



# 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\*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

## ARTICLE INFO

### Article history:

Received 22 April 2014

Received in revised form

11 June 2014

Accepted 19 June 2014

Available online 26 June 2014

### Keywords:

Formamide

Fluorenone

Fluorene

Aggregate fluorescence change

AIEE

Highly fluorescent

## 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.

© 2014 Elsevier Ltd. All rights reserved.

## 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 literature. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). <sup>1</sup>H NMR spectra are reported as followed: chemical shift in ppm ( $\delta$ ) relative to the chemical

\* Corresponding authors. Tel./fax: +86 27 67867725.

E-mail addresses: [yinj@mail.ccnu.edu.cn](mailto:yinj@mail.ccnu.edu.cn) (J. Yin), [chshliu@mail.ccnu.edu.cn](mailto:chshliu@mail.ccnu.edu.cn) (S.H. Liu).

shift of TMS at 0.00 ppm, integration, multiplicities (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet), and coupling constant (Hz). <sup>13</sup>C NMR chemical shifts reported in ppm ( $\delta$ ) relative to the central line of triplet for CDCl<sub>3</sub> at 77 ppm. EI-MS was obtained using Thermo scientific DSQII. 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 (GF<sub>254</sub>) 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<sub>2</sub>CO<sub>3</sub> (28.8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 mmol) were stirred in THF (50 ml) and H<sub>2</sub>O (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 (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 60.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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]<sup>+</sup>. Anal. Calcd. for C<sub>51</sub>H<sub>48</sub>Br<sub>2</sub>: 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), K<sub>2</sub>CO<sub>3</sub> (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 (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 58.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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]<sup>+</sup>. Anal. Calcd. for C<sub>65</sub>H<sub>60</sub>N<sub>2</sub>O<sub>4</sub>: C, 83.66; H, 6.48; N, 3.00. Found: C, 83.70; H, 6.40; N, 3.02.

**Synthesis of 2c:** A mixture of 2,7-dibromofluorene (2.6 mmol, 0.85 g), **2b** (6.6 mmol), K<sub>2</sub>CO<sub>3</sub> (19.7 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03 mmol) were stirred in THF (50 ml) and H<sub>2</sub>O (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 (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 56.7%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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 C<sub>63</sub>H<sub>70</sub>Br<sub>4</sub>: 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<sub>2</sub>CO<sub>3</sub> (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 (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected orange red solid product in a yield of 51.8%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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 C<sub>91</sub>H<sub>94</sub>N<sub>4</sub>O<sub>8</sub>: C, 79.68; H, 6.91; N, 4.08. Found: C, 79.62; H, 6.86; N, 4.15.

### 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<sub>2</sub>CO<sub>3</sub> (14.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 mmol) were stirred in THF (50 ml) and H<sub>2</sub>O (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 (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 61.2%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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]<sup>+</sup>. Anal. Calcd. for C<sub>38</sub>H<sub>40</sub>O: 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), K<sub>2</sub>CO<sub>3</sub> (34.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) were stirred in THF (50 ml) and H<sub>2</sub>O (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 (Na<sub>2</sub>SO<sub>4</sub>), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected yellow solid product in a yield of 64.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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]<sup>+</sup>. Anal. Calcd. for C<sub>63</sub>H<sub>72</sub>O: C, 89.52; H, 8.59. Found: C, 89.59; H, 8.55.

## 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

Download English Version:

<https://daneshyari.com/en/article/175931>

Download Persian Version:

<https://daneshyari.com/article/175931>

[Daneshyari.com](https://daneshyari.com)