Supporting Information

An efficient size-selective anion binding cleft-shaped receptor: A novel $[F_2(H_2O)_3]^{2-}$ cluster with pseudo-encapsulated F^- ion

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1. General

1.1. Instruments

Electronic absorption and emission spectra were recorded on by a Hitachi UV–Vis (Model U–3501) spectrophotometer and Perkin Elmer LS–55 fluorimeter respectively. IR spectra (KBr pellet, 4000–400 cm^{-1}) were recorded on a Parkin Elmer modal 883 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker, Avance 300 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as internal standards.

Suitable single crystal of the complex between **1** and fluoride ion was mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.71073 Å) radiation. The crystal was positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 5s. The structure was solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift / error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program.[2] All calculations were carried out using SHELXS 97, SHELXL 97, PLATON 99, ORTEP-32 and WinGX system Ver-1.64.[3]

2. Materials and Methods

All reagents and solvents were used as received from commercial sources without further purification. All anions in the form of tetrabutylammonium salts such as $Bu_4N^+F^-$, $Bu_4N^+AcO^-$, $Bu_4N^+H_2PO_4^-$, $Bu_4N^+Cl^-$, $Bu_4N^+Br^-$, $Bu_4N^+I^-$, $Bu_4N^+NO_2^-$, $Bu_4N^+NO_3^-$, $Bu_4N^+ClO_4^-$, $Bu_4N^+HSO_3^-$ and $Bu_4N^+HSO_4^-$ were purchased from Sigma-Aldrich Chemical Company. Solvents used for the spectroscopic studies are spectroscopic grade.

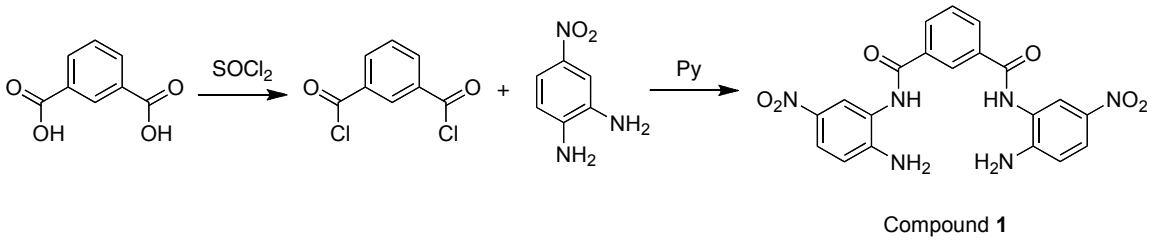
Due to poor solubility in nature of receptor **1**, firstly we dissolved it in small volume of DMSO solvent and then it was diluted into the 4% H_2O-CH_3CN mixed solvent, where percentage of DMSO solvent was 1% and this aqueous-acetonitrile solution was used for experimental investigation.

3. Syntheses and characterization

3.1. Synthesis of receptor 1

N,N/-Bis-(2-amino-5-nitro-phenyl)-isophthalamide (Receptor 1): Phenyl-1,3-dicarbonyl dichloride was obtained from the reaction of phenyl-1,3-dicarboxylic acid with $SOCl_2$ (7 ml) according to the literature procedure and was used without further characterization.[3] Pyridine solution of 4-nitro-benzene-1,2-diamine (0.75 gm, 4.90 mmol) was added dropwise to a pyridine (2 ml) solution of phenyl-1,3-dicarbonyl dichloride (0.50 gm, 2.47 mmol) at 0ºC. The reaction mixture was stirred for 12 hr at room temperature and then poured into CH_2Cl_2 solution. A brown precipitate was appeared, which was filtered and washed with CH_2Cl_2 and cold acetonitrile solvent, respectively. The yellow color solid was dried under vacuum, yield 85% (0.84 g, 3.0 mmol). ^{1}H NMR in d_6-DMSO, 300MHz, δ (ppm): 6.59 (broad, 4H, –NH_2), 6.78(d, J = 9Hz, 2H), 7.65(t, J = 7.5Hz, 1H), 7.89(dd, J = 9Hz, J = 2.7Hz, 2H), 8.09(s, 2H), 8.15(d, J = 7.5Hz, 2H),

8.61(s, 1H), 9.87(s, 2H, –CONH). ^{13}C NMR (75.5 MHz, d_6-DMSO, 20 ºC) δ (ppm): 114.05, 123.67, 123.67, 127.74, 128.44, 131.13, 161.96. IR (KBr): 3345, 3209, 1646, 1592, 1514, 1319, 1152, 1094, 898, 825, 742, 591 cm^{-1}.



Scheme S1. Synthetic scheme of compound **1**

3.2. ^{1}H and ^{13}C NMR Spectra

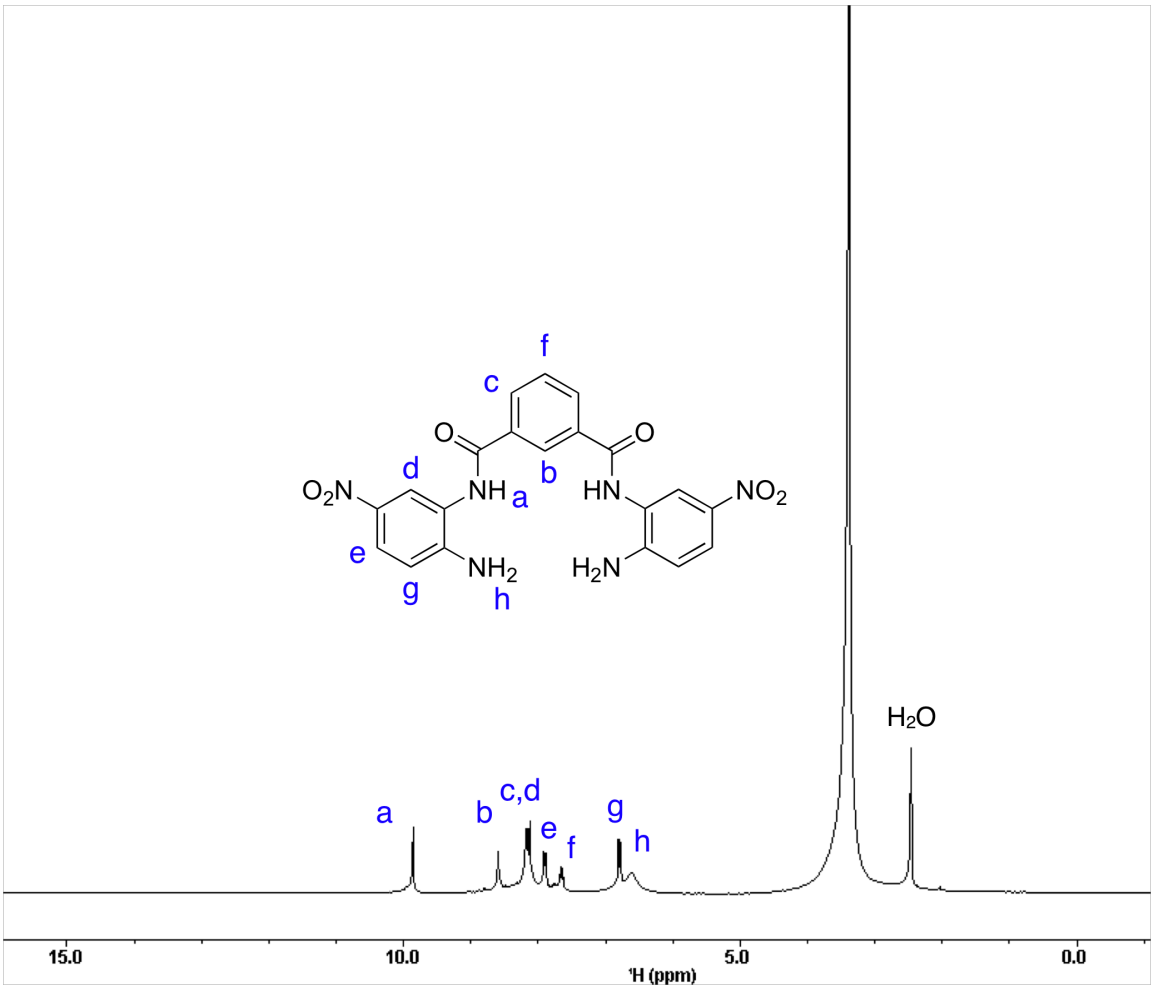


Figure S1. ^{1}H NMR (300 MHz) spectrum of **1** in d_6-DMSO at 20 ºC

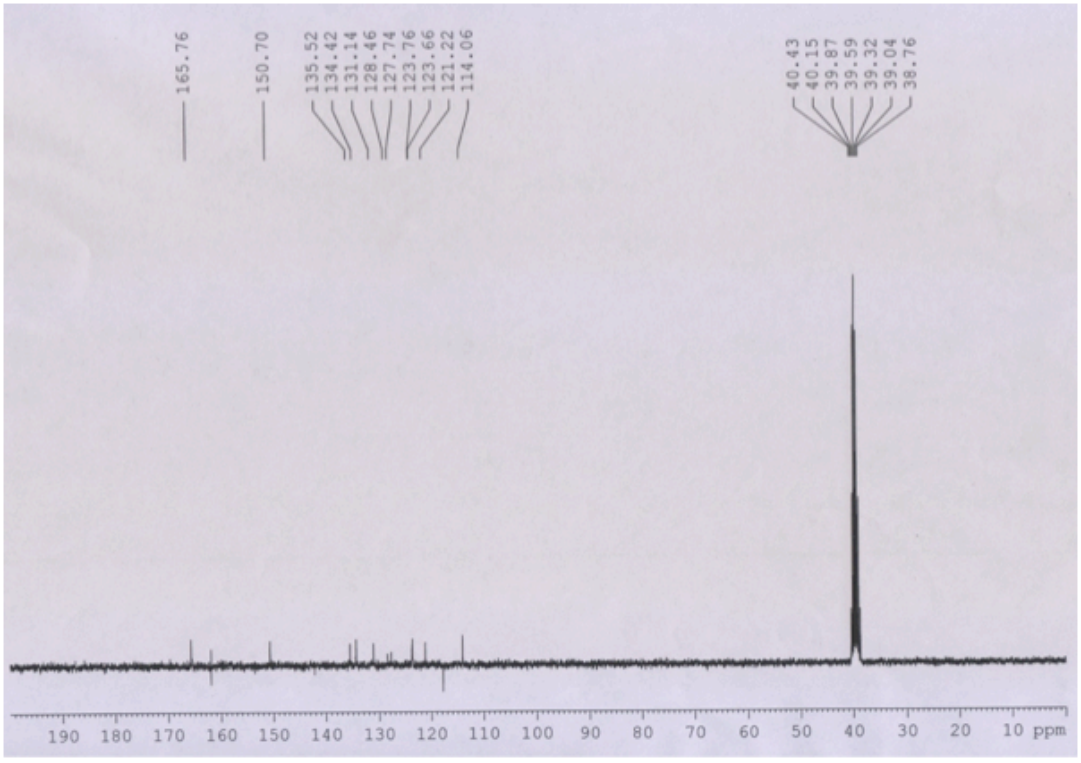


Figure S2. ^{13}C NMR (75.5 MHz) spectrum of **1** in d_6-DMSO at 20 ºC

4. Naked-eye color change

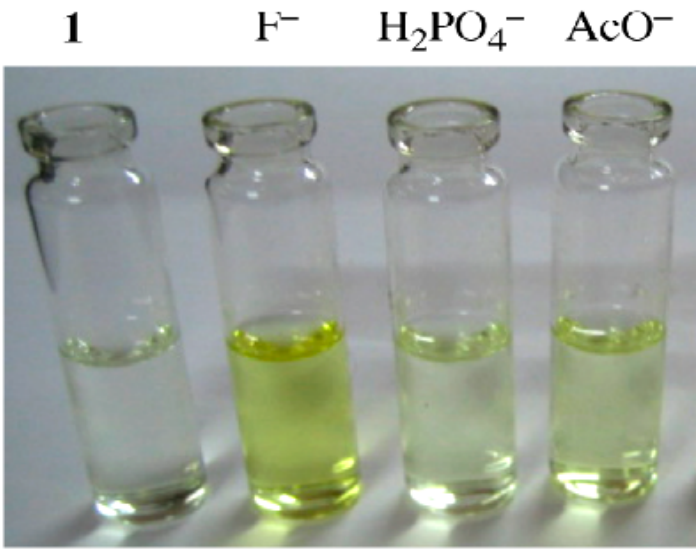


Figure S3. Naked-eye color changes of **1** (1×10^{-5}) in presence of various ions (0–2.0 equiv.) in aqueous-acetonitrile solvent.

5. UV–Vis Spectra

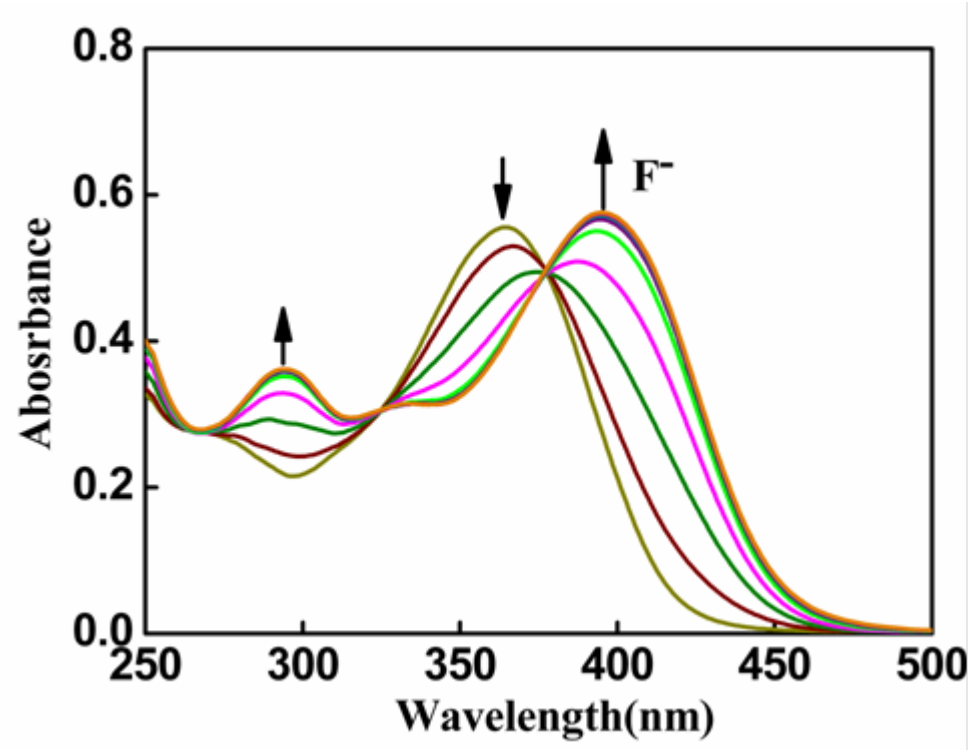


Figure S4. UV-vis spectral changes of **1** (0.5 μM) in presence of F^- ion (0-2.5eqv.) in aqueous-acetonitrile solvent.

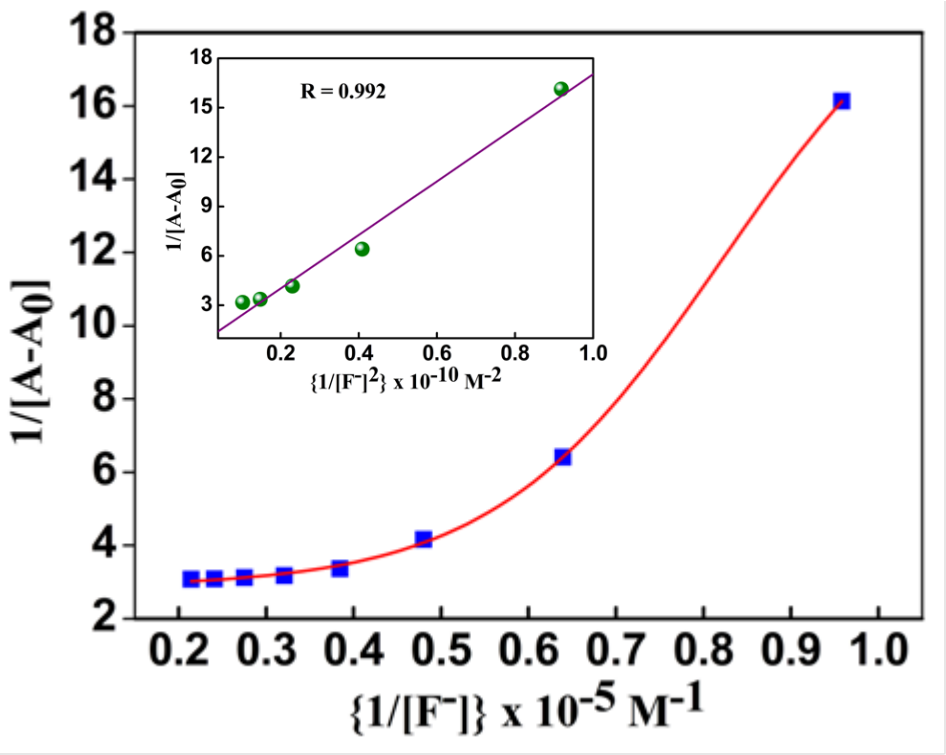


Figure S5. Benesi-Hildebrand plot (non-linear plot) of relative absorbance ($1/[A-A_0]$) vs concentration of fluoride anion ($1/[F^-]$) added during UV-vis titration (Fig. S4). (Inset) Plot (linear) of $1/[A-A_0]$ vs $1/[F^-]^2$.

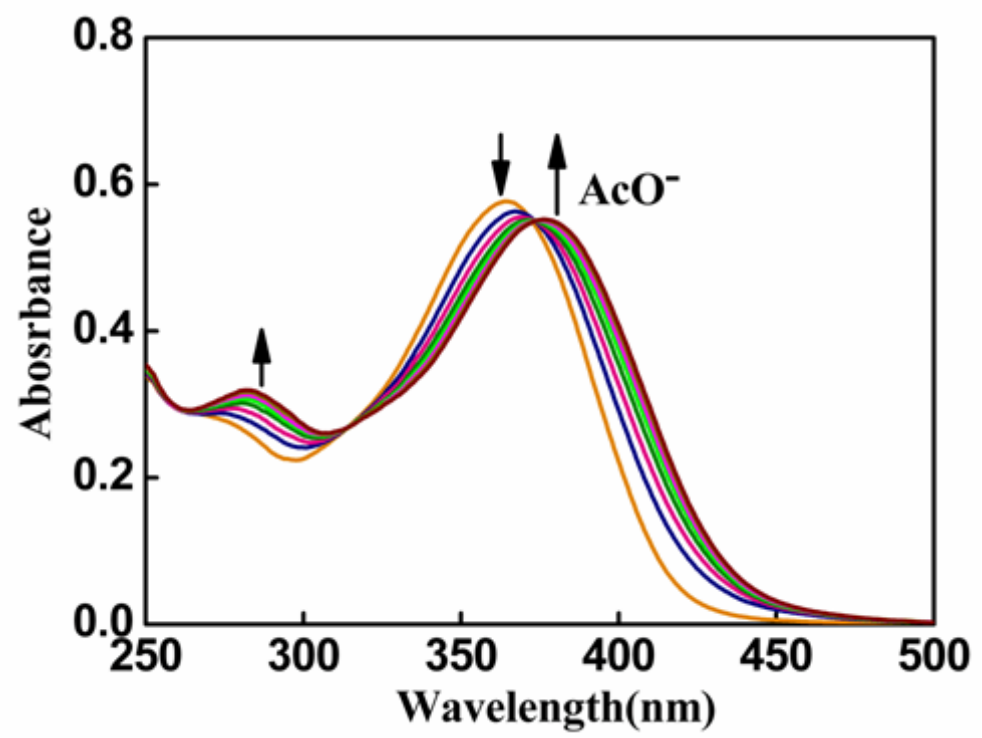


Figure S6. Spectral changes of **1** (0.5 μM) in presence of OAc^- ion (0–2.5eqv.) in aqueous-acetonitrile solvent.

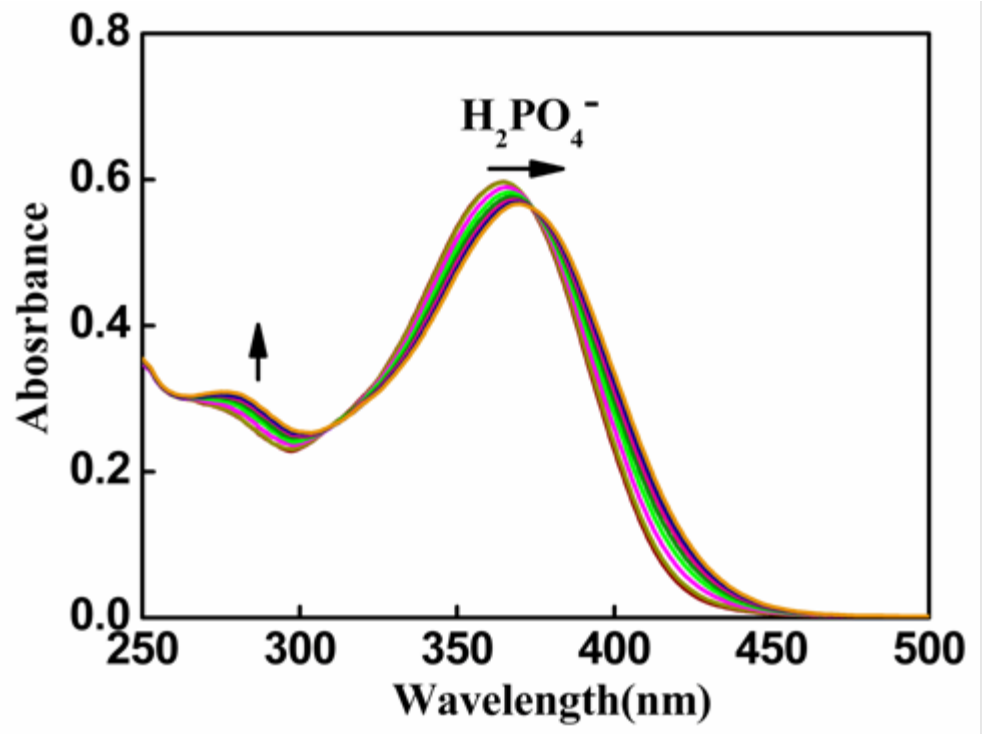


Figure S7. Spectral changes of **1** (0.5 μM) in presence of $H_2PO_4^-$ ion (0–2.5eqv.) in

aqueous-acetonitrile solvent

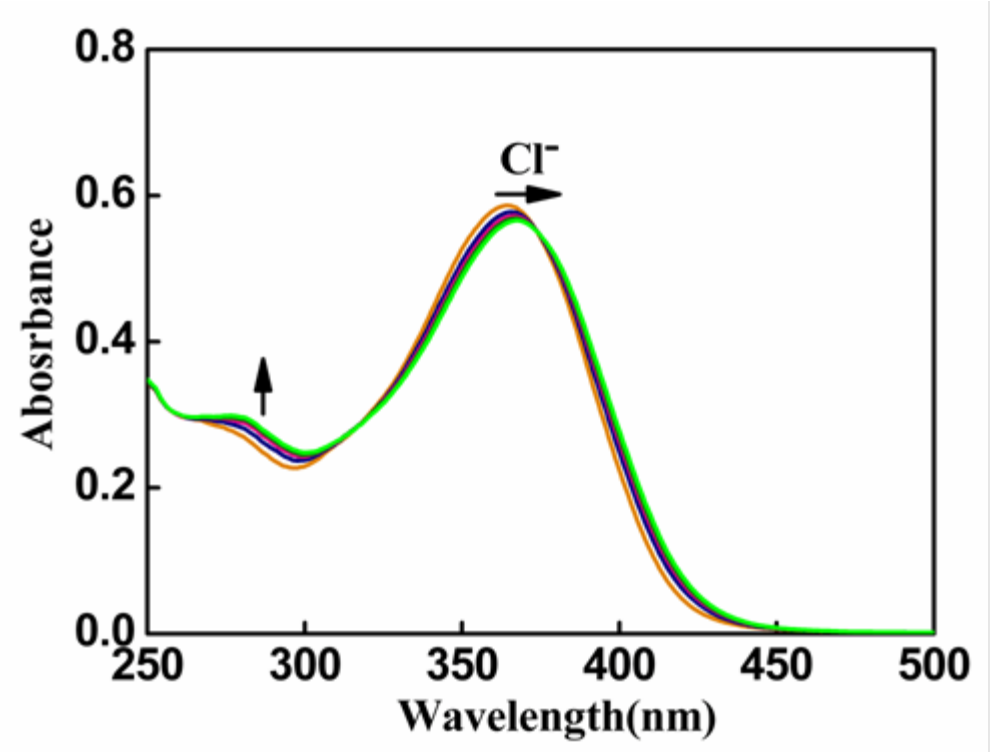
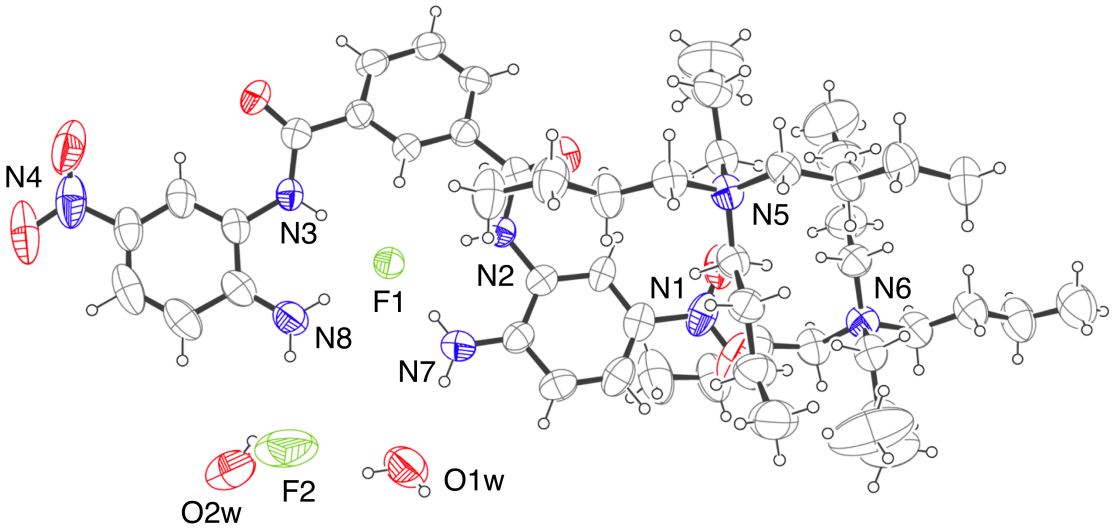


Figure S8. Spectral changes of **1** (0.5 μM) in presence of Cl^- ion (0–2.5eqv.) in aqueous-acetonitrile solvent.

6. X–ray Crystallographic Data and Structures

Crystals of **1** and fluoride ion suitable for X-ray structural analysis was grown by



slow diffusion of diethyl ether into acetonitrile solution of 1:2 mixture of **1** and tetrabutylammonium fluoride. It should be noted that a mixture of 1:1 or 1:3 mixtures of **1** and F^- also exhibit the similar X-ray crystal structural analysis.

Figure S9. ORTEP diagram of **1**.fluoride complex (thermal ellipsoids set to 30% probability). Tetrabutylammonium cation (n-Bu_4N^+) as a charge balancing counter ions.

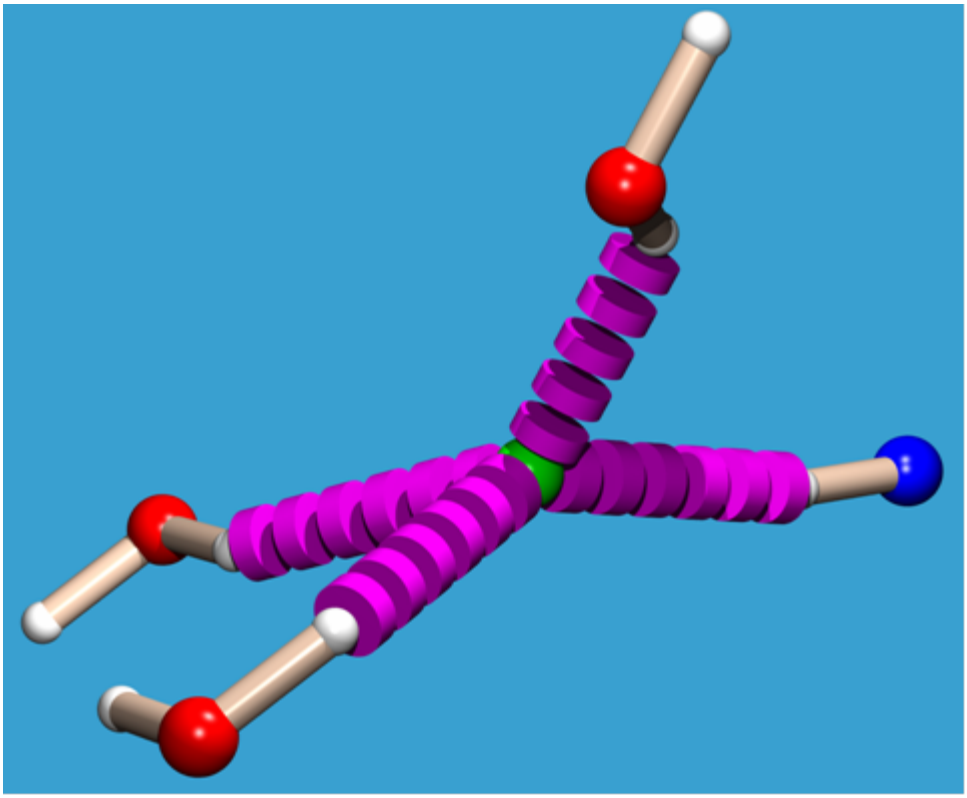


Figure S10. Partial structure of fluoride-water cluster, distorted trigonal pyramidal shape where the water molecule (O2W) is at the apex of the pyramid.

Table S1. Crystal data and refinement details of the receptor **1**-F^- complex

Parameters	**1**.F^-
Formula	$C_{52}H_{92}N_8F_2O_{7.5}$
Formula Weight	987.34
Crystal System	Monoclinic
Space group	$P2_1/c$
a /Å	9.9923(9)
b /Å	39.407(4)
c /Å	14.7337(14)
α /º	90
β /º	94.433(2)
γ /º	90
V /Å^3	5784.3(10)
Z	4
D_c/g cm^{-3}	1.134
R(int)	0.1355
No. of unique data	5506
No. of data with I >2σ(I)	3881
R1, *w*R2	0.1060, 0.2911
GOF on F^2	1.072

Table S2. Hydrogen bonding interactions of **1**-F^- complex

D-H…A	D-H	H…A	D…A	<D-H…A
N2-H2A..F1	0.8600	1.9100	2.764(7)	177.00
N3-H3A..F1	0.8600	1.9200	2.780(8)	177.00
N7-H7A..F1	0.8600	2.0000	2.768(9)	148.00
N8-H8A..F1	0.8600	1.9500	2.752(10)	154.00
N8-H8B..F2	0.8600	2.0400	2.895(11)	171.00
O1W-H1W1..F2	0.8500	1.8500	2.521(13)	135.00
O1W-H2W1..F2	0.8500	1.9500	2.709(15)	148.00
N7-H7B..O1W	0.8600	2.0700	2.931(11)	173.00

7. References

(1). SAINT, version 6.02; SADABS, version 2.03; Bruker AXS, Inc.: Madison, WI, **2002**.

(2). (a) G. M. Sheldrick, SHELXS 97, Program for Structure Solution, University of Göttingen, Germany, **1997**. (b) G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, **1997**. (c) A. L. Spek, PLATON, Molecular Geometry Program, *J. Appl. Crystallogr.* **2003**, 36, 7. (d) L. J. J. Farrugia, *Appl. Crystallogr.* **1997**, 30, 565. (e) Farrugia, L. J.; *J. Appl. Crystallogr.* **1999**, 32, 837.

(3). X. Bao, J. Yu, Y. Zhou, *Sens. and Actuators B (Chem.)* **2009**, 140, 467.