# Organic & Biomolecular Chemistry Supporting Information

## Self-Assembly of Indolocarbazole-Containing Macrocyclic Molecular

Yingjie Zhao,<sup>a,b</sup> Yuliang Li,\*<sup>a</sup> Yongjun Li,\*<sup>a</sup> Changshui Huang,<sup>a</sup> Huibiao Liu,<sup>a</sup> Siu-Wai Lai,<sup>c</sup> Chi-Ming Che<sup>c</sup> and Daoben Zhu<sup>a</sup>

## Table of contents

- 1. Synthesis of Compounds 6 and 7
- 2. Conformation Study of the Macrocycle 2 by NOESY
- 3. <sup>1</sup>H NMR and UV Spectroscopic Titration Studies
- 4. Binding Studies
- 5. X-ray Diffraction Analysis

## S1. Synthesis of macrocycles compounds 6 and 7

#### General

All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed on silica gel (160 - 200 mesh), and thin-layer chromatography (TLC) was performed on precoated silica gel plates and observed under UV light. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance DPS-400 and Bruker Avance DPS-600 spectrometers at room temperature (298 K). Chemical shifts were referenced to the residual solvent peaks. Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Biflex III mass Electronic absorption spectra were measured on a JASCO V-579 spectrometer. spectrophotometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500. All single crystal X-ray diffraction data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 173 K. Intensities were collected for absorption effects using the multi-scan technique SADABS. The structures were solved by direction methods and refined by a full matrix least squares technique based on F2 using SHELXL 97 program (Sheldrick, 1997). The extended packing plots and data from crystal packing were obtained using the software Mercury 1.4.1.

Compound **5** was synthesized in accordance with literature procedures.<sup>[1]</sup>



### 2-(2-azidoethoxy)ethanol, S2:

To a solution of 2-(2-chloroethoxy)ethanol **S1** (1.86 g, 15 mmol) in water (40 mL) was added sodium azide (1.69 g, 26 mmol) and the solution was refluxed for 3 d. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to give pure 2-(2-azidoethoxy)ethanol **S2** as a colorless oil (1.55 g, yield = 79%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  = 3.77~3.71 (m, 2 H), 3.71~3.67 (m, 2 H), 3.62 (t, 2 H, *J* = 3.9 Hz), 3.41 (t, 2 H, *J* = 4.8 Hz), 2.03 (t, 1 H, *J* = 4.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  = 72.1, 69.5, 61.1, 50.3. MS (HiResESI) Calcd for C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub> (M)<sup>+</sup> 131.0695; Found 131.0019 (M)<sup>+</sup>.

#### 2-(2-azidoethoxy)ethyl 4-methylbenzenesulfonate, S3:

A solution of 2-(2-azidoethoxy)ethanol **S2** (1.31 g, 10 mmol) and Et<sub>3</sub>N (2.0 mL, 14.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was cooled to 0°C. p-toluenesulfonyl chloride (2.17 g, 11.4 mmol) was added and the solution was stirred at RT for 18 h. The reaction was quenched with water (20 mL). The organic layer was separated, dried over MgSO<sub>4</sub>, filtered, concentrated under reduced pressure and the resulting crude oil was purified by column chromatography (petroleum ether:CH<sub>2</sub>Cl<sub>2</sub> 9:1 then 1:1 as eluent) to yield 2-(2-azidoethoxy)ethyl 4-methylbenzenesulfonate **S3** as a colorless oil (2.31 g, yield = 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  = 7.81 (d, 2 H, J = 8.1 Hz), 7.35 (d, 2 H, J = 8.1 Hz), 4.18 (t, 2 H, J = 4.5 Hz), 3.70 (t, 2 H, J = 4.8 Hz), 3.61 (t, 2 H, 5.1 Hz), 3.32 (t, 2 H, J = 5.1 Hz), 2.45 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  = 144.7, 132.5, 129.6, 127.6, 69.7, 68.9, 68.3, 50.3, 21.3. MS (HiResESI) Calcd for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>NaS (M+Na)<sup>+</sup> 308.0681; Found 308.0683 (M+Na)<sup>+</sup>, 593.1510 (2M+Na)<sup>+</sup>.

#### 1, 3-bis(2-(2-azidoethoxy)ethoxy)benzene, 6:

To a solution of resorcinol S4 (0.11 g, 1 mmol) in DMF (20 mL) was added K<sub>2</sub>CO<sub>3</sub> (0.55 g, 4 mmol) and 2-(2-azidoethoxy)ethyl 4-methylbenzenesulfonate S3 (0.7 g, 2.5 mmol), then the solution was heat to 70 °C for 10 h. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in  $CH_2Cl_2$  (50 mL), washed with  $H_2O$  (50 mL  $\times$  3), dried over anhydrous MgSO<sub>4</sub> and concentrated. The crude oil was purified by column chromatography (petroleum ether: ethyl acetate 1:1 as eluent) to yield 1,3-bis(2-(2-azidoethoxy)ethoxy)benzene 6 (0.24 g, yield = 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (t, J = 8.1 Hz, 1H), 6.53 (s, 1H), 6.51 (s, 2H), 4.14 – 4.09 (m, 4H), 3.87 – 3.83 (m, 4H), 3.76 – 3.71 (m, 4H), 3.41 (t, J = 5.1 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.8, 129.8, 107.1, 101.8, 70.1, 69.5, 67.3, 50.6. MS (ESI) Calcd  $C_{14}H_{20}N_6O_4Na$  $(M+Na)^+$ Found 359.2  $(M+Na)^+$ . for 359.14; Anal. Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>6</sub>O<sub>4</sub>: C, 49.99; H, 5.99; N, 24.99. Found: C, 49.82; H, 5.93; N 24.41.

#### 4-(2-(2-hydroxyethoxy)ethoxy)benzaldehyde, S6:

To a solution of 4-hydroxybenzaldehyde **S5** (2.44 g, 20 mmol) and 2-(2-chloroethoxy)ethanol **S1** (2.48 g, 20 mmol) in CH<sub>3</sub>CN (150 mL), were added potassium carbonate (11.0 g , 80 mmol). The suspension was heated at 70°C for 3 d under an atmosphere of nitrogen. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> (200 mL), washed with H<sub>2</sub>O (150 mL × 3), dried over anhydrous MgSO<sub>4</sub> and concentrated. The residue was purified by column chromatography to give **S6** (3.3 g, yield = 80%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 9.87 (s, 1H), 7.82 (d, J = 9.3 Hz, 2H), 7.01 (d, J = 10.3 Hz, 2H), 4.21 (m, 2H), 3.88 (m, 2H), 3.76 (m, 2H), 3.68 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 162.8, 131.9, 129.3, 114.7, 72.6, 69.3, 67.6, 61.6. MS (EI) Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> (M) 210.09; Found 210.1 (M).

#### 2-(2-(4-formylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate, S7:

A solution of **S6** (2.1 g, 10 mmol) and Et<sub>3</sub>N (5.0 mL) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was cooled to 0°C. p-toluenesulfonyl chloride (2.17 g, 11.4 mmol) was added and the solution was stirred at R.T. for 18 h. The reaction was quenched with water (20 mL). The organic layer was separated, dried over MgSO<sub>4</sub>, filtered, concentrated under reduced pressure and the resulting crude oil was purified by column chromatography (petroleum ether : CH<sub>2</sub>Cl<sub>2</sub> 1:4 as eluent) to yield 2-(2-(4-formylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate **S7** (2.8 g, yield = 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.89 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 4.20 (t, *J* = 4.4 Hz, 2H), 4.17 – 4.10 (m, 2H), 3.86 – 3.80 (m, 2H), 3.80 – 3.71 (m, 2H), 2.41 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.8, 163.8, 145.0, 132.9, 132.0, 130.1, 129.9, 128.0, 114.9, 69.6, 69.3, 68.9, 67.7, 21.6. HRMS (ESI) Calcd for C<sub>18</sub>H<sub>20</sub>O<sub>6</sub>S (M+Na)<sup>+</sup> 387.0878; Found 387.0915 (M+Na)<sup>+</sup>.

# 4,4'-(2,2'-(2,2'-(1,3-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy)bis(ethane-2,1-diyl))bis(o xy)dibenzaldehyde S8:

To a solution of resorcinol S4 (0.31 g, 2.8 mmol) in DMF (70 mL) was added K<sub>2</sub>CO<sub>3</sub> (1.55 g, 11.2 mmol) and S7 (2.55 g, 7 mmol), then the solution was heat to 70 °C for 10 h. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), washed with H<sub>2</sub>O (100 mL  $\times$  3), dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether: ethyl acetate : CH<sub>2</sub>Cl<sub>2</sub> 1:1:1 as eluent) to yield **S8** (0.98 g, yield = 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 9.88 (s, 2H), 7.82 (d, J = 7.7 Hz, 4 H), 7.15 (t, J = 8.1Hz, 1H), 7.02 (d, J = 7.9 Hz, 4H), 6.53 (s, 1H), 6.50 (d, J = 5.1 Hz, 2H), 4.23 (t, J = 4.2 Hz, 4H), 4.12 (t, J = 4.2 Hz, 4H), 3.95 (t, J = 4.2Hz, 4H), 3.91 (t, J = 4.1 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.8, 163.8, 159.9, 132.0, 130.1, 129.9, 114.9, 107.2, 101.9, 70.0, 69. 7, 67.8, 67.5. MALDI-TOF, Calcd for C<sub>28</sub>H<sub>30</sub>O<sub>8</sub>Na  $(M+Na)^+$  $(M+Na)^+$ . 517.18; Found 517.2 Anal. Calcd for C<sub>28</sub>H<sub>30</sub>O<sub>8</sub>: C, 68.00; H, 6.11; Found: C, 67.92; H, 6.13.

## (4,4'-(2,2'-(2,2'-(1,3-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy)bis(ethane-2,1-diyl))bis( oxy)bis(4,1-phenylene))dimethanol, S9:

To a solution of S8 (0.9 g, 1.8 mmol) in CH<sub>3</sub>OH (30 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added NaBH<sub>4</sub> (0.14 g, 3.6 mmol), then was stirred at R.T. for 2h, the solution was concentrated under reduced pressure. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), washed with HCl (5 %) (100 mL  $\times$  2), dried over anhydrous MgSO<sub>4</sub> and concentrated. The solution was concentrated under reduced pressure to yield **S9** (0.8 g, yield = 90%). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.26 (d, J = 6.8 Hz, 4H), 7.15 (t, J = 8.2 Hz, 1H), 6.90 (d, J = 7.6 Hz, 2H), 6.52 (s, 1H), 6.49 (d, J = 7.5 Hz, 2H), 4.60 (s, 4H), 4.18 - 4.05 (m, 8H), 3.95 - 3.84 (m, 8H), 1.68 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 160.0, 158.4, 133.5, 129.9, 128.6, 114.8, 107.2, 101.9, 70.0, 67.6, 67.5, 65.0. MALDI-TOF,  $(M+Na)^+$ Calcd for  $C_{28}H_{34}O_8Na$ 521.22; Found 521.2  $(M+Na)^+$ . Anal. Calcd for C<sub>28</sub>H<sub>34</sub>O<sub>8</sub>: C, 67.45; H, 6.87; Found: C, 67.21; H, 6.82

#### 1,3-bis(2-(2-(4-(azidomethyl)phenoxy)ethoxy)ethoxy)benzene, 7:

To a solution of S9 (0.8 g, 1.6 mmol) in PhMe (30 mL) was added hydrogen bromide 33% acetic acid solution (3.9 g, 16 mmol), then was heated to 40 °C for 2 h under an atmosphere of nitrogen. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in  $CH_2Cl_2$  (50 mL), washed with  $H_2O$  (50 mL  $\times$  3), dried over anhydrous MgSO<sub>4</sub> and concentrated. Without further purification, the product was dissolved in DMF (20 mL) containing NaN<sub>3</sub> (0.5 g, 7.7 mmol). The solution was heated to 70 °C for 10 h. After concentration, the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with H<sub>2</sub>O (50 mL  $\times$  3), dried over anhydrous MgSO<sub>4</sub> and concentrated, the residue was purified by column chromatography (ethyl acetate : petroleum ether 1:3 as eluent) to yield 7. Two steps yield 0.3 g (35%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (d, J = 8.6 Hz, 4H), 7.19 - 7.10 (m, 1H), 6.93 (d, J = 8.6 Hz, 4H), 6.53 (s, 1H), 6.52 (d, J = 2.8)Hz, 2H), 4.26 (s, 4H), 4.19 – 4.04 (m, 8H), 3.98 – 3.84 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 158.9, 129.8, 127.7, 115.0, 107.2, 101.9, 70.0, 69.9, 67.6, 67.5, 54.4. MALDI-TOF, Calcd  $(M+Na)^+$ Found for  $C_{28}H_{32}N_6O_6Na$ 571.23; 571.2  $(M+Na)^+$ . Anal. Calcd for C<sub>28</sub>H<sub>32</sub>N<sub>6</sub>O<sub>6</sub>: C, 61.30; H, 5.88; N, 15.32; Found: C, 61.15; H, 6.01; N, 15.38

 $^1\text{H}$  NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of S2



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of **S2** 



<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of **S3** 



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of **S3** 



<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of **S6** 



 $^1\text{H}$  NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of S7



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of **S7** 



## $^1\text{H}$ NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of S8



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of **S8** 



 $^1\text{H}$  NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of S9



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of **S9** 



<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of 6



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of 6



 $^{1}$ H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of **7** 



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of **7** 



## <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of Macrocycle 1



 $^{13}\text{C}$  NMR spectrum (100 MHz, 298 K, CDCl\_3) of Macrocycle 1



<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of Macrocycle 2



<sup>13</sup>C NMR spectrum (100 MHz, 298 K, CDCl<sub>3</sub>) of Macrocycle 2



<sup>1</sup>H NMR spectrum (600 MHz, 298 K, CDCl<sub>3</sub>) of Macrocycle 3





## <sup>1</sup>H NMR spectrum (600 MHz, 298 K, CDCl<sub>3</sub>) of Macrocycle 4



<sup>13</sup>C NMR spectrum (150 MHz, 298 K, CDCl<sub>3</sub>) of Macrocycle 4



## S2. Conformation Study of the Macrocycle 2 by NOESY

The 2D NMR at 0 °C showed the correlation between the indole ring and the chain (Figure S1). NOEs between N-H protons H<sub>a</sub> and the chain protons 1, 2, 3 and 4 indicate the folded conformation of the macrocycle **2**. But the two indole ring planes must not overlap very well and the two planes should slip to each other and keep the folded conformation by the chain (Figure S2). So the correlation from H<sub>a</sub> to the H<sub>1-4</sub> could be seen. However, the correlation of H<sub>a</sub> and H<sub>1-4</sub> must not be seen if the folded conformation was not formed. NOE cross peaks connecting H<sub>b</sub> and H<sub>1-4</sub> also proved this. The triazole H<sub>b</sub> should turn outside of the cavity so it could interact with the chain H<sub>1-4</sub> when the macrocycle **2** exist in a fold conformation. The correlation between the N-H<sub>a</sub> and the triazole-N atom turn to the internal of the cavity, there will be a correlation between the N-H<sub>a</sub> in one of the indol ring plane and the trazole H<sub>b</sub> in the other will have an intermolecular correlation. The correlation between H<sub>b</sub> and H<sub>1</sub> will prove the rotate of the trazole.



Figure S1. NOESY of the macrocycle 2 in D2-Tetrachloroethane at 0 °C.



Figure S2. The schematic description of the sliding movement of the folded macrocycle  $\mathbf{2}$ 

## S3. <sup>1</sup>H NMR and UV Spectroscopic Titration Studies



Scheme 1.	The	interaction	between	the macroc	ycle 1	1, 2	and	the	anions	5.
					2					

(a) 5.0 eqa				b	c d e	
3.0 eq				(		Lur
2.0 eq					III.	L.m.
1.8 eq						L
1.6 eq				^		<u> </u>
1.4 eq				~^		
1.2 eq.				^		Lun
1.0 eq				^		L
0.8 eq						1
0.6 eq					A	<u> </u>
0.4 eq.					lul	
0.2 eq						1 mr
0.1eq						fur
0.0 eq.			a		iiii	l
13.5	12.5	11.5	10.5 9 ō / ppm (macro	.5 9.0 cycle1-F)	8.5 8.0 7.5	7.0 6.5

20.0 eq.  1  1  1  1    10.0 eq.  1  1  1  1    5.0 eq.  1  1  1  1    3.0 eq.  1  1  1  1    2.0 eq.  1  1  1  1    1.6 eq.  1  1  1  1    1.0 eq.  1  1  1  1    0.6 eq.  1  1  1  1    0.4 eq.  1  1  1  1    0.2 eq.  1  1  1  1    0.0 eq.  1  1  1  1	(a)	2	h	o d e		
10.0 eq.  1  1  1    5.0 eq.  1  1  1    3.0 eq.  1  1  1    2.0 eq.  1  1  1    1.6 eq.  1  1  1    1.0 eq.  1  1  1    0.6 eq.  1  1  1	20.0 eq	a				
5.0 eq.	10.0 eq					
3.0 eq.	5.0 eq	A				
2.0 eq.  1  1    1.6 eq.  1  1    1.0 eq.  1  1    1.0 eq.  1  1    0.8 eq.  1  1    0.6 eq.  1  1    0.4 eq.  1  1    0.2 eq.  1  1    0.0 eq.  1  1	3.0 eq.—		۸			
1.6 eq.	2.0 eq		l			r
1.0 eq.	1.6 eq.—					
0.8 eq / /// // // // // // // // // //	1.0 eq	λ			_	
0.6 eq //// /// /// /// /// /// /// //	0.8 eq		Λ	M(		r
0.4 eq / U/	0.6 eq				_	
0.2 eqade c	0.4 eq		/	U		
a b <sup>a</sup> e c	0.2 eq				_	r
	0.0 eq.—	a ^^		bili		K



Figure S3 <sup>1</sup>H NMR spectra (aromatic region) of macrocycle **1** and macrocycle **2** in CDCl<sub>3</sub> at 298 K upon titrational addition of (a) TBAF·3H<sub>2</sub>O, (b) TBACl, (c) TBABr, and (d) TBAI. (a'), (b'), (c'), (d') is for the macrocycle **2**.(The concentration of the receptors is  $4.5 \times 10^{-3}$  M for macrocycle **1** and  $2.25 \times 10^{-3}$  M for macrocycle **2**)

## **S4. Binding Studies**

Job's plots<sup>[2]</sup>: Stock solutions of the macrocycle  $(1.0 \times 10^{-4} \text{ M for } 2 \text{ and } 2.0 \times 10^{-4} \text{ M for } 1)$  and an anion  $(1.0 \times 10^{-4} \text{ M or } 2.0 \times 10^{-4} \text{ M})$  were separately prepared in CH<sub>2</sub>Cl<sub>2</sub>. The UV/Vis spectra

(Figure S4) was taken for each of 10 different solutions containing a total of 2.0 mL of the macrocycle and TBAX in the following ratios: 1:0, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.3:0.7, 0.2:0.8, and 0.1:0.9. Job's plots were constructed by plotting  $A_{obs}-A_M-A_x$  against the  $\gamma$ -coordinate.





Figure S4. Job's Plot for complexation of the macrocycle and anion by UV spectroscopy. (a, b, c, d for macrocycle 1 and a', b', c', d' for macrocycle 2)



Figure S5. Absorption and fluorescence spectrumof macrocycle 1, 2 and 3 in CH<sub>2</sub>Cl<sub>2</sub>





Figure S6. Change in the chemical shift of triazoles- $H_b$  on addition of anions(F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) to a solution of macrocycle **1** (a, b, c, d) and macrocycle **2** (a', b', c', d') in CDCl<sub>3</sub> at 293 K. Square symbols represent experimental data points; continuous lines represent calculated curves. All anions were added as their TBA salts.

## **S5. X-ray Diffraction Analysis**

Table 1. Crystal data and structure refinement for macrocycle 1 and macrocycle 2.

	Crystal data of Macrocycle 1	Crystal data of Macrocycle 2		
Identification code	Macrocycle 1	Macrocycle 2		
Empirical formula	C45H52N8O5	C46H51N9O4		
Formula weight	784.95	793.96		
Temperature	173(2) K	173(2) K		
Wavelength	0.71073 Å	0.71073 Å		
Crystal system	Monoclinic	Monoclinic		
space group	P2(1)/c	P2(1)/c		
Unit cell dimensions	a = 15.612(3) Å α= 90°	$a = 21.048(4) \text{ Å} \alpha = 90^{\circ}$		
	$b = 13.356(3) \text{ Å} \beta = 102.05(3)^{\circ}$	b = 11.504(2) Å β= 102.01(3) °		
	$c = 20.763(4) \text{ Å} \gamma = 90^{\circ}$	$c = 17.527(4) \text{ Å } \gamma = = 90^{\circ}$		
Volume	4234.0(15) Å <sup>3</sup>	4151.2(14) Å <sup>3</sup>		
Z	4	4		
Calculated density	1.231 Mg/m <sup>3</sup>	1.270 Mg/m <sup>3</sup>		
Absorption coefficient	$0.082 \text{ mm}^{-1}$	0.084 mm <sup>-1</sup>		
F(000)	1672	1688		
Crystal size	$0.31 \times 0.20 \times 0.10 \text{ mm}^3$	0.18×0.17×0.09 mm <sup>3</sup>		
Theta range for data	2.65 to 25.00°	1.98 to 27.47°		
collection				
Limiting indices	-18<=h<=18, -15<=k<=15,	-25<=h<=27, -14<=k<=13,		
	-21<=l<=24	-22<=1<=22		
Reflections collected	28188	28221		
unique	7444 [R(int) = 0.0442]	9486 [R(int) = 0.0430]		
Completeness to theta	= 25.00 99.7 %	=27.47 99.7 %		
Absorption correction	Semi-empirical from	Numerical		
	equivalents			
Max. and min.	0.9918 and 0.9750	0.9925 and 0.9851		

transmission		
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints /	7444 / 0 / 524	9486 / 0 / 539
parameters		
Goodness-of-fit on $F^2$	1.198	1.140
Final R indices	$R_1 = 0.0649, wR_2 = 0.1380$	$R_1 = 0.0646, wR_2 = 0.1309$
[I>2sigma(I)]		
R indices (all data)	$R_1 = 0.0756, wR_2 = 0.1434$	$R_1 = 0.0775, wR_2 = 0.1378$
Largest diff. peak and	0.343 and -0.281 e.Å <sup>-3</sup>	0.218 and -0.240 e.Å <sup>-3</sup>
hole		



Figure S7. Top and side views of the crystal structure of macrocycle 1 and the unit cell diagram



Figure S8. Top and side views of the crystal structure of macrocycle 2 and the unit cell diagram

- [1] K. J. Chang, D. Moon, M. S. Lah, K. S. Jeong, Angew. Chem. Int. Ed. 2005, 44, 7926-7929.
- [2] C. Schalley, Analytical Methods in Supramolecular Chemistry, WILEY-VCH Verlag, Weinheim 2007.