Supporting Information

A New Red Fluorophore with Aggregation Enhanced Emission by an Unexpected “One-step” Protocol

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Synthesis of compound BT-CHO

Scheme S1. The synthetic route for BT-CHO.

Synthesis of compound A1-1

Compound A1-1 were synthesized according to previously reported method.[1]

Synthesis of compound A1-2

A 100 mL of Schlenk flask containing A1-1 (700 mg, 1.02 mmol) was added DMF (15 mL). NBS (670 mg, 3.76 mmol dissolved in 15 mL of DMF) was dropped slowed and the solution was stirred at room temperature for overnight. After the reaction was complete, the reaction mixture was poured into water and then extracted with CH$_2$Cl$_2$. The organic extract was dried over anhydrous Na$_2$SO$_4$ and was further purified by column chromatography using a dichloromethane/hexanes (2:3) mixture as the eluent. Compound A1-2 was isolated as a bright red powder in 99% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.77 (s, 1H), 8.29 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 9.0$ Hz, 2H), 7.85 (d, $J = 7.2$ Hz, 1H), 7.42 (d, $J = 12.0$ Hz, 4H), 7.19 (d, $J = 6.0$ Hz, 2H), 7.05 (d, $J = 8.4$ Hz, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 188.80, 153.99, 153.83, 148.33, 145.87, 139.55, 132.69, 132.44, 130.75, 130.54, 126.49, 126.11, 125.98, 122.80, 116.80.

Synthesis of compound BT-CHO

Compound A1-2 (800 mg, 1.42 mmol), (4- (tert-butyl) phenyl) boronic acid (755 mg, 4.24 mmol), Pd(PPh$_3$)$_4$ (97 mg, 0.084 mmol) were loaded into 100 ml Schlenk flask. A mixture of aqueous solution of K$_2$CO$_3$ (7.04 ml, 2 M) and THF (35 ml) were added to flask and stirred at reflux (65 °C) for overnight under argon ambience. After the reaction was complete, the reaction mixture was poured into water and then extracted with CH$_2$Cl$_2$, and evaporated under reduced pressure. The remaining crude product was purified by column chromatography using a dichloromethane/hexanes (2:3) mixture as the eluent. Compound BT-CHO was isolated as a red powder in 84% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.77 (s, 1H), 8.28 (d, $J = 7.8$ Hz, 1H), 7.98
(d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 8H), 7.47 (d, $J = 8.4$ Hz, 4H), 7.29 (t, $J = 8.4$ Hz, 6H), 1.37 (s, 16H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 188.82, 154.07, 153.90, 150.15, 149.19, 145.96, 139.91, 137.63, 136.63, 132.60, 130.60, 129.51, 127.95, 126.43, 125.79, 125.75, 125.43, 122.37, 34.53, 31.38.

**Parallel experiments of A1 with different substrates**

Scheme S2. Three parallel experiments of A1 with different substrates.

**Synthesis of compound A2**

Scheme S3. The synthetic route for A2.

**Synthesis of compound A2-1**

Compound A2-1 were synthesized according to previous reported method.[2]

**Synthesis of compound A2-2**

Compound A2-1 (500 mg, 0.96 mmol), (4-(tert-butyl) phenyl) boronic acid (514 mg, 2.88 mmol), Pd(PPh$_3$)$_4$ (66.7 mg, 0.058 mmol) were loaded into 100 ml Schlenk flask. A mixture of aqueous solution of K$_2$CO$_3$ (4.80 ml, 2 M) and THF (30 ml) were added to flask and stirred at reflux (65 °C) for overnight under argon ambience. After the reaction was complete, the reaction mixture was
poured into water and then extracted with CH$_2$Cl$_2$, and evaporated under reduced pressure. The remaining crude product was purified by column chromatography using a dichloromethane/hexanes (3:2) mixture as the eluent. Compound A2-2 was isolated as an orange powder in 95% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.91 (s, 1H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.52 (dd, $J = 8.4, 4.2$ Hz, 8H), 7.47 (d, $J = 8.4$ Hz, 4H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.16 (d, $J = 9.0$ Hz, 2H), 4.42 (m, $J = 7.8$ Hz, 2H), 4.38 (m, $J = 8.4$ Hz, 2H), 1.36 (s, 18H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 179.36, 150.08, 148.18, 145.98, 137.59, 137.03, 136.37, 132.48, 128.00, 127.92, 127.88, 126.40, 125.74, 125.11, 122.74, 114.92, 65.15, 64.54, 34.53, 31.38.

**Synthesis of compound A2**

To a solution of A2-1 (300 mg, 0.45 mmol) and malononitrile (90 mg, 1.36 mmol) in 15 mL of toluene was added 0.20 mL of triethylamine. After being stirred at 90 °C for 1 h under argon atmosphere, the reaction mixture was poured into water and then extracted with CH$_2$Cl$_2$. The organic extract was dried over anhydrous Na$_2$SO$_4$ and was further purified by column chromatography using a dichloromethane/hexanes (1:1) mixture as the eluent. Compound A2 was isolated as a dark powder in 53% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.83 (s, 1H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.53 (dd, $J = 8.4, 1.8$ Hz, 8H), 7.46 (d, $J = 8.4$ Hz, 4H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.13 (d, $J = 8.4$ Hz, 2H), 4.42 (d, $J = 3.0$ Hz, 2H), 4.36 (s, 2H), 1.36 (s, 24H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 150.22, 149.45, 149.03, 145.60, 144.76, 144.76, 137.48, 136.95, 136.88, 132.07, 128.40, 127.98, 126.44, 125.77, 125.49, 124.13, 121.96, 115.47, 114.54, 109.65, 65.60, 64.48, 34.55, 31.38. HRMS (APCI): calcd for C$_{48}$H$_{44}$N$_3$O$_2$S [M + H]$^+$: 726.3149, found 726.3155.
**HPLC analysis**

Fig. S1 HPLC profile showing the reactions of A1 with different substrates: (i) A1 alone, (ii) A1H2 alone, (iii) A1+toluene, (iv) A1+toluene+malononitrile, (v) A1+toluene+triethylamine.

**TLC plate**

Fig. S2 a, b and c correspond to the reactions using piperidine, diethylamine and hexylamine as base, respectively; d represents the pure A1H2.
**Fig. S3** a and c represent the pure A1 and A1H2, respectively. b is the reaction of A1 with amantadine.

**Fig. S4** a represents the pure A2. b is the reaction using the hexylamine as the base.
PL spectra of A1 and A1H2 in solid state

Fig. S5 PL spectra of A1 (purple line) and A1H2 (red line) in solid state (excitation wavelength for A1: 550 nm, excitation wavelength for A1H2: 385 nm).

Fig. S6 Normalized Absorption spectra of A1H2-NPs at different water fractions aged for (a) 1 day and (b) 7 days.

Table S1. The maximum absorption wavelength of A1H2-NPs at different water fractions after aging for 1 day and 7 days.

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**Table S2. Data calculated at the B3LYP/6-31G (d)* level**

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<th>Sample</th>
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<th>Orb: Compos (%)</th>
<th>( \lambda_{calc\ em}^b/\text{nm} )</th>
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<td>A1H2</td>
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<td>A1</td>
<td>0.5136</td>
<td>HOMO→LUMO:99.2</td>
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*Oscillator strength. b Emission maximum (\( \lambda_{em} \)) derived from theoretical DFT calculations.

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**Influence of pH on fluorescent intensity of A1H2-NPs**

![Graph showing fluorescence intensity of A1H2-NPs at 616 nm in PBS (pH 7.4) and other buffer solutions with pH ranging from 2 to 9, compared with that in deionized water.]

**Fig. S7** Fluorescence intensity of the A1H2-NPs at 616 nm in PBS (pH 7.4), and other buffer solutions with pH ranging from 2 to 9, compared with that in deionized water.
$^1$H-NMR, $^{13}$C-NMR, and MS spectra

Fig. S8 $^1$H NMR spectrum of A1-2 in CDCl$_3$

Fig. S9 $^1$H NMR spectrum of BT-CHO in CDCl$_3$
Fig. S10 $^1$H NMR spectrum of A1 in CDCl$_3$

Fig. S11 $^1$H NMR spectrum of A1H2 in CDCl$_3$
Fig. S12 $^1$H NMR spectrum of A2-2 in CDCl$_3$

Fig. S13 $^1$H NMR spectrum of A2 in CDCl$_3$
Fig. S14 $^{13}$C NMR spectrum of A1-2 in CDCl$_3$

Fig. S15 $^{13}$C NMR spectrum of BT-CHO in CDCl$_3$
Fig. S16 $^{13}$C NMR spectrum of A1 in CDCl$_3$

Fig. S17 $^{13}$C NMR spectrum of A1H2 in CDCl$_3$
Fig. S18 $^{13}$C NMR spectrum of A2-2 in CDCl$_3$

Fig. S19 $^{13}$C NMR spectrum of A2 in CDCl$_3$
Fig. S20 MALDI-TOF-MS of A1
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<th>Measured m/z</th>
<th>Calc m/z</th>
<th>Diff (ppm)</th>
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<td>A1H2</td>
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<td>C48 H44 N5 S</td>
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**Fig. S21** HRMS of A1H2

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<th>Measured m/z</th>
<th>Calc m/z</th>
<th>Diff (ppm)</th>
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<tbody>
<tr>
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<td>C48 H43 N3 O2 S</td>
<td>C48 H44 N3 O2 S</td>
<td>726.3155</td>
<td>726.3149</td>
<td>0.97</td>
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**Fig. S22** HRMS of A2
References
