

## Selective synthesis and aggregation-induced emissions of thienyl substituted cyclobutene derivatives

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## Experimental Section

### *Materials and Instrumentations*

All reagents were used as received from commercial resources unless otherwise specified.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker ADVANCE 400 NMR Spectrometer.  $^1\text{H}$  NMR spectra were referenced to  $\text{CDCl}_3$  (7.26 ppm) and  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CDCl}_3$  solvent (77.36 ppm). High resolution mass spectra (HRMS) were determined on IonSpec 4.7 Tesla Fourier Transform Mass Spectrometer. UV-vis absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Absolute quantum yield measurement (LabSphere®, FluoroMax-4, HORIBA Jobin Yvon, PLQY software package) was used for powder sample. In this experimental setup, it is possible to measure the Photoluminescence Quantum Yields (PLQY) via using the integrating sphere in combination with a commercial fluorimeter. Emission spectrum including the scattering region of excitation light were measured for both blank and test samples, and these spectra were corrected with instrumental factors to calculate the quantum yield. X-ray diffraction intensity data were collected at 173 K on a Saturn724 + CCD diffractometer with graphite monochromated Mo  $\text{K}\alpha$  radiation. And the structure and refinement were carried out using the Crystal Clear (Rigaku Inc., 2008).

### *Synthesis of compounds 4a and 4b*

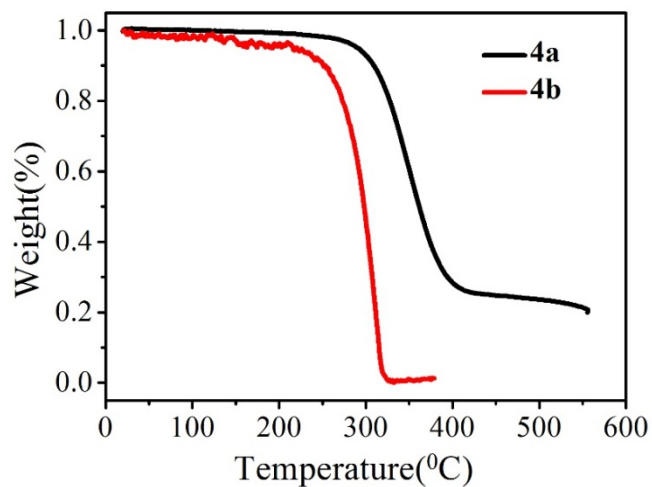
**Compound 3a:** *n*-BuLi (1.6 M in THF, 6.9 mL, 1.1 equiv.) was added to a solution of 2-ethynylthiophene (10 mmol, 1.0 equiv.) in dry THF at  $-78\text{ }^\circ\text{C}$  under the atmosphere of argon. After the resulting solution was stirred for 40 min at  $-78\text{ }^\circ\text{C}$ , a solution of benzophenone (10 mmol, 1 equiv.) in dry THF was added slowly. After 15 min, the resulting solution was slowly warmed up to room temperature and stirred for another 10 h. Finally, the resulting mixture was quenched by saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 30$  mL). The combined organic layers were washed with brine (20 mL), dried with  $\text{MgSO}_4$ , concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane: $\text{CH}_2\text{Cl}_2 = 1:2$ ) to give brown solids of the title compound (**3a**). (7.5 mmol, yield: 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.69 (d, 4H), 7.38 (t, 4H), 7.32 (d, 4H), 7.01 (s, 1H), 2.97 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 145.2, 133.1, 128.9, 128.6, 128.3, 128.1, 127.9, 127.7, 127.7, 127.6, 126.6, 122.8, 95.90, 81.1, 75.5. HR-MS (EI) for  $\text{C}_{19}\text{H}_{14}\text{OS}$ : Calculated: 290.0765; Found: 290.0674.

**Compound 4a:** Propargyl alcohol **3a** (2.9 g, 10 mmol, 10 equiv) was dissolved in dry toluene (30 mL) with moderate heating, then the solution was cooled and stirred at  $0\text{ }^\circ\text{C}$  under a nitrogen atmosphere. Ethyldiisopropylamine (14 mmol, 14 equiv) and acetic anhydride (11.7 mmol, 11.7 equiv) were added drop wise to the solution successively to keep the temperature of the reaction below  $10\text{ }^\circ\text{C}$ . After the addition, the solution was stirred at  $0\text{ }^\circ\text{C}$  for 15 min, then warmed up to room temperature for 15 min and then heated to  $110\text{ }^\circ\text{C}$  for 4 h. Finally, the reaction was cooled, diluted with ethyl acetate (100 mL) and washed with 2.0 M HCl. The organic layers were collected, dried over  $\text{MgSO}_4$ , concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane) to give yellow solids of the title compound (**4a**) (820 mg, 1 mmol. yield: 30%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (d, 6.8 Hz, 6H), 6.95 (d, 2H), 6.76 (dt, 6.8 Hz, 3H), 6.60 (s, 1H), 6.01 (s, 1H), 6.01 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 148.3, 141.6, 141.4, 139.7, 133.6, 131.9, 131.5, 130.7, 128.0, 127.6, 127.5, 127.3, 127.1, 126.9, 126.7. HR-MS (EI) for  $\text{C}_{38}\text{H}_{26}\text{S}_2$ : Calculated: 546.1476; Found: 546.1260.”

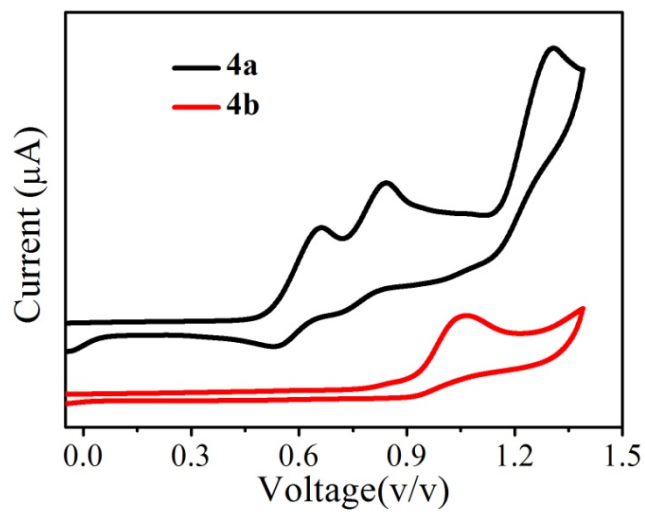
**Compound 3b:** *n*-BuLi (1.6 M in THF, 6.9 mL, 1.1 equiv.) was added to a solution of 2-ethynylthiophene (10 mmol, 1.0 equiv.) in dry THF at  $-78\text{ }^\circ\text{C}$  under the atmosphere of argon. After the resulting solution

was stirred for 40 min at -78 °C, a solution of (perfluorophenyl) (phenyl) methanone (10 mmol, 1 equiv.) in dry THF was added slowly. After 15 min, the resulting solution was slowly warmed up to room temperature and stirred for another 10 h. Finally, the resulting mixture was quenched by saturated aqueous NH<sub>4</sub>Cl (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were washed with brine (20 mL), dried with MgSO<sub>4</sub>, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1:2) to give brown solids of the title compound (**3b**). (7mmol, yield: 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.71 (d, 2H), 7.44 – 7.37 (m, 3H), 7.35 – 7.29 (m, 2H), 7.02 (d 1H), 3.30 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 142.3, 133.2, 129.0, 128.7, 128.4, 127.2, 125.7, 121.5, 91.9, 81.5, 72.6. HR-MS (EI) for C<sub>19</sub>H<sub>9</sub>OSF<sub>5</sub>: Calculated: 380.0294; Found: 380.0274.

**Compound 4b:** compound **3b** (3.8 g, 10 mmol, 10 equiv) was dissolved in dry toluene (30 mL) with moderate heating, then the solution was cooled and stirred at 0 °C under a nitrogen atmosphere. Ethyldiisopropylamine (14 mmol, 14 equiv) and acetic anhydride (11.7 mmol, 11.7 equiv) were added drop wise to the solution successively to keep the temperature of the reaction below 10 °C. After the addition, the solution was stirred at 0 °C for 15 min, then warmed up to room temperature for 15 min and then heated to 110 °C for 12 h. Finally, the reaction was cooled, diluted with ethyl acetate (100 mL) and washed with 2.0 M HCl. The organic layers were collected, dried over MgSO<sub>4</sub>, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane) to give yellow solids of the title compound (**4b**) (1.12 g, 1.5 mmol. yield: 31%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.32 (d, 2H), 7.31 (d, 2H), 7.24 (d, 2H), 7.17 (d, 2H), 6.89 (d, 2H), 6.73 (m, 2H), 6.64 (d, 2H), 5.93 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 150.7, 147.9, 139.2, 138.7, 131.9, 131.2, 130.6, 130.1, 129.7, 129.4, 128.8-127.9, 127.8, 127.2, and 127.0. HR-MS (EI) for C<sub>38</sub>H<sub>16</sub>S<sub>2</sub>F<sub>10</sub>: Calculated: 726.0534; Found: 726.0421.



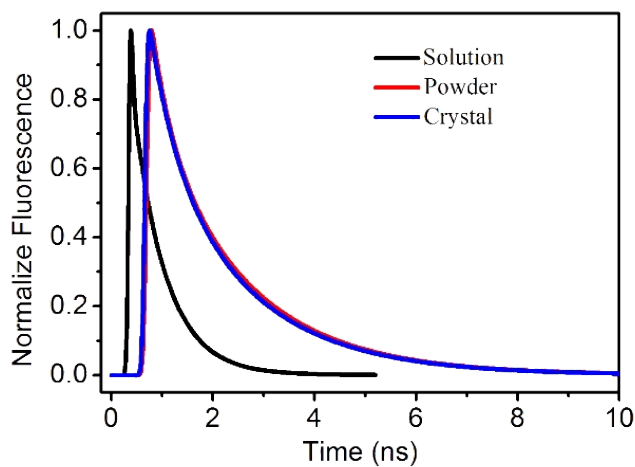
**Fig. S1** TGA curves of compounds **4a** and **4b**, measured with a heating rate of 10 °C /min in nitrogen.



**Fig. S2** Oxidative cyclic voltammogram of **4a** and **4b** in  $\text{CH}_2\text{Cl}_2$  versus  $\text{Fc}/\text{Fc}^+$ . Scan rate:  $0.1 \text{ V s}^{-1}$  (electrolyte, 0.1 M TBAPF<sub>6</sub>).

**Table S1.** TGA, HOMO-LUMO levels and energy gaps of compound **4a**, **4b**.

Compound	TGA(°C)	HOMO(eV)	LUMO(eV)	Gap(eV)
<b>4a</b>	298	-5.31	-2.55	2.76
<b>4b</b>	276	-5.67	-2.91	2.76



**Fig. S3** Lifetime of compounds **4a**.

Solution: lifetime-1= 0.63494 ns $\pm$ 0.0093855ns; lifetime-2= 0.017252 ns $\pm$ 0.022547ns

Powder: lifetime-1= 1.8176 ns $\pm$ 0.062689 ns; lifetime-2= 0.39552 ns $\pm$ 0.059877ns

Crystal: lifetime-1= 1.8275 ns $\pm$ 0.11377ns; lifetime-2= 0.49592 ns $\pm$ 0.10472ns

**Table S2** Single crystal diffraction data and structure refinement for compounds **4a** (CCDC 973432)

Parameters	<b>4a</b>
Empirical formula	C <sub>38</sub> H <sub>26</sub> S <sub>2</sub>
Formula weight	546.71
Temperature	173(2)K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	P 2(1)
Unit cell dimensions	a= 11.459(2)Å , $\alpha$ =90.00 b= 5.9687(10) Å, $\beta$ = 93.659(3) c= 20.744(4)Å, $\gamma$ =90.00
Z	2
Density (calculated)	1.282 g/cm <sup>3</sup>
Absorption coefficient	0.214
F(000)	572
Crystal size(mm)	0.28×0.27×0.13
Theta range for data collection	3.04° to 27.48°
Index ranges	-14<=h<=14 -7<=k<=7 -26<=l<=14
Reflections collected	7411
Independent reflections	5503
R <sub>int</sub>	0.0500
Completeness to theta	98.6%
Absorption correction	multi-scan
Max. and min. transmission	0.9424 and 0.9727
Data / restraints / parameters	5503/333/370
Goodness-of-fit on F <sup>2</sup>	1.053
Final R indices [I>2sigma(I)]	R <sub>1</sub> = 0.0588  wR <sub>2</sub> = 0.1490
R indices (all data)	R <sub>1</sub> = 0.0563, wR <sub>2</sub> = 0.1460
Largest diff. peak and hole	0.879 and -0.472 e.Å <sup>-3</sup>

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