

## Supplementary Information

# Aryl-triazole Foldamers Incorporating a Pyridinium Motif for Halide Anion Binding in Aqueous Media

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## 1. Complete Reference 15 in the Main Text

15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian03 Revision D.02; Gaussian, Inc.: Pittsburgh, PA, 2004

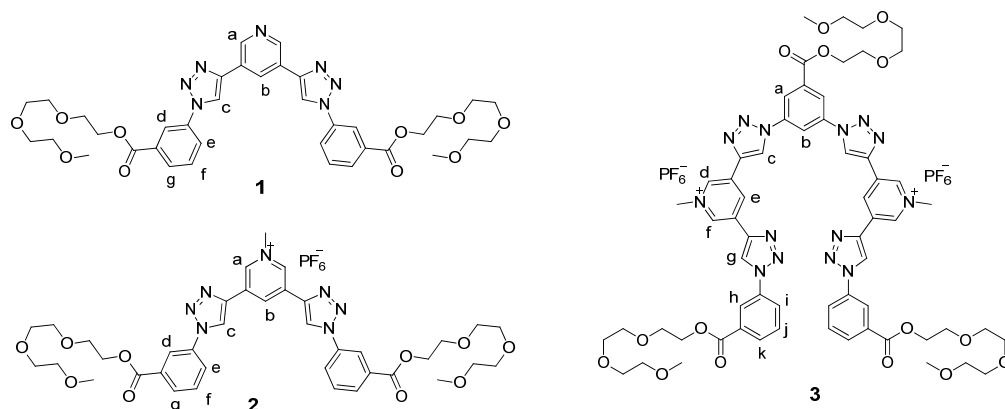
## 2. General Procedures and Materials.

All starting materials and solvents were commercially available and used without further purification unless otherwise noted. Dry tetrahydrofuran (THF) and toluene were dried from sodium/benzophenone and then distilled under inert atmosphere. Anhydrous diisopropylamine (*iso*-Pr<sub>2</sub>NH) and DCM were distilled over CaH<sub>2</sub> under argon. Compounds **4**<sup>[S1]</sup>, **5**<sup>[S2]</sup> and **7**<sup>[S2]</sup> were prepared according to the procedure previously reported.

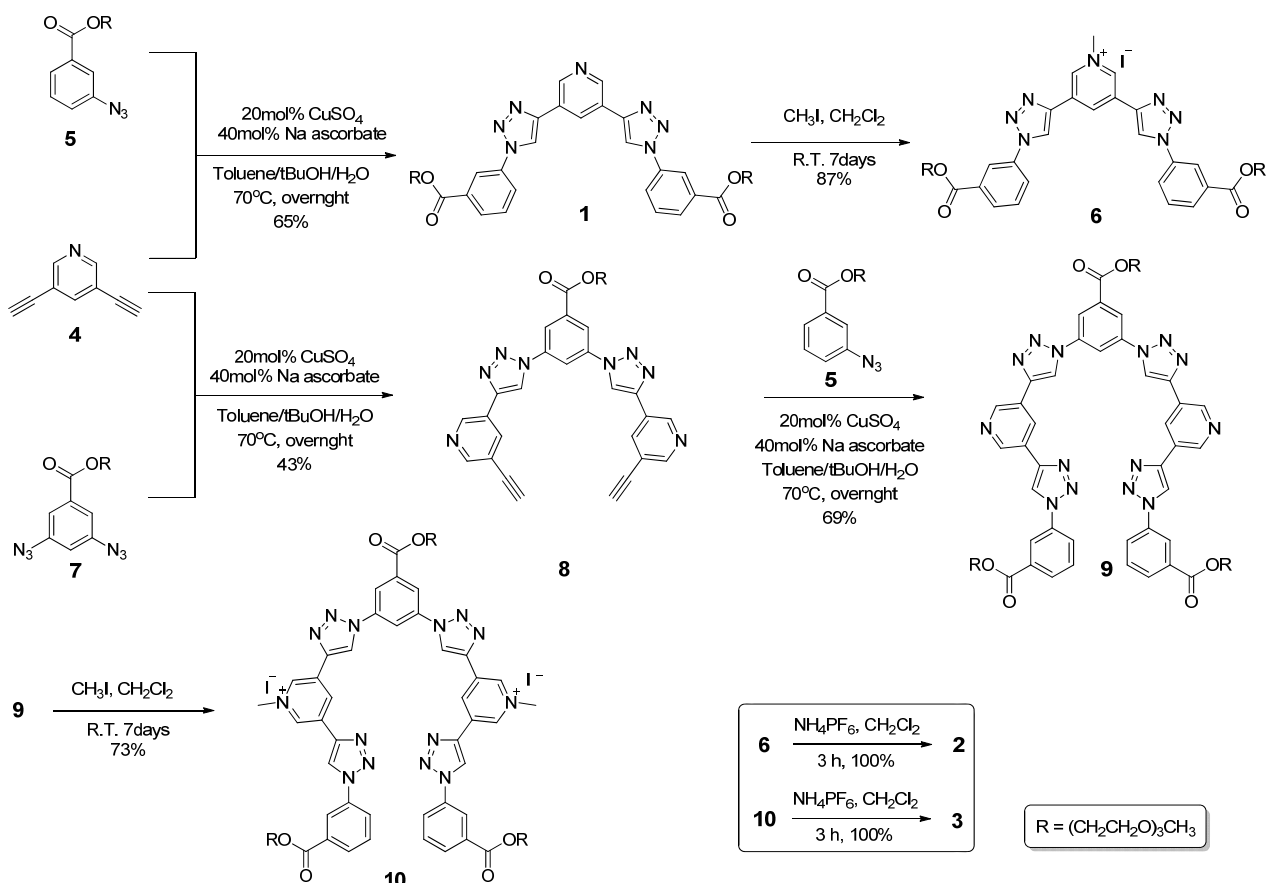
Column chromatography was carried out on flash grade silica gel, using 0 – 20 psig pressure. NMR spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR and 2D NMR) were obtained using commercial spectrometers (<sup>1</sup>H, 400, 500 and 600 MHz) using chloroform-*d* (CDCl<sub>3</sub>), acetone-*d*<sub>6</sub>, methanol-*d*<sub>4</sub> (CD<sub>3</sub>OD), pyridine-*d*<sub>5</sub> and dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as solvent at ambient temperature (298 K). The chemical shift references were as follows: (<sup>1</sup>H) chloroform, 7.26 ppm; (<sup>13</sup>C) chloroform-*d*, 77.16 ppm (chloroform-*d*); (<sup>1</sup>H) DMSO-*d*<sub>5</sub>, 2.50 ppm; (<sup>13</sup>C) DMSO-*d*<sub>6</sub>, 39.52 ppm (DMSO-*d*<sub>6</sub>); (<sup>1</sup>H) acetone-*d*<sub>5</sub>, 2.05 ppm; (<sup>13</sup>C) acetone-*d*<sub>6</sub>, 29.92 ppm (acetone-*d*<sub>6</sub>). Typical 1D FID was subjected to exponential multiplication with an exponent of 0.3 Hz. High resolution mass spectra (HRMS-ESI) were acquired on FT-ICR spectrometer.

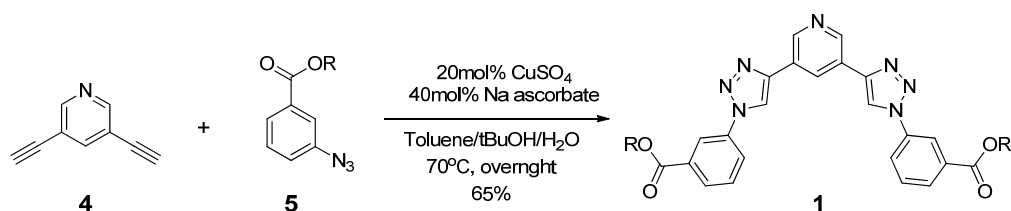
### 3. Synthesis of Methylpyridine-appended Aryl-triazole Oligomers.

Scheme S1. Structure of oligomer 1–3.

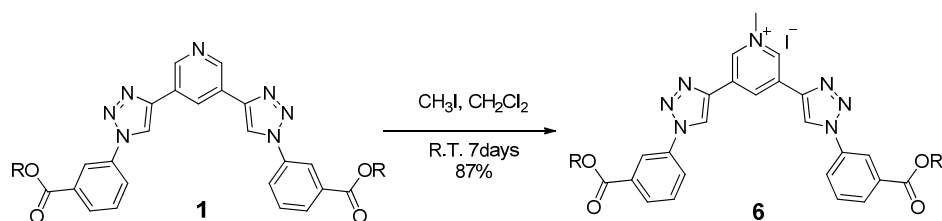


Scheme S2. Synthesis of oligomer 1–3.



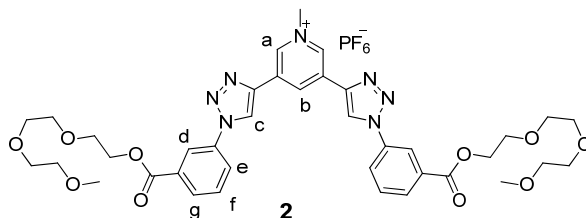


**Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3'-(4,4'-(pyridine-3,5-diyl)bis(1H-1,2,3-triazole-4,1-diyl))dibenzoate (1).** Compound **4** (63.5 mg, 0.5 mmol) and **5** (0.34 g, 1.1 mmol) were dissolved in the mixture of toluene and *tert*-butanol, then the solution was degassed with bubbling of argon for half an hour. To the solution, CuSO<sub>4</sub> (15.9 mg, 0.1 mmol) dissolved in H<sub>2</sub>O (1 mL) and sodium ascorbate (39.9 mg, 0.2 mmol) dissolved in H<sub>2</sub>O (1 mL) were added. The reaction solution protected by Ar was stirred at 70 °C overnight. When the reaction finished, most of the solvents were removed under reduced pressure. The residue was resolved in DCM and the organic layer was washed with saturated NH<sub>4</sub>Cl (100 mL×2) and NaCl (100 mL×2) respectively. The crude product was purified by flash chromatography (SiO<sub>2</sub>, DCM : EA = 10:1) to provide **1** (0.26 g, 65%) as a white yellow solid. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz, 298 K): δ = 9.41 (s, 2H), 9.22 (d, *J* = 2.0 Hz, 2H), 8.95 (t, *J* = 2.0 Hz, 1H), 8.62 (d, *J* = 2.1 Hz, 2H), 8.33 (dd, *J* = 1.3 Hz, 8.0 Hz, 2H), 8.20 (d, *J* = 7.6 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 2H), 4.55 (t, *J* = 4.4 Hz, 4H), 3.89 (t, *J* = 4.8 Hz, 4H), 3.70-3.67 (m, 4H), 3.634-3.61 (m, 4H), 3.59-3.57 (m, 4H), 3.46-3.43 (m, 4H), 3.25 (s, 6H). <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 125 MHz, 298 K): δ = 165.8, 147.3, 145.9, 138.3, 133.1, 131.3, 130.3, 129.9, 127.7, 125.4, 121.7, 120.9, 72.7, 71.38, 71.28, 71.14, 69.6, 65.5, 58.8. HRMS (ESI-FT-ICR) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>37</sub>H<sub>44</sub>N<sub>7</sub>O<sub>10</sub> 746.3144, found 746.3141.

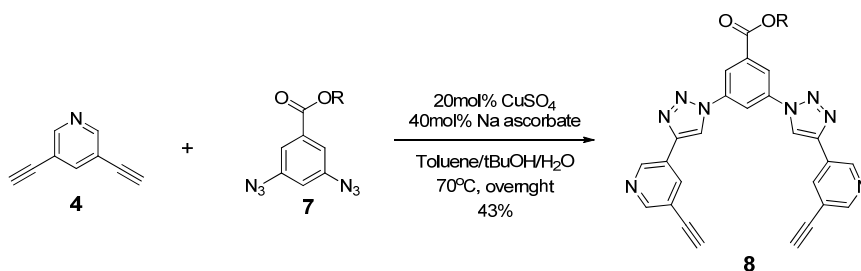


**3,5-Bis(1-(3-(2,5,8,11-tetraoxadodecan-1-oyl)phenyl)-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium iodide (6).** To the solution of Compound **1** (0.2 g, 0.27 mmol) in dry DCM, CH<sub>3</sub>I (0.2 mL) was added. The reaction solution was sealed and stirred for 7 days at room temperature. Solvents were removed under reduced pressure. The crude product was purified by flash chromatography (SiO<sub>2</sub>, DCM : MeOH = 100:2) to provide **6** (0.21 g, 87%) as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K): δ = 10.13 (s, 2H), 9.74 (s, 1H), 9.55 (s, 2H), 8.55 (s, 2H), 8.20-8.14 (m, 4H), 7.70 (t, *J* = 8.0

Hz, 2H), 4.76 (s, 3H), 4.59 (t,  $J = 4.4$  Hz, 4H), 4.0 (t,  $J = 4.8$  Hz, 4H), 3.81-3.79 (m, 4H), 3.73-3.71 (m, 4H), 3.62-3.60 (m, 4H), 3.49-3.46 (m, 4H), 3.27 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100M Hz, 298 K)  $\delta = 165.4, 141.1, 140.0, 136.3, 135.9, 131.99, 131.76, 130.29, 130.18, 124.38, 124.05, 121.0, 72.0, 70.77, 70.72, 70.61, 69.3, 64.7, 59.0, 50.1$ . HRMS (ESI-FT-ICR)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{38}\text{H}_{46}\text{N}_7\text{NaO}_{10}$  910.2243, found 910.2243.

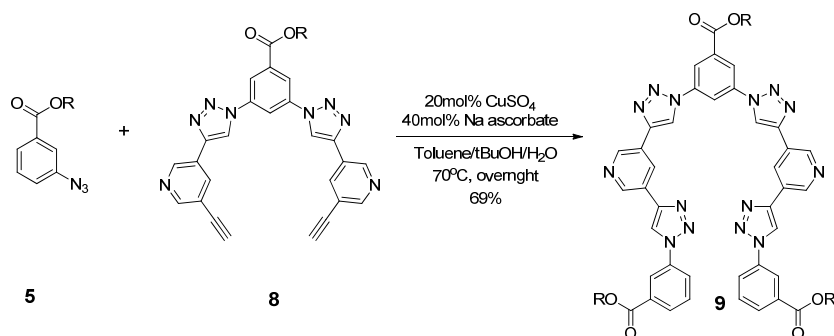


**3,5-Bis(1-(3-(2,5,8,11-tetraoxadodecan-1-oyl)phenyl)phenyl)-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium hexafluorophosphate (2).** Compound **6** (0.2 g, 0.22 mmol) was dissolved in DCM (30 mL) and it was stirred with aqueous  $\text{NH}_4\text{PF}_6$  (0.1 mM, 20 mL) for 3 hours. The mixture changed colour from yellow to colourless. The organic layer was washed with further aqueous  $\text{NH}_4\text{PF}_6$  (0.1 molL $^{-1}$ , 20 mL $\times$ 6) and water (20 mL $\times$ 2). Solvents were removed under reduced pressure and the residue was dried to give compound **2** as a pale solid (100%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 400 MHz, 298 K):  $\delta = 9.69$  (s, 2H), 9.61 (s, 2H), 9.59 (s, 1H), 8.56 (s, 2H), 8.30 (dd,  $J = 1.2$  Hz, 8.0 Hz, 2H), 8.24 (d,  $J = 8.0$  Hz, 2H), 7.89 (t,  $J = 8.0$  Hz, 2H), 4.88 (s, 3H), 4.56 (t,  $J = 4.4$  Hz, 4H), 3.90-3.87 (m, 4H), 3.70-3.68 (m, 4H), 3.64-3.61 (m, 4H), 3.60-3.57 (m, 4H), 3.45-3.43 (m, 4H), 3.24 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COC}_3$ , 125 MHz, 298 K):  $\delta = 165.6, 142.51, 142.01, 137.8, 136.9, 133.22, 132.74, 131.5, 130.9, 125.6, 123.3, 121.8, 72.6, 71.36, 71.28, 71.13, 69.6, 65.6, 58.8, 50.0$ . HRMS (ESI-FT-ICR)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{37}\text{H}_{46}\text{N}_7\text{O}_{10}$  760.3300, found 760.3322.

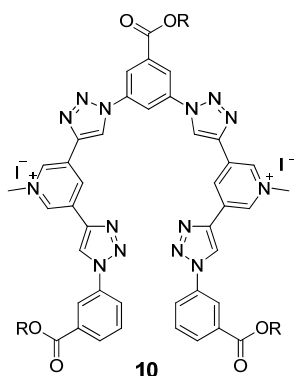


**2-(2-(2-Methoxyethoxy)ethoxy)ethyl 3,5-bis(4-(5-ethynylpyridin-3-yl)-1H-1,2,3-triazol-1-yl)benzoate (8).** Compound **8** was obtained by a similar procedure to compound **1** starting with compound **4** and **7**. Yield 43%, pale solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 9.11$  (d,  $J = 2.0$  Hz, 2H), 8.75 (d,  $J = 1.6$  Hz, 2H), 8.74 (t,  $J = 2.0$  Hz, 1H), 8.56-8.55 (m, 4H), 8.41 (t,  $J = 2.0$  Hz, 4.0 Hz, 2H), 4.63-4.61 (m, 2H), 3.92-3.90 (m, 2H), 3.76-3.66 (m, 6H), 3.55-3.52 (m, 2H), 3.31 (s, 3H), 3.30 (s, 2H).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 100M Hz, 298 K):  $\delta$  = 163.7, 151.5, 145.7, 144.0, 137.6 135.0, 133.1, 125.6, 121.2, 119.28, 119.05, 114.6, 84.7, 79.9, 71.2, 69.90, 69.75, 69.61, 68.2, 65.0, 58.0. HRMS (MALDY-FT-ICR)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{32}\text{H}_{29}\text{N}_8\text{O}_5$  605.2259, found 605.2255.



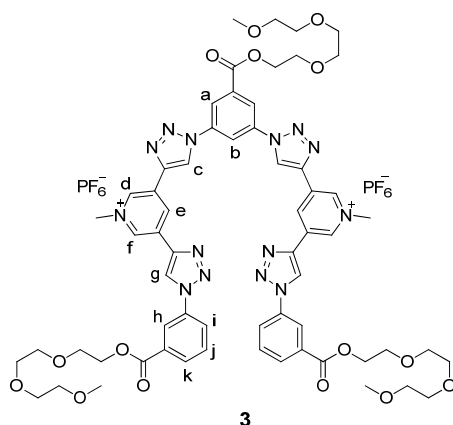
**Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl) 3,3'-(4,4'-(5,5'-(1,1'-(5-(2,5,8,11-tetraoxadodecan-1-oyl)-1,3-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(pyridine-5,3-diyl))bis(1*H*-1,2,3-triazole-4,1-diyl))dibenzoate (9).** Compound **9** was obtained by a similar procedure to compound **1** starting with compound **8** and **5**. Yield 69%, white solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 400M Hz, 298 K):  $\delta$  = 9.87 (s, 2H), 9.71(s, 2H), 9.19(d,  $J$  = 6.0 Hz, 4H), 8.96 (s, 1H), 8.92 (s, 2H), 8.64 (s, 2H), 8.52 (s, 2H), 8.30 (d,  $J$  = 8.0 Hz, 2H), 8.11 (d,  $J$  = 7.6 Hz, 2H), 7.86 (t,  $J$  = 8.0 Hz, 2H), 4.59 (t,  $J$  = 3.6 Hz, 2H), 4.50 (t,  $J$  = 4.4 Hz, 4H), 3.88 (t,  $J$  = 4.4 Hz, 2H), 3.82 (t,  $J$  = 4.8 Hz, 4H), 3.67-3.61 (m, 6H), 3.58-3.50 (m, 12H), 3.40-3.37 (m, 6H), 3.19 (s, 6H), 3.17 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 100M Hz, 298 K):  $\delta$  = 164.5, 163.6, 145.72, 145.58, 144.23, 144.02, 137.13, 136.38, 132.60, 131.08, 130.28, 128.9, 127.7, 125.86, 125.57, 123.8, 119.87, 119.74, 119.55, 118.34, 113.2, 71.2, 69.94, 69.89, 69.77, 69.74, 69.60, 68.20, 64.86, 64.42, 57.97, 57.95. HRMS (ESI-FT-ICR)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{60}\text{H}_{67}\text{N}_{14}\text{O}_{15}$  1223.4905, found 1223.4877.



**5,5'-(1,1'-(5-(2,5,8,11-Tetraoxadodecan-1-oyl)-1,3-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(3-(1-(3-(2,5,8,11-tetraoxadodecan-1-oyl)phenyl)-1*H*-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium) iodide (10).** Compound **10** was obtained by a similar procedure to compound **6** starting with compound **9** and  $\text{CH}_3\text{I}$ . Yield 73%, yellow solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 400M Hz,

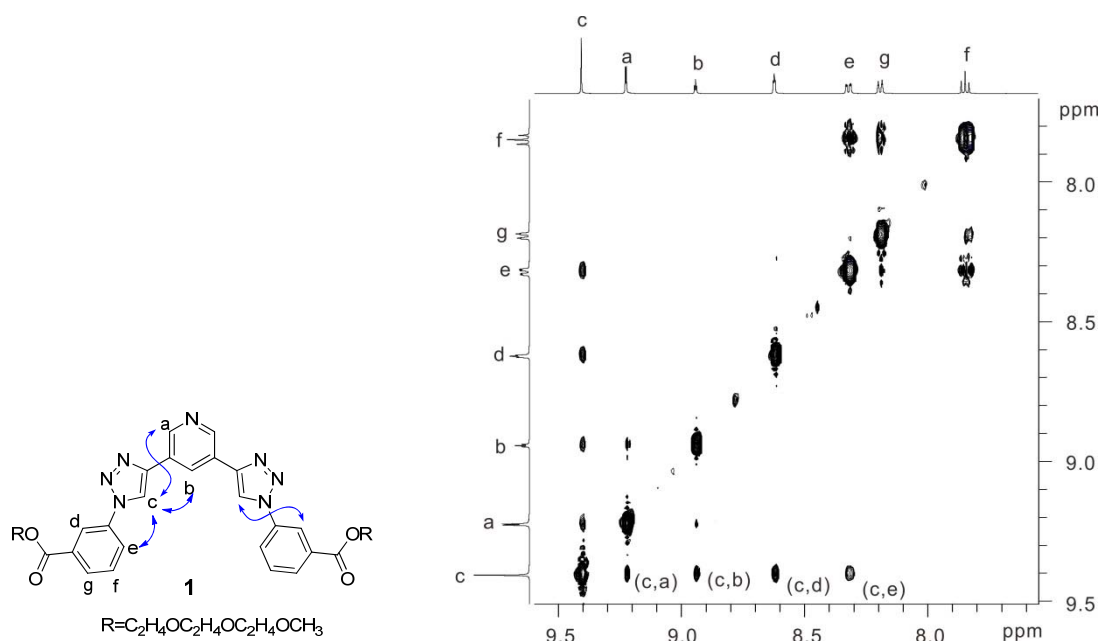


298 K):  $\delta$  = 10.11 (s, 2H), 9.87 (s, 2H), 9.66 (d,  $J$  = 3.6 Hz, 4H), 9.55 (s, 2H), 9.01 (s, 1H), 9.68 (d,  $J$  = 1.6 Hz, 2H), 8.50 (s, 2H), 8.32 (d,  $J$  = 8.0 Hz, 2H), 8.17 (d,  $J$  = 7.6 Hz, 2H), 7.91 (t,  $J$  = 8.0 Hz, 2H), 4.60 (t,  $J$  = 5.2 Hz, 2H), 4.57 (s, 6H), 4.50 (t,  $J$  = 4.0 Hz, 4H), 3.87 (t,  $J$  = 4.4 Hz, 2H), 3.81 (t,  $J$  = 4.8 Hz, 4H), 3.64-3.60 (m, 6H), 3.56-3.49 (m, 12H), 3.39-3.56 (m, 6H), 3.18 (s, 6H), 3.16 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 100M Hz, 298 K):  $\delta$  = 164.4, 163.4, 141.53, 141.14, 140.95, 140.61, 136.9, 135.9, 134.7, 133.2, 131.2, 130.69, 130.31, 129.86, 129.52, 123.99, 123.18, 122.8, 119.58, 119.03, 114.0, 71.24, 69.86, 69.74, 69.59, 68.18, 65.20, 64.58, 58.0, 48.8. HRMS (ESI-FT-ICR)  $m/z$ :  $[\text{M}]^{2+}$  Calcd for  $\text{C}_{62}\text{H}_{72}\text{N}_{14}\text{O}_{15}$  626.2645, found 626.2631.

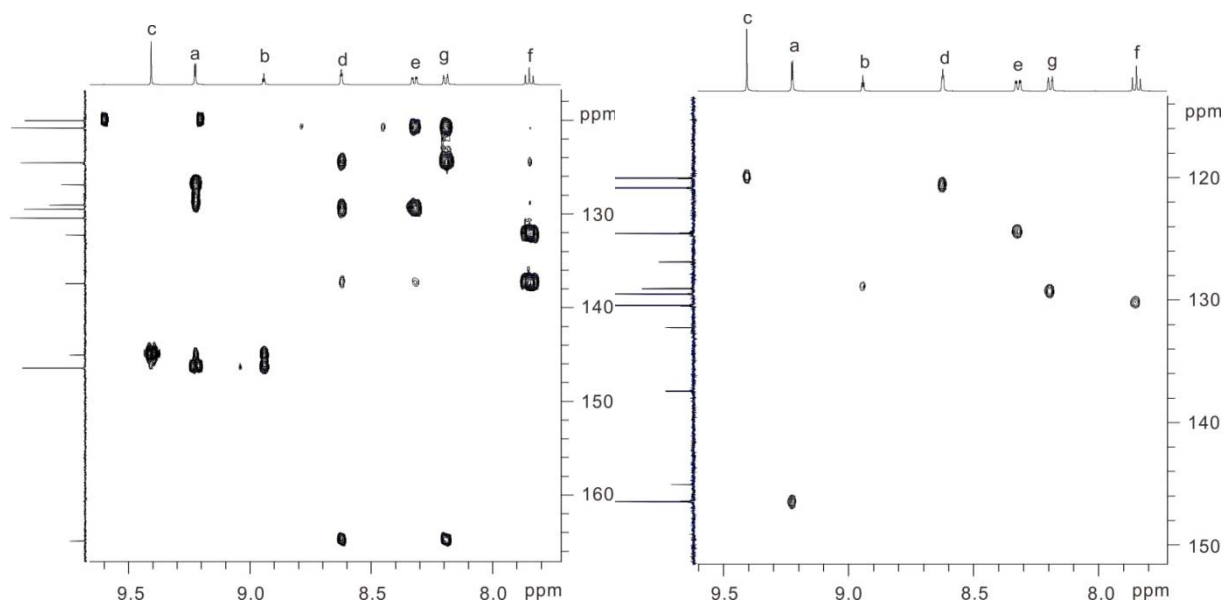


**5,5'-(1,1'-(5-(2,5,8,11-Tetraoxadodecan-1-oyl)-1,3-phenylene)bis(1H-1,2,3-triazole-4,1-diyl))bis(3-(1-(3-(2,5,8,11-tetraoxadodecan-1-oyl)phenyl)-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium) hexafluorophosphate (3).** Compound **3** was obtained by a similar procedure to compound **2** starting with compound **10**. Yield 100%, white solid.  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 400M Hz, 298 K):  $\delta$  = 10.06 (s, 2H), 9.83 (s, 2H), 9.64 (d,  $J$  = 3.2 Hz, 4H), 9.48 (s, 2H), 8.96 (s, 1H), 8.61 (s, 2H), 8.46 (s, 2H), 8.29 (d,  $J$  = 8.0 Hz, 2H), 8.15 (d,  $J$  = 8.0 Hz, 2H), 7.89 (t,  $J$  = 8.0 Hz, 2H), 4.62 (s, 2H), 4.61 (s, 6H), 4.49 (s, 4H), 3.88 (s, 2H), 3.81 (s, 4H), 3.67-3.61 (m, 6H), 3.59-3.50 (m, 12H), 3.40-3.37 (m, 6H), 3.19 (s, 6H), 3.16 9s, 3H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 125 MHz, 298 K):  $\delta$  = 164.7, 163.8, 141.85, 141.51, 141.43, 141.16, 137.59, 136.4, 135.2, 133.4, 131.56, 131.01, 130.58, 130.31, 129.9, 124.7, 123.53, 123.08, 120.35, 120.22, 115.6, 71.2, 69.87, 69.76, 69.74, 69.60, 68.24, 65.23, 64.67, 58.00, 57.99, 48.8. HRMS (ESI-FT-ICR)  $m/z$ :  $[\text{M}]^{2+}$  Calcd for  $\text{C}_{62}\text{H}_{72}\text{N}_{14}\text{O}_{15}$  626.2645, found 626.2631.

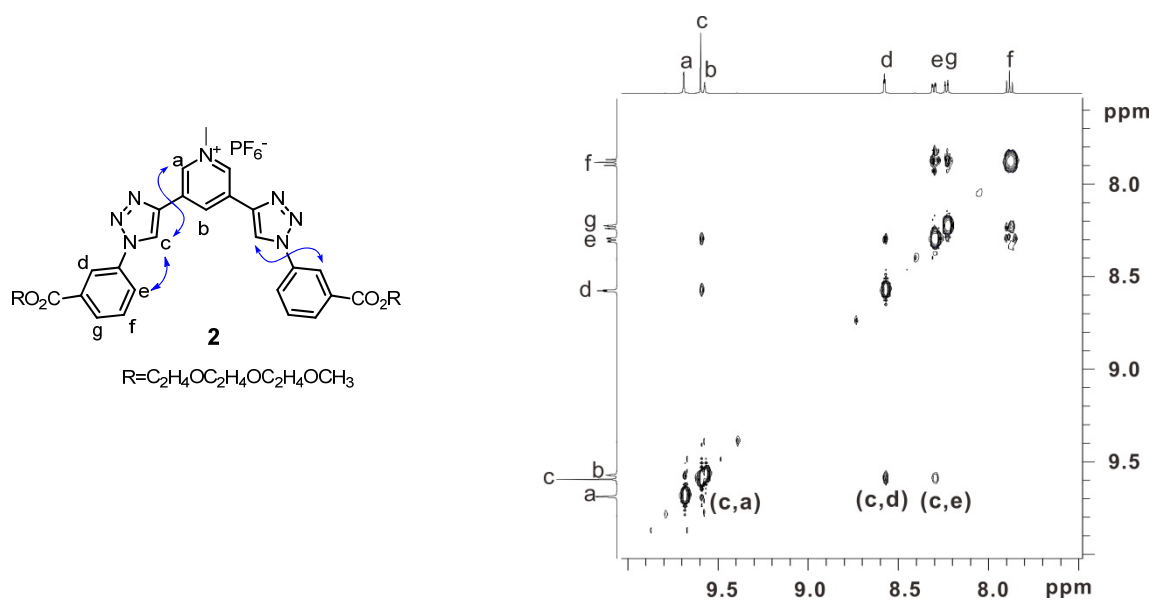
#### 4. 2D NMR Studies on Oligomer 1–3.



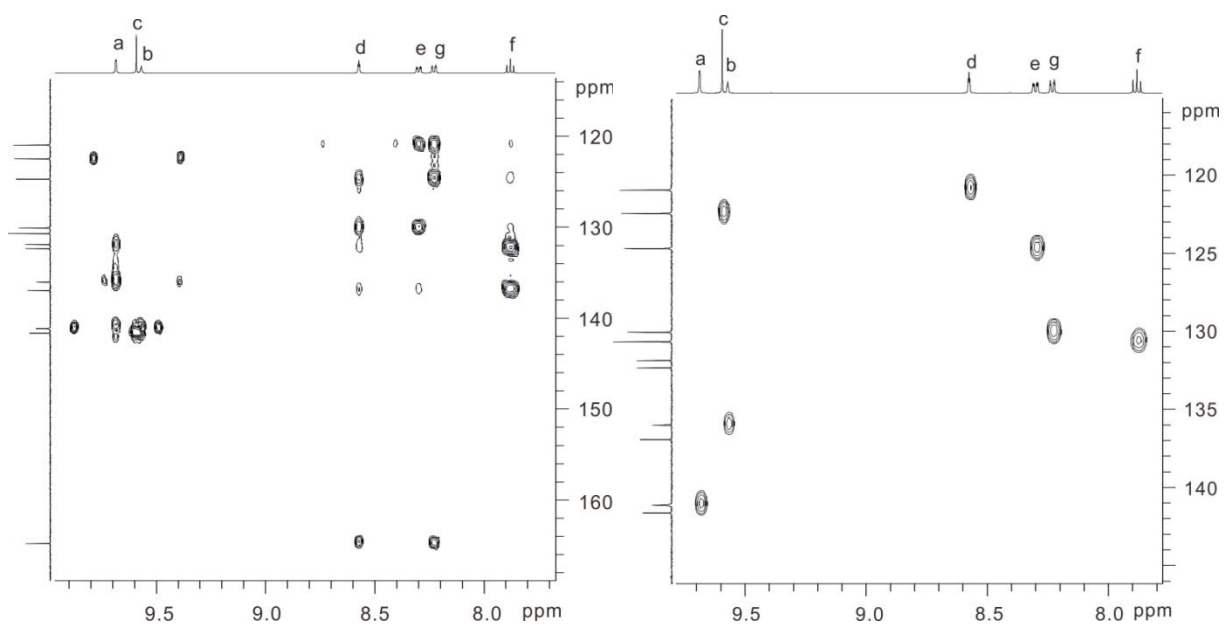
**Figure S1.** Partial NOESY spectrum (500 MHz, 298 K, acetone-*d*<sub>6</sub>) of compound 1. [1] = 6.0 mM.



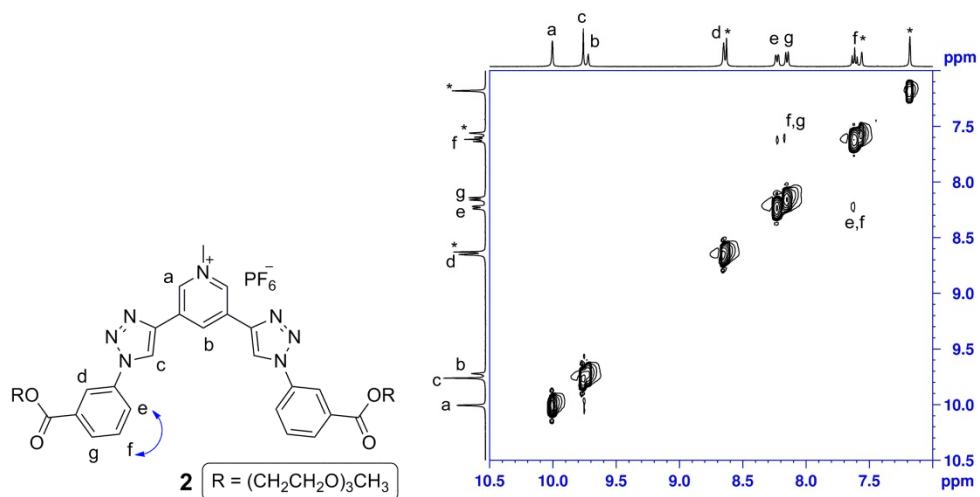
**Figure S2.** Partial HMBC (left) and HSQC (right) spectra (500 MHz, 298 K, acetone-*d*<sub>6</sub>) of compound 1. [1] = 6.0 mM.



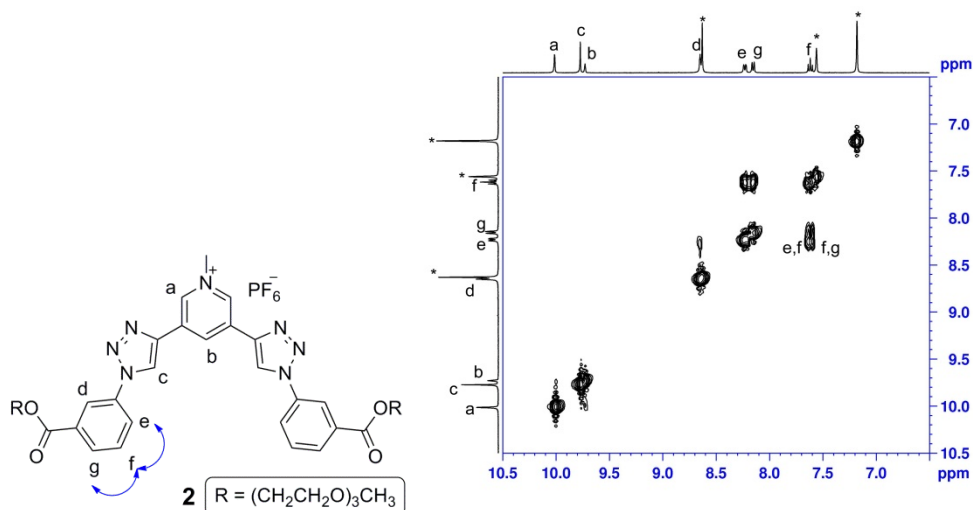
**Figure S3.** Partial NOESY spectrum (500 MHz, 298 K, acetone- $d_6$ ) of compound **2**. [**2**] = 6.0 mM.



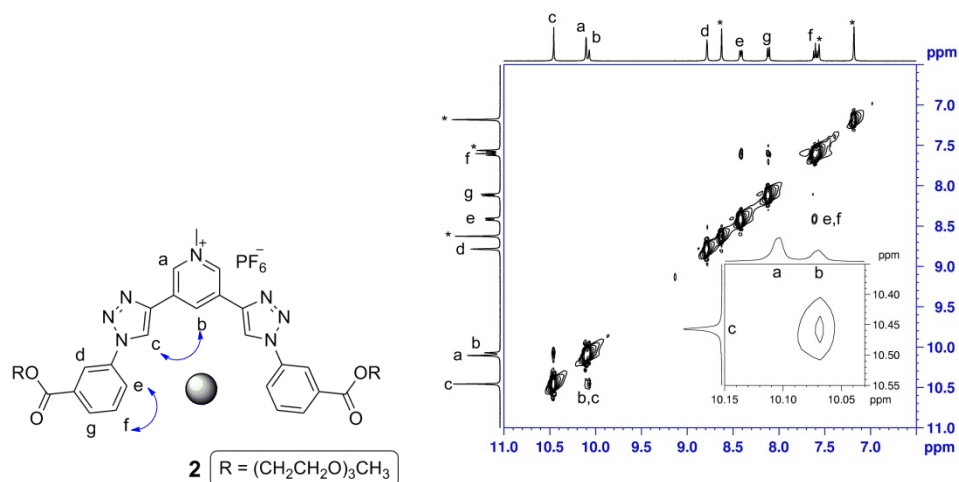
**Figure S4.** Partial HMBC (left) and HSQC (right) spectra (500 MHz, 298 K, acetone- $d_6$ ) of compound **2**, [**2**] = 6.0 mM.



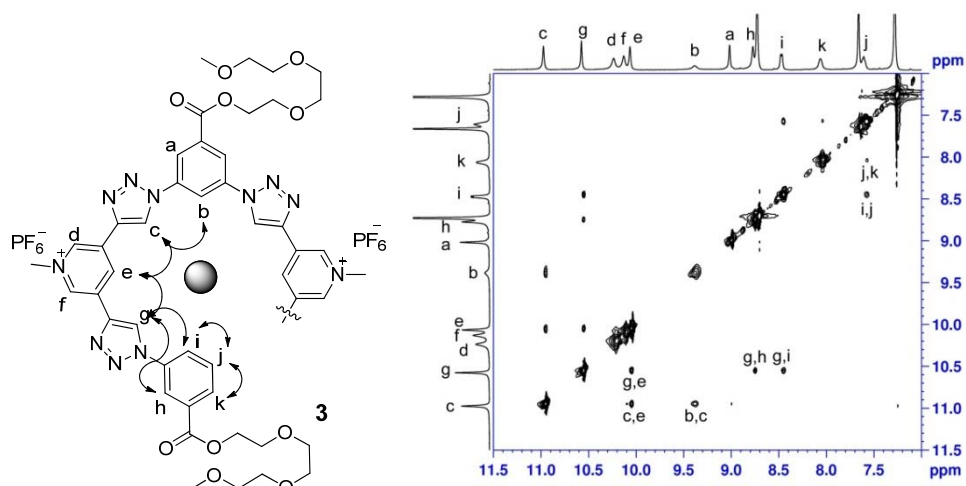
**Figure S5.** Partial  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum (400 MHz, 298 K, 6:94 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ ) of compound **2**.  $[\mathbf{2}] = 6.0$  mM.



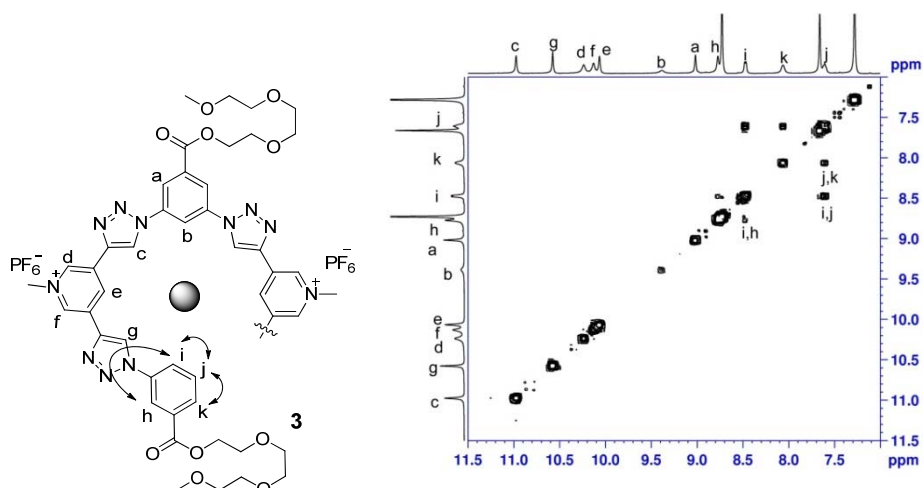
**Figure S6.** Partial  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (400 MHz, 298 K, 6:94 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ ) of compound **2**.  $[\mathbf{2}] = 2.0$  mM.



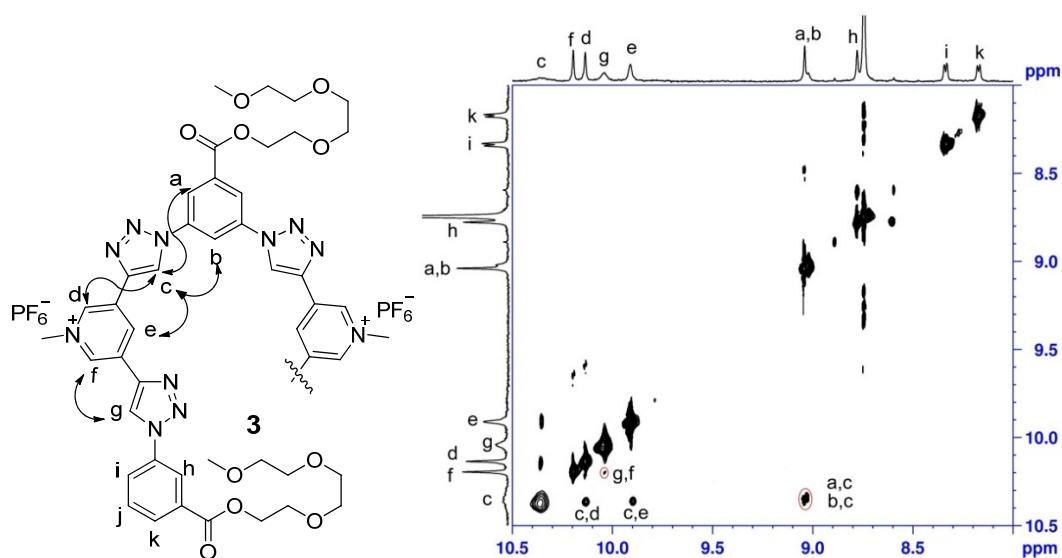
**Figure S7.** Partial  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum (400 MHz, 298 K, 6:94 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ ) of compound **2** with 2.0 equivalents of  $n\text{Bu}_4\text{N}^+\text{Br}^-$ ,  $[\mathbf{2}] = 5.0$  mM.



**Figure S8.** Partial  $^1\text{H}$ - $^1\text{H}$  ROESY spectrum (6:94 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ , 500 MHz, 298 K) of compound **3** in the presence of 5.0 equivalents of  $n\text{Bu}_4\text{N}^+\text{Br}^-$ . [**3**] = 2.0 mM.

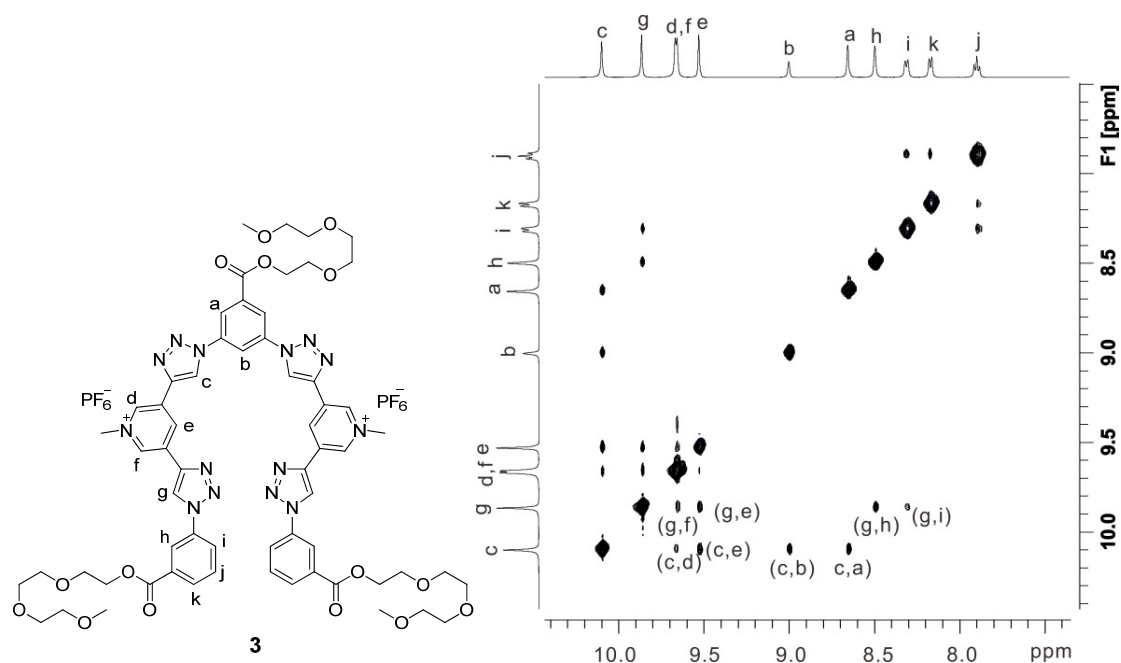


**Figure S9.** Partial  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (6:94 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ , 500 MHz, 298 K) of compound **3** with 5.0 equivalents of  $n\text{Bu}_4\text{N}^+\text{Br}^-$ , [**3**] = 2.0 mM.

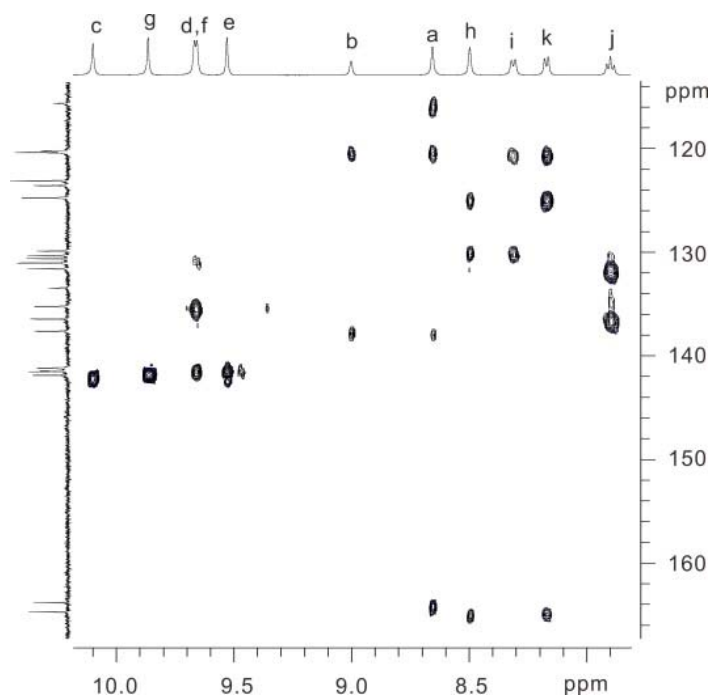


**Figure S10.** Partial  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum (5:95 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ , 600 MHz, 298 K) of compound **3** with 0.3 equivalent of  $n\text{Bu}_4\text{N}^+\text{Br}^-$ . [**3**] = 1.0 mM.

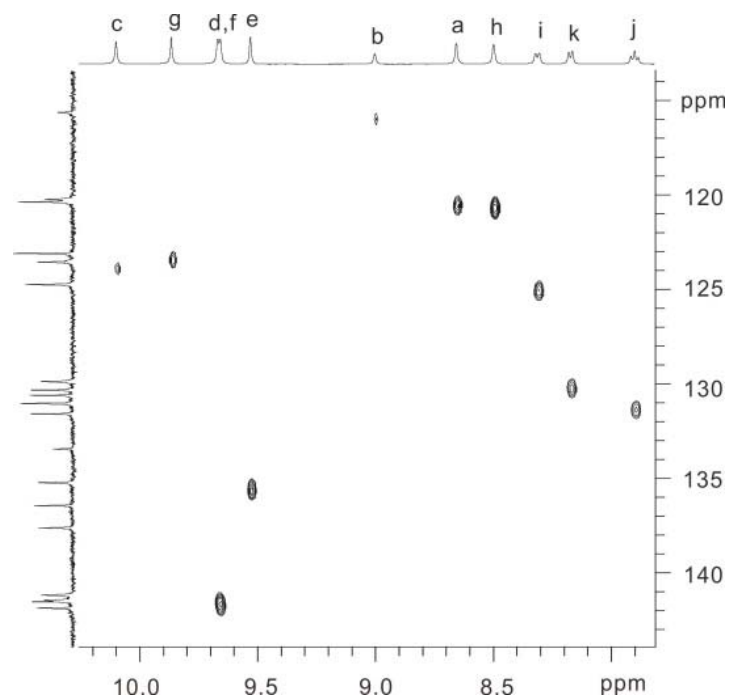
Nonaggregation of **3** takes places in polar solvent DMSO-*d*<sub>6</sub>, with evidence given by the corresponding <sup>1</sup>H NMR spectrum showed one set of sharp signals.



**Figure S11.** Partial <sup>1</sup>H-<sup>1</sup>H NOESY spectrum (DMSO-*d*<sub>6</sub>, 500 MHz, 298 K) of compound **3**. [**3**] = 6.0 mM.



**Figure S12.** Partial <sup>1</sup>H-<sup>13</sup>C HMBC spectrum (DMSO-*d*<sub>6</sub>, 500 MHz, 298 K) of compound **3**. [**3**] = 6.0 mM.



**Figure S13.** Partial  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum (DMSO- $d_6$ , 500 MHz, 298 K) of compound **3**. [**3**] = 6 mM.

## 5. $^1\text{H}$ NMR Titration Experiments.

### 5.a Summary of Binding Affinity Measurements.

**$^1\text{H}$  NMR Titration Experiments.** To a solution of **oligomer 1** (1 mM, 0.5 mL) in acetone- $d_6$ , a solutions of tetrabutylammonium halide ( $n\text{Bu}_4\text{N}^+\text{X}$ , X =  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ ) ( $[\text{X}] = 50$  mM) in the same solvent was gradually added. In this process, a serial of  $^1\text{H}$  NMR spectra of the sample were recorded by a Bruker Advance 400 MHz spectrometer at 298 K. More than 18 points were recorded and the data were processed by non-linear multivariate regression analysis by using the WinEQNMR program.<sup>[S3]</sup>

**Job Plot Experiments.** Stock solutions of **1** (1 mM) and  $n\text{Bu}_4\text{N}^+\text{X}^-$  (1 mM) were separately prepared in Acetone- $d_6$ .  $^1\text{H}$  NMR spectra was recorded for each of 10 different samples containing a total of 0.5 mL of **1** and  $n\text{Bu}_4\text{N}^+\text{X}^-$  in the following ratio: 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9. The Job plot was constructed by the change of chemical shift multiply proportion of **1** in each sample against the proportion of **1** in each solution.



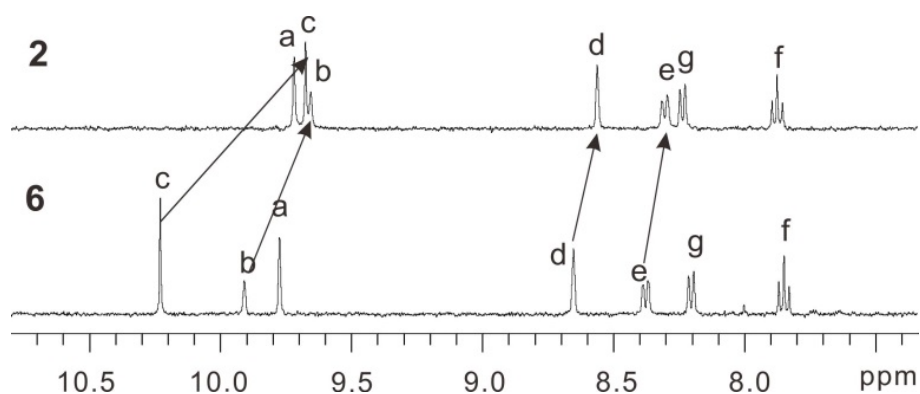
**Table S1.** Summary of Binding properties of **1**, **2** and **3** for Halide Anions <sup>a</sup>

Receptor	Anion	Proton <sup>b</sup>	In Acetone- <i>d</i> <sub>6</sub>				In 6:94 (v/v) D <sub>2</sub> O/Pyridine- <i>d</i> <sub>5</sub>			
			<i>K</i> <sub>a</sub> (M <sup>-1</sup> )	Δδ (ppm)	Mean <i>K</i> <sub>a</sub> <sup>c</sup>	SE/ ( <i>K</i> <sub>a</sub> or mean <i>K</i> <sub>a</sub> )	<i>K</i> <sub>a</sub> (M <sup>-1</sup> )	Δδ (ppm)	Mean <i>K</i> <sub>a</sub> <sup>c</sup>	SE/ ( <i>K</i> <sub>a</sub> or mean <i>K</i> <sub>a</sub> )
<b>1</b>	Cl <sup>-</sup>	Hc	327±20	1.40	/	6.12%	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
	Br <sup>-</sup>	Hc	134±5	1.23	/	3.73%	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
	I <sup>-</sup>	Hc	39±1	0.67	/	2.56%	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
<b>2</b>	Cl <sup>-</sup>	Hc	(5.40±0.21)×10 <sup>4</sup> <sup>e</sup> [7.35 ± 0.74]	1.49	(6.35± 0.30) × 10 <sup>4</sup> [6.74 ± 0.59]	4.72% [8.75%]	(3.28±0.11)×10 <sup>3</sup>	0.67	(3.28±0.11)×10 <sup>3</sup>	3.35%
		Hb	(7.29±0.15)×10 <sup>4</sup> <sup>e</sup> [6.13 ± 0.69]	0.79			<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
	Br <sup>-</sup>	Hc	(1.79±0.07)×10 <sup>4</sup>	1.32	/	3.91%	(2.49±0.09)×10 <sup>3</sup>	0.64	(2.49±0.09)×10 <sup>3</sup>	3.61%
	I <sup>-</sup>	Hc	(3.84±0.11)×10 <sup>3</sup>	1.00	/	2.86%	(1.13±0.04)×10 <sup>3</sup>	0.40	(1.13±0.04)×10 <sup>3</sup>	3.54%
<b>3</b>	Cl <sup>-</sup>	Hc	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	(7.49±0.29)×10 <sup>4</sup>	0.68	(4.62±0.17)×10 <sup>4</sup>	3.68%
		Hg	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	(1.75±0.17)×10 <sup>4</sup>	0.51		
	Br <sup>-</sup>	Hc	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	(9.91±0.52)×10 <sup>4</sup>	0.77	(6.99±0.30)×10 <sup>4</sup>	4.29%
		Hg	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	(4.08±0.27)×10 <sup>4</sup>	0.60		
	I <sup>-</sup>	Hc	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	(4.13±0.24)×10 <sup>4</sup>	0.69	(3.32±0.14)×10 <sup>4</sup>	4.22%
		Hg	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	(2.52±0.13)×10 <sup>4</sup>	0.55		

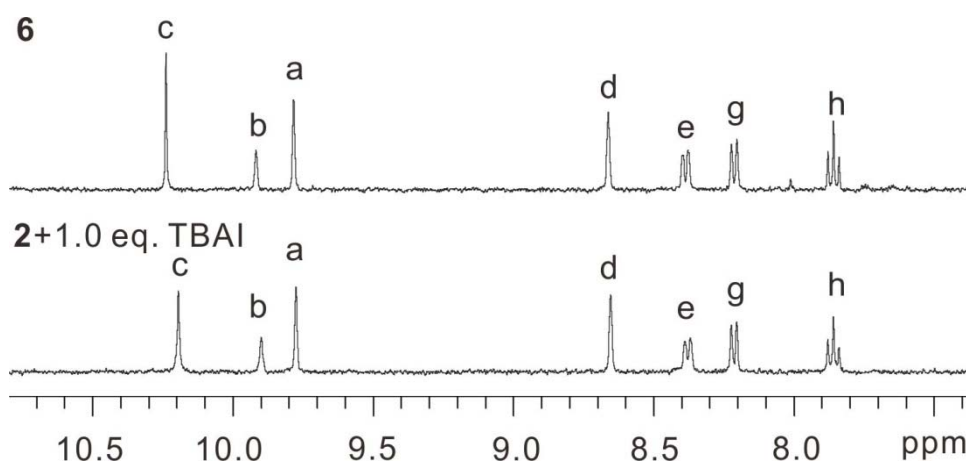
<sup>a</sup> The association constants were calculated by WinEQNMR. The association constant (*K*<sub>21</sub>) of the 1:2 (receptor : anion) complex is included in square brackets when it is applicable. <sup>b</sup> Titration profile of the proton used for *K*<sub>a</sub> calculation. <sup>c</sup> Standard error of mean *K*<sub>a</sub> was calculated according to error propagation of that  $K_a = \frac{K_a^{H_b} + K_a^{H_d}}{2}$  and  $\delta K_a = \frac{\sqrt{\delta K_a^{H_b} + \delta K_a^{H_d}}}{2}$  if two *K*<sub>a</sub> was derived from the binding isotherms of two protons, for example, H<sub>b</sub> and H<sub>d</sub>, independently. <sup>d</sup> Not investigated. <sup>e</sup> Fitted the binding profile in a 1:2 (receptor : anion) binding model. Since WinEQNMR provides only the values of β<sub>1</sub> (β<sub>1</sub> = *K*<sub>11</sub>) and β<sub>2</sub> (β<sub>2</sub> = *K*<sub>11</sub>*K*<sub>21</sub>), *K*<sub>21</sub> was consequently obtained by  $K_{21} = \beta_2/\beta_1$ , in which the standard deviation was propagated according to  $\Delta K_{21} = K_{21} \cdot [(\Delta(\beta_1)/\beta_1)^2 + (\Delta(\beta_2)/\beta_2)^2]^{1/2}$ .

## 5.b $^1\text{H}$ NMR Titration on Receptor **1** and **2** in Acetone- $d_6$ .

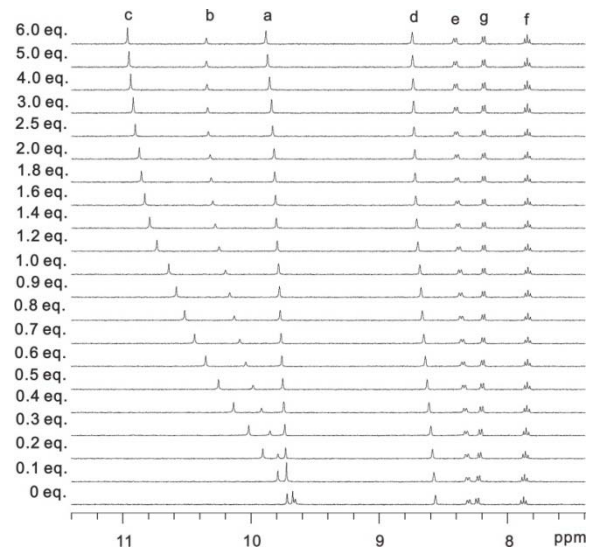
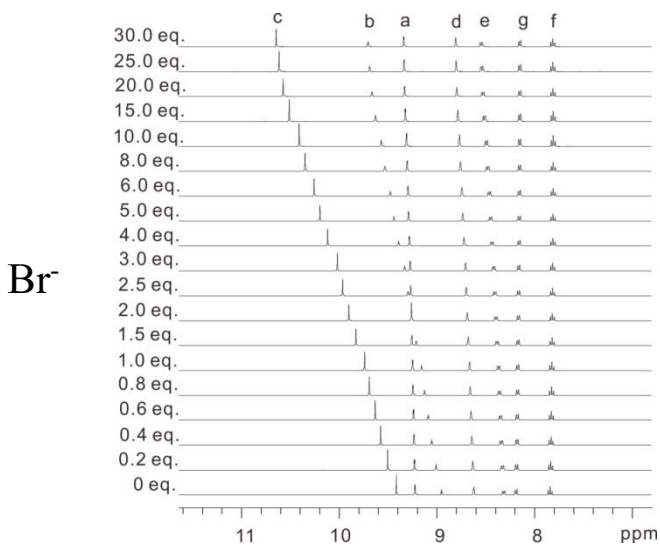
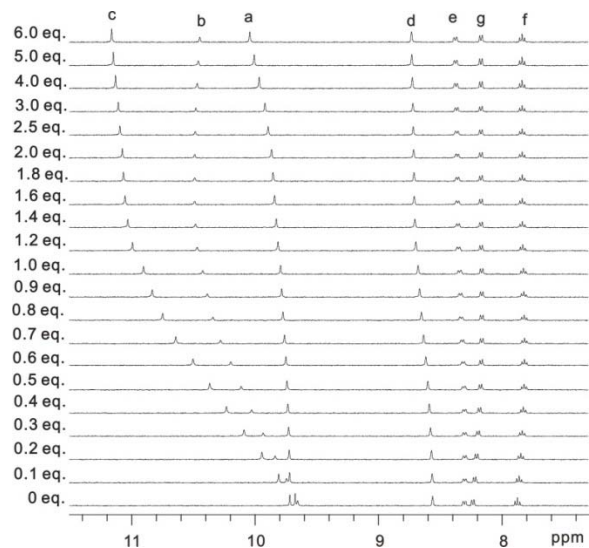
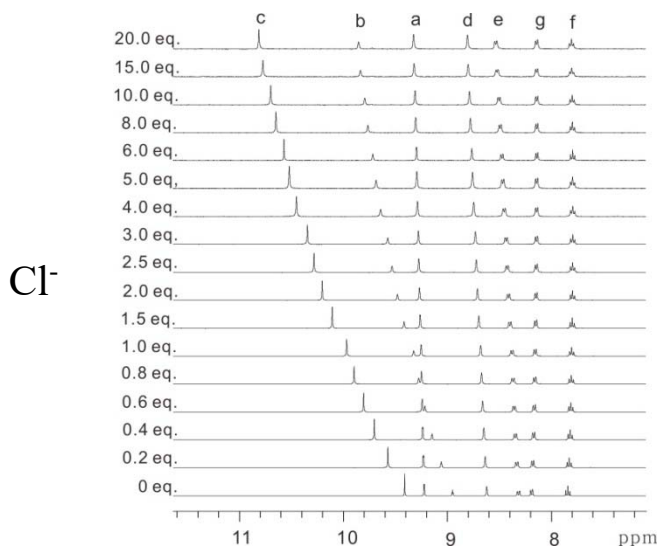
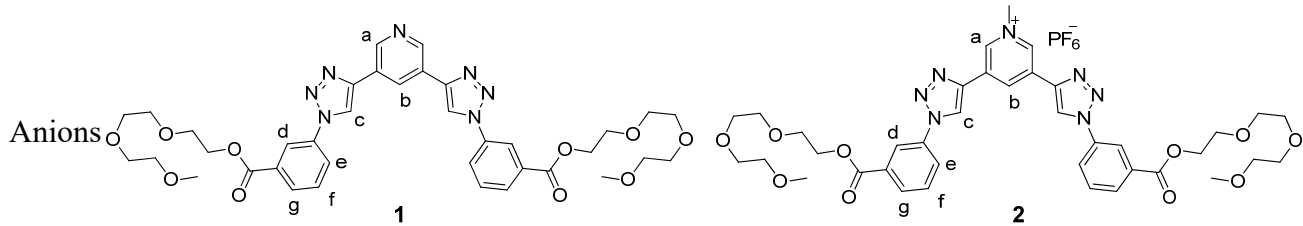
Compared the  $^1\text{H}$  NMR spectrum of **2** to that of **6**, the significant upshifts of  $\text{H}_b$  and  $\text{H}_a$  indicate the receptor binds very weakly to hexafluorophosphate anions, providing hexafluorophosphate to be a good counter anions for the studied systems. In the synthesis of **2**, the iodide-to-hexafluorophosphate exchange procedure should give a completely displacement of iodide anions, as demonstrated by that the  $^1\text{H}$  NMR spectrum of **6** is identical to that of **2** in the presence of 1.0 equiv of iodide anions (Figure S15).

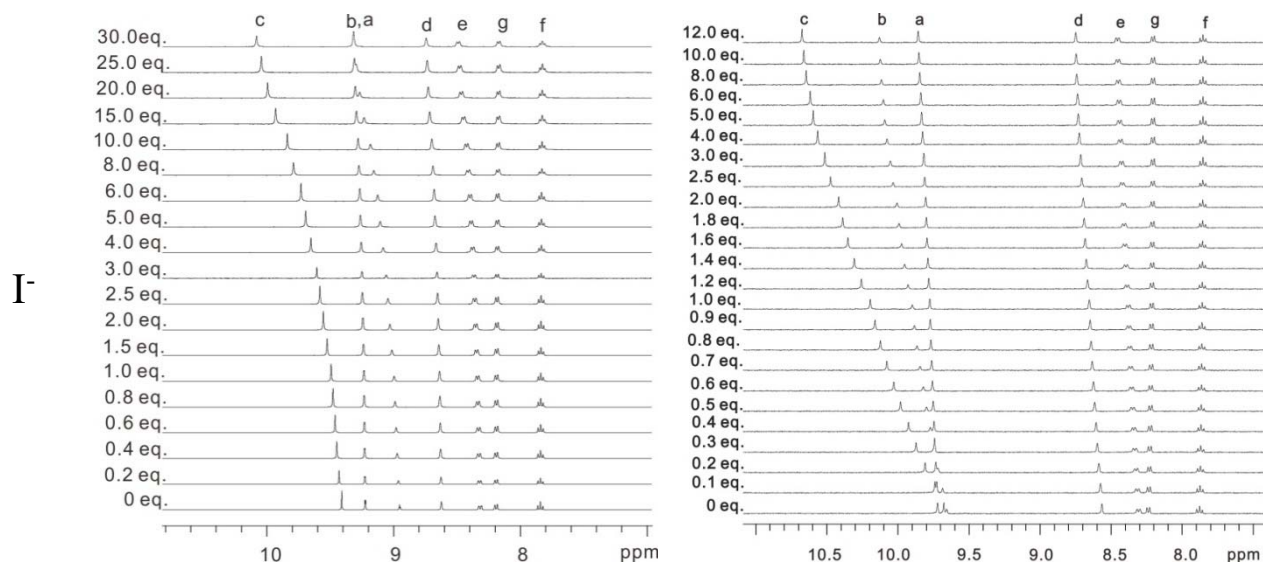


**Figure S14.** Partial  $^1\text{H}$  NMR spectra (400 MHz, 298K) of compound **2** and **6** in acetone- $d_6$ .  $[\mathbf{2}] = [\mathbf{6}] = 0.5$  mM.

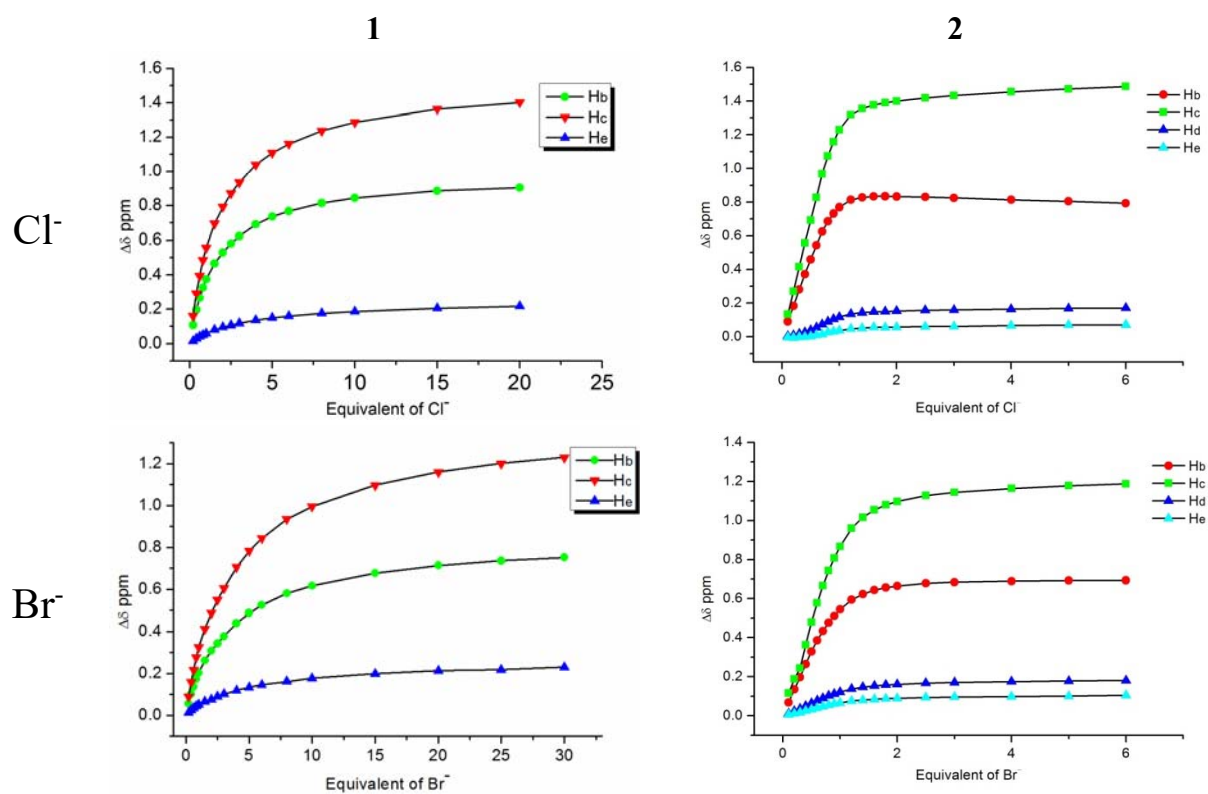


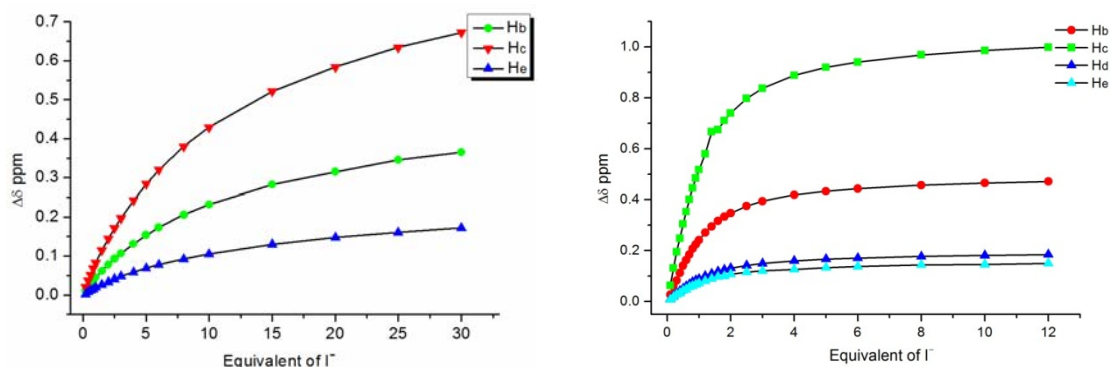
**Figure S15.** Partial  $^1\text{H}$  NMR spectra (400 MHz, 298 K) of acetone- $d_6$  solution of compound **6** and **2** in the presence of 1 equiv  $n\text{Bu}_4\text{N}^+\text{I}^-$ .  $[\mathbf{6}] = [\mathbf{2}] = [n\text{Bu}_4\text{N}^+\text{I}^-] = 0.5$  mM.



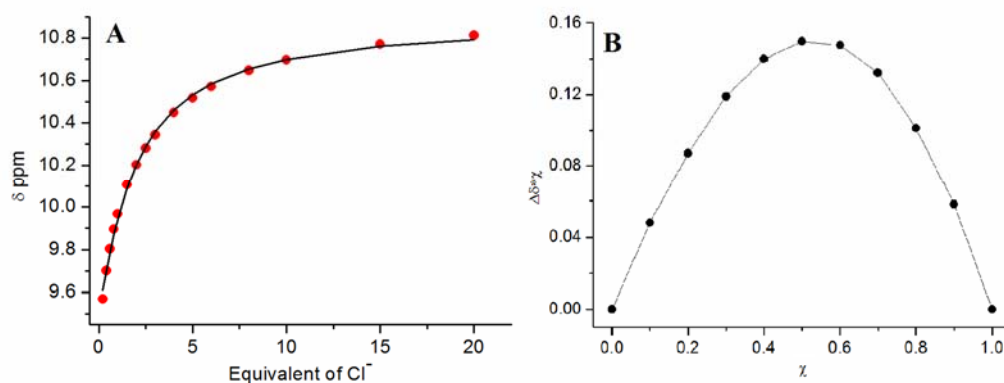


**Figure S16.** Changes of partial  $^1\text{H}$  NMR spectra (400 MHz, 298 K) of **1** (left column) and **2** (right column) in acetone- $d_6$  upon titration with  $n\text{Bu}_4\text{N}^+\text{Cl}^-$  (top),  $n\text{Bu}_4\text{N}^+\text{Br}^-$  (middle) and  $n\text{Bu}_4\text{N}^+\text{I}^-$  (bottom). ( $[\mathbf{1}] = 2 \text{ mM}$ ,  $[\mathbf{2}] = 0.5 \text{ mM}$ )

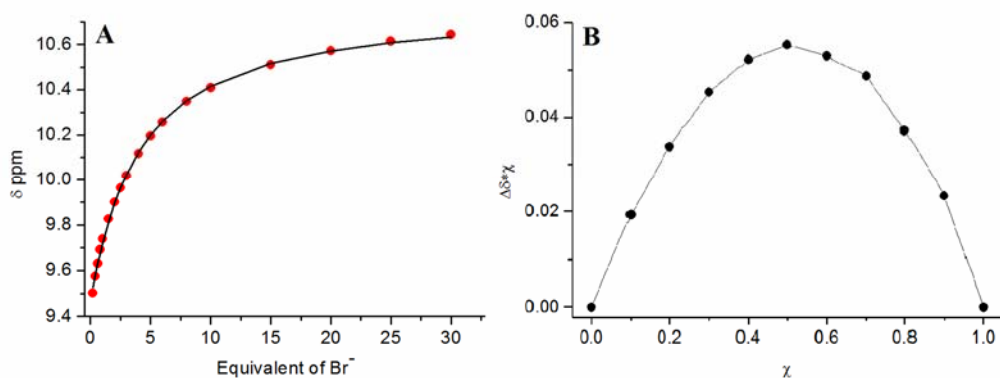


I<sup>-</sup>

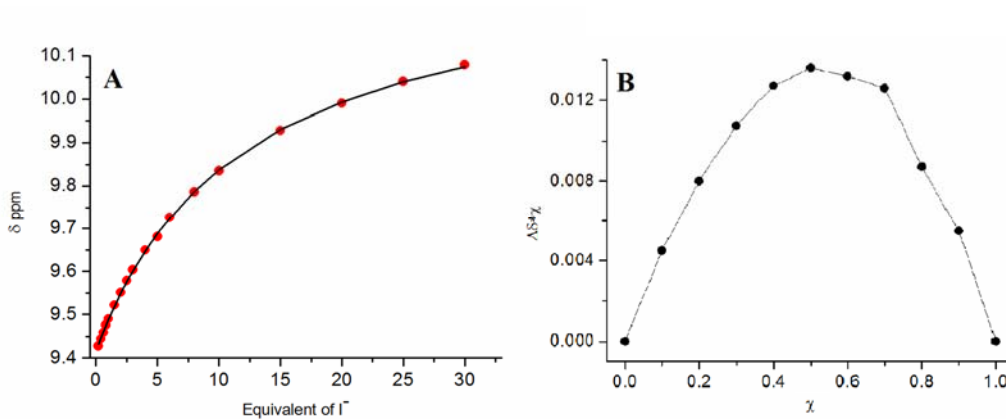
**Figure S17.** Changes in  $^1\text{H}$  chemical shifts of some protons on **1** (left column) and **2** (right column) in acetone- $d_6$  with increasing the concentrations of chloride (top), bromide (middle) and iodide (bottom) ions. ( $[\mathbf{1}] = 2 \text{ mM}$ ,  $[\mathbf{2}] = 0.5 \text{ mM}$ , 400 MHz, 298 K)



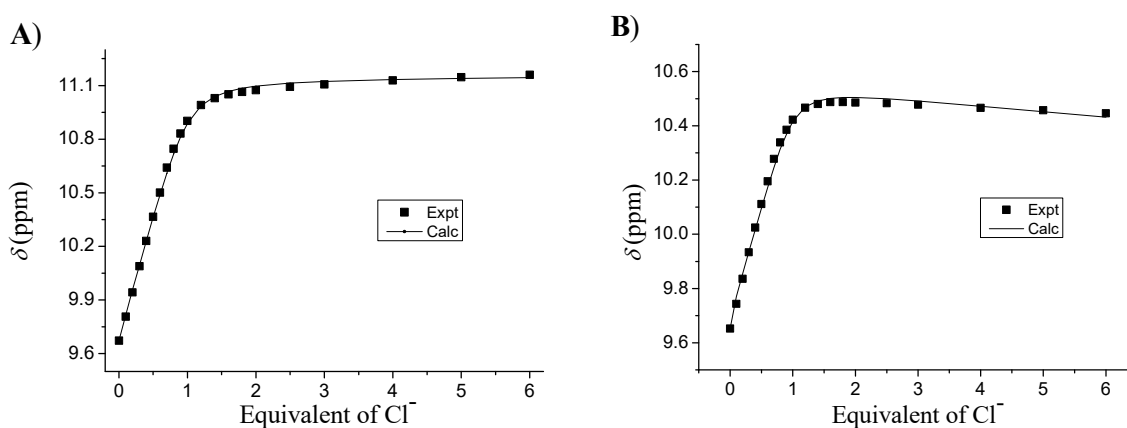
**Figure S18.** A) Changes in the triazole ( $\text{H}_c$ )  $^1\text{H}$  chemical shift of **1** in acetone- $d_6$  with increasing concentration of chloride anions at ambient temperature. The data ( $\bullet$ ) were curve-fitted to a 1:1 binding model (fitting-curve was represented by line).  $[\mathbf{1}] = 2.0 \text{ mM}$ . B) Job Plot for complexation of **1** in acetone- $d_6$  with  $n\text{Bu}_4\text{N}^+\text{Cl}^-$  by NMR spectroscopy, in which the chemical shift of triazole ( $\text{H}_c$ ) was monitored.  $[\mathbf{1}] + [\text{Cl}^-] = 1.0 \text{ mM}$ .



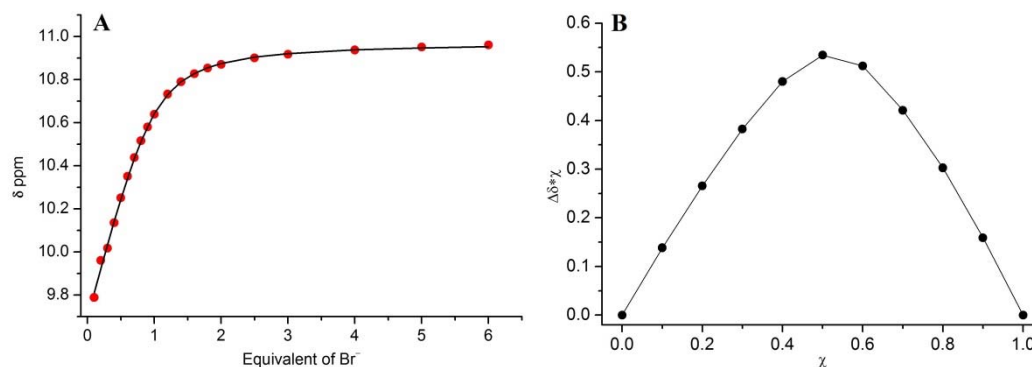
**Figure S19.** A) Changes in the triazole ( $\text{H}_c$ )  $^1\text{H}$  chemical shift of **1** in acetone- $d_6$  with increasing concentration of bromide anions at ambient temperature. The data ( $\bullet$ ) were curve-fitted to a 1:1 binding model (fitting-curve was represented by line).  $[\mathbf{1}] = 2.0 \text{ mM}$ . B) Job Plot for complexation of **1** in acetone- $d_6$  with  $n\text{Bu}_4\text{N}^+\text{Br}^-$  by NMR spectroscopy, in which the chemical shift of triazole ( $\text{H}_c$ ) was monitored.  $[\mathbf{1}] + [\text{Br}^-] = 1.0 \text{ mM}$ .



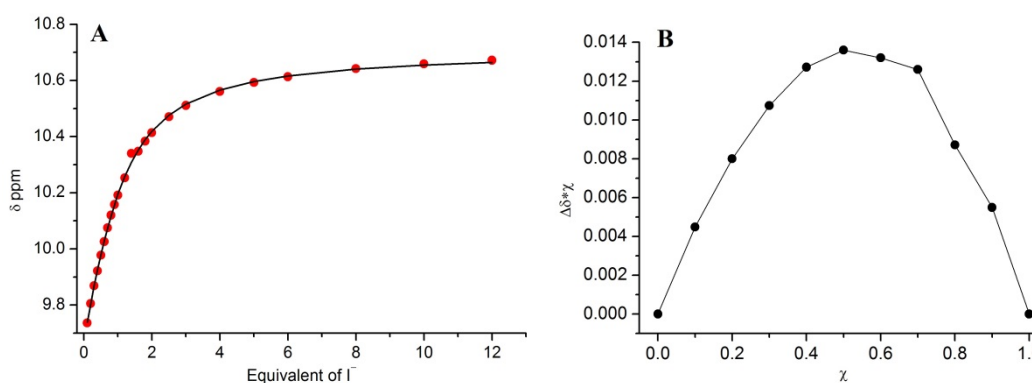
**Figure S20.** A) Changes in the triazole ( $H_c$ )  $^1H$  chemical shift of **1** in acetone- $d_6$  with increasing concentration of iodide anions at ambient temperature. The data ( $\bullet$ ) were curve-fitted to a 1:1 binding model (fitting-curve was represented by line).  $[1] = 2.0$  mM. B) Job Plot for complexation of **1** in acetone- $d_6$  with  $nBu_4N^+I^-$  by NMR spectroscopy, in which the chemical shift of triazole ( $H_c$ ) was monitored.  $[1] + [I^-] = 1.0$  mM.



**Figure S21.** Changes in the chemical shift of A) triazole proton  $H_c$  and B) pyridinium proton  $H_b$  of **2** in acetone- $d_6$  with increasing concentration of chloride anions at ambient temperature. The data ( $\blacksquare$ ) were curve-fitted to a 1:2 (**2** to chlorides) binding model (fitting-curves were represented by lines).  $[2] = 0.5$  mM.

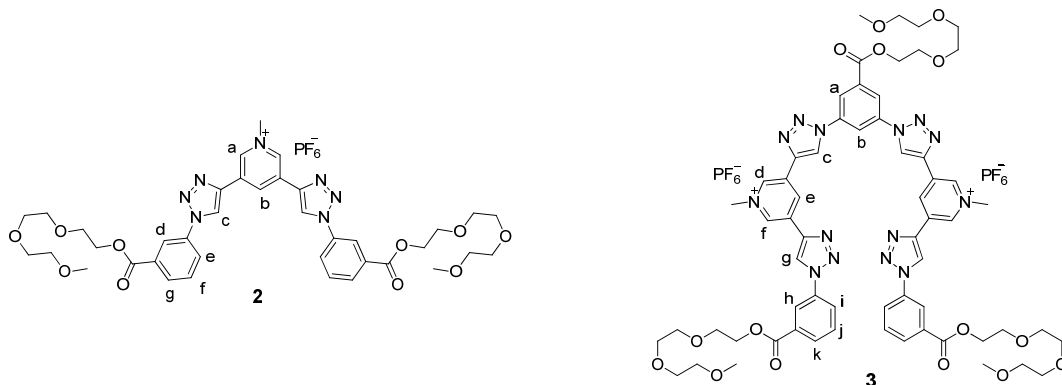


**Figure S22.** A) Changes in the triazole (H<sub>c</sub>) <sup>1</sup>H chemical shift of **2** in acetone-*d*<sub>6</sub> with increasing concentration of bromide anions at ambient temperature. The data (●) were curve-fitted to a 1:1 binding model (fitting-curve was represented by line). [2] = 0.5 mM. B) Job Plot for complexation of **2** in acetone-*d*<sub>6</sub> with *n*Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup> by NMR spectroscopy, in which the chemical shift of triazole (H<sub>c</sub>) was monitored. [2] + [Br<sup>-</sup>] = 1.0 mM.

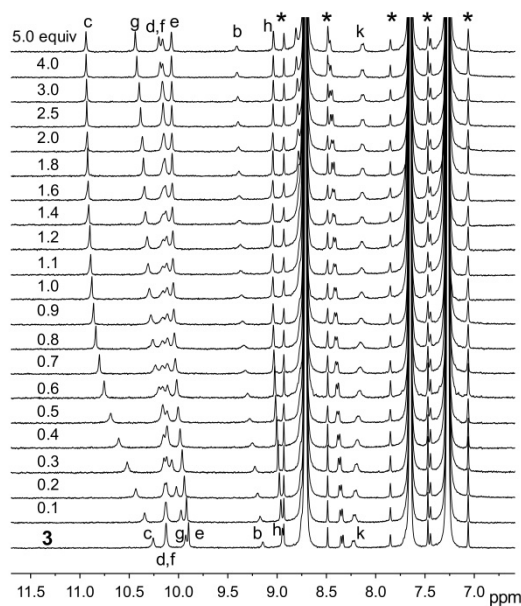
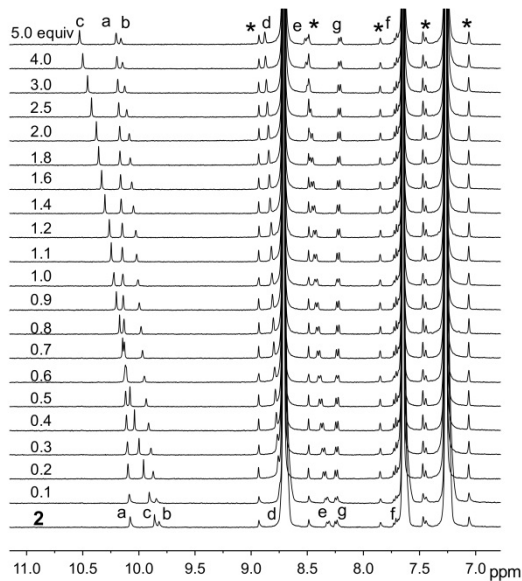


**Figure S23.** A) Changes in the triazole (H<sub>c</sub>) <sup>1</sup>H chemical shift of **2** in acetone-*d*<sub>6</sub> with increasing concentration of iodide anions at ambient temperature. The data (●) were curve-fitted to a 1:1 binding model (fitting-curve was represented by line). [2] = 0.5 mM. B) Job Plot for complexation of **2** in acetone-*d*<sub>6</sub> with *n*Bu<sub>4</sub>N<sup>+</sup>I<sup>-</sup> by NMR spectroscopy, in which the chemical shift of triazole (H<sub>c</sub>) was monitored. [2] + [I<sup>-</sup>] = 1.0 mM.

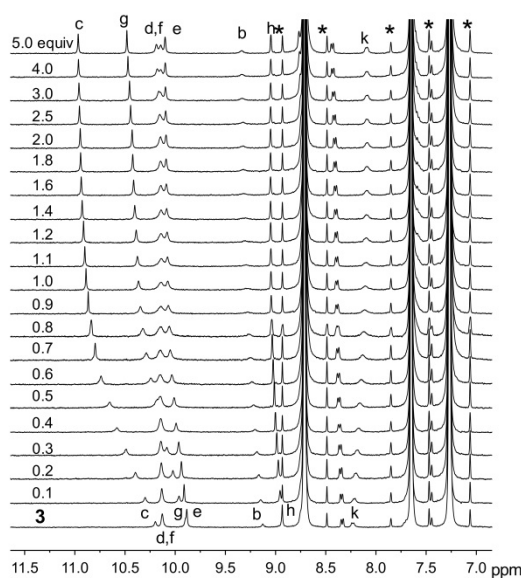
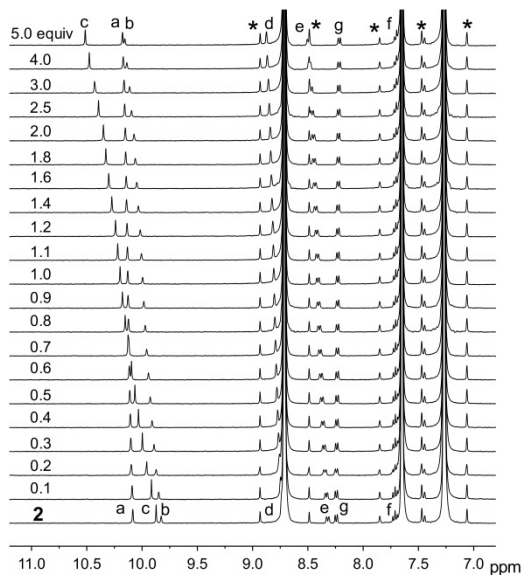
5.c  $^1\text{H}$  NMR Titration on Receptor 2 and 3 in 6:94 (v/v)  $\text{D}_2\text{O}/\text{Pyridine-}d_5$ .



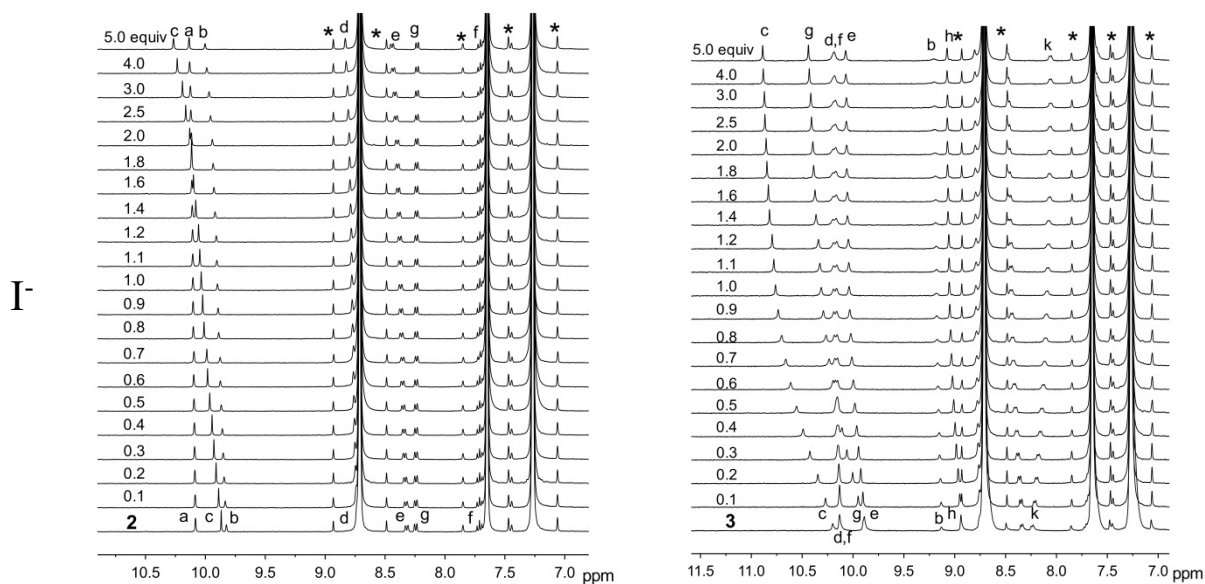
$\text{Cl}^-$



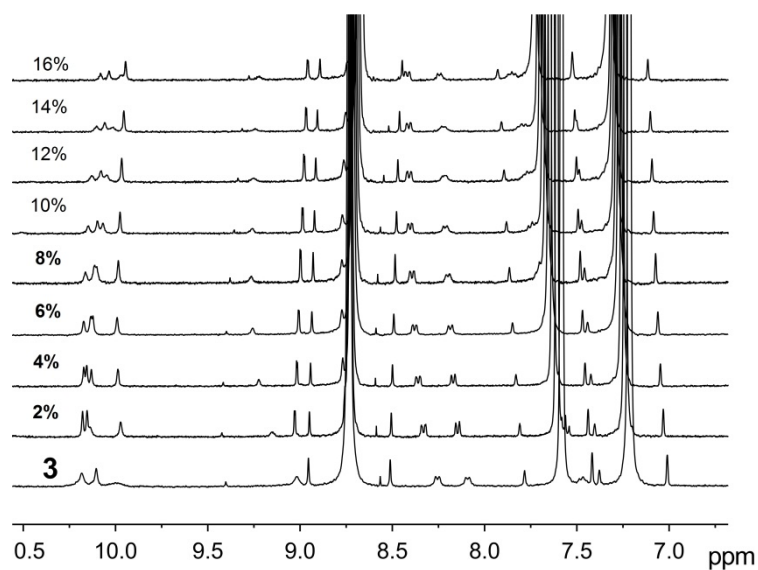
$\text{Br}^-$



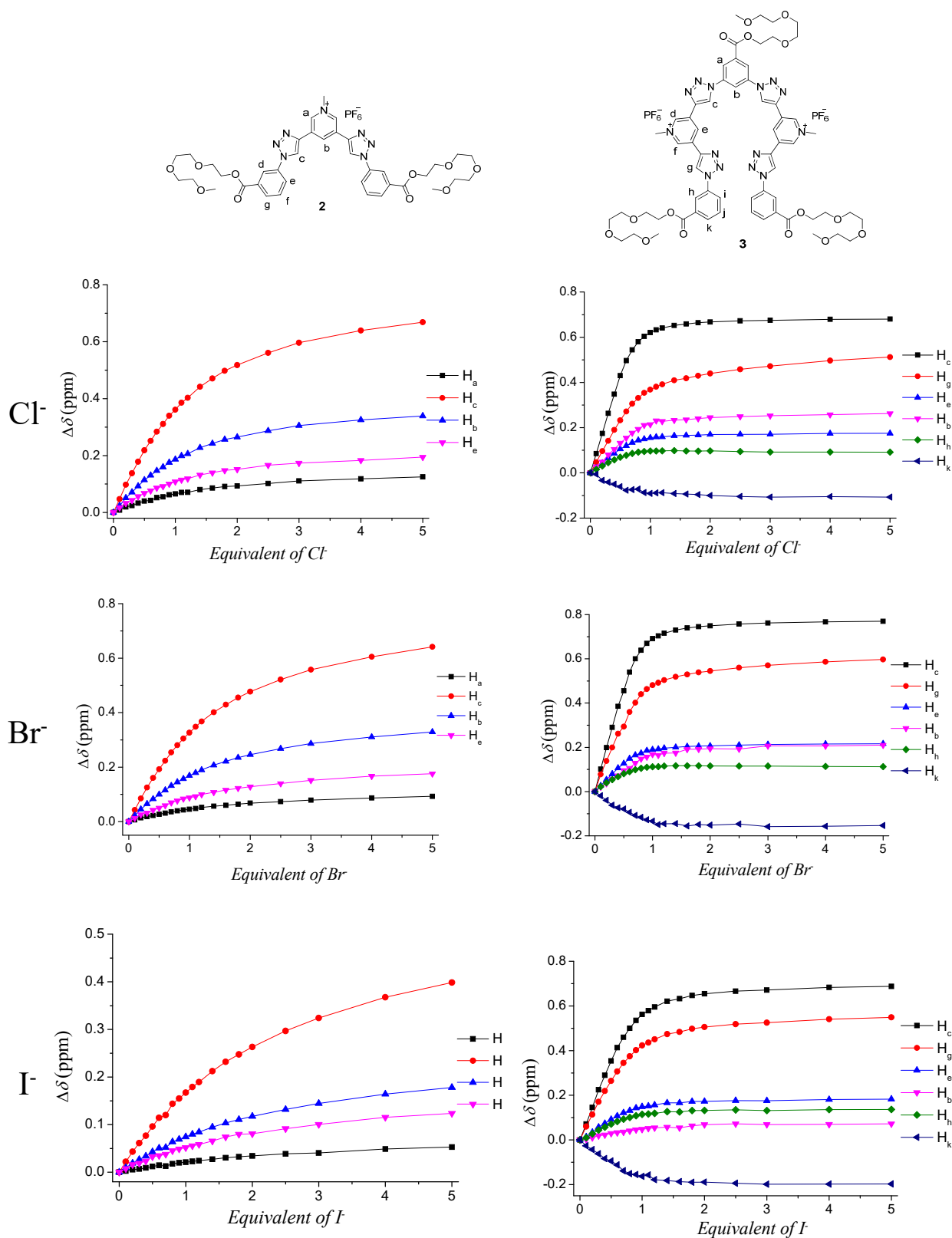




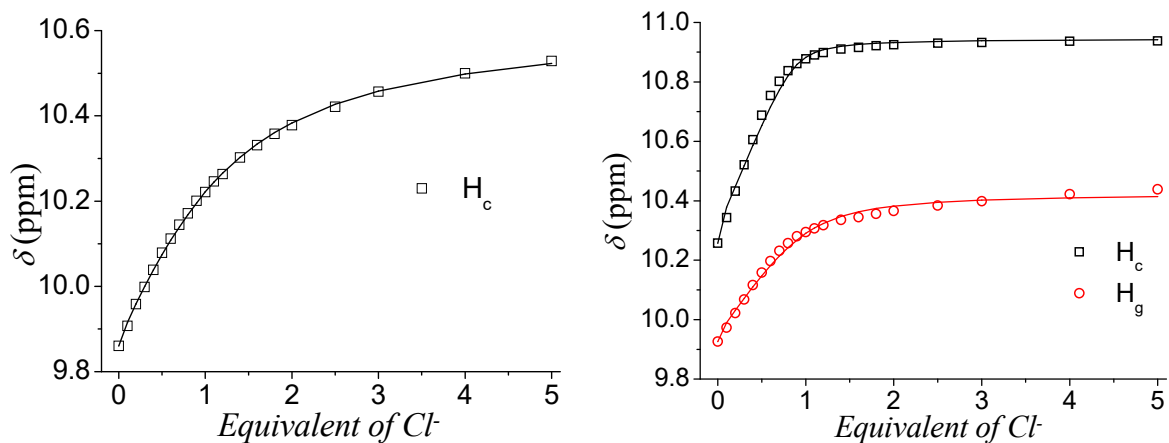
**Figure S24.** Changes of partial  $^1\text{H}$  NMR spectra (400 MHz, 298 K) of **2** (left column) and **3** (right column) in 6:94 (v/v)  $\text{D}_2\text{O}$ /pyridine- $d_5$  upon titration with  $n\text{Bu}_4\text{N}^+\text{Cl}^-$  (top),  $n\text{Bu}_4\text{N}^+\text{Br}^-$  (middle) and  $n\text{Bu}_4\text{N}^+\text{I}^-$  (bottom). ( $[\mathbf{2}] = [\mathbf{3}] = 0.5 \text{ mM}$ )



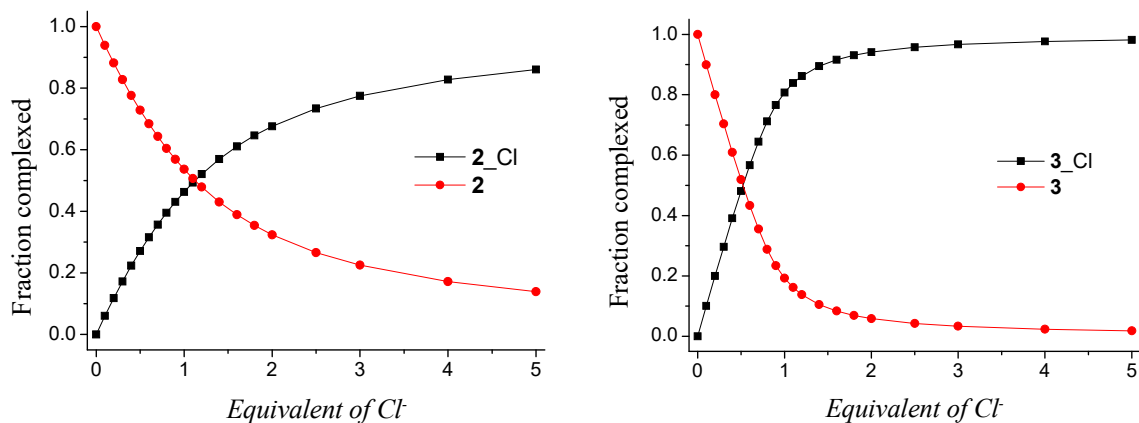
**Figure S25.** Changes of partial  $^1\text{H}$  NMR spectrum (400 MHz, 298 K) of **3** during the increasing of  $\text{D}_2\text{O}$  in pyridine- $d_5$ . ( $[\mathbf{3}] = 0.5 \text{ mM}$ )



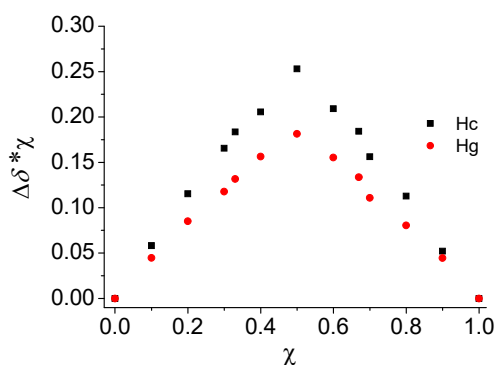
**Figure S26.** Changes in  $^1\text{H}$  chemical shifts of some protons on **2** (left column) and **3** (right column) in 6:94 (v/v)  $\text{D}_2\text{O}$ /pyridine- $d_5$  with increasing the concentrations of chloride (top), bromide (middle) and iodide (bottom) ions. ( $[\mathbf{2}] = [\mathbf{3}] = 1 \text{ mM}$ , 400 MHz, 298 K)



**Figure S27.** Changes in chemical shift of triazole proton in **2** (left) and **3** (right) upon titration of chloride ions. The experiment dates (point) were curved-fitted (line) to 1:1 model by WinEQNMR. ( $[2] = [3] = 0.5$  mM, 400 MHz, 6:94 (v/v)  $D_2O/Pyridine-d_5$ , 298 K)



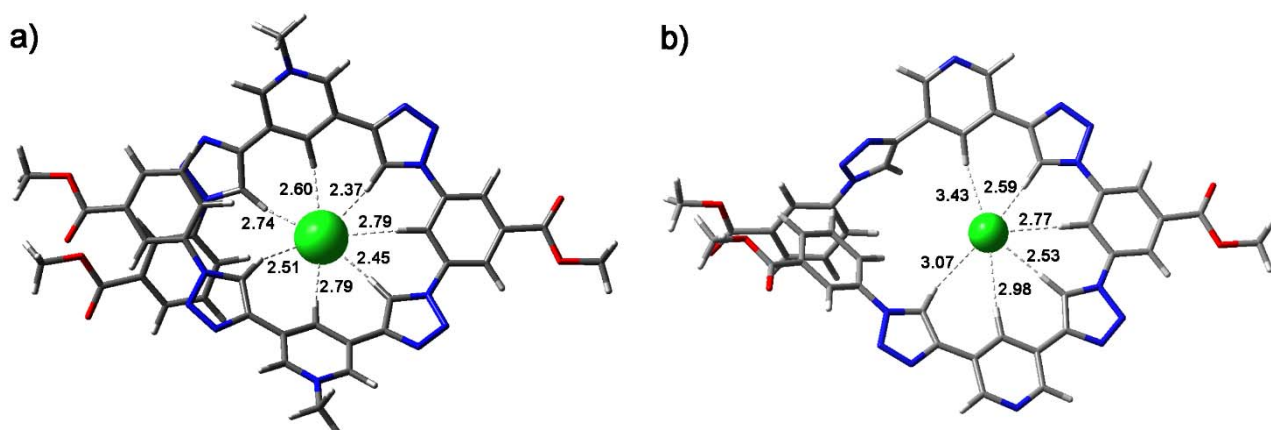
**Figure S28.** The changes in the fraction of complexed **2** and **3** upon titration of  $nBu_4N^+Cl^-$  as determined by 1:1 model. ( $[2] = [3] = 0.5$  mM, 400 MHz, 6:94 (v/v)  $D_2O/pyridine-d_5$ , 298 K)



**Figure S29.** Job plot of **3** with  $nBu_4N^+Br^-$ . ( $\chi = [3]/([3]+[Br^-])$ , 400 MHz, 6:94 (v/v)  $D_2O/pyridine-d_5$ , 298 K)

## 6. DFT Calculations

**Computational Details.** The fully optimized geometries (gas phase) for  $\mathbf{3}\cdot\text{Cl}^-$  and an analog of it, in which all the pyridinium groups in  $\mathbf{3}\cdot\text{Cl}^-$  were displaced with pyridyl ones (denoted  $\mathbf{3Py}\cdot\text{Cl}^-$ ), were calculated by using DFT with the B3LYP hybrid functional and 3-21G basis set within the Gaussian 09 software package, wherein the final geometries obtained were confirmed as minima by vibrational analysis. Four processing cores and 10 GB physical memory were used for the optimization. To reduce computational costs, all the long PEG esters were replaced with methyl ones. For the same reason, tetramethyl ammonium cation was used as the counterion for chloride, and hexafluorophosphate anions as the counterions of pyridinium in the calculations.



**Figure S30.** Energy-minimized structures (RB3LYP/3-21G, gas phase) of a)  $\mathbf{3}\cdot\text{Cl}^-$  and b)  $\mathbf{3Py}\cdot\text{Cl}^-$ . To reduce computational costs, long PEG ester chains were replaced with methyl ones. Counterions were omitted for clarities.

### Optimized geometries/coordinate obtained from Gaussian

#### $\mathbf{3}\cdot\text{Cl}^-$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.190554	3.882592	-0.750421
2	6	0	1.137830	3.336571	-0.526262
3	7	0	2.194525	4.163163	-0.180407
4	7	0	3.265543	3.432182	0.108463
5	7	0	2.854471	2.060832	-0.064708

6	6	0	3.727095	1.009671	0.341787
7	6	0	5.105392	1.160476	0.205977
8	6	0	3.195796	-0.136706	0.939467
9	6	0	-7.381192	-1.649298	-2.202961
10	6	0	-6.920485	-0.335993	-2.335066
11	6	0	-6.538391	-2.699088	-1.822631
12	6	0	-5.199728	-2.416193	-1.570994
13	6	0	-5.575780	-0.076998	-2.071994
14	6	0	-4.724676	-1.111182	-1.689340
15	7	0	-5.028786	1.230643	-2.107566
16	7	0	-5.848219	2.414709	-1.964348
17	7	0	-4.989624	3.411026	-1.758371
18	6	0	-3.689148	2.922434	-1.756446
19	6	0	-3.713690	1.565895	-1.995761
20	7	0	-4.266000	-3.400780	-1.156202
21	7	0	-4.638839	-4.597392	-0.431568
22	7	0	-3.484083	-5.150266	-0.051866
23	6	0	-2.424765	-4.374216	-0.494344
24	6	0	-2.913459	-3.286113	-1.187530
25	6	0	-1.021195	-4.606460	-0.197530
26	6	0	-2.532492	3.710289	-1.360116
27	6	0	-1.244284	3.151645	-1.302834
28	6	0	-0.034900	-3.884466	-0.881967
29	6	0	-0.622285	-5.466332	0.816936
30	6	0	1.314219	-4.031799	-0.559069
31	6	0	1.653514	-4.910756	0.468310
32	7	0	0.693712	-5.605407	1.120124
33	6	0	2.339824	-3.267783	-1.240169
34	7	0	3.684112	-3.583626	-1.173027
35	7	0	4.386213	-2.704608	-1.885510
36	7	0	3.416357	-1.776518	-2.416990
37	6	0	2.170765	-2.128706	-2.010512
38	6	0	3.825315	-0.689116	-3.236848
39	6	0	2.892702	-0.037894	-4.054042
40	6	0	5.156851	-0.273730	-3.208719
41	6	0	3.298887	1.035661	-4.846966
42	6	0	5.546572	0.799864	-4.007498
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46	8	0	7.329576	2.281968	-4.648054
47	6	0	9.091624	1.116783	-2.873164
48	6	0	-8.803779	-1.997612	-2.460838
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57	1	0	-1.339648	-6.020265	1.403210
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64	1	0	0.330095	5.748053	0.192818
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66	1	0	2.675878	-5.028648	0.784801
67	1	0	-0.319515	-3.178024	-1.650074
68	1	0	5.530455	2.053966	-0.228774
69	1	0	4.971927	2.291263	-5.424337

70	1	0	5.870613	-0.767071	-2.568561
71	1	0	2.574050	1.536802	-5.476234
72	1	0	1.859731	-0.361632	-4.073202
73	1	0	9.251819	2.004164	-3.487208
74	1	0	9.788458	0.323052	-3.149915
75	1	0	1.063068	-5.605202	3.183227
76	1	0	2.066793	-6.763123	2.247269
77	1	0	-2.637307	7.600778	-0.325766
78	1	0	-2.431426	6.752502	1.262613
79	1	0	-1.033382	7.538305	0.468878
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81	1	0	-11.356511	-0.171680	-3.398301
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86	1	0	9.135479	1.342947	-1.809290
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90	8	0	7.942211	1.344906	0.030934
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93	1	0	9.936773	-0.832227	-0.043206
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97	6	0	5.419324	-1.018031	1.246369
98	1	0	6.097325	-1.785113	1.590691
99	1	0	3.596606	-2.015472	1.863726
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108	9	0	-2.146539	3.665973	1.613267
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110	9	0	-0.061565	-1.993597	4.450834
111	9	0	1.153473	-1.501425	2.493571
112	9	0	-0.085196	-3.470526	2.641919
113	9	0	2.267677	-3.573856	2.629396
114	9	0	2.318726	-2.096052	4.471110
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127	1	0	-3.645051	0.649614	1.062086
128	1	0	-3.325433	1.929039	2.281977
129	1	0	-4.361248	0.524458	2.702970
130	1	0	-2.920654	0.161703	4.634161
131	1	0	-1.811375	1.487494	4.147216
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### 3Py•Cl<sup>-</sup>

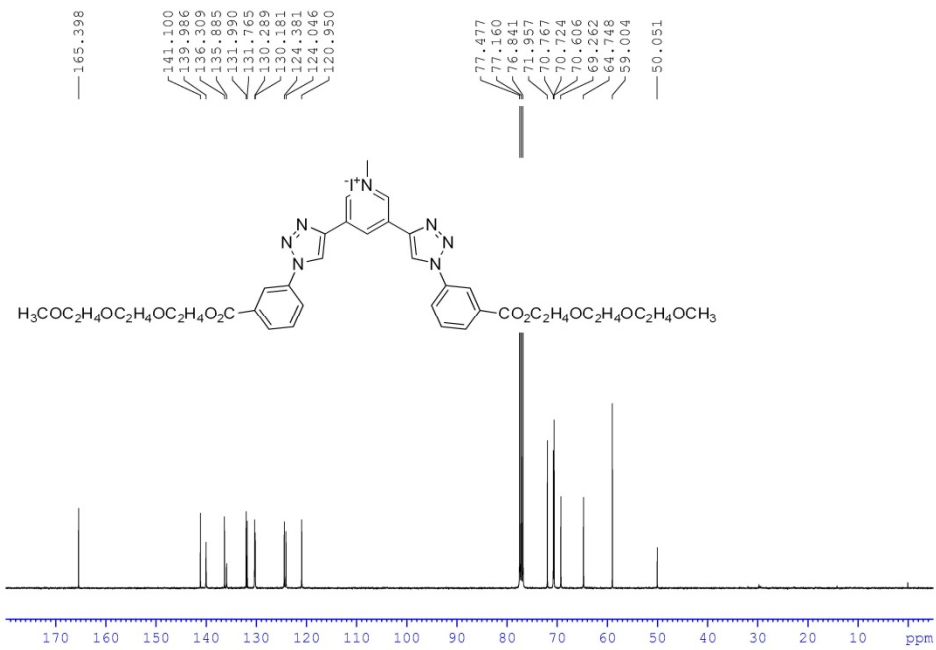
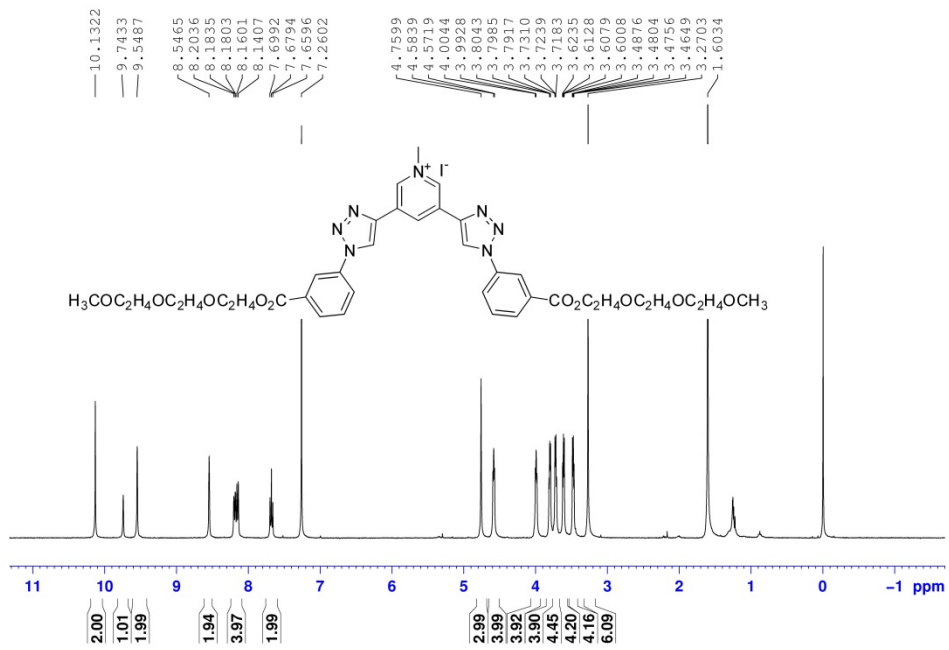
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13	6	0	6.096510	0.703999	0.598080
14	6	0	5.252238	-0.337671	0.210903
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37	6	0	-4.014387	-2.516989	2.348894
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56	1	0	2.465711	-5.960846	-2.464810

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66	1	0	-5.896167	-2.784404	1.333321
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68	1	0	-2.297138	-2.121763	3.594716
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72	1	0	11.949481	0.768406	1.587073
73	1	0	-1.448318	-3.796550	2.035149
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75	1	0	-0.596582	2.542362	0.061901
76	1	0	-9.973793	-1.410162	2.108020
77	1	0	11.745074	-0.959448	2.050765
78	6	0	-5.584129	2.378008	-1.581861
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80	8	0	-6.922331	4.132618	-2.565277
81	8	0	-7.699554	1.976516	-2.561426
82	6	0	-8.916817	2.466016	-3.239622
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85	1	0	-8.662389	2.923411	-4.198772
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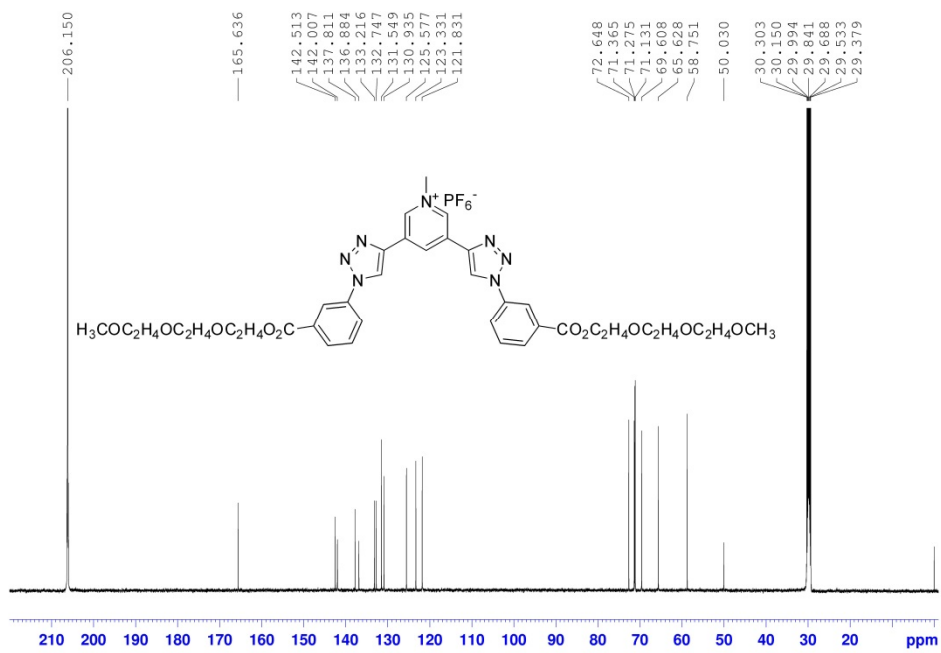
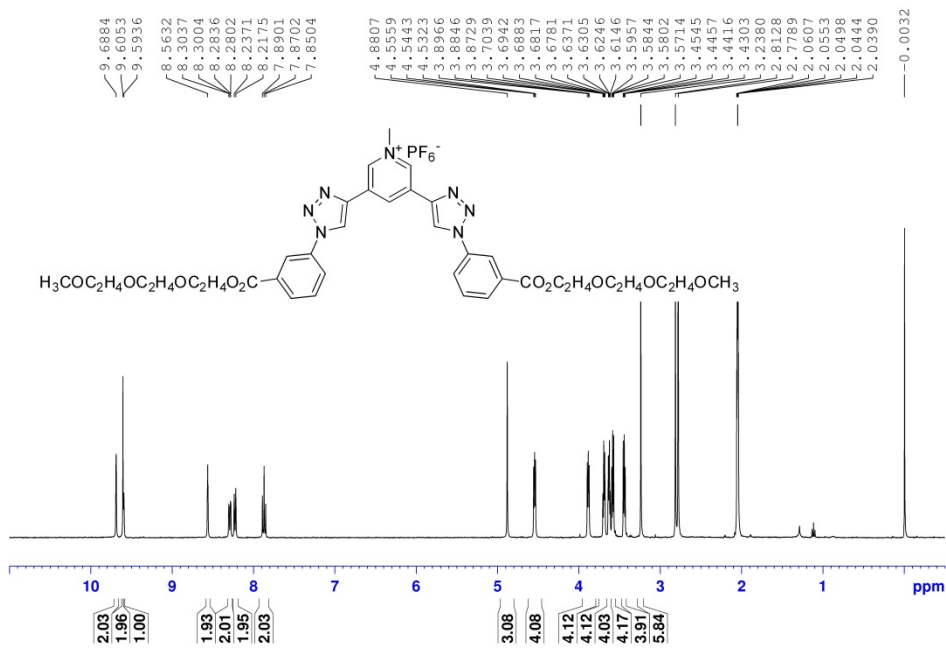
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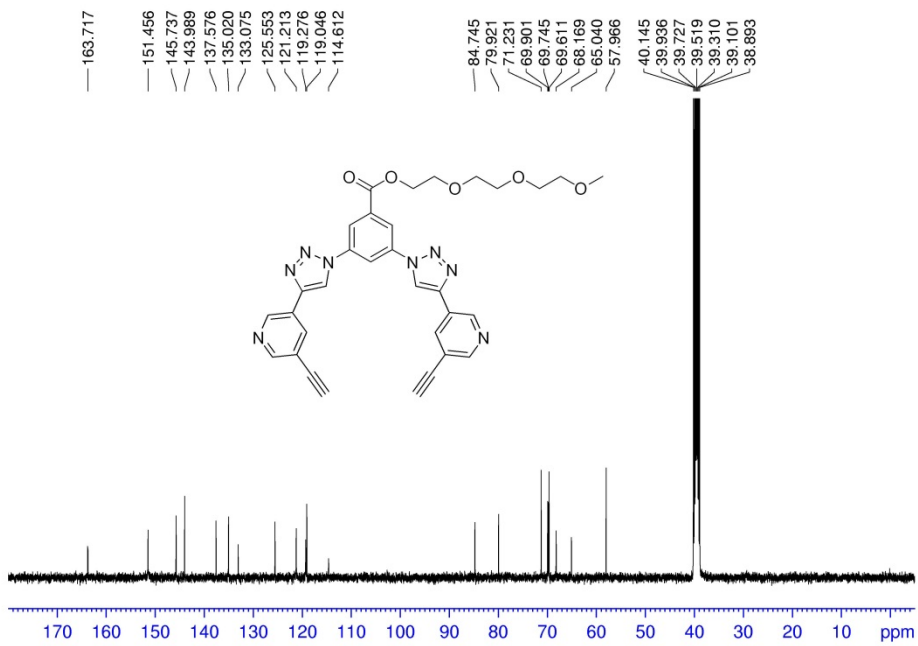
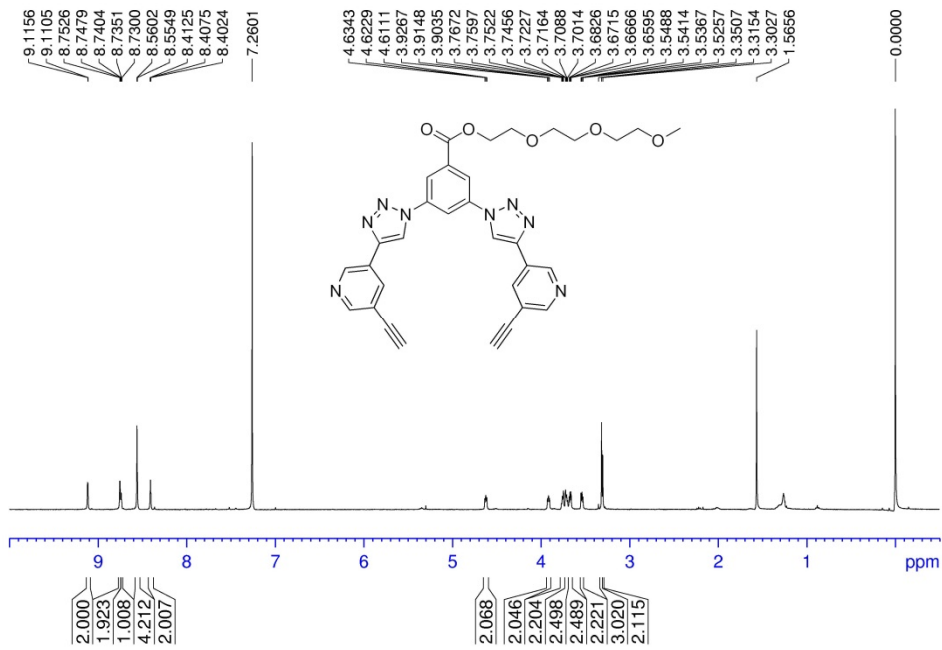




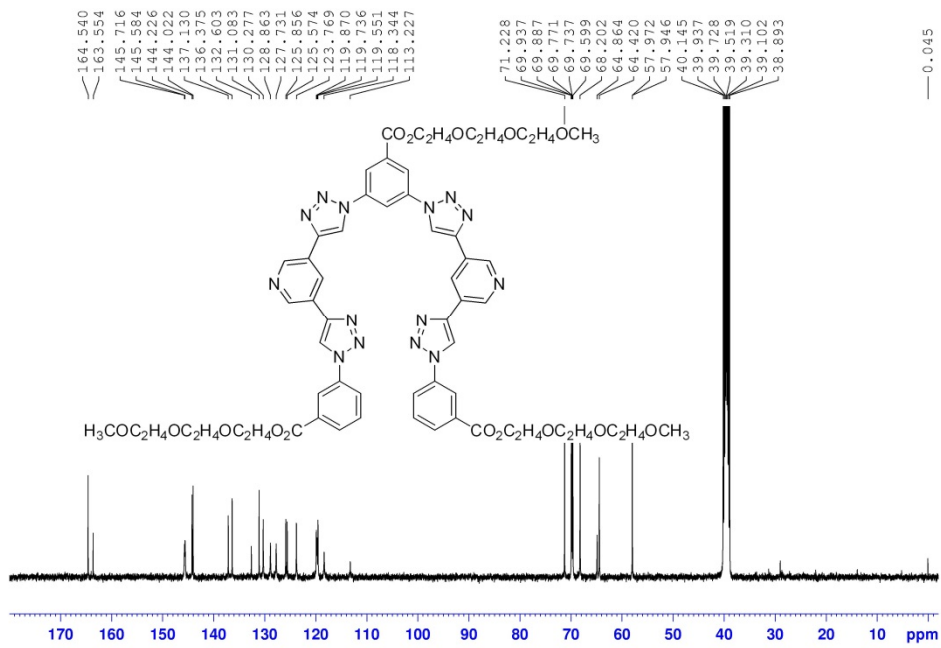
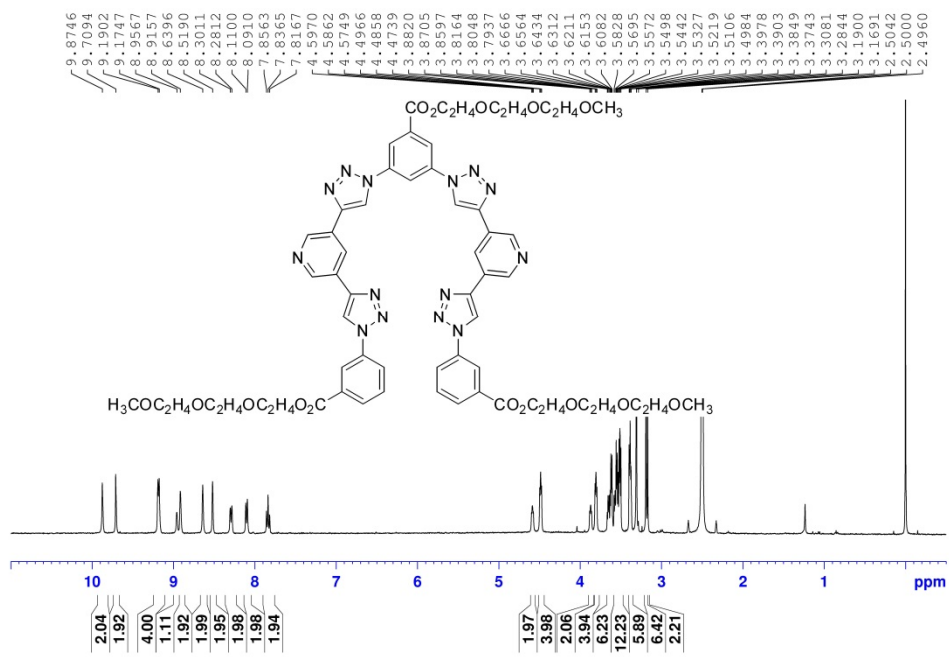
<sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 6



<sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 2

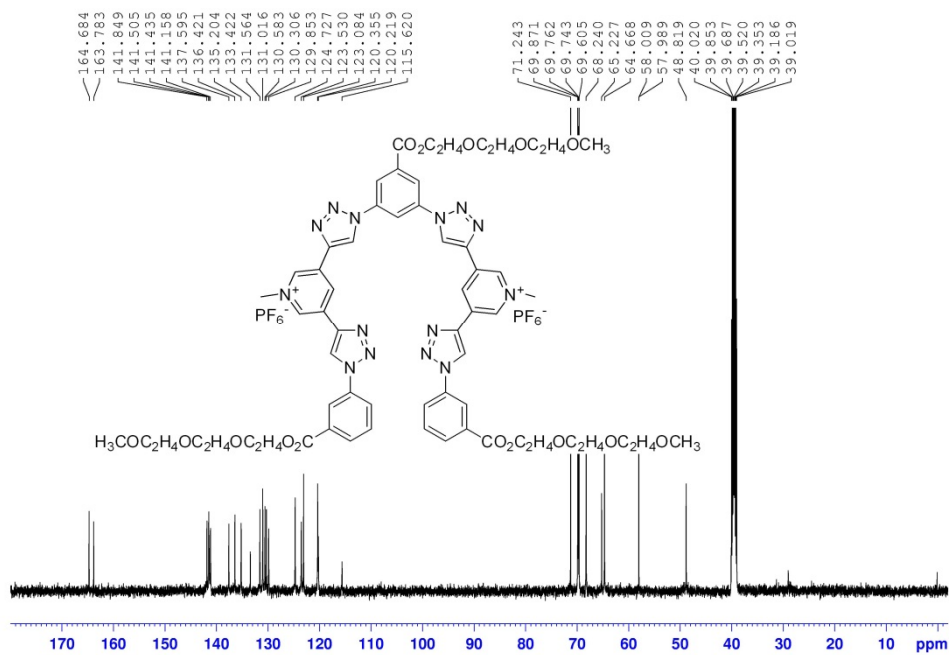
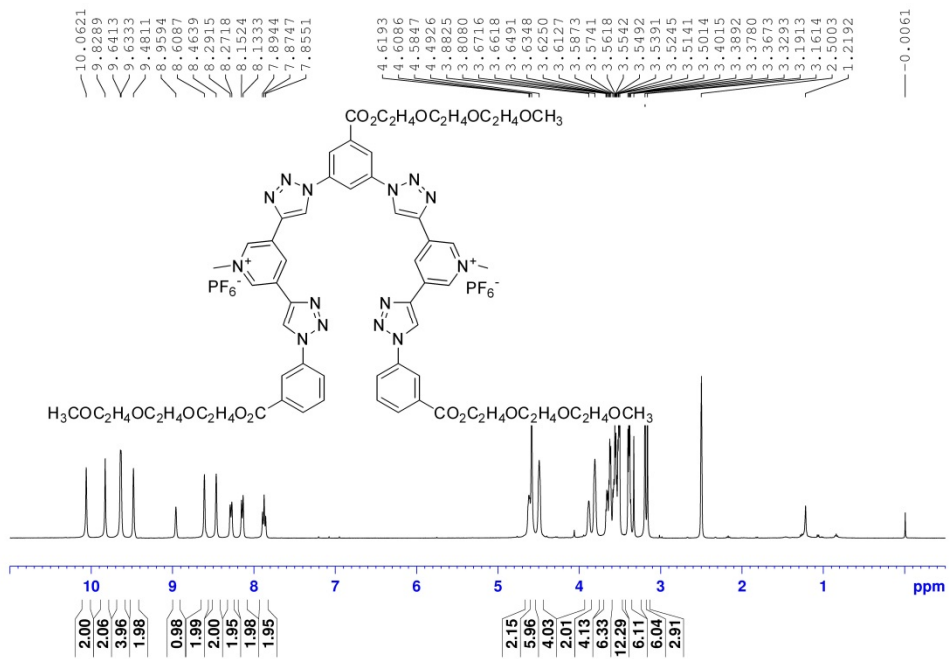


<sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 8



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 9





<sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 3

## 8. Supporting References.

[S1] Robinson, S. W.; Mustoe, C. L.; White, N. G.; Brown, A.; Thompson, A. L.; Kennepohl, P. and Beer, P. D. *J. Am. Chem. Soc.* **2015**, *137*, 499–507.

[S2] Meudtner, R. M. and Hecht, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4926–4930

[S3] Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311–312.