

**Supporting Information  
for**  
**Ion-induced FRET On-Off in fluorescent calix[4]arene**

Min Hee Lee,<sup>1</sup> Duong Tuan Quang,<sup>1</sup> Hyo Sung Jung,<sup>1</sup> Juyoung Yoon,<sup>2</sup> Chang-Hee Lee,<sup>3</sup> and Jong Seung Kim<sup>1,\*</sup>

<sup>1</sup>*Department of Chemistry, Dankook University, Seoul 140-714, Korea.*

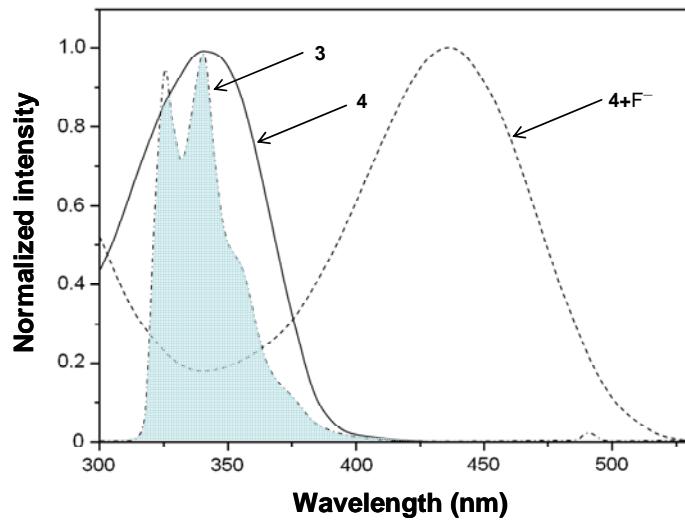
<sup>2</sup>*Department of Chemistry and Division of Nano Sciences, Ewha Womans University, Seoul 120-750, Korea.*

<sup>3</sup>*Department of Chemistry, Kangwon National University, Chun-Chon, 200-701, Korea*

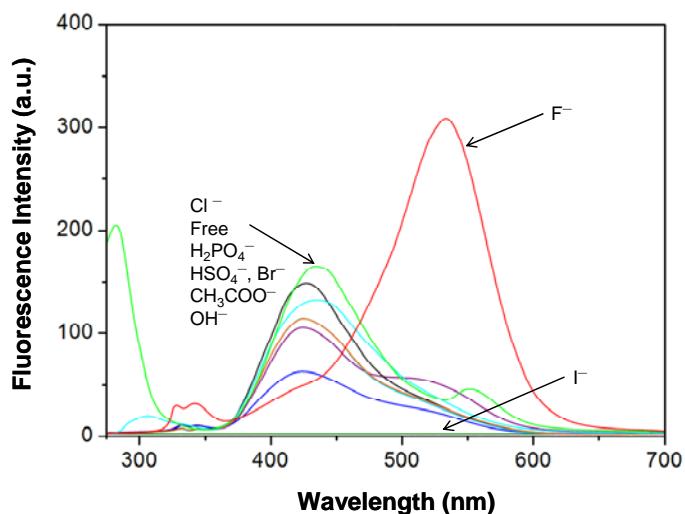
Corresponding author: [jongskim@dankook.ac.kr](mailto:jongskim@dankook.ac.kr), Fax: +82-2-797-3277

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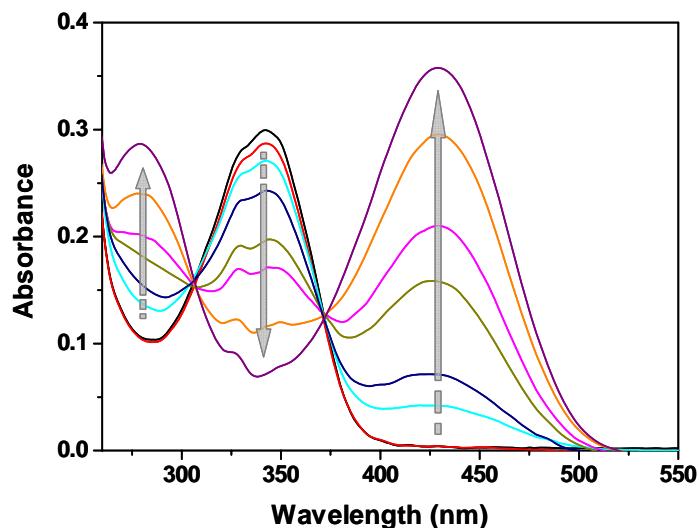
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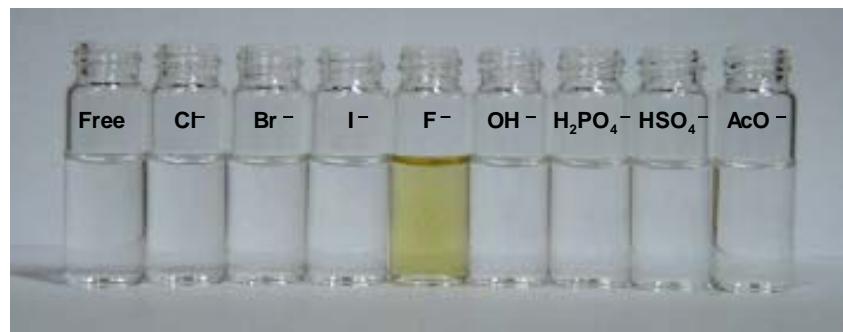
**Figure S1.** Spectral overlap of **3** (FRET donor) and **4** (FRET acceptor). Grayish band is for the emission of **3** excited at 245 nm (naphthalene). Solid line is for the absorption of **4**. Dotted line is for the absorption of **4+F<sup>-</sup>** which was treated with 100 eq of TBA<sup>+</sup>F<sup>-</sup> in CH<sub>3</sub>CN.



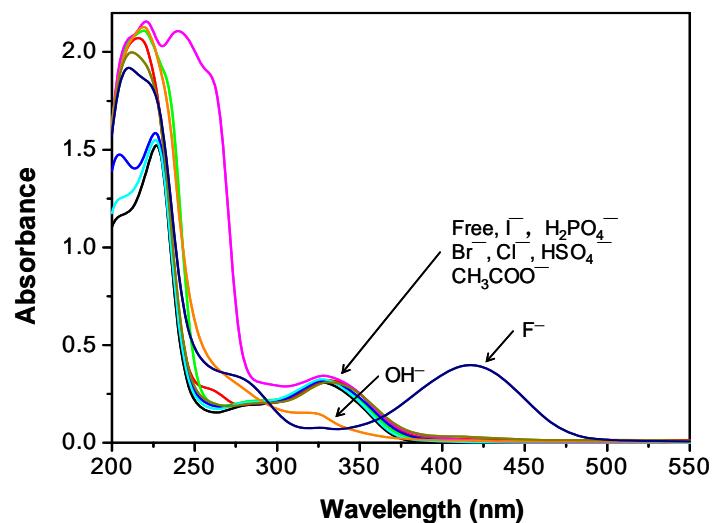
**Figure S2.** Fluorescence spectra of **1** (6.0  $\mu\text{M}$ ) upon addition of TBA<sup>+</sup> salts of OH<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (0.6 mM) in CH<sub>3</sub>CN with an excitation at 245 nm.



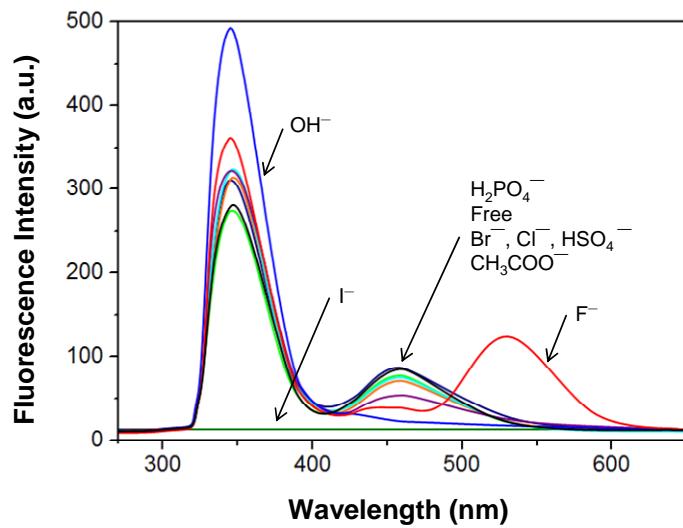
**Figure S3.** Absorption spectra of **1** (20.0  $\mu\text{M}$ ) upon addition of various concentrations (0, 5, 10, 20, 50, 60, 100, 400 eq) of TBA<sup>+</sup> F<sup>-</sup> in CH<sub>3</sub>CN.



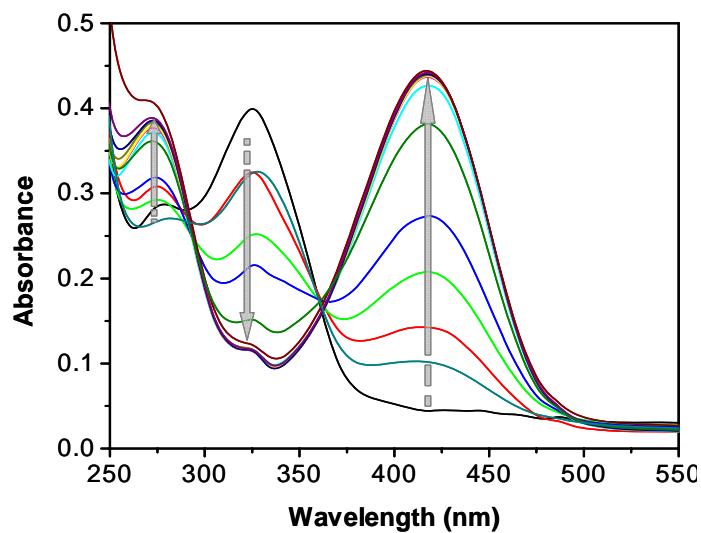
**Figure S4.** Visual color changes of **1** with 20 eq of  $\text{F}^-$  in  $\text{CH}_3\text{CN}$ .



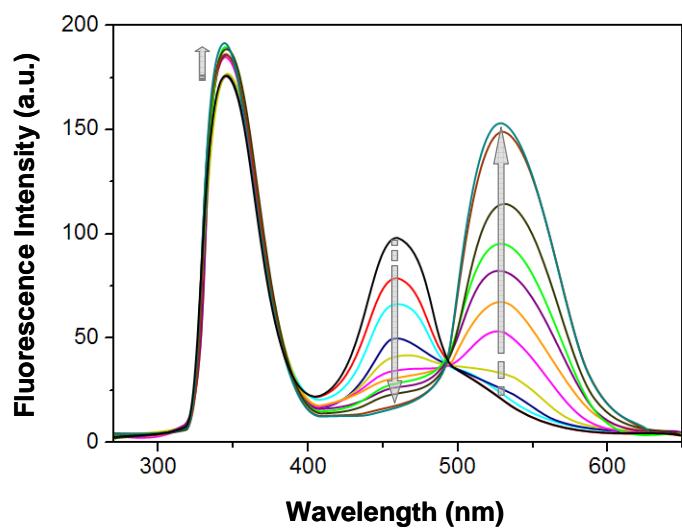
**Figure S5.** Absorption spectra of **5** ( $20.0 \mu\text{M}$ ) upon addition of  $\text{TBA}^+$  salts of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{OH}^-$ ,  $\text{HSO}_4^-$ , and  $\text{H}_2\text{PO}_4^-$  ( $10.0 \text{ mM}$ ) in  $\text{CH}_3\text{CN}$ .



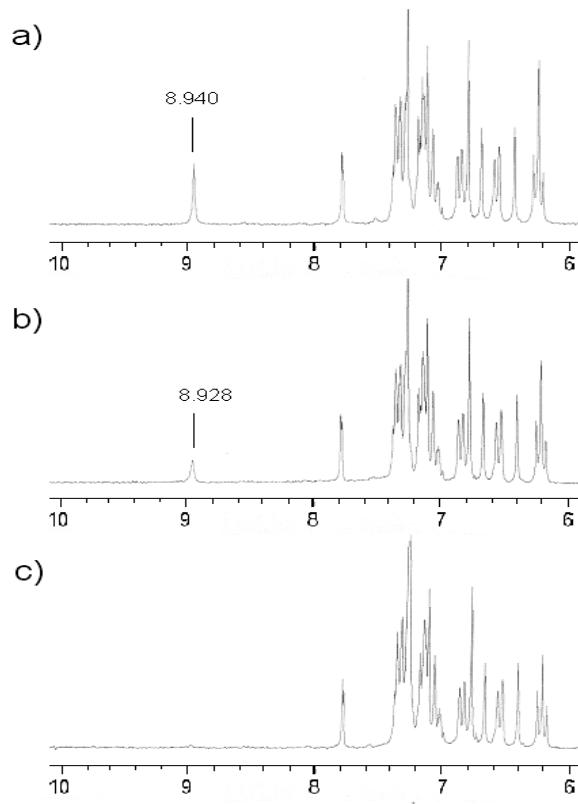
**Figure S6.** Fluorescence spectra of **5** (6.0  $\mu\text{M}$ ) upon addition of TBA $^+$  salts of OH $^-$ , F $^-$ , Cl $^-$ , Br $^-$ , I $^-$ , CH<sub>3</sub>COO $^-$ , HSO<sub>4</sub> $^-$ , and H<sub>2</sub>PO<sub>4</sub> $^-$  (0.6 mM) in CH<sub>3</sub>CN with an excitation at 245 nm.



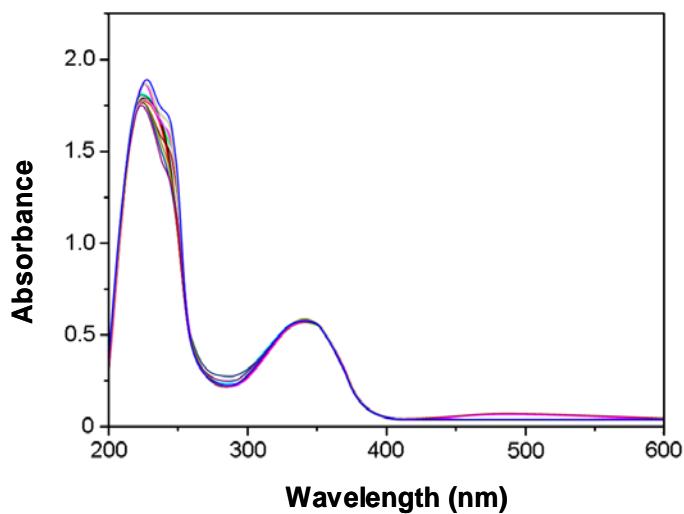
**Figure S7.** Absorption spectra of **5** (20.0  $\mu\text{M}$ ) upon addition of various concentrations (0, 5, 10, 20, 30, 60, 80, 90, 100, 150, 200, 400 eq) of TBA $^+$  F $^-$  in CH<sub>3</sub>CN.



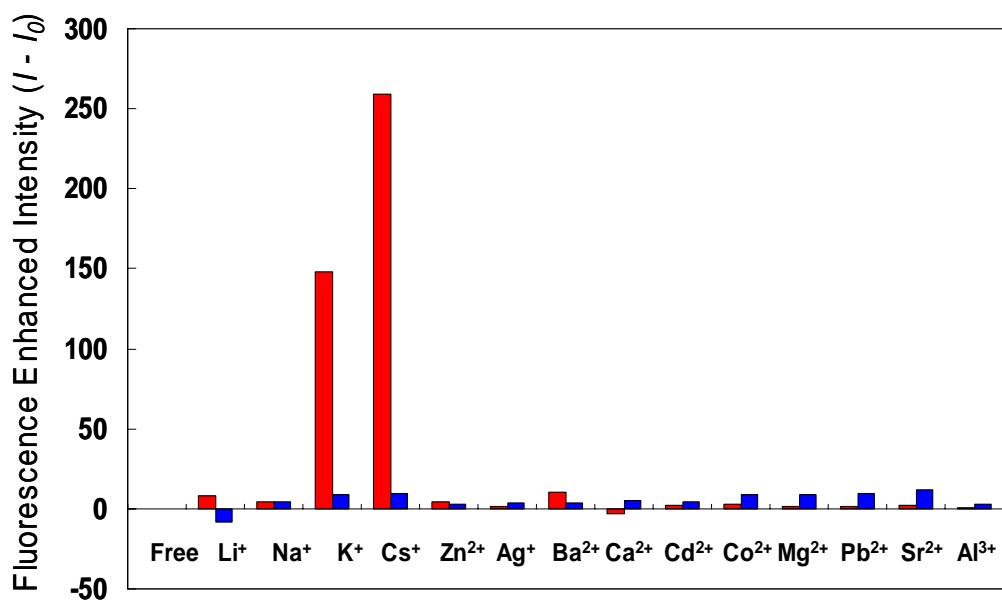
**Figure S8.** Fluorescence spectra of **5** (6.0  $\mu$ M) upon addition of various concentrations (0, 5, 6, 7, 10, 20, 30, 60, 80, 100, 200, 400 eq) of TBA $^+$  F $^-$  in CH<sub>3</sub>CN with an excitation at 245 nm.



**Figure S9.** Partial <sup>1</sup>H NMR spectra of the ligand **1** (8.0 mM) in the absence and presence of fluoride ion in CDCl<sub>3</sub>. a) 0 eq b) 0.1 eq and c) 0.58 eq.



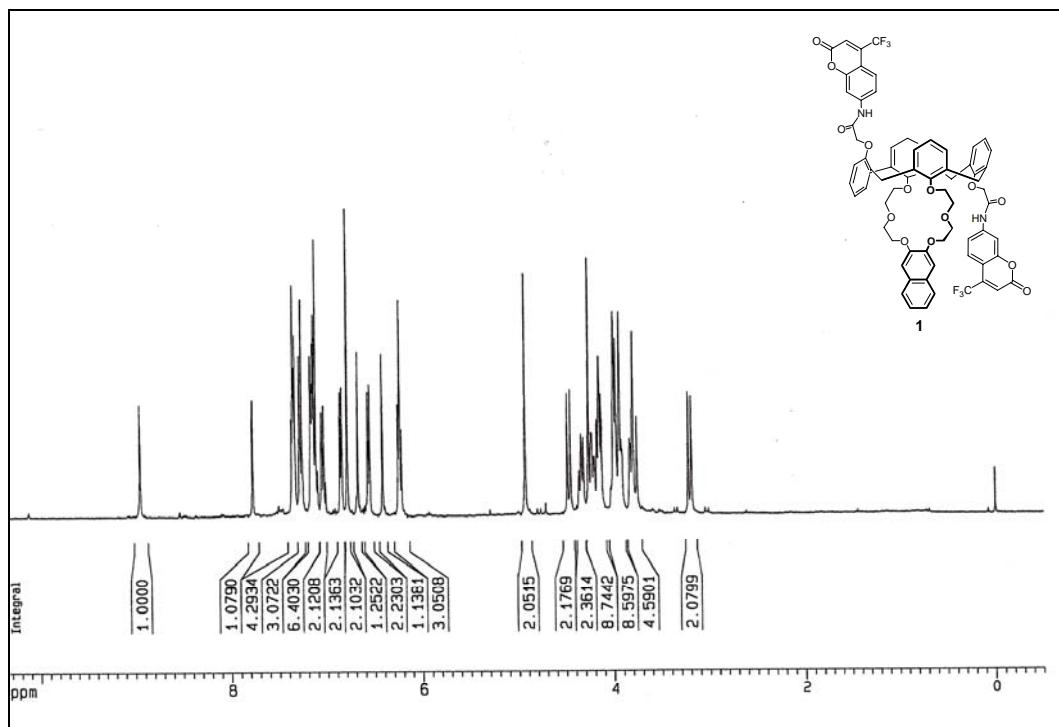
**Figure S10.** Absorption spectra of **1** (20.0  $\mu\text{M}$ ) upon addition of  $\text{ClO}_4^-$  salts of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$  (10.0 mM) in  $\text{CH}_3\text{CN}$ .



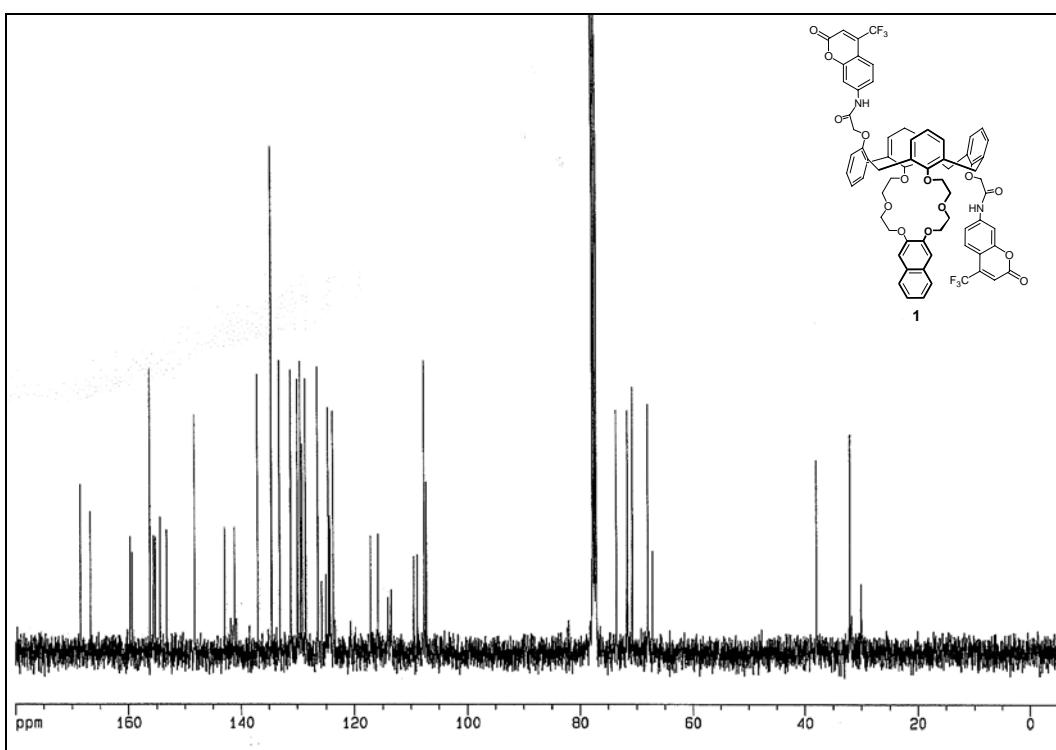
**Figure S11.** Fluorescence enhanced intensity of **1** (6.0  $\mu\text{M}$ , red) and **5** (6.0  $\mu\text{M}$ , blue) upon addition of various metal ions (3.0 mM) in  $\text{CH}_3\text{CN}$  with an excitation at 245 nm.

### NMR of 1.

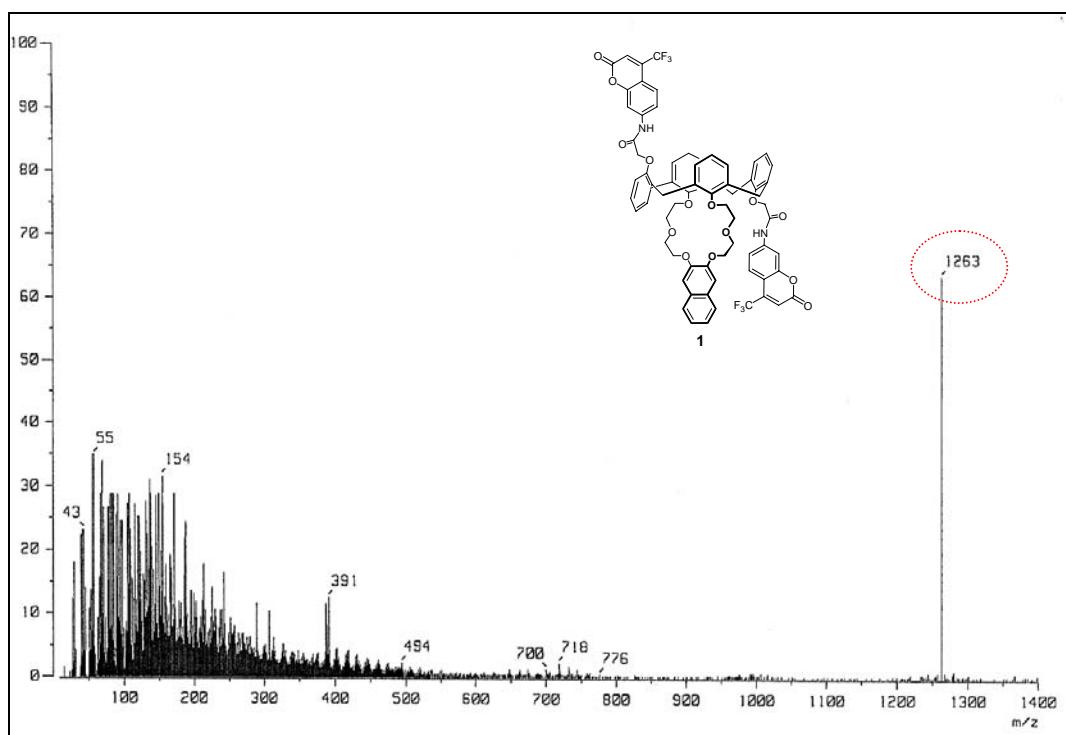
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.95 (s, 1 H), 7.77 (s, 1 H), 7.35 (m, 4 H), 7.17 (m, 3 H), 7.11 (m, 2 H), 6.84 (m, 2 H), 6.78 (s, 2 H), 6.56 (d, 1 H, *J* = 7.52 Hz), 4.93 (s, 2 H), 4.48 (d, 2 H, *J* = 12.88 Hz), 4.43 (m, 2 H), 4.26~4.12 (m, 8 H), 3.99~3.93 (m, 8 H), 3.75 (m, 4 H), 3.22 (d, 2 H, *J* = 12.92 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 168, 166, 159, 156, 155, 153, 148, 142, 141, 136, 133, 129, 123, 117, 115, 114, 107, 73, 71, 70, 68, 67, 38, 31, 30 ppm.



**Figure S12.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of compound 1.



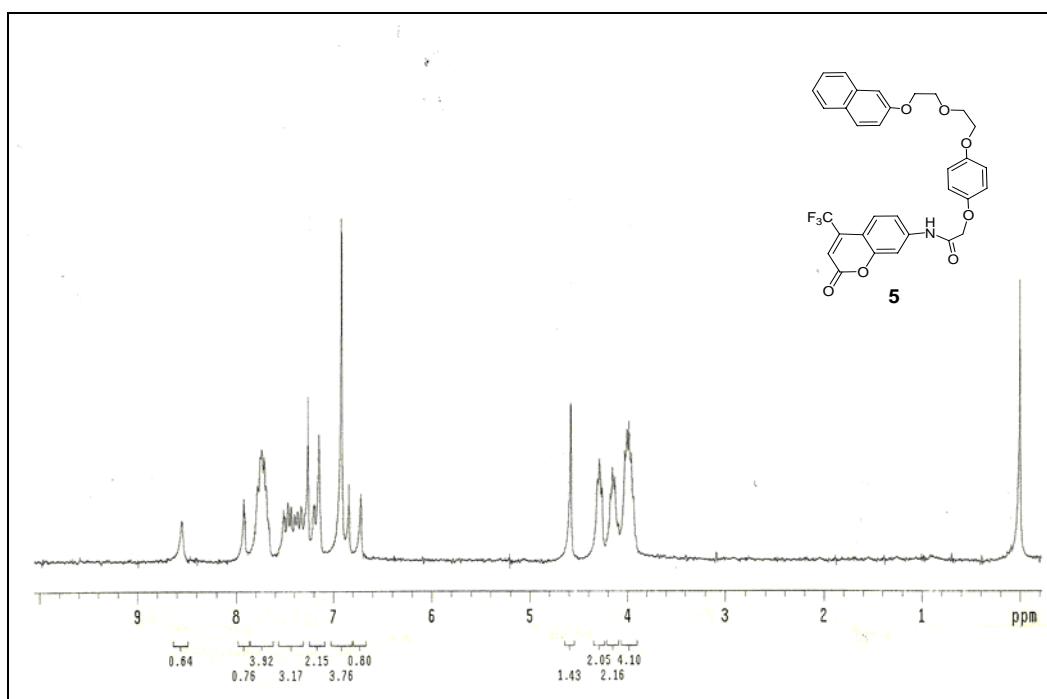
**Figure S13.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) spectrum of compound **1**.



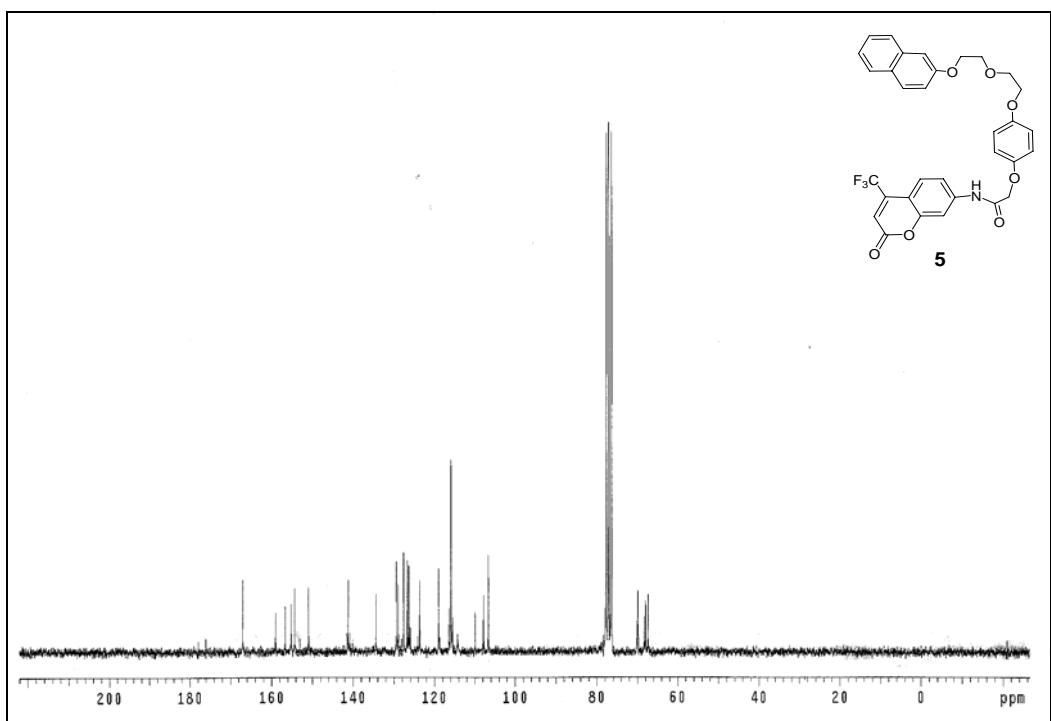
**Figure S14.** Mass spectrum of compound **1**.

**NMR of 5.**

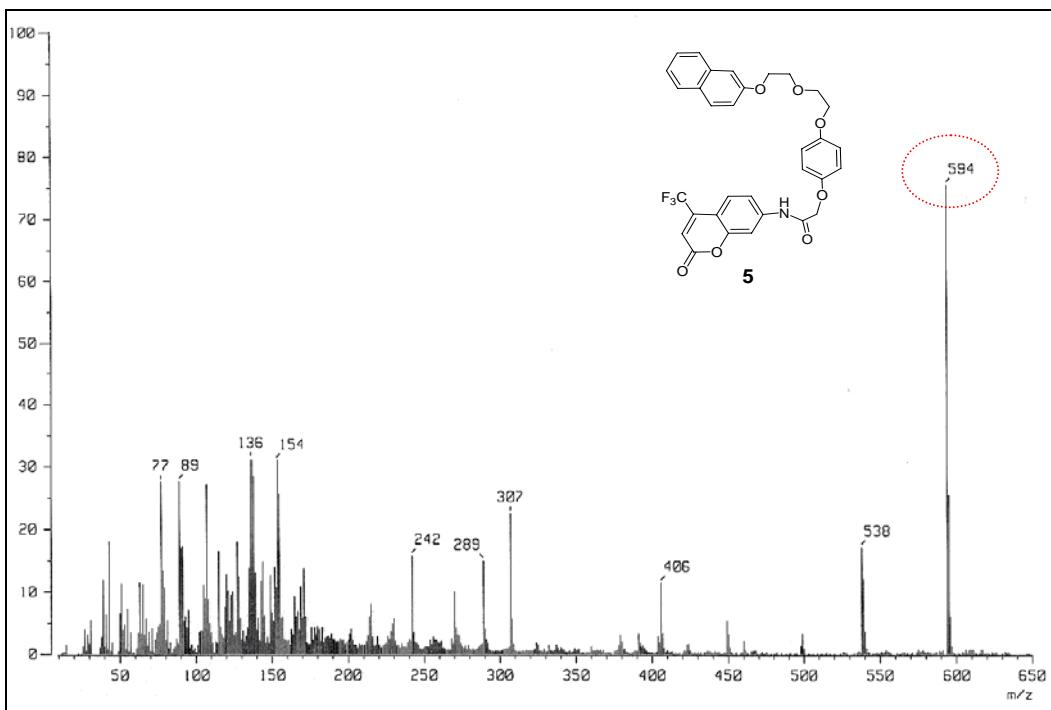
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.59 (s, 1 H), 7.95 (s, 1 H), 7.85~7.62 (m, 4 H), 7.60~7.27 (m, 3 H), 7.15 (m, 2 H), 6.91 (m, 4 H), 6.78 (s, 1 H), 4.58 (s, 2 H), 4.75 (t, 2 H), 4.19 (t, 2 H), 4.00~3.98 (m, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz): 166, 158, 156, 155, 154, 150, 141.1, 141.0, 134, 129, 127, 123, 118, 116, 115, 109, 107, 106, 69, 68, 67, 67 ppm.



**Figure S15.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of compound 5.



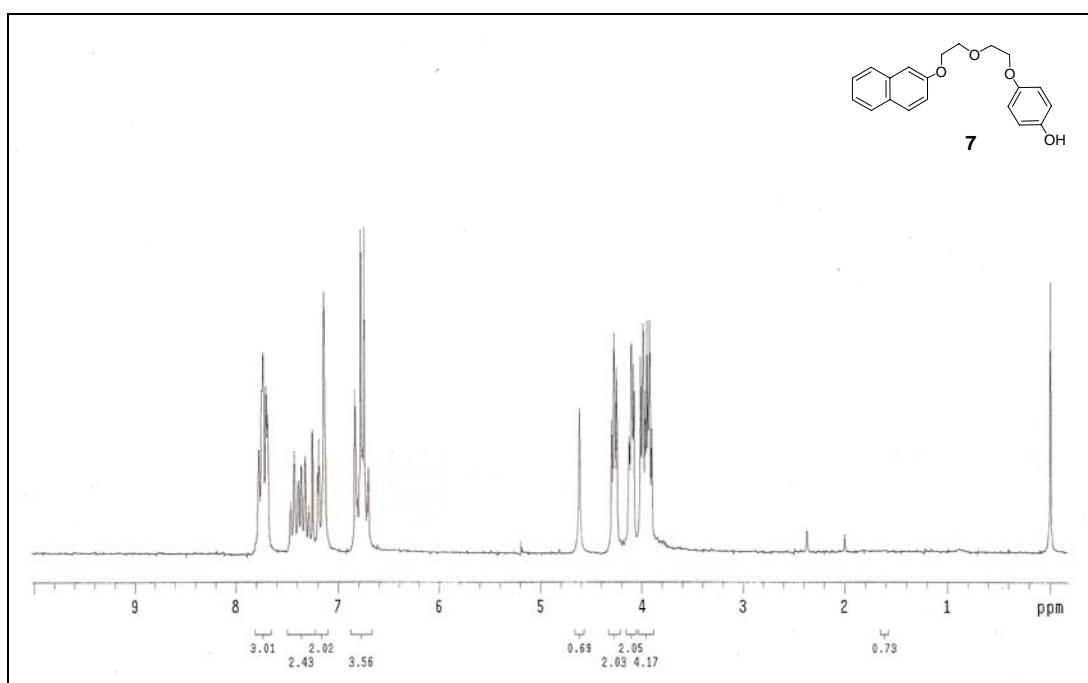
**Figure S16.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz) spectrum of compound **5**.



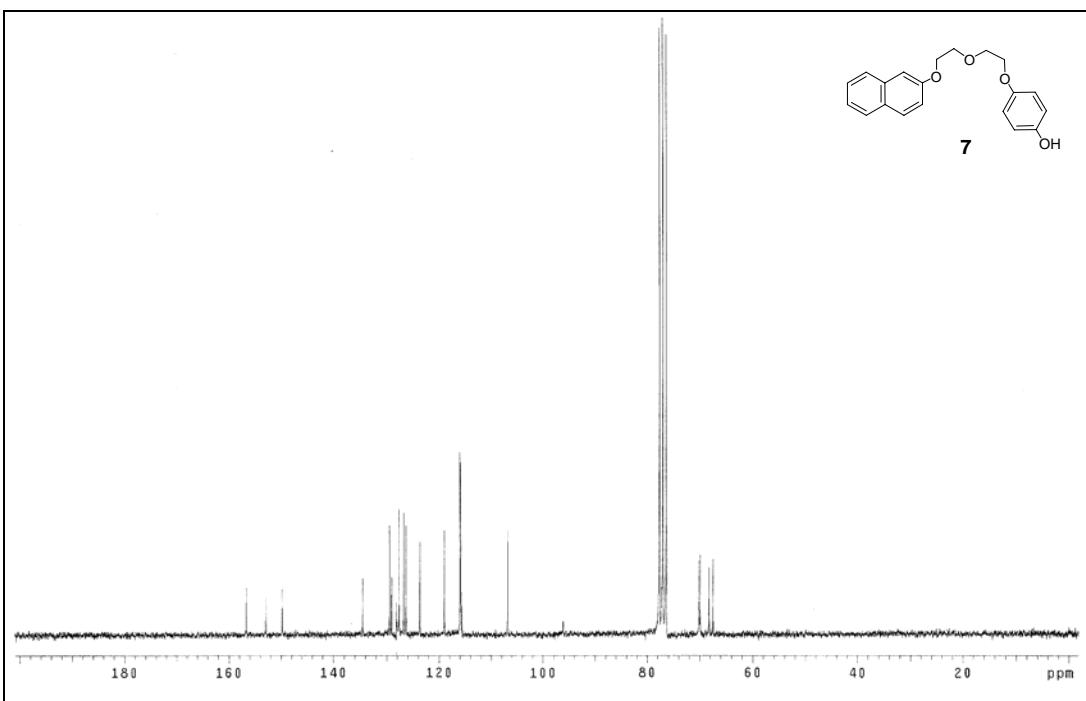
**Figure S17.** Mass spectrum of compound **5**.

**NMR of 7.**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.82~7.69 (m, 3 H), 7.56~7.25 (m, 2 H), 7.143 (m, 2 H), 6.84~6.75 (m, 4 H), 4.62 (s, 1 H), 4.72 (t, 2 H), 4.11 (t, 2 H), 4.02~3.91 (m, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz): 157, 150, 134, 129, 127, 124, 118, 117, 105, 69 ppm.



**Figure S18.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz) spectrum of compound 7.



**Figure S19.** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) spectrum of compound 7.