH$_3$), 1.94 (m, 2H, −CH$_2$−C$_4$H$_9$), 4.11 (t, J = 5.1 Hz, 2H, −CH$_2$−OH), 4.37 (br, 2H, −N−CH$_2$−C$_5$H$_{11}$), 4.53 (br, 2H, −N−CH$_2$−), 7.28 (m, 1H, ArH), 7.35 (t, J = 7.5 Hz, 1H, ArH), 7.47−7.57 (m, 8H, ArH), 7.75 (d, J = 7.2 Hz, 3H, ArH), 7.84 (d, J = 8.1 Hz, 2H, ArH), 8.19 (d, J = 7.2 Hz, 1H, ArH), 8.46 (m, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.4, 22.9, 27.3, 29.3, 31.9, 43.6, 45.8, 61.8, 109.2, 109.3, 119.1, 119.2, 119.5, 120.8, 123.4, 123.8, 125.5, 125.9, 126.0, 126.2, 126.7, 127.5, 129.1, 132.5, 133.5, 134.0, 140.0, 140.3, 140.7, 141.4, 142.4. IR (thin film), v (cm^{-1}): 1601, 800, 747, 699 (Ar); 1065 (−C−O−). MS (EI), m/z [M$^+$]: 536.2, calcd: 536.3. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 305; ϵ_{max} = 8.28 × 10^4 mol^{-1} L cm^{-1}. C$_{38}$H$_{36}$N$_2$O (EA) (%, found/calcd): C, 84.76/85.04; H, 7.25/6.76; N, 4.96/5.22.

Compound 10. Compound **19** (0.40 g, 1.08 mmol), compound **18** (1.20 g, 3.24 mmol). Purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/2) as eluent to afford light yellow solid (0.42 g, 45.1%). Mp = 138−140 °C. ^{1}H (CDCl$_3$) δ (ppm): 0.89 (t, J = 6.6 Hz, 6H, −CH$_3$), 1.33−1.45 (m, 12H, −CH$_2$−CH$_2$−CH$_2$−CH$_3$), 1.94 (m, 4H, −CH$_2$−C$_4$H$_9$), 4.18 (br, 2H, −CH$_2$−OH), 4.37 (br, 4H, −N−CH$_2$−C$_5$H$_{11}$), 4.60 (br, 2H, −N−CH$_2$−), 7.33 (t, J = 7.5 Hz, 2H, ArH), 7.44−7.54 (m, 8H, ArH), 7.58−7.61 (br, 2H, ArH), 7.74 (d, J = 7.2 Hz, 6H, ArH), 7.87 (d, J = 8.7 Hz, 4H, ArH), 8.43 (s, 2H, ArH), 8.50 (d, J = 11.7 Hz, 4H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.0, 21.5, 26.0, 28.0, 30.6, 42.3, 44.6, 60.6, 107.9, 108.0, 108.1, 117.8, 117.9, 122.5, 122.8, 124.1, 124.6, 124.7, 125.3, 126.2, 127.7, 131.2, 132.1, 132.7, 139.0, 139.2, 139.3, 141.0. IR (thin film), v (cm^{-1}): 1602, 800, 755, 698 (Ar); 1066 (−C−O−). MS (EI), m/z [M$^+$]: 861.4, calcd: 861.5. UV−vis (THF, 1 × 10^{-5} mol/L): λ_{max} (nm): 307; ϵ_{max} = 1.38 × 10^5 mol^{-1} L cm^{-1}. C$_{62}$H$_{59}$N$_3$O (EA) (%, found/calcd): C, 85.94/86.37; H, 6.56/6.90; N, 4.62/4.87.

General Procedure for the Synthesis of Compounds 11 and 12. Compound **20** or **22** (1.00 equiv) and tetraphenylcyclopentadienone (**21**) (1.00 equiv for compound **20**, 2.00 equiv for compound **22**) was dissolved in *o*-xylene. The resultant mixture was refluxed for 24 h. After being cooled to room temperature, the solution was evaporated to remove *o*-xylene. The crude product was purified by column chromatography.

Compound 11. Compound **20** (0.37 g, 1.57 mmol), tetraphenylcyclopentadienone (**21**) (0.61 g, 1.57 mmol). Purified by

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132.3, 133.2, 139.1, 139.6, 139.8, 140.3, 140.5, 140.7, 141.0, 141.4, 142.1. IR (thin film), ν (cm^{-1}): 1600, 810, 763, 698 (Ar); 1073 (−C−O−). MS (EI), m/z [M$^+$]: 971.7, calcd: 971.4. UV−vis (THF, 1×10^{-5} mol/L): λ_{max} (nm): 304; ϵ_{max} = 4.95 $\times 10^4$ mol^{-1} L cm^{-1}. C$_{74}$H$_{53}$NO (EA) (%, found/calcd): C, 91.06/91.42; H, 5.83/5.49; N, 1.21/1.44
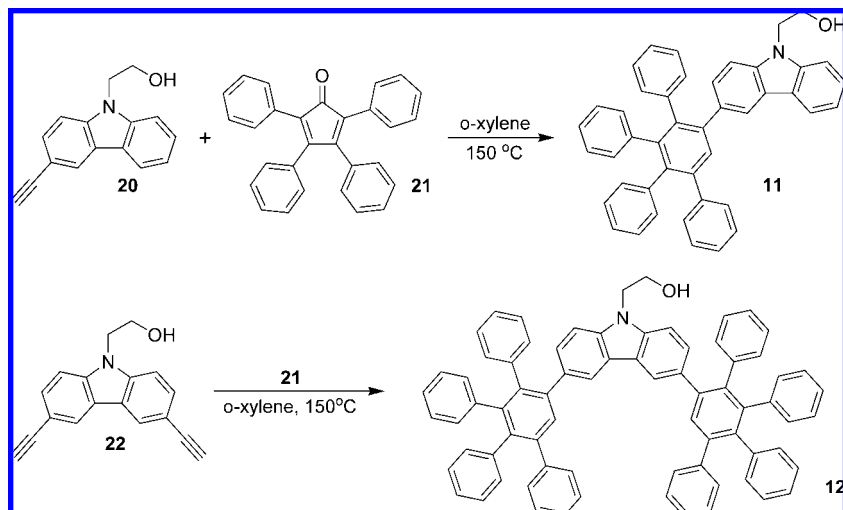
Results and Discussion

Synthesis and Structural Characterization. As shown in Schemes 1 and 2 and S1−S4, the 12 carbazole-based lumino-phores (**1**−**12**) and the reactive intermediate compounds were prepared with satisfactory yields. The reactions used in the synthetic route, including the nucleophilic substitution reaction, the Sonogashira coupling reaction, the Diels−Alder and Suzukii reaction, were easy to handle, and the yields were relatively OK. All the 12 luminophores could be divided into two classes: one was the monosubstituted carbazole-based luminophores, for example, **1**, **3**, **5**, **7**, **9**, and **11**, in which only the 3-position in the carbazole ring underwent the Suzukii or Diels−Alder reaction and there was still one hydrogen atom present at the 6-position; and another class was the disubstituted ones, in which both of the 3- and 6-positions in the carbazole ring were substituted. Thus, we could compare the photophysical proper-ties of the two classes of carbazole-based luminophores due to their similar chemical structures.

It should be pointed out that there was one hydroxyl group present in all the 12 luminophores **1**−**12**, which could be utilized to introduce them to the polymeric system or for the further functionalization according to the different requirements. This would surely benefit the application of the carbazole-based luminophores in different fields. All the 12 luminophores (**1**−**12**) and other compounds were well characterized by ^{1}H, ^{13}C NMR, FT-IR, elemental analysis, and EI-MS, and all gave satisfactory data (in Experimental Section and Supporting Information).

Aggregation-Induced Emission Enhancement (AIEE) Prop-erties and Photophysics. All the obtained carbazole-based luminophores were soluble in common solvents, such as chloroform, acetone, ethanol, THF, acetonitrile, and dichlo-romethane. However, they demonstrated bad solubility in water. The UV−vis absorption spectra are shown in Figure S24. As they have the same carbazole core, the spectra were nearly similar with different molar absorption coefficients.

Compounds **1**−**12** emitted detectable fluorescence upon excitation in diluted solutions. Figure 1 showed their fluorescent

column chromatography on silica gel using dichloromethane as eluent to afford yellow powder (0.61 g, 65.6%). Mp = 145−150 °C. ^{1}H (CDCl$_3$) δ (ppm): 4.02 (br, 2H, −CH$_2$−OH), 4.41 (t, J = 5.1 Hz, 2H, N−CH$_2$−), 6.82 (m, 3H, ArH), 6.89 (m, 9H, ArH), 6.93 (m, 3H, ArH), 7.19 (m, 8H, ArH), 7.42 (d, J = 3.6 Hz, 2H, ArH), 7.70 (s, 1H, ArH), 7.91 (d, J = 7.2 Hz, 1H, ArH), 7.97 (s, 1H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 45.8, 61.7, 108.0, 109.0, 119.5, 120.5, 122.1, 122.8, 123.3, 125.5, 125.8, 126.0, 126.5, 126.8, 127.1, 127.2, 127.8, 128.4, 130.2, 131.7, 131.8, 131.9, 132.2, 133.2, 139.1, 139.5, 139.6, 140.3, 140.5, 140.7, 141.0, 141.2, 141.4, 142.0, 142.1. IR (thin film), ν (cm^{-1}): 1600, 803, 738, 699 (Ar); 1073 (−C−O−). MS (EI), m/z [M$^+$]: 591.3, calcd: 591.3. UV−vis (THF, 1×10^{-5} mol/L): λ_{max} (nm): 286; ϵ_{max} = 5.59 $\times 10^4$ mol^{-1} L cm^{-1}. C$_{44}$H$_{33}$NO (EA) (%, found/calcd): C, 88.57/ 89.31; H, 4.97/5.62; N, 1.73/ 2.37.

Compound 12. Compound **22** (0.12 g, 0.46 mmol), tetraphe-nylcyclopentadienone (**21**) (0.18 g, 0.46 mmol). Purified by column chromatography on silica gel using dichloromethane as eluent to afford yellow powder (0.34 g, 76.0%). Mp = 225−228 °C. ^{1}H (CDCl$_3$) δ (ppm): 3.95 (t, J = 5.1 Hz, 2H, −CH$_2$−OH), 4.31 (t, J = 5.1 Hz, 2H, N−CH$_2$−), 6.82 (m, 4H, ArH), 6.90 (m, 28H, ArH), 7.14 (s, 6H, ArH), 7.18 (d, 6H, ArH), 7.68 (s, 2H, ArH), 7.90 (s, 2H, ArH). ^{13}C NMR (CDCl$_3$) δ (ppm): 45.8, 61.7, 108.0, 121.9, 123.0, 125.5, 125.8, 126.4, 126.8, 127.1, 127.2, 127.8, 128.5, 130.2, 131.7, 131.8, 131.9,

SCHEME 2

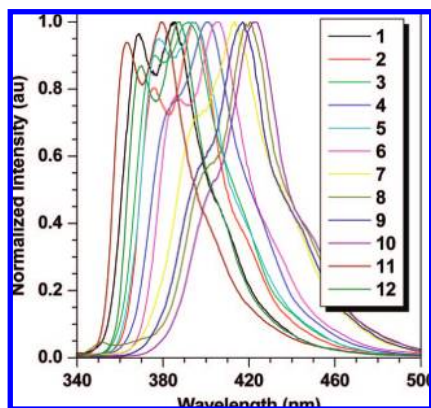**438** *J. Phys. Chem. B, Vol. 113, No. 2, 2009*

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Figure 1. Normalized PL spectra of compounds **1**−**12** in their diluted THF solution.

Figure 2. (A) PL spectra of dilute solution of **1** (10 μM) in water/THF mixtures with different water contents. Excitation wavelength: 299 nm. (B) Changes in the quantum yield of **1** with different water fractions in the water/THF mixtures.
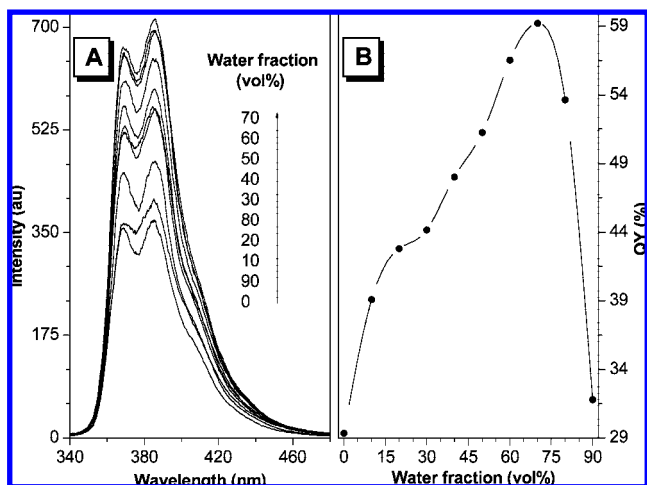

Figure 3. (A) PL spectra of dilute solution of **2** (10 μM) in water/THF mixtures with different water contents. Excitation wavelength: 305 nm. (B) Changes in the quantum yield of **2** with different water fractions in the water/THF mixtures.

spectra in the THF solutions. The intensity was normalized for the comparison of their different maximum emission wavelengths. It was easily seen that the disubstituted luminophores demonstrated red-shifted maximum emission wavelengths, in comparison with their corresponding monosubstituted analogues. This should be attributed to the prolonged conjugated π system. Also, from compounds **1**−**10**, there was an increasing trend in the maximum emission wavelengths.

To determine whether compounds **1**−**12** were AIEE active or not, the fluorescent behavior of their diluted solutions were studied in the mixture solvents of THF and water with different water fractions, since they could be easily dissolved in THF but were insoluble in water. Figure 2 showed the tested results of compound **1**. While the water fraction was increased from 0% to 70%, the fluorescent intensity of **1** was enhanced correspondingly. Since **1** was insoluble in water, the increase of the water fraction in the mixture solvent would reduce the solubility of **1**. Then, the existing formation of **1** would change from molecules in pure THF to particles of molecular aggregation in the mixture solvent step by step. Thus, the enhanced fluorescent intensity implied that **1** emitted stronger fluorescence upon aggregation than in diluted solution. Or, in other words, it was aggregation-induced emission enhancement (AIEE) active. However, further increase in the water fraction in the mixture solvent resulted in the decrease of the fluorescent intensity. It was reasonable. According to the aggregation of **1**
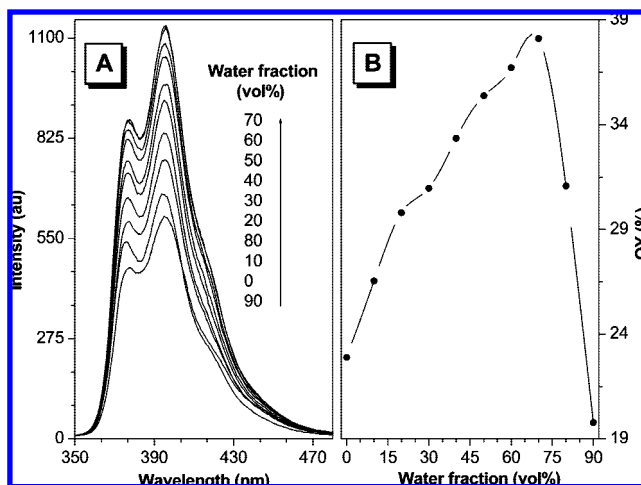
upon the increasing of the water fraction in solvent, only the molecules on the surface of the nanoparticles emitted light and contributed to the fluorescent intensity upon excitation, leading to the decrease of the fluorescent intensity; but the restriction of intramolecular rotations (RIR) of the aromatic rings around the carbon−carbon single bonds in the aggregation state would enhance light emission. The net outcome of these two antagonistic processes was the observed AIEE effect, when the water fraction was not higher than 70% in the mixture solvent. This indicated that the RIR process played a predominant role in affecting the fluorescent behavior of the aggregated molecules. Moreover, when the water fraction was higher than 70%, the solubility of **1** in the mixture solvent even decreased to yield more insoluble particles; thus, the number of the emission molecules became even less. Then, the enhancement of the fluorescent intensity from the PIR process could not make up the decreasing trend of the intensity caused by the less and less emitting molecules. Hence, the fluorescent intensity decreased. The calculated quantum yields of **1** in the solutions at different water fractions also exhibited the similar changing trend, further confirming that compound **1** was AIEE active.

Just as obtained in the fluorescent behavior of compound **1**, nearly the same trend was observed in the case of compound **2** (Figure 3). However, if we compared the results of these two compounds in detail, we could still find some differences. The maximum emission wavelength of compound **2** was red-shifted about 9 nm, in comparison with that of compound **1**. As mentioned above, this was caused by the prolonged π system, since there were two phenyl rings bonded to the carbazole ring at both of the 3 and 6 positions in compound **2**. However, its quantum yield (22.9%) was lower than that of compound **1** (29.4%) in diluted THF solutions, in spite of the prolonged π system.

To know whether this phenomenon was special for **1** and **2** or not, we studied the fluorescent behavior of the other 10 carbazole-based luminophores (**3**-**12**). Similar phenomena were observed (Figure S25−S34). When a little amount of water was added to the THF solution of them, their emission intensity was boosted up immediately; it began to go down when the water fraction was higher than a special point. Also, the maximum emission wavelengths of the disubstituted ones were red-shifted, and longer than their corresponding monosubstituted ones. As to the quantum yields in diluted THF

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CHART 3
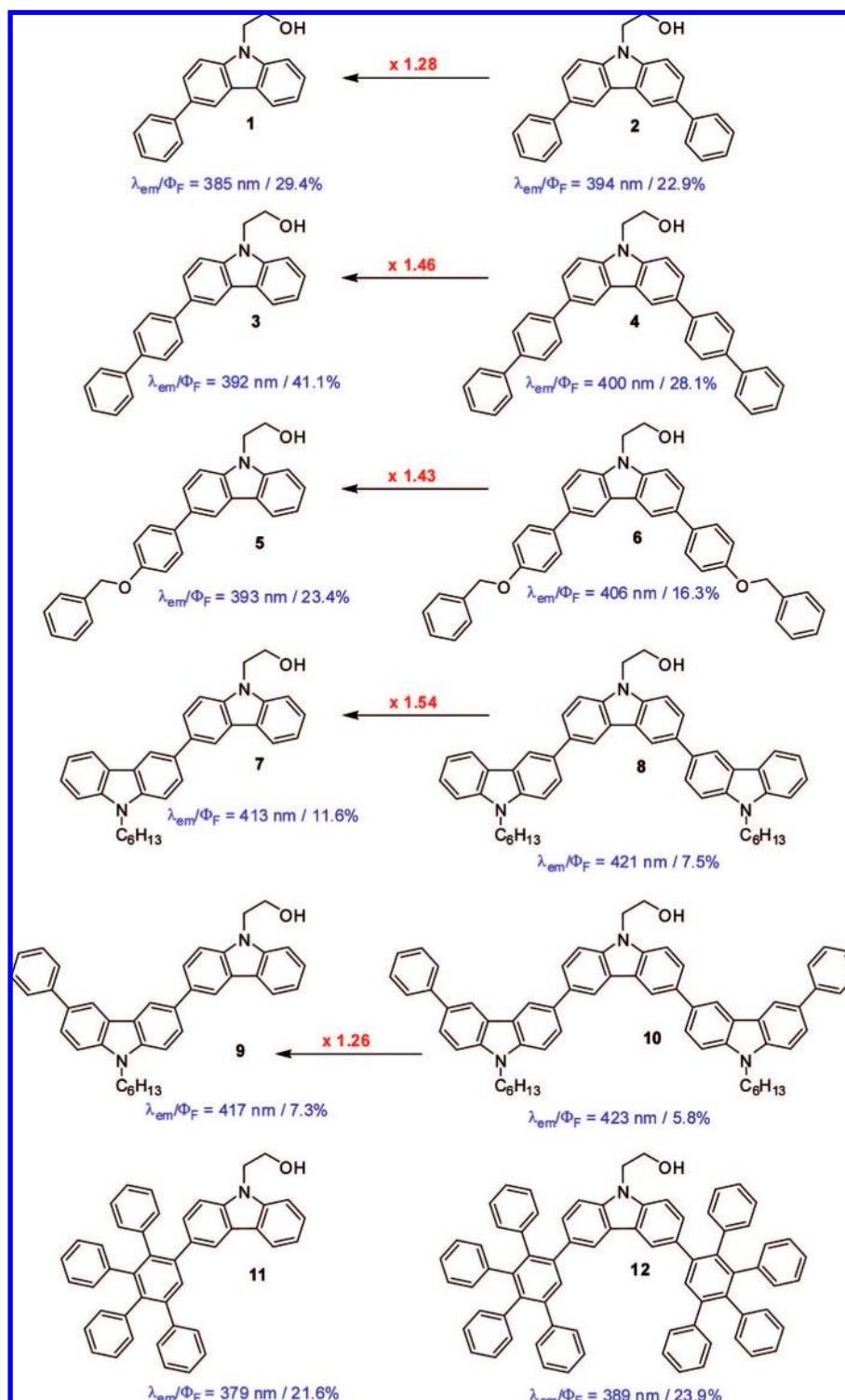
solutions, those of the monosubstituted ones were relatively higher in the cases of compounds **1**–**10**. This confirmed that the higher quantum yield of compound **1**, the monosubstituted carbazole-based luminophore, was not a special example but nearly a common rule. To demonstrate the changes more visually, we summarized their maximum emission wavelengths and quantum yields in Chart 3. As mentioned in the Introduction, we have attributed the AIE and AIEE phenomena to the restrictions of the intramolecular phenyl vibrational and rotational motions.[12] Thus, accordingly, it was expected that if the emitting unit was the same, the quantum yields in

diluted solutions would decrease when some aromatic moieties with rotational motions were linked to the emitting group, and the more aromatic rotors linked, the smaller the quantum yields that would result. Here, in compounds **1**–**10**, we could consider the carbazole moieties as the emitting units; then, after some aromatic groups are introduced, actually the quantum yields of the resultant compounds decreased in comparison with that of carbazole.[16] As the linked aromatic groups in the disubstituted luminophores were more than their monosubstituted ones, correspondingly, their quantum yields were even lower. Thus, the obtained experi-
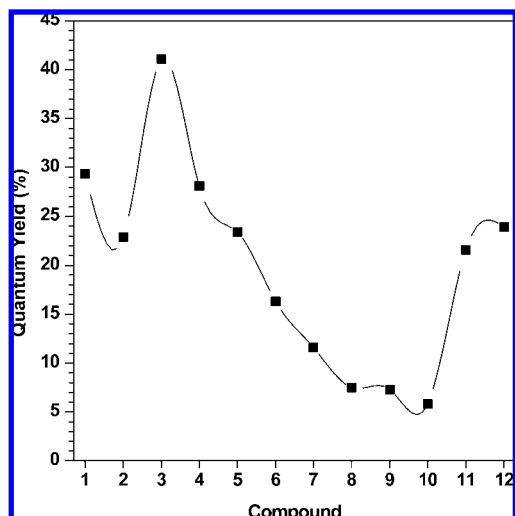
Figure 4. Changes in the quantum yield of compounds **1**−**12** in their diluted solutions of THF.

Figure 5. Normalized PL spectra of **1** in dilute THF solution (10 μM) and PMMA film (30%).

mental results further confirmed the mechanism of AIE and AIEE phenomena on another side.

Compound **11** possessed lower quantum yield (21.6%) than its disubstituted analogue, compound **12** (23.9%), not in accordance with the above-mentioned rule. This was a little strange at the first glance, but might be reasonable after careful consideration. In both compounds **11** and **12**, the bonded aromatic groups were very large; then the rotation of the phenyl rings would be affected by themselves to a large degree since they were placed in very limited space, and thus, all the phenyl rings could not rotate freely as the aromatic rings in compounds **1**−**10**. So, the absorbed energy could not easily be consumed by the intramolecular phenyl vibrational and rotational motions, directly leading to the relatively higher quantum yields of them in comparison with those of compounds **1**−**10**.[12d] As the π system of compound **12** was longer than that of compound **11**, the restriction of the rotational motions resulted in the higher quantum yield of compound **12**.

If we summarized the quantum yields of the 12 compounds visually (Figure 4), it is seen that from compound **1** to **12**, the changing trend of quantum yields was becoming lower, except the abnormal ones of compounds **3** and **4**. As mentioned above, the emitting unit was the same, the quantum yields in diluted solutions would decrease when some aromatic moieties with rotational motions were linked to the emitting group, and the more aromatic rotors linked, the smaller the quantum yields that would result. However, the results of compounds **3** and **4** reminded us another fact: the π system would be prolonged after the linkage of the additional aromatic moieties, which would benefit the increase of the quantum yields of the resultant compounds. Thus, the change of the quantum yields would be the result of two conflicting effective parameters: one is the prolonged π system, and another is the intramolecular phenyl vibrational and rotational motions. And in our case, the intramolecular phenyl vibrational and rotational motions were the main reason, which led to the above results. This reason could also be applied to explain the fact that the quantum yields of compounds **11** and **12** are not higher than those of all compounds **1**−**10**, but higher than some of them. Although the obtained experimental results partially proved our thought, more work is still needed to further confirm this idea.

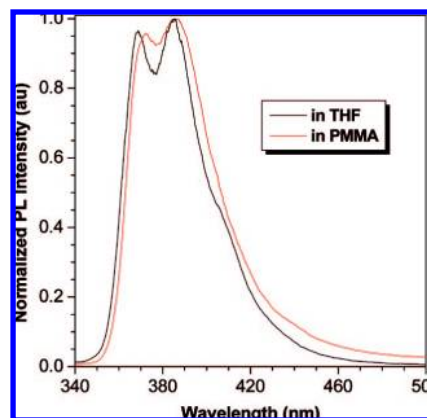As mentioned above, there was one hydroxyl group present in all the 12 luminophores **1**−**12**, which could be utilized to introduce them to the polymeric system or for the further functionalization according to the different requirements. Then, if there were no hydroxyl groups in them, how about their photophysical properties? Or in other words, did the hydroxyl groups play an important role for the experimental results obtained so far? To answer this question, we prepared another two carbazole-based luminophores, **23** and **24**, with similar structures as those of **1** and **2** but without the hydroxyl group (Chart S1). The experimental results demonstrated that they were AIEE active and obeyed the same rule as **1** and **2** (Figures S35 and S36), confirming that the hydroxyl groups had nothing to do with our experimental results.

We also doped the luminophores into poly(methylmethacrylate) (PMMA) with the concentration of 30% and then prepared their thin films. As shown in Figure 5 and Figures S37 −S47, there was no big difference between the maximum emission wavelengths of the films and those of their corresponding ones in diluted THF solutions; also nearly no apparent additional shoulder peaks appeared in the fluorescent spectra of the films. These results indicated that there were nearly no delocalized excitons or excimers formed in the solid state of these luminophores. This property would surely benefit the potential application of compounds **1**−**12**, and our examples might provide a new way to develop efficiently AIEE active carbazole-based LED materials.

Conclusions

With the aim to broaden the family of AIE and AIEE luminophores, a series of carbazole-based molecules were successfully synthesized. All of them possessed good solubility and demonstrated AIEE properties. Our preliminary results demonstrated that the attachment of some aromatic rotors to the luminescent moieties would decrease their quantum yields in diluted solutions: the more rotors that were attached, the smaller the quantum yields that resulted. These results further confirmed the reported mechanism of AIE and AIEE phenomena

Supporting Information Available: Figures of ¹HNMR and ¹³CNMR spectra, and PL spectra; and the synthetic procedure for some reaction intermediates. This information is available free of charge via the Internet at http://pubs.acs.org.

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