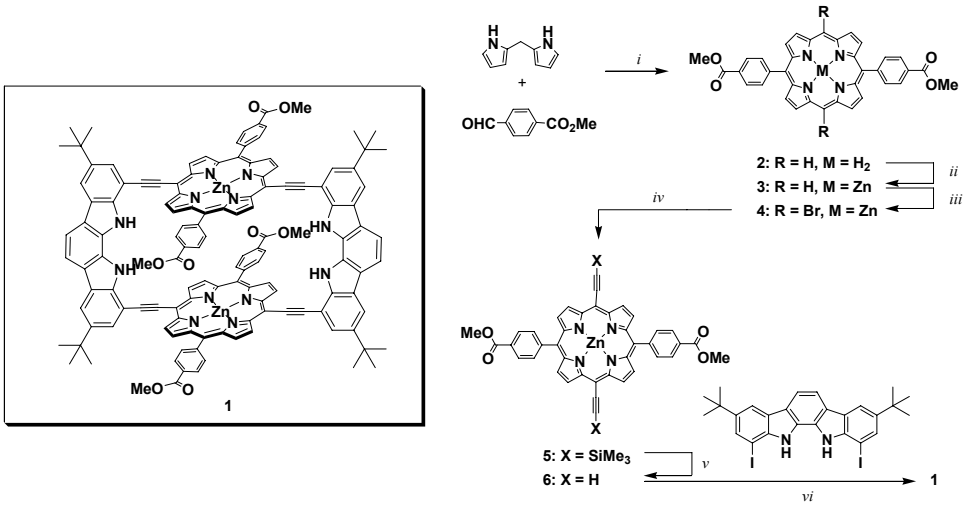
Supporting Information

Measurements. Electronic absorption spectra were recorded on a JASCO model V-660 spectrometer.^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 and DPX 400 spectrometer, respectively, at 25°C in $CDCl_3$,DMSO-d_6, or THF-d_8. MALDI-TOF-MS was performed on an Applied Biosystems 4700 proteomics analyzer with α-cyano-4-hydroxycinnamic acid as the matrix.



Synthesis.3: To a mixturesolution of 4-formyl-benzoate(2.25 g, 13.68 mmol) and dipyrromethane(2.0 g, 13.68 mmol) in CH_2Cl_2 (830 mL) and MeOH(170 mL), BF_3•Et_2O(2 mL, 15.92 mmol) was added and stirred for 12 h at 25°C. Then, *p*-chloranil(8.49 g, 34.2 mmol) was added and the reaction mixture was further stirred for 4 h. The reaction mixture was concentrated to a volume of 200 mL and then chromatographed in silica gel with 5% MeOH/CH_2Cl_2. Without further purification, the product was dissolved in 10% MeOH/CH_2Cl_2 containing $Zn(OAc)_2$ (6.0 g, 27.36 mmol) and then stirred for 12 h at 25°C. Thereaction mixture was purified by column chromatography with 3% MeOH/CH_2Cl_2, where the first fraction was collected and evaporated to dryness.The residue was recrystallized from CH_2Cl_2/hexane to give **3**, a reddish purple powder (1.1 g, 25%) (Rf = 0.33 in MeOH/CH_2Cl_2(1:99)): ^{1}H

NMR(250 MHz, $CDCl_3$, 25°C) δ = 10.23(s, 2H), 9.36-9.38(d, J = 5 Hz, 4H), 8.98-9.00(d, J = 5 Hz 4H), 8.40-8.43(d, J = 7.5 Hz, 4H), 8.29-8.33(d, J = 10 Hz, 4H), 4.09ppm (s, 6H); MALDI-TOF-MS:*m/z*: calcd. for $C_{36}H_{24}N_4O_4Zn$: 641.99 [M^+]; found: 640.15.

4: *N*-bromosuccinimide (NBS; 0.58 g, 3.26 mmol) was added to a solution of **3** (1.0 g, 1.56 mmol) in CH_2Cl_2 (200 mL) and MeOH (20 mL), and then stirred for 30 min at 25°C. The reaction mixture was quenched with acetone (20mL) and evaporated. MeOH was added to the crude mixture, andprecipitate was filtered. The residue was again washed with MeOH to give **4**, a purple powder (1.12 g, 90%) (Rf = 0.33 in Hex/CH_2Cl_2(1:9)): ^{1}H NMR (250 MHz, [D_6]DMSO, 25°C) δ 9.62-9.64 (d, J = 5 Hz, 4 H), 8.79-8.77(d, J = 5 Hz, 4 H), 8.28-8.31 (d, J = 7.5 Hz, 4 H), 8.13-8.16 (d, J = 7.5 Hz, 4 H), 4.06 ppm (s, 6H); MALDI-TOF-MS:*m/z*: calcd. for $C_{36}H_{22}Br_2N_404Zn$: 799.78 [M^+]; found 800.0.

5: **4** (1.0 g, 1.26 mmol), CuI (20 mg, 0.06 mmol), and $Pd(PPh_3)_2Cl_2$ (44 mg, 0.06 mmol) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with N_2;this process was repeated three times. Dried THF (70 mL), Et_3N (3 mL),andtrimethylsilyl- acetylene (0.7 mL, 5.04 mmol) were added. The reaction mixture was stirred for 16 h at 25°C and then filtered through Celite. The filtrate was concentrated and then purified by column chromatography with CH_2Cl_2 to give **5** (0.81g, 78%)(Rf = 0.27 in Hex/EtOAc(8:2)): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C)δ = 9.70-9.69 (d, J=4 Hz, 4 H), 8.84-8.83 (d, J=4 Hz, 4 H), 8.41-8.39 (d, J=8 Hz, 4 H), 8.25-8.23 (d, J=8 Hz, 4 H), 4.08 (s, 6 H), 0.59ppm (s, 18 H); ^{13}C NMR (100 MHz,$CDCl_3$, 25°C)δ = 176.29, 152.36, 149.68, 134.38, 132.43, 131.74, 129.55, 127.89,121.38, 107.01, 102.49, 101.91, 77.22, 53.42, 52.42, 0.31 ppm;MALDI-TOF-MS:*m/z*: calcd. for $C_{46}H_{40}N_404Si_2Zn$: 834.4 [M^+]; found: 832.29.

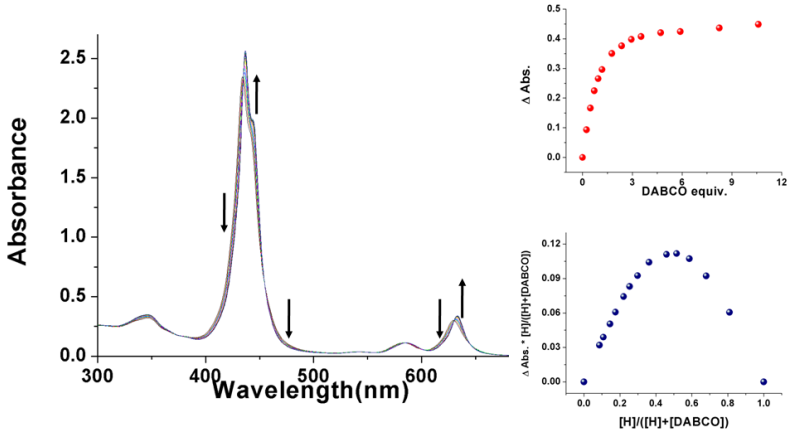
6: Tetrabutylammonium fluoride (5 mL, 1 M in THF) was added to solution of **5** (0.6 g, 0.72 mmol) in CH_2Cl_2 (100 mL) and stirred for 30 min at 25°C, then removed the solvent under reduced pressure. The residue was purified by column chromatography with CH_2Cl_2/MeOH (99/1) as an eluent. Recrystallization from CH_2Cl_2/hexane gives **6** (0.42 g, 85%), a purple crystal(Rf = 0.23 in

Hex/EtOAc(7:3)): ^{1}H NMR (400 MHz, [D_6]DMSO, 25°C) δ= 9.63-9.62 (d, J = 4 Hz, 4 H), 8.79-8.78 (d, J = 4 Hz, 4 H), 8.43-8.41 (d, J = 8 Hz, 4 H), 8.34-8.32 (d, J =8 Hz, 4 H), 5.30 (s, 2 H), 4.07ppm (s, 6H); ^{13}C NMR (100MHz, [D_6]DMSO, 25 °C) δ= 166.38, 151.53,148.96, 146.60, 134.38, 132.42, 131.23, 129.26, 127.49, 123.77, 120.82, 104.97, 101.43, 99.66, 85.67, 52.37, 40.33. ppm; MALDI-TOF-MS:*m/z*: calcd. for $C_{40}H_{24}N_4O_4Zn$: 690.03 [M^+]; found 688.12.

1:**6** (0.1 g, 0.15 mmol), CuI (1 mg, 5.3 μmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 1.4 μmol), and **7**(0.09 g, 0.15 mmol) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with N_2; this process was repeated three times. Dried THF (29 mL), Et_3N (2.9 mL) were added. The reaction mixture was stirred for 48 h at 25°C, and then the solution was evaporated. The residue was purified by column chromatography with ethyl acetate/hexane (3:7) to give **1** (10 mg, 7%)(Rf = 0.25 in Hex/EtOAc(7:3)):^{1}H NMR(400 MHz, [D_8]THF, 25°C) δ= 10.46 (s, 4 H), 9.42-9.41(d, J = 4 Hz, 8 H), 8.43-8.42(d, J = 4 Hz, 8 H), 8.30(s, 4 H), 8.26-8.23(m, 8 H), 8.02-7.99 (m, 8 H), 7.88 (s, 4 H), 7.60-7.59(d, J = 4 Hz, 4 H), 3.98 (s, 12 H), 1.47 ppm (s, 36 H); ^{13}C NMR (100 MHz, [D_8]THF, 25°C)δ= 165.76, 151.42, 148.83, 146.49, 141.84, 138.96, 133.84, 133.33, 131.13, 130.67, 129.31, 127.14, 127.05, 126.03, 125.09, 124.26, 121.26, 120.51, 117.16, 111.75, 105.12, 100.40, 93.75, 91.33, 59.07, 51.09, 34.20, 31.09, 29.26 ppm; MALDI-TOF-MS: *m/z*: calcd. for $C_{132}H_{96}N_{12}O_8Zn_2$:2109.03 [$M^+$]; found 2108.5.

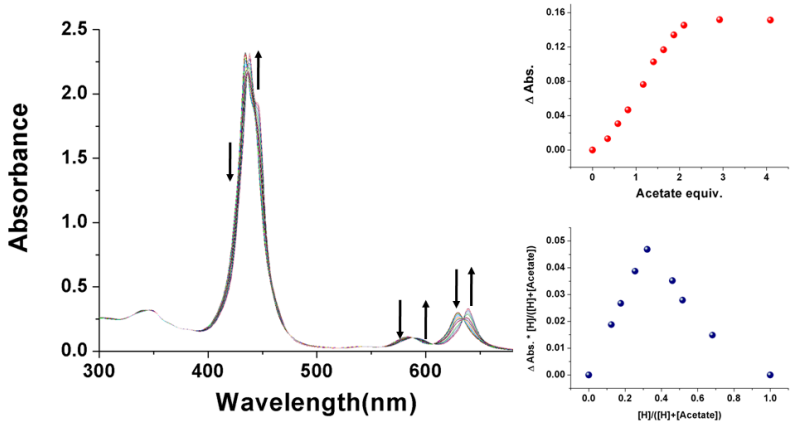
Spectroscopic titration of macrocycle 1 with DABCO

[**1**] = 4.3 x 10^{-6} M, [DABCO]/[**1**] = 0-10.6, 1 cm thick optical cell; ΔAbs was monitored at 437 nm.

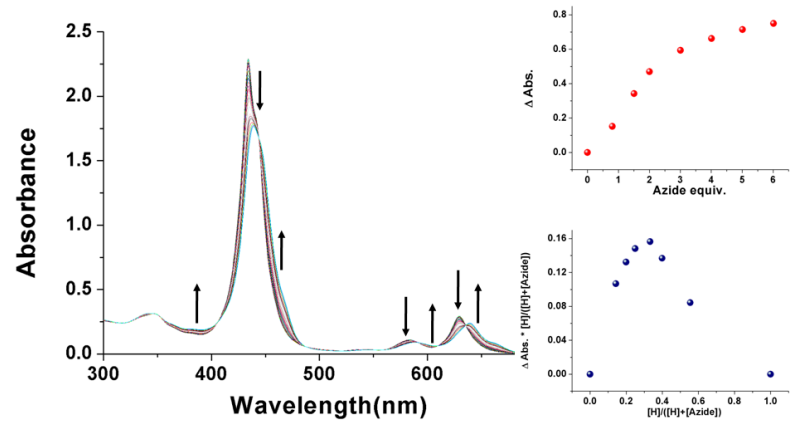


Spectroscopic titration of macrocycle 1 with guests (a)acetate, (b)azide, (c)fluoride in THF at 25 °C

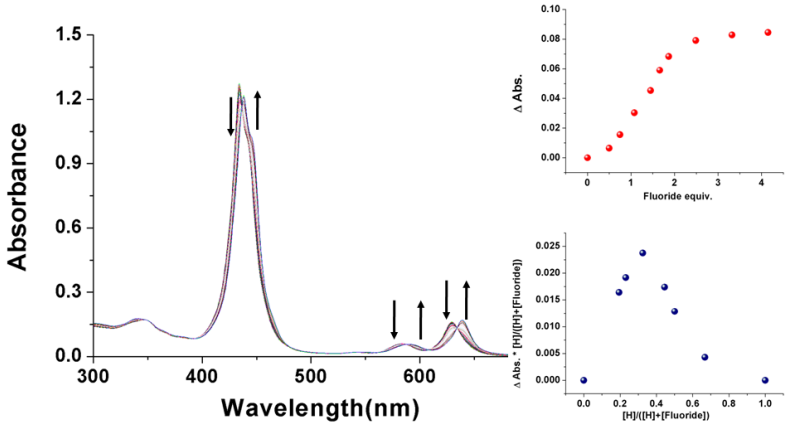
(a) [**1**] = 4.4 x 10^{-6} M, [acetate]/[**1**] = 0-4.1, 1 cm thick optical cell; ΔAbs was monitored at 639 nm.



(b) [**1**] = 4.3 x 10^{-6} M, [azide]/[**1**] = 0-6.0, 1 cm thick optical cell; ΔAbs was monitored at 434 nm.



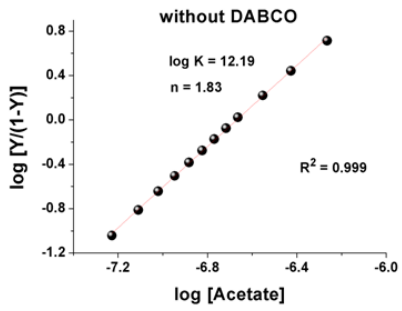
(c) [**1**] = 2.4 x 10^{-6} M, [fluoride]/[**1**] = 0-4.1, 1 cm thick optical cell; ΔAbs was monitored at 640 nm.



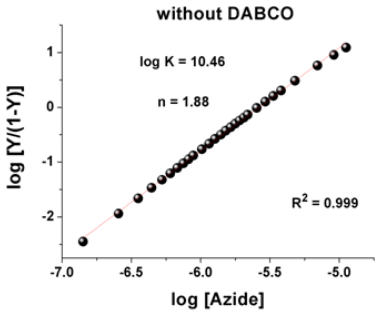
Hill plots of macrocycle 1 with guests (a)acetate, (b)azide, (c)fluoride in THF at 25 °C

Cooperative guest-binding process was analyzed according to the Hill equation: $\log(y/(1-y)) = n\log[\text{guest}] + \log K$, where K, y, and n are the association constant, the extents of complexation and Hill coefficient, respectively. From the slope and the intercept of the linear plots (Hill plot) one can estimate K and n, which are useful as measures of the cooperativity. A higher value of n is related to a higher degree of cooperativity. The maximum is equal to the number of binding sites.

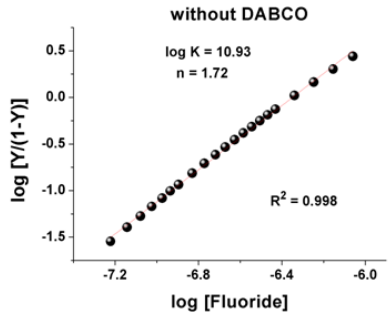
(a) 1 with acetate



(b) 1 with azide

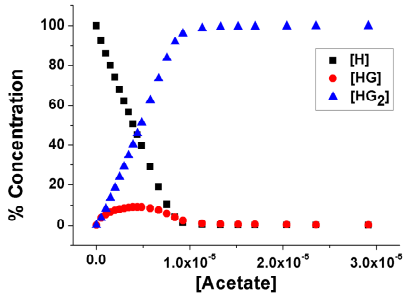


(c) 1 with fluoride

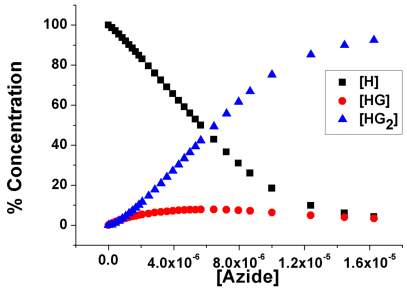


% formation of macrocycle 1 with guests (a)acetate, (b)azide, (c)fluoride in THF at 25 °C

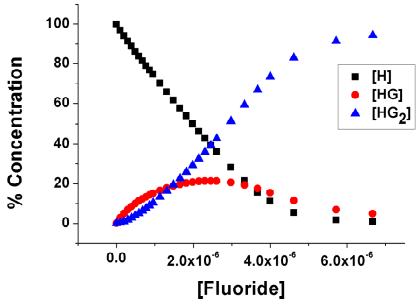
(a) 1 with acetate



(b) 1 with azide



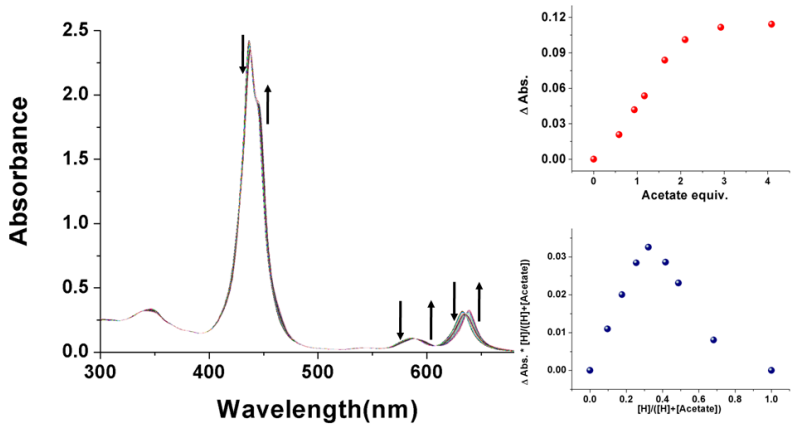
(c) 1 with fluoride



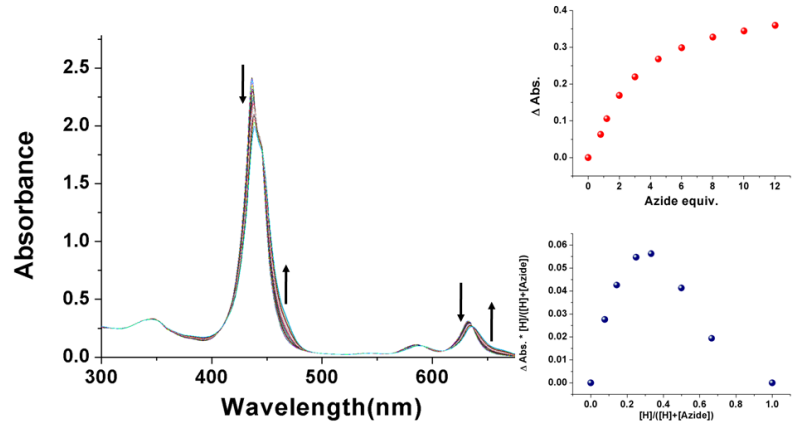
	K_1 [M^{-1}]	K_2 [M^{-1}]
F^-	1.60 x 10^6	5.42 x 10^6
Acetate	1.06 x 10^6	2.60 x 10^7
N_3^-	7.11 x 10^4	2.50 x 10^6

Spectroscopic titration of macrocycle 1⊃DABCO with guests (a)acetate, (b)azide, (c)fluoride in THF at 25 °C

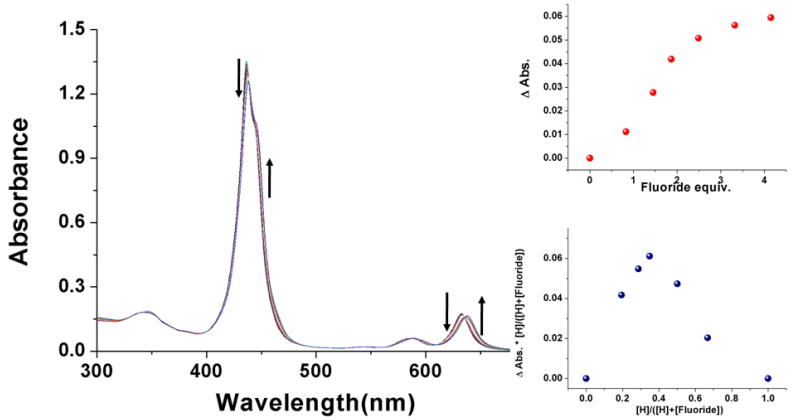
(a) [**1**] = 4.4 x 10^{-6} M, [acetate]/[**1**] = 0-4.1, 1 cm thick optical cell; ΔAbs was monitored at 639 nm.



(b) [**1**] = 4.3 x 10^{-6} M, [azide]/[**1**] = 0-12.0, 1 cm thick optical cell; ΔAbs was monitored at 455 nm.

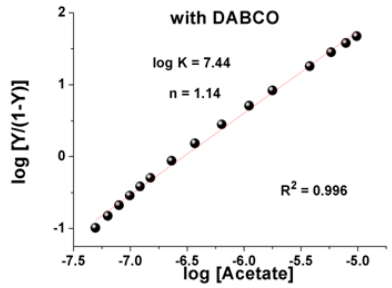


(c) [**1**] = 2.4 x 10^{-6} M, [fluoride]/[**1**] = 0-4.1, 1 cm thick optical cell; ΔAbs was monitored at 640 nm.

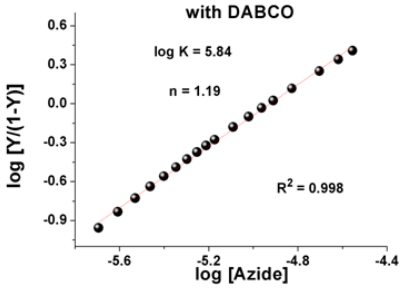


Hill plots of macrocycle 1⊃DABCO with guests (a)acetate, (b)azide, (c)fluoride in THF at 25 °C

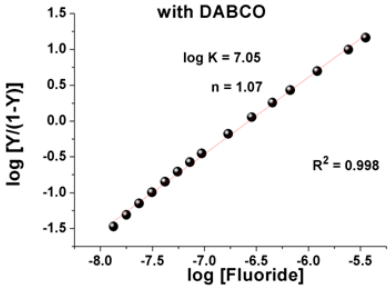
(a) 1⊃DABCO with acetate



(b) 1 ⊃DABCO with azide

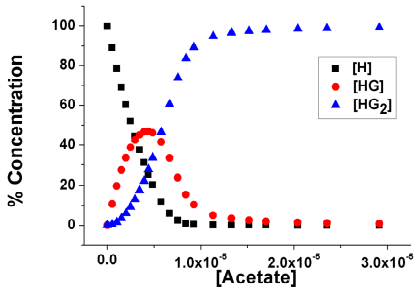


(c) 1 ⊃DABCO with fluoride

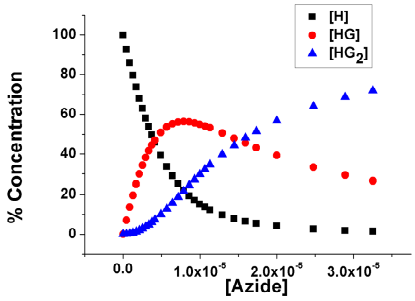


% formation of macrocycle 1⊃DABCO with guests (a)acetate, (b)azide, (c)fluoride in THF at 25 °C

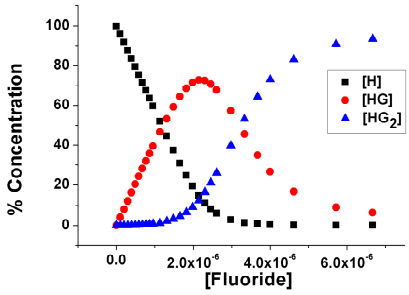
(a) 1⊃ DABCO with acetate



(b) 1 ⊃ DABCO with azide



(c) 1 ⊃ DABCO with fluoride



	K_1 [M^{-1}]	K_2 [M^{-1}]
F^-	1.18×10^8	4.09×10^6
Acetate	1.50×10^7	4.86×10^6
N_3^-	6.44×10^5	9.69×10^4