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Highlights

• A series of luminogens containing formamide or fluorenone units, based on fluorene, have been synthesized.

• Fluorene-based luminogens with formamide units exhibited aggregate fluorescence change.

• Fluorene-based luminogens with fluorenone unit exhibited AIEE characteristics.

CERTER MARK

Fluorene-based novel highly emissive fluorescent molecules with aggregate fluorescence change or aggregation-induced emission enhancement characteristics

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ABSTRACT

A series of luminogens containing formamide or fluorenone units, based on fluorene, have been synthesized and characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Their aggregate fluorescence change and aggregation-induced emission enhancement (AIEE) characteristics were investigated by luminescence and UV/Vis spectroscopies. The results indicate that luminogens **1d** and **2d**, containing formamide units, exhibit significant fluorescence color changing upon aggregate formation, which is a newly observed uncommon and interesting aggregation-induced emission phenomenon. Although the luminogen **3d**, with one fluorenone unit and one fluorene unit, was weakly emissive in solution, it was highly fluorescent in the aggregated state and demonstrates typical AIEE characteristics. In comparison with **3d**, the luminogen **4d** with one fluorenone unit and two fluorene units showed weaker AIEE

behavior. In thin-films and in the solid state, luminogen **1d** shows intense yellow-green emission, and other luminogens show strong yellow emitting. Among these luminogens, **4d** exhibits the highest solid-state emission quantum yield.

Keywords: formamide; fluorenone; fluorene; aggregate fluorescence change; AIEE

1. Introduction

Research into efficient luminescent organic molecules has attracted widespread attention on account of their practical applications in sensors, displays, storage and photoelectronic devices [1–5]. When aggregated in the condensed phase, emission is often partially or wholly quenched, which largely limits practical applications of fluorophores. Generally this phenomenon is known as aggregation-caused quenching (ACQ) [6–7]. In 2001, Tang *et al.* observed an unusual fluorescence phenomenon in some propeller-shaped molecules known as aggregation-induced emission (AIE) [8]. These AIE luminogens are weakly-emissive or non-emissive in solution, but exhibit intense emission upon aggregate formation (as opposed to the ACQ effect) [9–10]. Many research groups are now working in the field of AIE research and this has led to the synthesis of many new AIE fluorogens [11–25]. In 2002, Park *et al.* reported that a new kind of organic CN-MBE nanoparticles displayed intensely enhanced fluorescence emission, referred to as aggregation-induced emission enhancement (AIEE) [26]. Since

then, many AIEE materials have also been prepared. In addition, oligomers and polymers with fluorene as a skeleton are valuable candidates for use in light emitting diodes because of their tunable electronic properties and facile structural fragility. It is therefore an exciting modern challenge to synthesize new fluorescent molecules based on fluorene with AIE or AIEE characteristics. However, the interrelated instance is quite rare [27]. Herein, we designed and synthesized a series of novel fluorescent molecules based on fluorene and investigated their aggregate fluorescence change and AIEE characteristics.

2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. All starting materials were obtained commercially as analytical-grade and used without further purification. Compounds **1a** [28], **1b** [29], **2a** [30], **2b** [29], **3a** [31], **3b** [29], **3c** [27], **4c** [32] and N-(4-hydroxyphenyl)formamide [33] were prepared by procedures described in the corresponding literatures. ¹H NMR (400 MHz) and ¹³C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ¹H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s=singlet, d=doublet, t=triplet,

m=multiplet), and coupling constant (Hz). ¹³C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. EI-MS was obtained using Thermo scientific DSQ II. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer and Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). The absolute fluorescence quantum yields and time-resolved luminescence of solids were measured by Edinburgh Instruments FLS900. Column chromatographic separations were carried out on silica gel (200-300 mesh). TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF₂₅₄) and visualization was effected at 254 nm.

2.2 Synthesis

2.2.1 Synthesis of luminogens 1d and 2d with formamide units

Synthesis of **1c**: A mixture of compounds **1a** (3.8 mmol, 2.5 g), **1b** (9.6 mmol), K_2CO_3 (28.8 mmol), Pd(PPh_3)_4 (0.04 mmol) were stirred in THF (50 ml) and H₂O (5 ml) for two days under an argon atmosphere at 80°C. After completion of present reaction, the mixtures were extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 60.0%. ¹H NMR (400 MH_z, CDCl₃): δ (ppm)= 7.89-7.79 (m, 8H), 7.72-7.66

(m, 4H), 7.63 (s, 2H), 7.58 (d, J= 8 Hz, 2H), 7.40 (d, J= 8 Hz, 2H), 7.34 (d, J= 8 Hz, 2H), 4.01 (s, 4H), 3.27 (t, J= 6 Hz, 4H), 2.10 (s, 4H), 1.65 (d, J= 8 Hz, 4H), 1.23 (s, 4H), 1.12 (s, 4H), 0.76 (s, 4H). ¹³C NMR (100 MH_z, CDCl₃): δ (ppm)= 151.31, 143.93, 143.42, 141.38, 140.88, 140.38, 140.13, 139.97, 126.80, 126.69, 126.22, 125.99, 125.02, 123.70, 121.30, 120.10, 119.93, 55.19, 40.27, 37.01, 33.81, 32.60, 29.01, 27.70, 23.62. EI-MS: m/z= 820.63[M]⁺. Anal. Calcd. for C₅₁H₄₈Br₂: C, 74.63; H, 5.89. Found: C, 74.69; H, 5.85.

Synthesis of **1d**: A mixture of compounds **1c** (1.8 mmol, 1.5 g), N-(4-hydroxyphenyl)formamide (5.5 mmol), K₂CO₃ (21.9 mmol) were stirred in DMF (50 ml) for overnight under an argon atmosphere at 60°C. After completion of present reaction, DMF was removed from reaction system by vacuum distillation. the residual mixtures were extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 58.0%, ¹H NMR (400 MH_z, CDCl₃): δ (ppm)= 8.39 (d, J= 12 Hz, 1H), 8.21 (s, 1H), 7.84-7.65 (m, 13H), 7.56 (d, J= 8 Hz, 2H), 7.40-7.24 (m, 8H), 7.12 (d, J= 12 Hz, 1H), 6.86 (d, J= 8 Hz, 2H), 6.71 (d, J= 8 Hz, 4H), 3.94 (s, 4H), 3.74 (d, J= 4 Hz, 4H), 2.11 (s, 4H), 1.54 (s, 4H), 1.25 (d, J= 4 Hz, 4H), 1.16 (d, J= 4 Hz, 4H), 0.79 (s, 4H). ¹³C NMR (100 MH_z, CDCl₃): δ (ppm)= 162.64, 158.57, 151.46, 143.98, 143.47, 141.42, 140.87, 140.28, 129.05, 126.87, 126.17, 126.01, 125.10, 123.72, 121.65, 121.42, 120.10,

119.97, 115.44, 114.86, 68.21, 55.31, 40.25, 37.03, 29.50, 28.98, 25.49, 23.64. EI-MS: $m/z= 933.71[M]^+$. Anal. Calcd. for C₆₅H₆₀N₂O₄: C, 83.66; H, 6.48; N, 3.00. Found: C, 83.70; H, 6.40; N, 3.02.

Insert Scheme 1

Synthesis of **2c**: A mixture of 2,7-dibromofluorene (2.6 mmol, 0.85 g), **2b** (6.6 mmol), K₂CO₃ (19.7 mmol), Pd(PPh₃)₄ (0.03 mmol) were stirred in THF (50 ml) and H₂O (5 ml) for two days under an argon atmosphere at 80°C. After completion of present reaction, the mixtures were extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 56.7%. ¹H NMR (400 MH_z, CDCl₃): δ (ppm)= 7.91 (t, J= 8 Hz, 4H), 7.80-7.63 (m, 10H), 7.35 (s, 6H), 4.10 (s, 2H), 3.28 (t, J= 8 Hz, 8H), 2.04 (s, 8H), 1.67 (t, J= 6 Hz, 8H), 1.21-1.10 (m, 16H), 0.68 (s, 8H). ¹³C NMR (100 MH_z, CDCl₃): δ (ppm)= 150.99, 150.50, 144.17, 140.74, 140.51, 140.27, 140.14, 127.08, 126.90, 126.08, 123.76, 122.73, 121.21, 120.20, 119.74, 55.00, 42.24, 37.10, 33.94, 32.58, 29.10, 27.70, 23.51. Anal. Calcd. for C₆₃H₇₀Br₄: C, 65.98; H, 6.15. Found: C, 65.91; H, 6.23.

Synthesis of **2d**: A mixture of compounds **2c** (1.5 mmol, 1.7 g), N-(4-hydroxyphenyl)formamide (8.9 mmol), K_2CO_3 (35.6 mmol) were stirred in DMF (50 ml) for overnight under an argon atmosphere at 60°C. After completion of present reaction, DMF was removed from reaction system by vacuum distillation. the residual mixtures were extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected orange red solid product in a yield of 51.8%. ¹H NMR (400 MH_Z, CDCl₃): δ (ppm)= 8.46-8.26 (m, 3H), 7.86 (d, J= 4 Hz, 3H), 7.79-7.60 (m, 12H), 7.37-7.30 (m, 14H), 6.94 (d, J= 8 Hz, 4H), 6.79-6.75 (m, 8H), 4.02 (s, 2H), 3.79 (t, J= 6 Hz, 8H), 2.05 (d, J= 8 Hz, 8H), 1.57 (s, 8H), 1.26-1.14 (m, 16H), 0.71 (s, 8H). ¹³C NMR (100 MH_Z, CDCl₃): δ (ppm)= 163.10, 159.02, 156.94, 156.04, 151.14, 150.62, 144.17, 140.69, 140.30, 140.13, 129.69, 129.21, 127.05, 126.86, 126.01, 123.72, 122.78, 121.63, 121.39, 120.19, 120.01, 119.75, 115.29, 114.64, 68.09, 68.00, 55.04, 40.26, 29.57, 28.95, 25.52, 23.64. Anal. Calcd. for C₉₁H₉₄N₄O₈: C, 79.68; H, 6.91; N, 4.08. Found: C, 79.62; H, 6.86; N, 4.15.

Insert Scheme 2

2.2.2 Synthesis of luminogens 3d and 4d with fluorenone unit

Synthesis of **3d:** A mixture of **3c** (1.9 mmol, 0.5 g), **3b** (2.4 mmol), K_2CO_3 (14.5 mmol), $Pd(PPh_3)_4$ (0.02 mmol) were stirred in THF (50 ml) and H_2O (5 ml) for two days under an argon atmosphere at 80°C. After completion of present reaction, the mixtures

were extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 61.2%. ¹H NMR (400 MH_Z, CDCl₃): δ (ppm)= 7.99 (s, 1H), 7.80-7.68 (m, 4H), 7.61-7.51 (m, 5H), 7.37-7.29 (m, 4H), 2.02 (t, J= 8 Hz, 4H), 1.13-1.05 (m, 12H), 0.76 (t, J= 6 Hz, 6H), 0.65 (d, J= 8 Hz, 4H). ¹³C NMR (100 MH_Z, CDCl₃): δ (ppm)= 194.00, 151.54, 150.93, 144.30, 142.89, 142.65, 141.05, 140.44, 138.44, 134.79, 134.38, 133.14, 128.89, 127.22, 126.78, 125.55, 124.36, 122.85, 120.91, 120.63, 120.32, 120.01, 119.79, 55.19, 40.39, 31.46, 29.66, 23.73, 22.55, 13.98. EI-MS: m/z= 512.53[M]⁺. Anal. Calcd. for C₃₈H₄₀O: C, 89.02; H, 7.86. Found: C, 89.08; H, 7.81.

Synthesis of **4d**: A mixture of **4c** (4.6 mmol, 1.56 g), **3b** (11.5 mmol), K₂CO₃ (34.6 mmol), Pd(PPh₃)₄ (0.05 mmol) were stirred in THF (50 ml) and H₂O (5 ml) for two days under an argon atmosphere at 80°C. After completion of present reaction, the mixtures were extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 64.0%. ¹H NMR (400 MH_Z, CDCl₃): δ (ppm)= 8.03 (s, 2H), 7.83-7.72 (m, 6H), 7.63-7.60 (m, 6H), 7.38-7.32 (m, 6H), 2.03 (t, J= 8 Hz, 8H), 1.14-0.63 (m, 44H). ¹³C NMR (100 MH_Z, CDCl₃): δ (ppm)= 194.02, 151.54, 150.90, 142.79, 142.45, 141.05, 140.41, 138.37, 135.11, 133.22, 127.22, 126.77, 125.55, 122.88, 122.82, 120.83, 120.68,

120.04, 119.80, 55.17, 40.39, 31.44, 29.65, 23.74, 22.54, 13.97. EI-MS: m/z= 845.24[M]⁺. Anal. Calcd. for C₆₃H₇₂O: C, 89.52; H, 8.59. Found: C, 89.59; H, 8.55.

Insert Scheme 3

3. Results and discussion

3.1 Synthesis

The target compounds 1d and 2d with formamide units were obtained by reacting *N*-(4-hydroxyphenyl)formamide with intermediates 1c and 2c. Luminogens 1d and 2d were prepared according to the synthetic routes presented in Schemes 1 and 2, respectively. The target compounds 3d and 4d, containing a fluorenone unit, were obtained by reacting intermediate 3b with intermediates 3c and 4c, respectively. Luminogens 3d and 4d were prepared according to the synthetic route presented in Scheme 3. All compounds were synthesized with high percentage yields

3.2 Fluorescence change behavior due to aggregate formation

To observe the novel aggregation-induced characteristics of luminogens 1d and 2d, the luminescence and UV/Vis spectra (Figs. S1 and S2) were recorded in DMF-H₂O mixtures with differing water fraction content (f_w). In pure DMF, the luminogen 1d absorption spectrum revealed a peak at 352 nm. This absorption blue-shifted at first, then red-shifted as the f_w values were increased. Luminogen 1d exhibited two emission bands with maxima (λ_{max}) at 375 nm, 460 nm (shoulder peak) and 480 nm and emitted a deep blue-green fluorescence under UV irradiation due to the existence of three fluorene units, as is shown in Fig. 1. Interestingly, when f_w reached 50%, two new emission bands were observed with λ_{max} at 401 nm (shoulder peak), 424 nm, 447 nm (shoulder peak) and 517 nm, while the luminescence color changed from blue-green to faint yellow-green. Moreover, when f_w exceeded 50%, the addition of water to the DMF solution resulted in an increase in intensity of the two new emission bands, producing a strong yellow-green emission. This is because as 1d is insoluble in water, an increase in the water content in the mixed solvent resulted in transformation of the luminogen from a dissolved or well dispersed state in pure DMF to aggregated particles in the mixtures with high f_w . The two new emission bands were thus caused by aggregation and luminogen 1d exhibited a uncommon AIE phenomenon involving a fluorescence color changing due to aggregate formation. The change of emission color was so distinct that it could be readily distinguished by the naked eye under 365 nm UV illumination. The interesting aggregate behavior of luminogen 1d might be related to the presence of the formamide units.

Insert Figure 1

Luminogen 2d has a similar structure to 1d, containing two formamide units and three fluorene units. Luminogen 2d in pure DMF solution showed a similar absorption spectrum to 1d, with the absorption maximum occurring at 352 nm (Fig. S2). However, in contrast to luminogen 1d, the absorption peak red-shifted at first, then blue-shifted when f_w was increased. As is illustrated in Fig. 2, in pure DMF two emission bands were observed with λ_{max} at 376 nm, 457 nm (shoulder peak) and 477 nm, corresponding to blue-green emission under 365 nm UV light. When f_w reached 40 %, two new emission bands were observed with λ_{max} at 406 nm and 554 nm, and the emission color changed from blue-green to light yellow. The luminescence intensity of the two new emission bands significantly increased as f_w was increased to 50 % and the emission became a stronger yellow. However, the changes to the luminescence spectra with further increases of water content were negligible. Therefore, luminogen 2d also exhibits outstanding fluorescence change behavior due to aggregate formation. It was speculated that the formamide units played a key role in the novel aggregate characteristics of luminogens 1d and 2d.

Insert Figure 2

3.3 AIEE characteristics

The AIEE properties of luminogens 3d and 4d were also investigated. The UV/Vis

absorption spectra in different DMF-H₂O mixtures with differing f_w are shown in Figs. S3 and S4. Both compounds show similar absorption spectra with absorption maxima at approximately 306 nm and 350 nm. Luminogens 3d and 4d belong to Donor-Acceptor (D-A) molecules. Due to an intramolecular charge transfer (ICT) transition from the electron-donating fluorene units to the electron-accepting fluorenone unit, luminogen 3d in pure DMF (2.0×10^{-5} mol L⁻¹) exhibited very weak yellow fluorescence with λ_{max} at 552 nm. The yellow emission disappear as f_w was increased to 10% due to twisted intramolecular charge transfer (TICT). Which commonly takes place in D-A molecules, decreasing the emission efficiency and red-shifting the emission wavelength. However, When f_w exceeded 40%, the emission intensity increased significantly and the emission maximum of luminogen 3d shifted to 536 nm. Furthermore, the fluorescence changed from weak yellow to strong yellow, which is typical of AIEE active species (Fig. 3).[26] Since the dissolution capacity of the mixture with high water content became quite poor, the luminogen 3d must have aggregated, and the AIEE phenomenon may be associated with the presence of fluorenone.

Insert Figure 3

Luminogen **4d** contains two fluorene units and one fluorenone unit. Owing to the remarkable ICT character, luminogen **4d** exhibited relatively strong yellow emission in

pure THF with a λ_{max} at 542 nm. However, the luminescence intensity of the emission band largely decreased when f_w was increased to 10 %, which is attributed to TICT as well. Excitingly, the presence of the fluorenone moiety induced AIEE in luminogen **4d**. As shown in Fig. 4, when f_w exceeded 50 %, the luminescence intensity again increased. Hence, we can adjust turning on or off this yellow fluorescence simply *via* control of the water fraction. Luminogen **4d** also exhibited some AIEE behavior, but it is weaker than in the case of **3b** (Fig. 4).

Insert Figure 4

3.4 Thin-film and solid state fluorescence behavior

Thin-film and solid state fluorescence spectra were used to further study the aggregation characteristics of luminogens **1d**, **2d**, **3d** and **4d**. As shown in Fig. 5, the thin-film fluorescence spectra of luminogens **1d** and **2d** showed two emission bands at around 423 nm and 530 nm, with the λ_{max} at around 530 nm. The thin-film fluorescence spectra of luminogens **3d** and **4d** showed single emission bands with λ_{max} at 549 nm and 572 nm, respectively. Consistent with the luminescence of all luminogens in DMF or THF-H₂O mixtures with high water content, thin-film of luminogen **1d** emitted yellow-green fluorescence, and thin-films of other luminogens emitted strong yellow fluorescence under illumination with a UV lamp (365 nm). In addition, their solid state

fluorescence spectra were similar to the thin-film spectra. The quantum yield of solid **1d** was 8.5 %, and the average lifetime was 6.92 ns. The quantum yield of solid **2d** was 6.4 %, which was lower than solid **1d**. The average lifetime was 4.47 ns, which was also lower than solid **1d**. Time-resolved luminescence of solids **1d** and **2d** are presented in Figs. S5 and S6. The luminescence quantum yield of solid **3d** was 15.8 %, and the average lifetime was 5.47 ns. The quantum yield of solid **4d** was 20.7 %, and the average lifetime was 9.70 ns. Therefore, the solid-state emission quantum yield of **4d** was the highest of all studied luminogens. The time-resolved luminescence of solids **3d** and **4d** are shown in Figs. S7 and S8.

Insert Figure 5

4. Conclusions

In this work, we report a series of novel fluorescent molecules based on fluorene. Through investigation of their aggregation properties it was discovered that luminogens **1d** and **2d**, containing formamide units, exhibit obvious fluorescence change due to aggregate formation, an novel and interesting aggregation-induced phenomenon. The occurrence of aggregate fluorescence change is most likely related to the presence of the formamide units. Luminogen **3d**, containing a fluorenone unit, exhibited excellent AIEE characteristics, which is very likely associated with the presence of the fluorenone unit.

Although luminogen **4d** demonstrates weaker AIEE behavior than **3d**, **4d** exhibits superior solid-state emission quantum yield. Additionally, in thin-films and in the solid state, these luminogens showed intense yellow-green or yellow emission. Future studies will focus on finding other fluorene-based luminogens with novel AIE or AIEE characteristics.

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Supporting Information Available

UV–Vis absorption spectra of luminogens 1d, 2d, 3d and 4d in DMF or THF-H₂O mixtures with different water contents. Time-resolved luminescence of solids 1d, 2d, 3d and 4d.

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Scheme 1. Synthesis of luminogen 1d with formamide units



Scheme 2. Synthesis of luminogen 2d with formamide units



Scheme 3. Synthesis of luminogens 3d and 4d with fluorenone unit



Figure 1. (a) PL spectra of the dilute solutions of luminogen **1d** $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ in DMF-H₂O mixtures with different volume fractions of water (0%, 30% and 50%). (b) PL spectra of the dilute solutions of luminogen **1d** $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ in DMF-H₂O mixtures with different volume fractions of water (50%-90%). Excitation wavelength= 330 nm. (c) The fluorescence images of luminogen **1d** (concentration: $2.0 \times 10^{-5} \text{ mol L}^{-1}$) in different DMF-H₂O mixtures with different water fractions (*f*_w) taken under 365 nm UV illumination.



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Figure 5. (a) Thin-film fluorescence spectra of luminogens **1d**, **2d**, **3d** and **4d** (excitation wavelength= 380 nm). (b) solid fluorescence spectra of luminogens **1d**, **2d**, **3d** and **4d** (excitation wavelength= 380 nm).

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Fluorene-based novel highly emissive fluorescent molecules with aggregate fluorescence change or aggregation-induced emission enhancement characteristics

Zhao Chen, Jinhua Liang, Xie Han, Jun Yin*, Guang-Ao Yu, Sheng Hua Liu*

Synopsis

Fluorene-based luminogens with formamide units exhibited fluorescence change of aggregate formation, which is a uncommon and novel aggregation-induced emission phenomenon. Fluorene-based luminogens with fluorenone unit exhibited AIEE characteristics.



aggregate fluorescence change



Electronic Supplementary Information (ESI)

Fluorene-based novel highly emissive fluorescent molecules with aggregate fluorescence change or aggregation-induced emission enhancement characteristics

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Figure S1. UV–Vis absorption spectra of 1d in DMF-water mixtures with different volume fractions of water (0-90%).

Figure S2. UV–Vis absorption spectra of 2d in DMF-water mixtures with different volume fractions of water (0-90%).

Figure **S3**. UV–Vis absorption spectra of **3d** in DMF-water mixtures with different volume fractions of water (0-90%).

Figure S4. UV–Vis absorption spectra of 4d in THF-water mixtures with different volume fractions of water (0-90%).

Figure S5. Time-resolved luminescence of solid 1d.

Figure S6. Time-resolved luminescence of solid 2d.

Figure S7. Time-resolved luminescence of solid 3d.

Figure S8. Time-resolved luminescence of solid 4d.

Figure **S9.** Fluorescence decays τ , photoluminescence quantum yields Φ of solids **1d**,

2d, 3d and 4d.



Figure S1. UV-Vis absorption spectra of 1d in DMF-water mixtures with different

volume fractions of water (0-90%).



Figure S2. UV–Vis absorption spectra of 2d in DMF-water mixtures with different volume fractions of water (0-90%).



Figure S3. UV–Vis absorption spectra of 3d in DMF-water mixtures with different volume fractions of water (0-90%).



Figure S4. UV–Vis absorption spectra of 4d in THF-water mixtures with different volume fractions of water (0-90%).



Figure S5. Time-resolved luminescence of solid 1d. Excitation wavelength:

375nm.



Figure **S6**. Time-resolved luminescence of solid **2d**. Excitation wavelength: 375nm.



Figure S7. Time-resolved luminescence of solid 3d. Excitation wavelength:

375nm.



Figure **S8**. Time-resolved luminescence of solid **4d**. Excitation wavelength: 375nm.

Solids	τ ₁ (ns)	A ₁ (%)	τ ₂ (ns)	A ₂ (%)	τ ₃ (ns)	A ₃ (%)	$< \tau >$ $(ns)^{a}$	Φ ^b (%)
1d	0.38	42.8	4.61	18.6	15.30	38.5	6.92	8.5
2d	2.89	52.1	6.20	47.9			4.47	6.4
3d	4.70	96.1	24.27	3.9			5.47	15.8
4d	7.55	53.4	12.14	46.6		7	9.70	20.7

Figure **S9.** Fluorescence decays τ , photoluminescence quantum yields Φ of solids **1d**,

2d, 3d and 4d.

^a The lifetime $\langle \tau \rangle$ was calculated according to the equation: $\langle \tau \rangle = (A_1\tau_1+A_2\tau_2+A_3\tau_3)/(A_1+A_2+A_3)$; A: the fractions; τ : lifetimes. ^b Φ : photoluminescence quantum yields.