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SUPPLEMENTARY INFORMATION (SI)

Ion-Mediated Single-Molecular Optical Switching and Sensing Based on Fluorophore-Tethered Calix[4]pyrrole

Divya Sareen, Ji Hye Lee, Hyonseok Hwang, Soeun Yoo, and Chang-Hee Lee*

Department of Chemistry, Kangwon National University, Chun Cheon 200-701 Korea
E-mail: chhlee@kangwon.ac.kr

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S1. Experimental

1. General

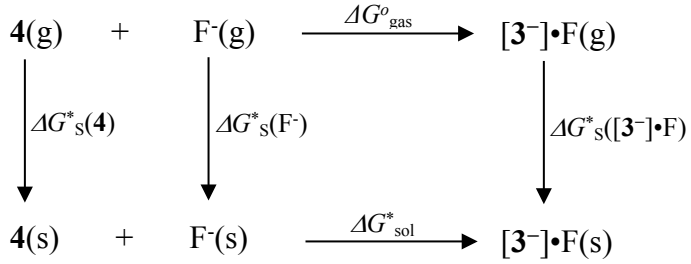
^{1}H NMR and ^{13}C NMR spectra have been recorded on Bruker Avance 300 MHz and 100 MHz, respectively with TMS as internal standard using $CDCl_3$ and CD_3CN as deuterated solvents. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet), coupling constant J (Hz), integration and assignment. Mass spectra were recorded on Voyager DE-STR MALDI-TOF (for higher molecular weights) and JEOL JMS-700 GC mass spectrometer. Emission studies were conducted on Scinco FluoroMate FS-2 fluorescence spectrophotometer within the range of 200-900 nm at a fixed slit width of 10 nm. The excitation wavelength employed for recordings was 320 nm. UV-visible spectral studies were performed using Varian Cary 100 Conc spectrophotometer and were recorded between 900 and 200 nm. The optical studies were carried out with a quartz cuvette of path length 1 cm. Thermodynamic data have been recorded using VP-ITC MicroCalorimeter.

2. Computational Methods

All theoretical calculations were carried out using the Gaussian 09 suite of programs[1] and visualizations were made by Gauss View 5.[2] For the conformational analysis for **3**, **4 and [3^{-}]•F**, total 100 initial structures for each compound were generated using the MMFF force fields as implemented in the Spartan 14 software.[3] In the conformation search, the calixpyrrole part was fixed and the hydrocarbon and coumarin part in each compound were freely rotated without any restraints. These 100 initial structures were optimized with the semi-empirical AM1 method. Then the 7 and 20 lowest energy structures for **4 and [3^{-}]•F**, respectively, were selected for further optimizations at the M06-2X/3-21G level of theory. Among them were chosen the 5 lowest energy structures for each compound which were finally optimized at the M06-2X/6-31G(d,p). The final lowest energy structure for each compound was selected and frequency analysis with the same basis set was performed to verify the optimized structure as a minimum. The electronic energy was refined by single point energy calculations at the M06-2X/6-31+G(d,p) level. The binding free energy difference (ΔG^{*}_{sol}) was evaluated using the thermodynamic cycle method (Scheme S1) and following equation:

$$\Delta G^{*}_{sol} = \Delta G^{o}_{gas} + \Delta G^{*}_{S}([\mathbf{3}^{-}]\bullet F) - \Delta G^{*}_{S}(\mathbf{4}) - \Delta G^{*}_{S}(F^{-}) + \Delta G_{S}^{o\rightarrow *}$$

where ΔG^*_{sol} and ΔG^o_{gas} are the binding free energy differences in solution and gas phase, respectively, and $\Delta G^*_S(X)$ is the solvation free energy for X. $\Delta G_S^{\circ\rightarrow *}$ is the free energy change of 1 mol of an ideal gas from 1 atm to 1 M, which is 1.89 kcal/mol at 298.15 K.[4] The solvation free energies of the two compounds and F^- ion in CH_3CN were evaluated using the integral-equation formalism polarizable continuum model (IEF-PCM).



Scheme S1 Thermodynamic cycle for the calculation of ΔG^*_{sol}.

3. Chemicals

The starting materials for syntheses have been purchased from Sigma-Aldrich, TCI or Alfa Aesar. Dry THF for reaction was obtained by refluxing it with sodium metal in the presence of benzophenone till it turns blue. Pyrrole was used after distillation under reduced pressure. Anionic salts (tetrabutylammonium salts) used in the spectrophotometric studies were of analytical grade bought from Sigma-Aldrich. The solvents used were also of analytical grade purchased from Fischer Scientific.

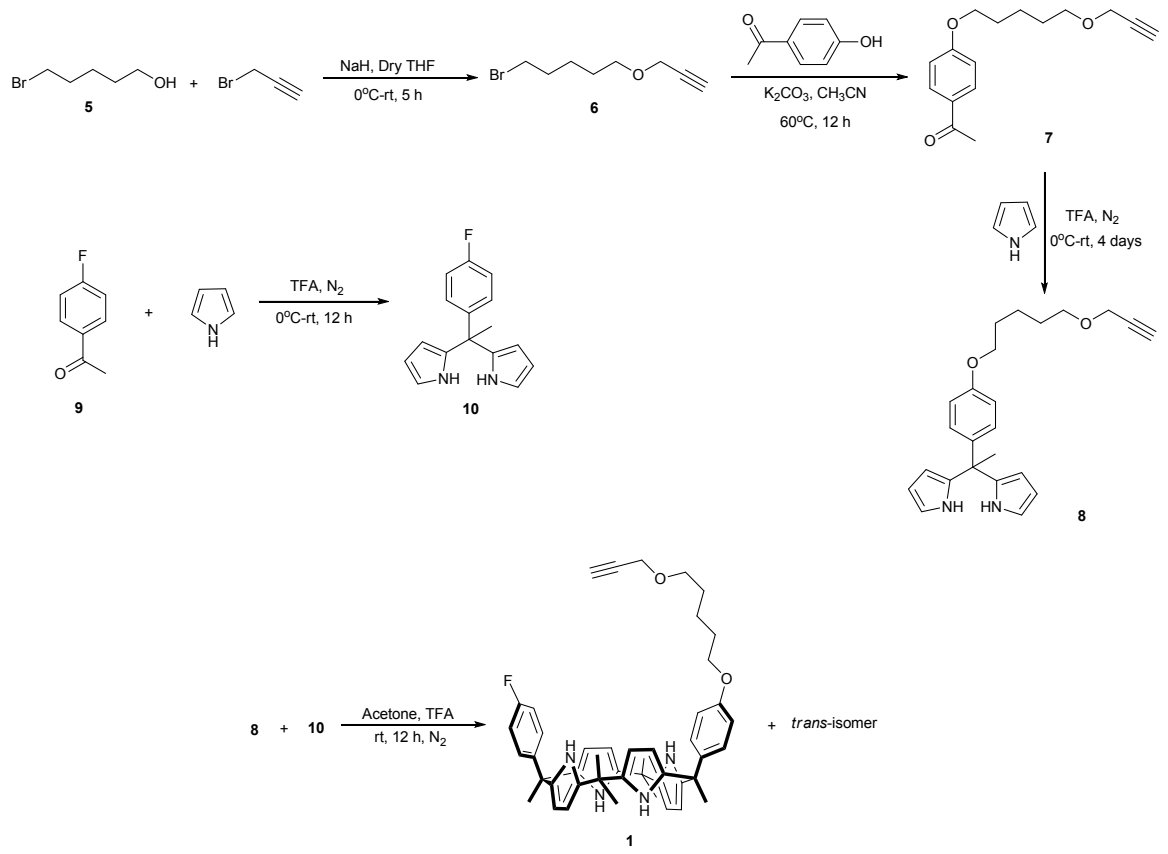
4. Quantum Yield Calculations

The fluorescence quantum yields were determined using an optically matching solution of 9,10-diphenylanthracene as a standard having a quantum yield of 0.90 in cyclohexane[5] using the equation:

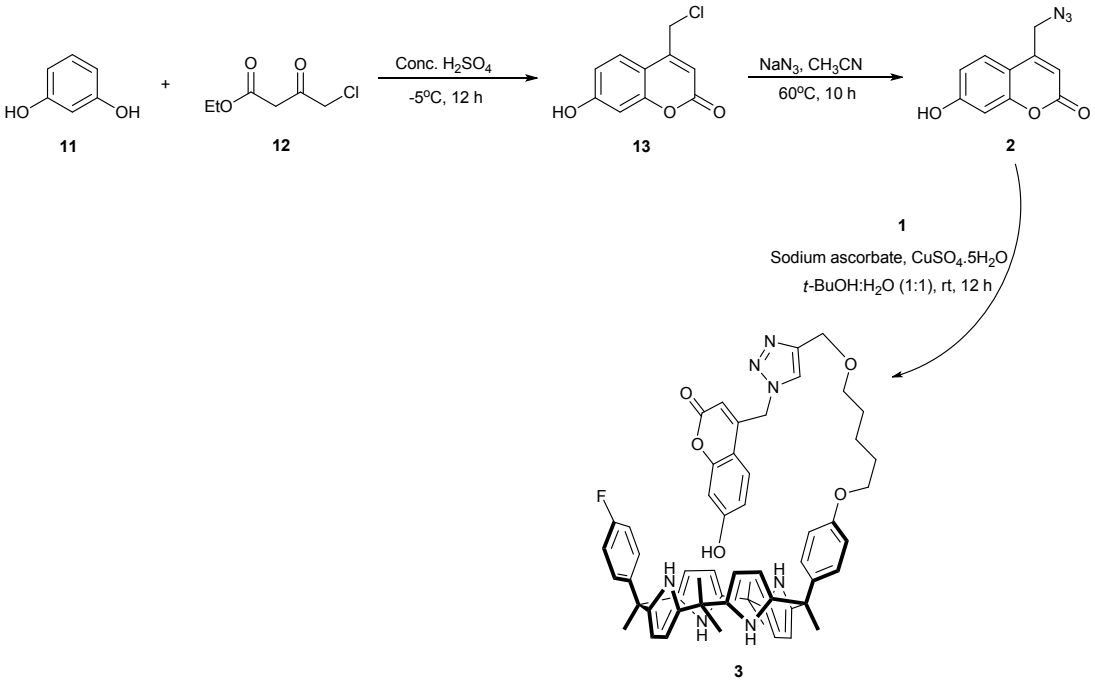
$$\Phi_x = \Phi_{st} \times (F_x A_{st} \times \eta_x^2) / (F_{st} A_x \times \eta_{st}^2)$$

where Φ_x and Φ_{st} are the quantum yields of the test sample and the standard sample respectively, A_x and A_{st} are the absorbances of the test sample and the standard sample respectively, F_x and F_{st} are the areas of emission bands for the test sample and the reference sample, η_x and η_{st} are the refractive indices of test sample and standard sample solutions in their respective pure solvents.

S2. Synthetic procedures and spectral data

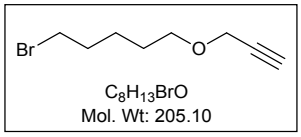


Scheme S2 (a) Synthesis of calix[4]pyrrole **1**.

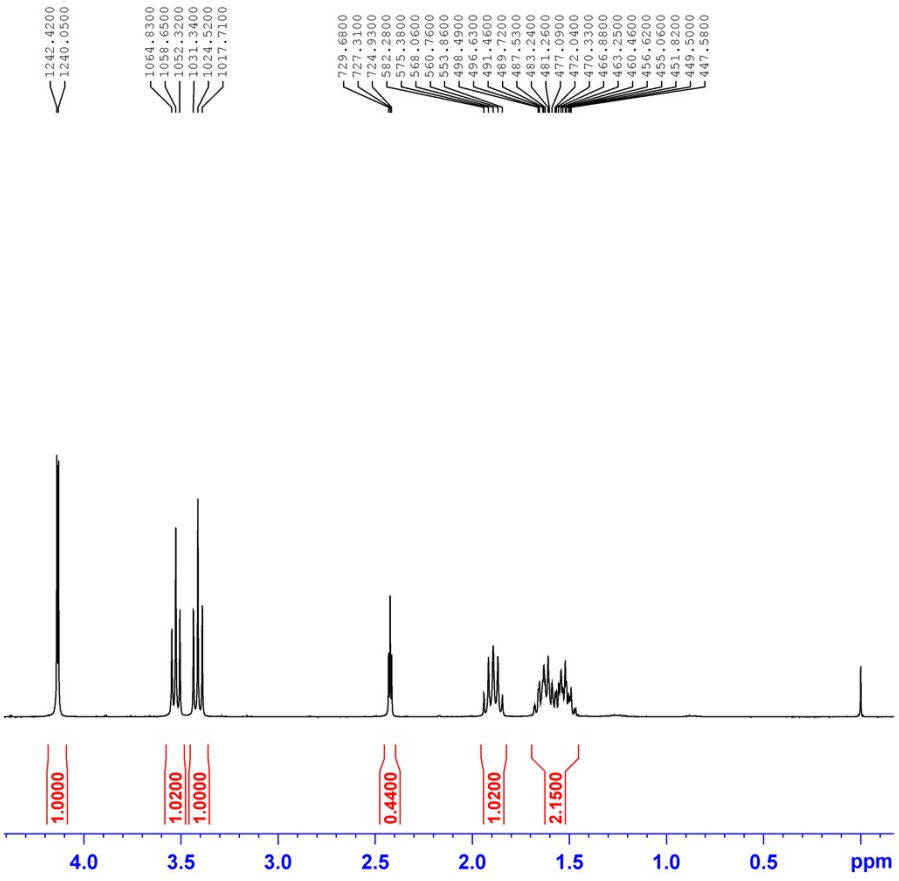


Scheme S2 (b) Synthesis of targeted molecular switch **3**.

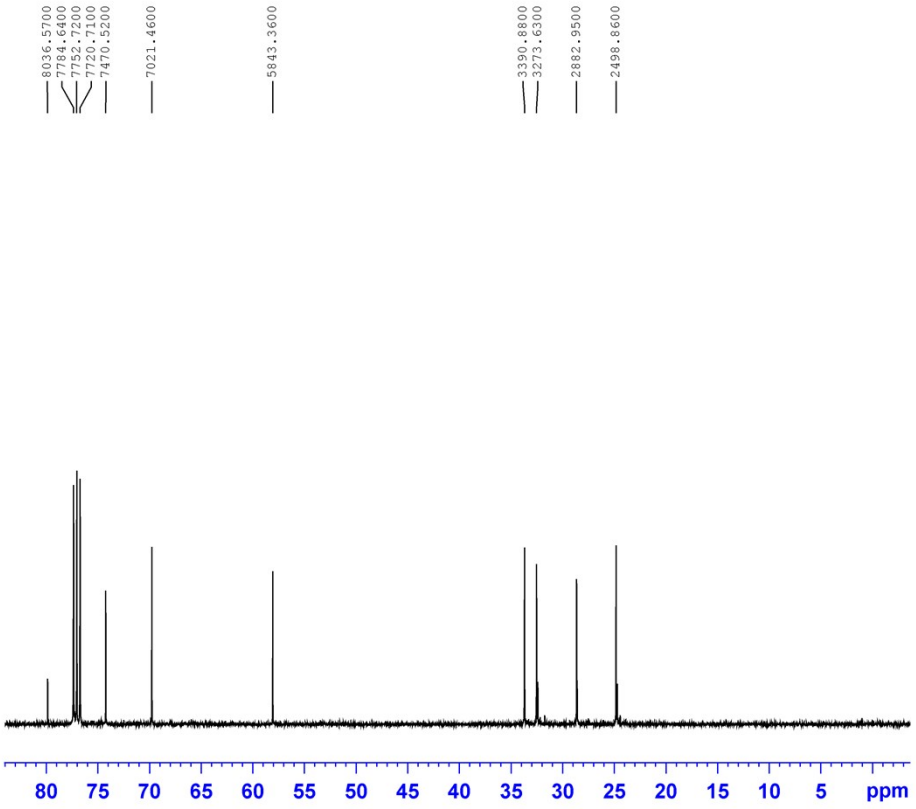
1-Bromo-5-(prop-2-yn-1-yloxy)pentane[6] (6)



5-Bromo-1-pentanol **5** (0.4 ml, 1 eq.) in dry THF was added to a suspension of NaH (0.3 g, 2 eq.) in 15 ml of dry THF with stirring under inert atmosphere at 0°C followed by addition of propargyl bromide (0.7 ml, 2 eq.) dissolved in THF (10 ml). The reaction mixture was shifted to room temperature and stirred for 12 h. The reaction mixture was quenched with water (15 ml) and extracted with DCM (3×15 ml). The organic layer was washed with brine (15 ml) and dried over Na_2SO_4. Solvent was removed under reduced pressure and residual oil was purified by column chromatography (Hex: EtOAc = 95:5) to yield **6** as a yellow oil. Yield 50%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.52-1.63 (4H, m, C**H**$_2$), 1.87-1.92 (2H, m, C**H**$_2$), 2.42 (1H, t, *J* = 2.38 Hz, ≡C**H**), 3.42 (2H, t, *J* = 6.82 Hz, C**H**$_2$-O), 3.53 (2H, t, *J* = 6.26 Hz, Br-C**H**$_2$), 4.14 (2H, d, *J* = 2.39 Hz, O-C**H**$_2$-); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 28.8, 32.7, 33.9, 58.4, 70.2, 74.7 and 80.4; MS: *m/z* 205 [M$^+$].

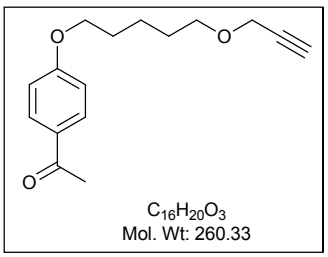


^{1}H NMR spectrum of **6**

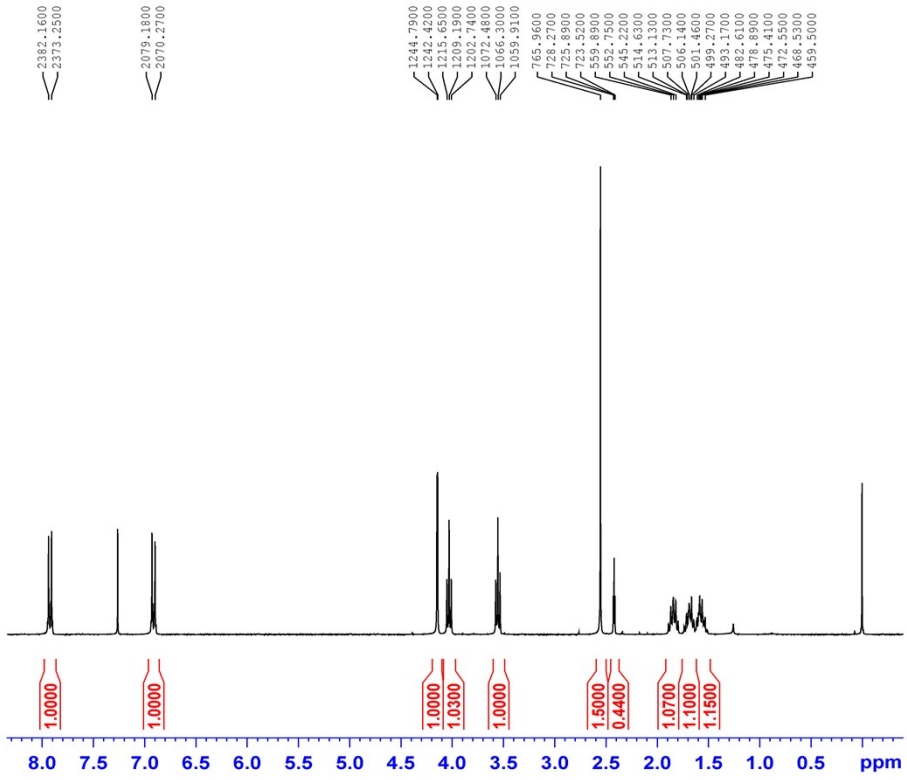


^{13}C NMR spectrum of **6**

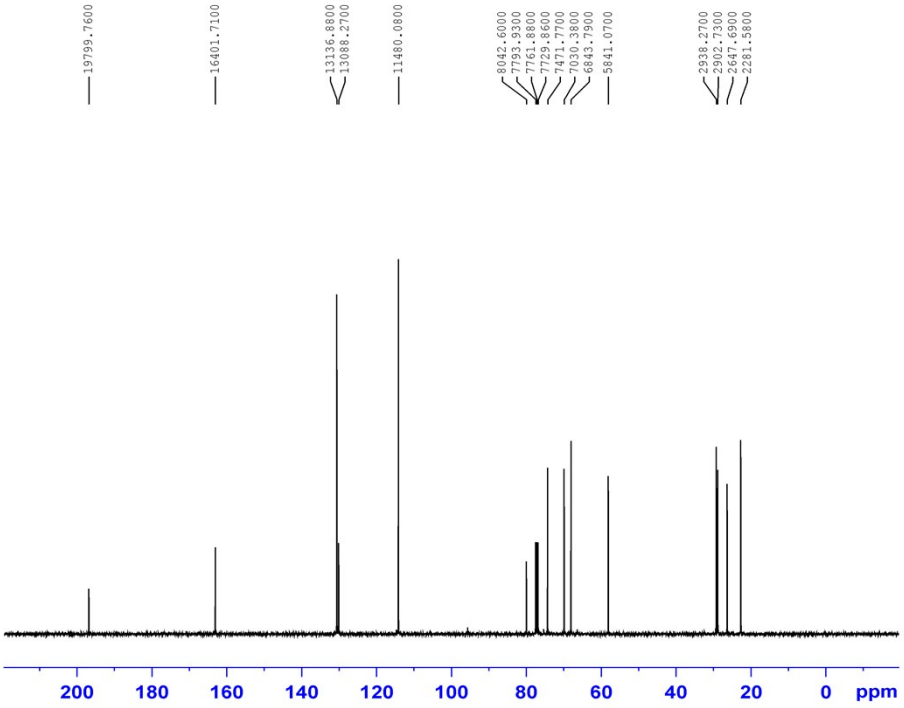
1-(4-((5-(prop-2-yn-1-yloxy)pentyl)oxy)phenyl)ethan-1-one[7] (7)



4-Hydroxyacetophenone (0.33 g, 1 eq.) and K_2CO_3 (0.7 g, 2 eq.) were dissolved in 15 ml of acetonitrile and the reaction mixture was stirred at 60°C for 30 min. Compound **6** (0.5 g, 1 eq.) dissolved in acetonitrile (10 ml) was added dropwise and the resulting reaction mixture was refluxed overnight. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was taken in water (15 ml) and extracted with DCM (3×15 ml). The organic extract was dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure to afford crude product which was purified by column chromatography (Hex: EtOAc = 93:7) to afford **7** as a yellow oil. Yield 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.57 (2H, m, C**H**$_2$), 1.69 (2H, m, C**H**$_2$), 1.84 (2H, m, C**H**$_2$), 2.42 (1H, t, *J* = 2.38 Hz, ≡C**H**), 2.55 (3H, s, C**H**$_3$), 3.55 (2H, t, *J* = 6.28 Hz, C**H**$_2$-O), 4.03 (2H, t, *J* = 6.45 Hz, ArO-C**H**$_2$), 4.14 (2H, d, *J* = 2.38 Hz, O-C**H**$_2$-), 6.92 (2H, d, *J* = 8.91 Hz, Ar**H**), 7.92 (2H, d, *J* = 8.91 Hz, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.8, 26.5, 29.0, 29.4, 58.4, 68.4, 70.3, 74.7, 80.4, 114.8 (2C), 130.9, 131.4 (2C), 164.0 and 198.0; MS: *m/z* 260 [M$^+$].

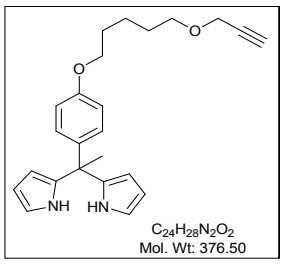


^{1}H NMR spectrum of **7**

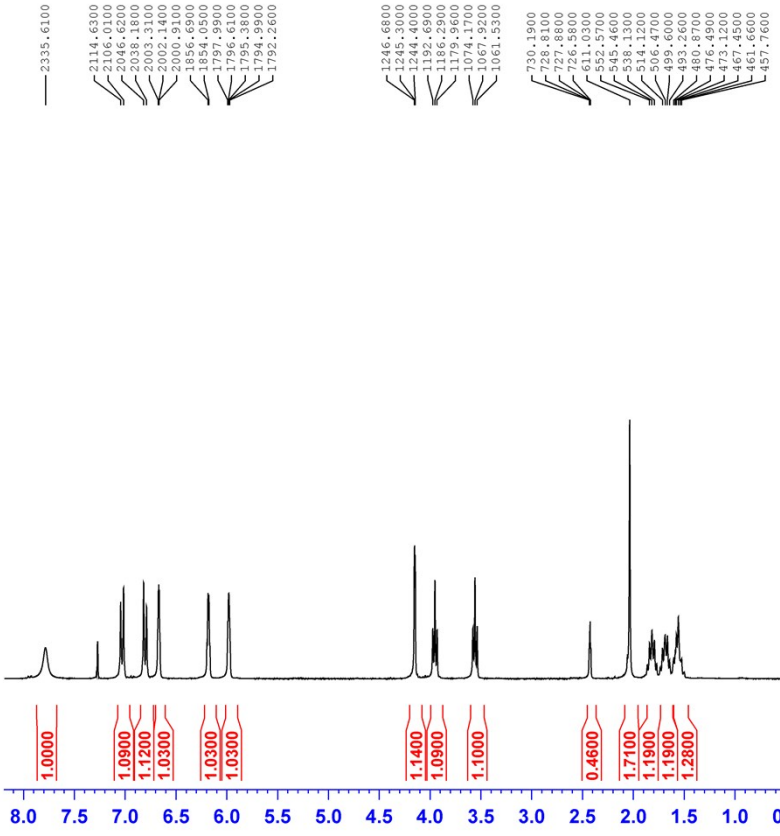


^{13}C NMR spectrum of **7**

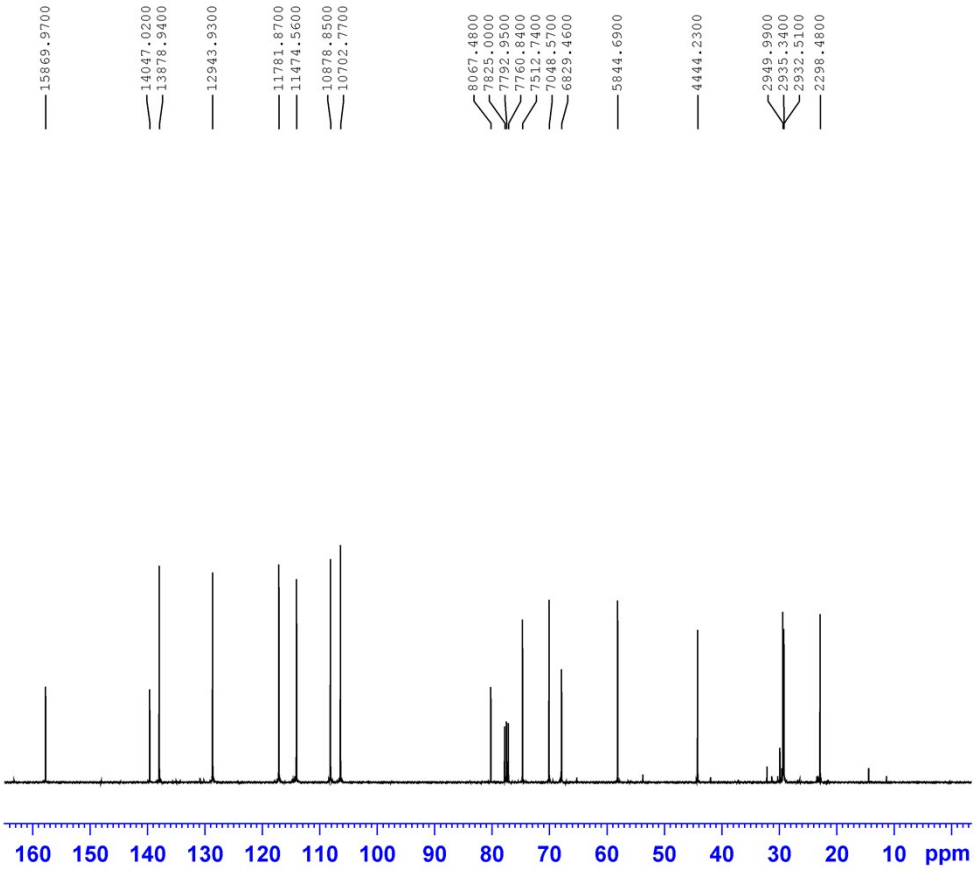
5-(4-((5-(prop-2-yn-1-yloxy)pentyl)oxy)phenyl)-5-methyldipyrromethane (8)



TFA (0.03 ml, 1 eq.) was added dropwise to the mixture of compound **7** (0.1 g, 1 eq.) and pyrrole (0.3 ml, 10 eq.) at 0°C under nitrogen atmosphere. The reaction mixture was shifted to room temperature and stirred for 4 days. The reaction mixture was quenched with aqueous 0.1 N NaOH and extracted with DCM (3×15 ml). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to afford crude product, which was purified by column chromatography (Hex: EtOAc = 94:6) to yield product **8** as a yellow oil. Yield 48%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.56 (2H, m, C**H**$_2$), 1.66 (2H, m, C**H**$_2$), 1.80 (2H, m, C**H**$_2$), 2.03 (3H, s, C**H**$_3$), 2.40 (1H, m, ≡C**H**), 3.54 (2H, t, *J* = 6.32 Hz, C**H**$_2$-O), 3.93 (2H, t, *J* = 6.36 Hz, ArO-C**H**$_2$), 4.13 (2H, d, *J* = 2.29 Hz, O-C**H**$_2$-), 5.96 (2H, m, pyrrolic-**H)**, 6.16 (2H, m, pyrrolic-**H)**, 6.65 (2H, m, pyrrolic-**H)**, 6.79 (2H, d, *J* = 8.42 Hz, Ar**H**), 7.01 (2H, d, *J* = 8.62 Hz, Ar**H**), 7.76 (2H, br s, N**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 23.0, 29.3, 29.4, 29.5, 44.4, 58.4, 68.3, 70.5, 75.1, 80.7, 107.0 (2C), 108.8(2C), 114.7 (2C), 117.8(2C), 129.4 (2C), 138.8 (2C), 140.5 and 158.7; MS: *m/z* 376 [M$^+$].

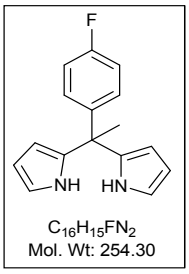


^{1}H NMR spectrum of **8**

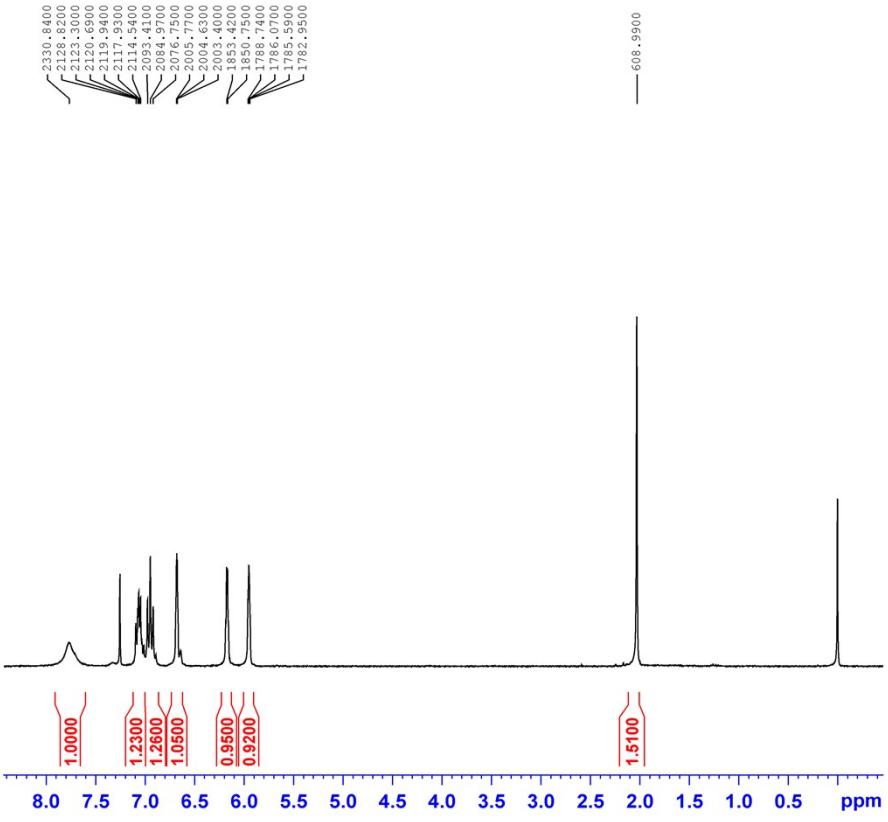


^{13}C NMR spectrum of **8**

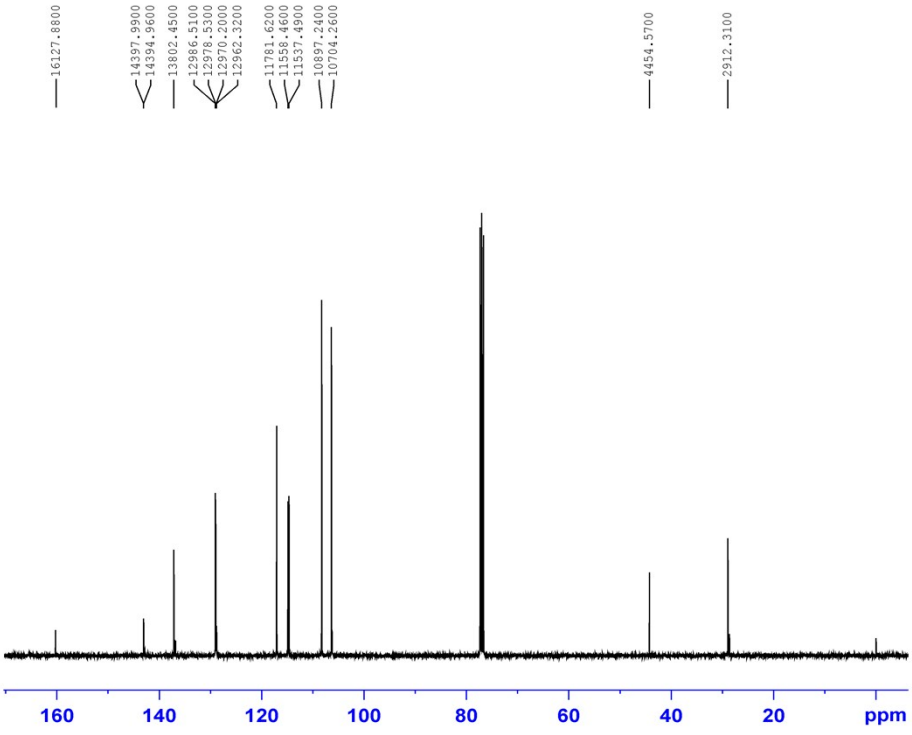
5-(4-fluorophenyl)-5-methyldipyrromethane[8] (10)



TFA (1.2 ml, 1 eq.) was added dropwise to the mixture of commercially available 4-fluoroacetophenone **9** (2 ml, 1 eq.) and pyrrole (11.4 ml, 10 eq.) at 0°C under nitrogen atmosphere. The reaction mixture was shifted to room temperature and stirred for 12 h. The reaction mixture was quenched with aqueous 0.1 N NaOH and extracted with DCM (3×15 ml). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (Hex: EtOAc = 95:5) to afford **10** as a white solid. Yield 66%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.03 (3H, s, C**H**$_3$), 5.95 (2H, m, pyrrolic-**H)**, 6.17 (2H, m, pyrrolic-**H)**, 6.68 (2H, m, pyrrolic-**H)**, 6.95 (2H, m, Ar**H**), 7.07 (2H, m, Ar**H**), 7.77 (2H, br s, N**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 29.1, 44.5, 107.0 (2C), 109.0 (2C), 115.4, 115.6, 117.8 (2C), 129.8 (2C), 138.0 (2C), 144.0 and 161.3; MS: *m/z* 254 [M^+].

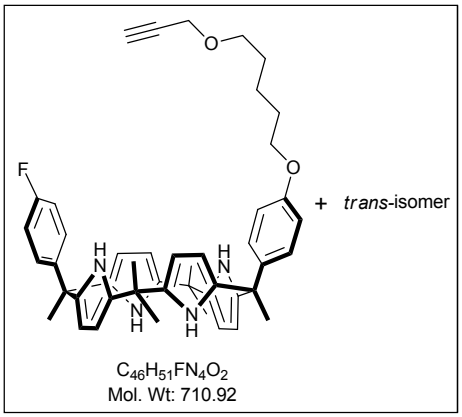


^{1}H NMR spectrum of **10**



^{13}C NMR spectrum of **10**

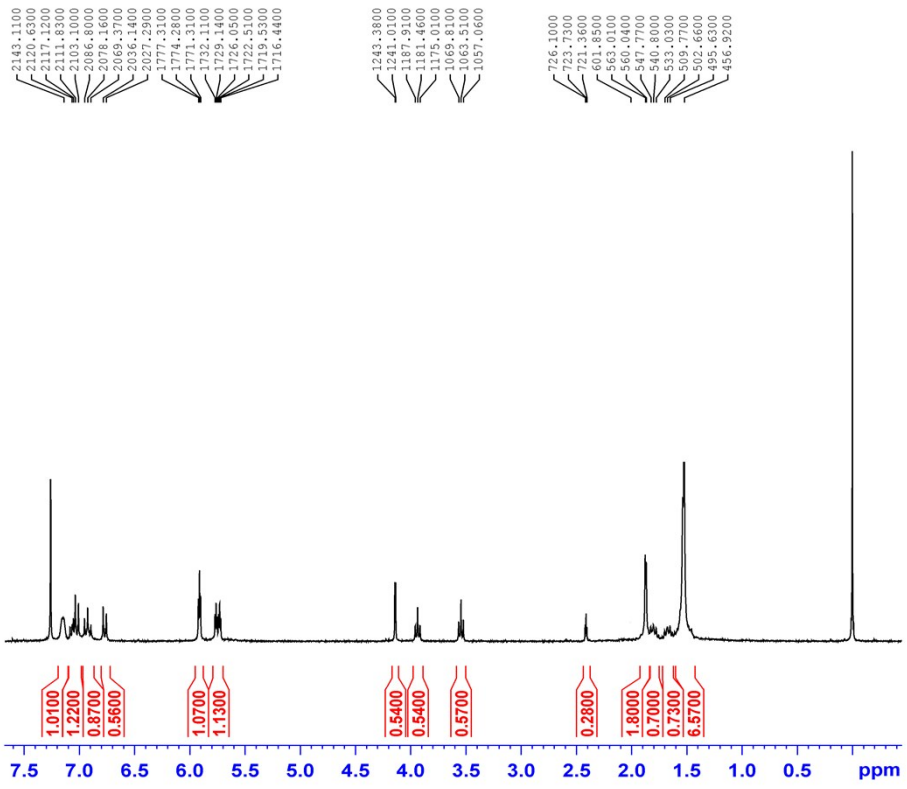
5-(4-fluorophenyl)-15-(4-((5-(prop-2-yn-1-yloxy)pentyl)oxy)phenyl)-5,10,10,15,20,20-hexamethylcalix[4]pyrrole (1)



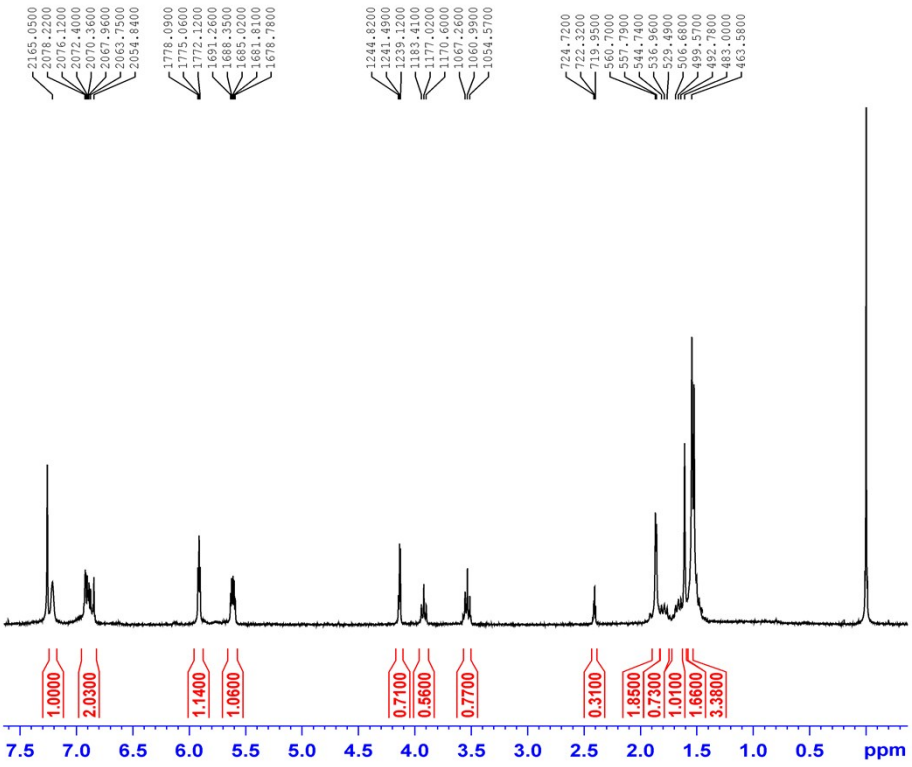
TFA (0.3 ml, 2 eq.) was added dropwise to the mixture of compounds **8** (0.5 g, 1 eq.) and **10** (0.34 g, 1 eq.) in acetone (150 ml) under nitrogen atmosphere and the resulting reaction mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with triethylamine (1.7 ml, 4 eq.). Acetone was removed under reduced pressure to obtain residue which was taken in water (15 ml) and extracted with DCM (3×15 ml). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed *in vacuo*. Column chromatography on silica afforded purification as well as separation of the two isomers. The first fraction containing *trans*- isomer (8%) was collected in 98:2 hexane/EtOAc mixture, while the second fraction (Hex: EtOAc = 97:3) gave the required *cis*-isomer **1** as a creamish white solid in 6% yield.

trans- isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.52 (12H, s, *meso*-C**H**$_3$), 1.58-1.83 (6H, m, C**H**$_2$), 1.87 (6H, d, *J* = 2.96 Hz, *meso*-C**H**$_3$), 2.41 (1H, t, *J* = 2.38 Hz, ≡C**H**), 3.54 (2H, t, *J* = 6.38 Hz, C**H**$_2$-O), 3.94 (2H, t, *J* = 6.45 Hz, ArO-C**H**$_2$), 4.14 (2H, d, *J* = 2.36 Hz, O-C**H**$_2$-), 5.72-5.77 (4H, m, pyrrolic-**H)**, 5.91 (4H, m, pyrrolic-**H)**, 6.76-7.04 (8H, m, Ar**H**), 7.15 (4H, br s, N**H**).

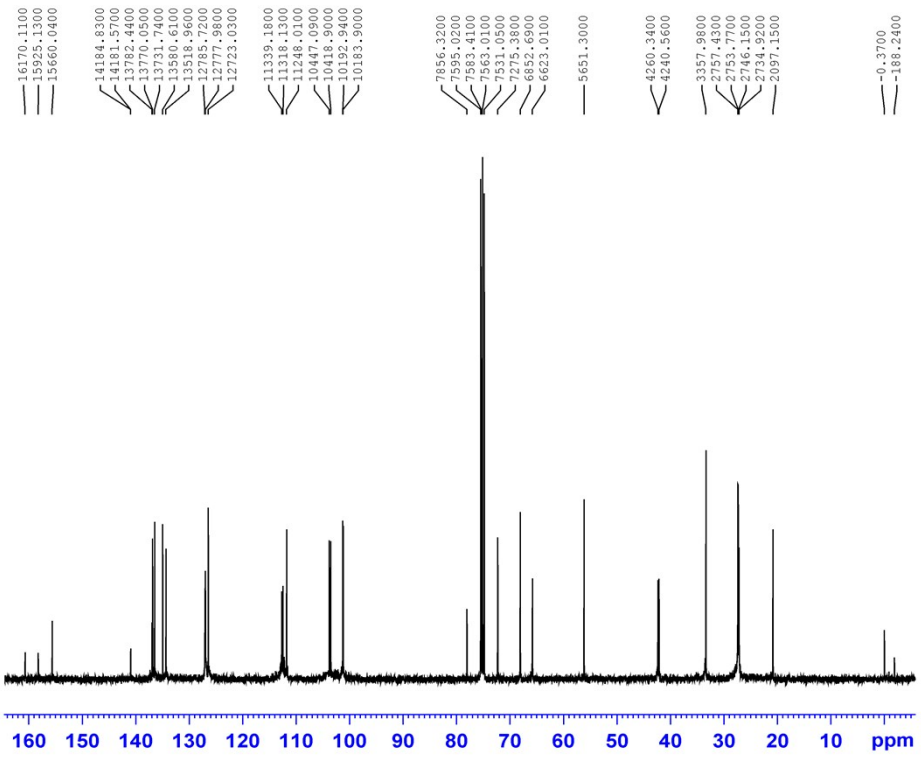
cis- isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.53 (6H, s, *meso*-C**H**$_3$), 1.61 (6H, s, *meso*-C**H**$_3$), 1.64-1.79 (6H, m, C**H**$_2$), 1.86 (6H, d, *J* = 2.92 Hz, *meso*-C**H**$_3$), 2.41 (1H, t, *J* = 2.39 Hz, ≡C**H**), 3.54 (2H, t, *J* = 6.44 Hz, C**H**$_2$-O), 3.92 (2H, t, *J* = 6.43 Hz, ArO-C**H**$_2$), 4.13 (2H, d, *J* = 2.37 Hz, O-C**H**$_2$-), 5.60-5.64 (4H, m, pyrrolic-**H)**, 5.92 (4H, m, pyrrolic-**H)**, 6.85-6.93 (8H, m, Ar**H**), 7.22 (4H, br s, N**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.0 (2C), 27.3, 27.5, 27.5, 27.6, 33.6 (4C), 42.4, 42.6, 56.5 (2C), 66.2, 68.5, 72.8, 78.6 (2C), 101.8 (2C), 101.9 (2C), 104.2 (2C), 104.5 (2C), 112.5 (2C), 113.2, 113.4, 127.2 (2C), 127.8, 127.9, 135.2, 135.8, 137.3 (2C), 137.7, 137.8, 141.8, 141.9, 156.6, 159.2 and 161.7; MS: *m/z* 709 [M^+-1].



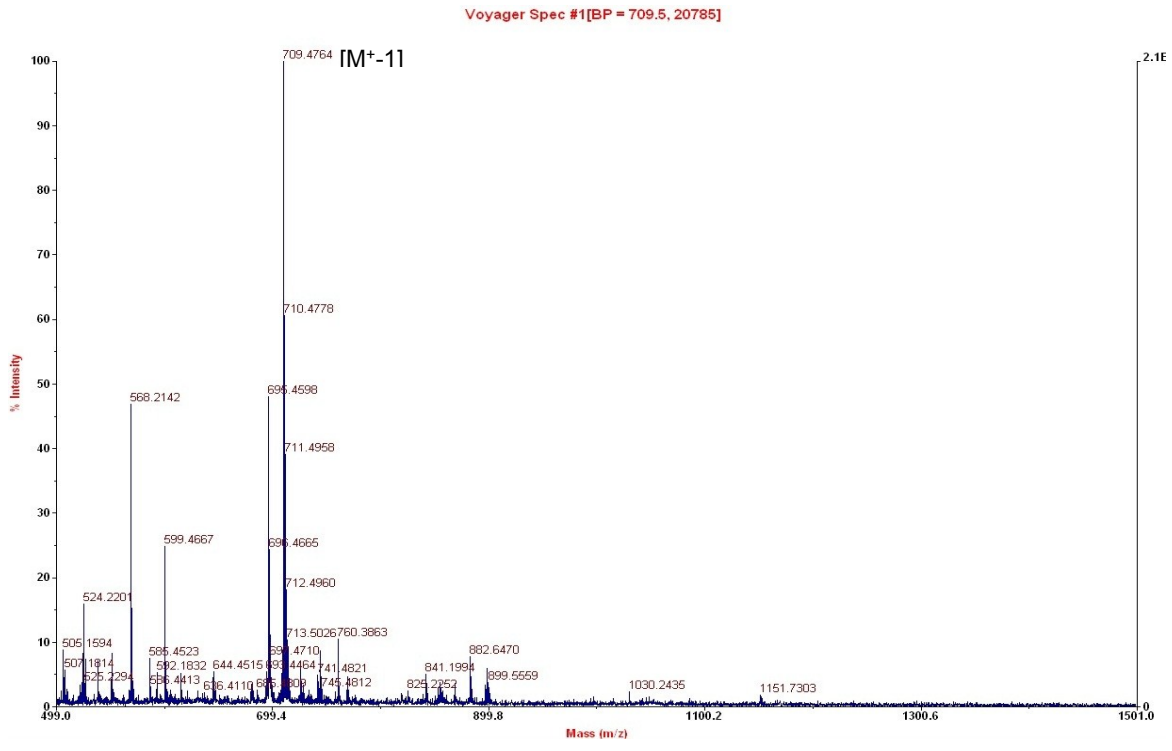
^{1}H NMR spectrum of *trans*-**1**



^{1}H NMR spectrum of *cis*-**1**

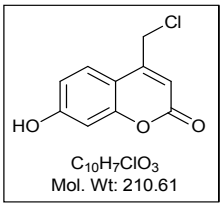


^{13}C NMR spectrum of *cis*-**1**

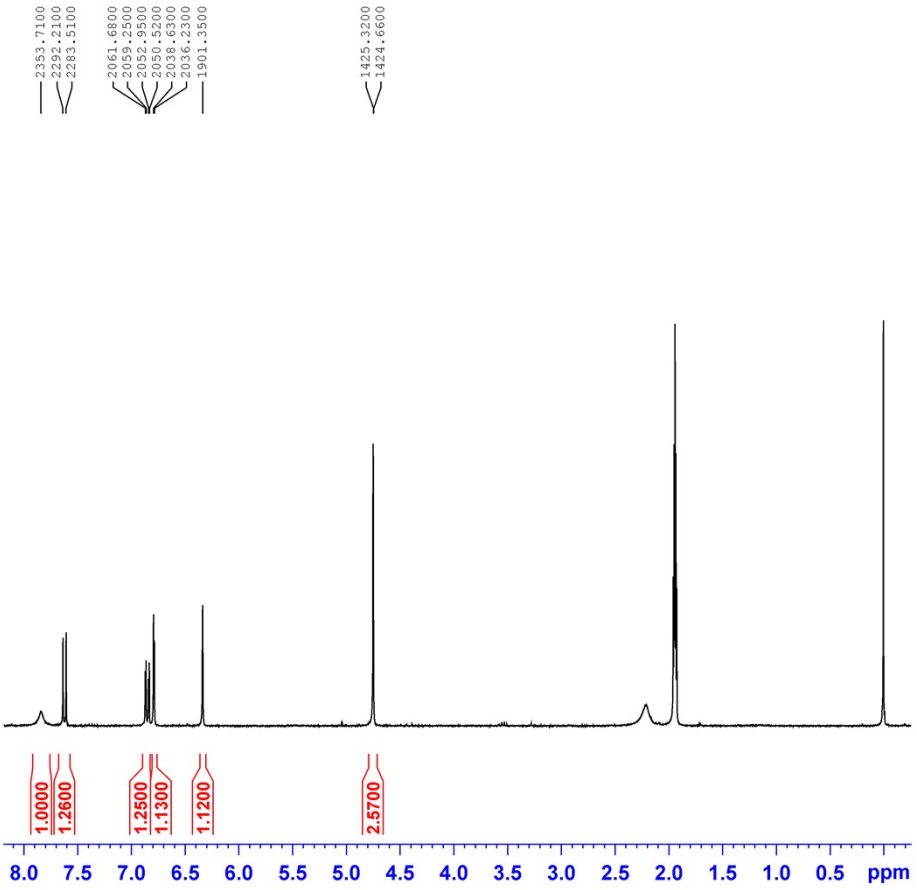


Mass spectrum of *cis*-**1**

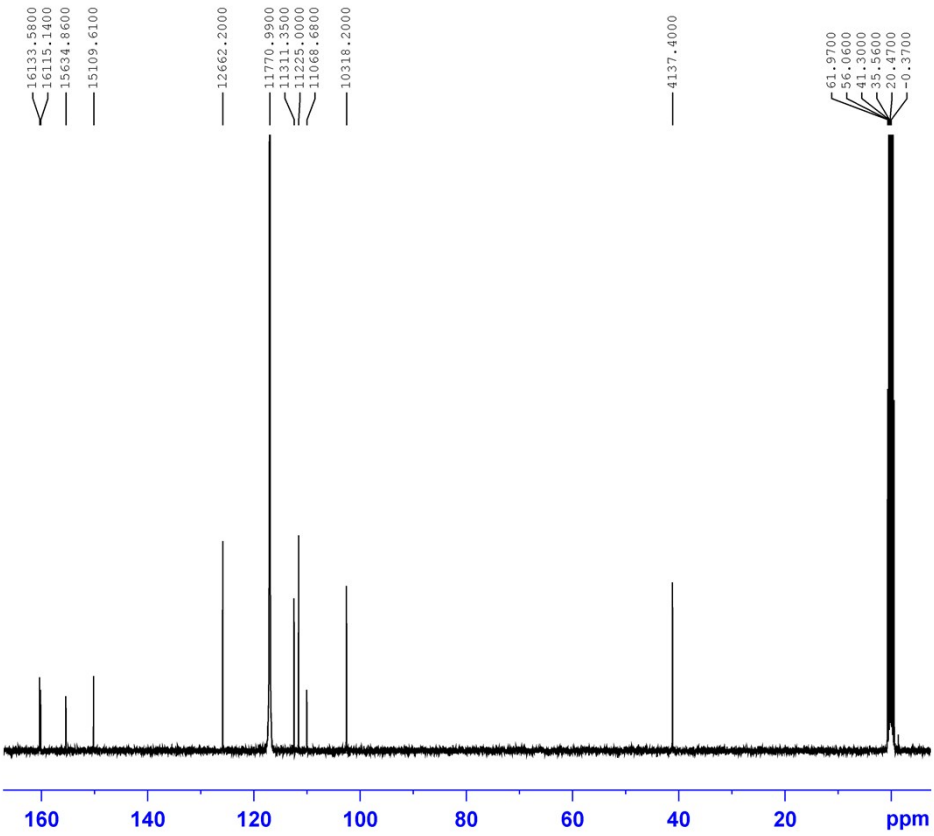
4-(Chloromethyl)-7-hydroxy-2H-chromen-2-one[9] (13)



Resorcinol **11** (4.45 g, 1 eq.) was added dropwise to a well stirred solution of concentrated sulphuric acid (40 ml) at -5°C followed by slow addition of ethyl-4-chloroacetoacetate **12** (5.5 ml, 1 eq.). After overnight stirring at -5°C, the reaction mixture was poured into 350 ml of ice cold water and stirred for 1 h. The resulting white precipitates were collected by filtration, washed with ice water until the filtrate became neutral and dried to afford crude product, which was further recrystallized from ethanol to obtain **13** as a white solid. Yield 76%; ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 4.75 (2H, s, C**H**$_2$), 6.34 (1H, s, Ar**H**), 6.79 (1H, d, *J* = 2.4 Hz, Ar**H**), 6.85 (1H, dd, *J* = 6.30, 2.42 Hz, Ar**H**), 7.63 (1H, d, *J* = 8.72 Hz, Ar**H**), 7.85 (1H, br s, O**H**); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 41.4, 103.2, 110.7, 112.2, 113.1, 126.6, 151.1, 156.3, 161.2 and 161.3; MS: *m/z* 210 [M^+].

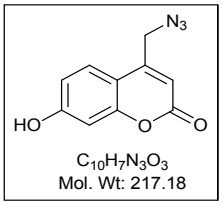


^{1}H NMR spectrum of **13**

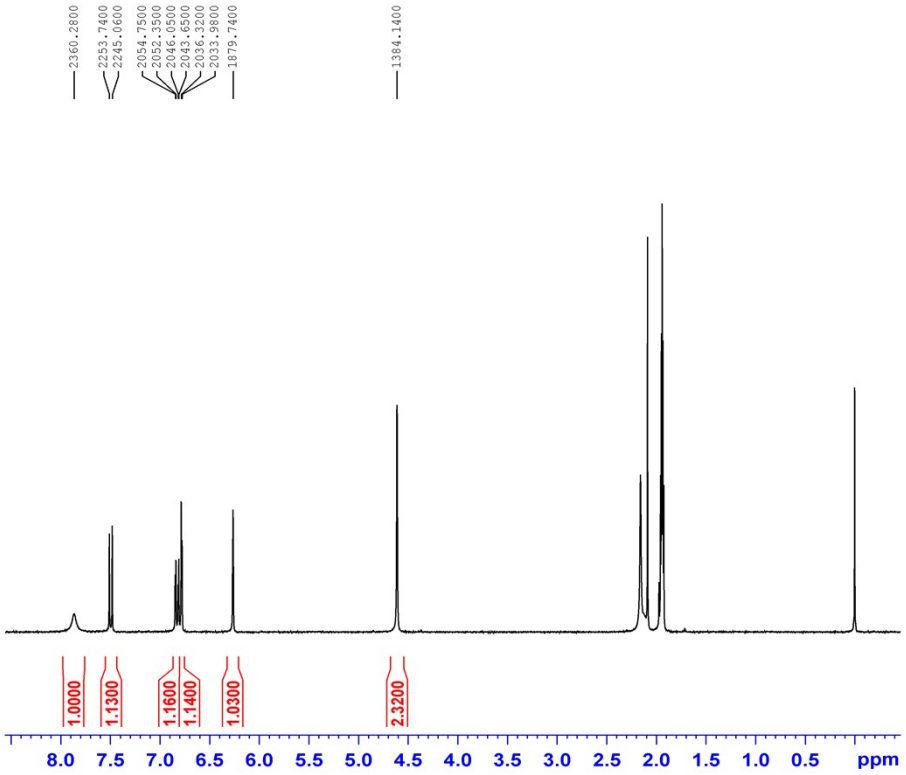


^{13}C NMR spectrum of **13**

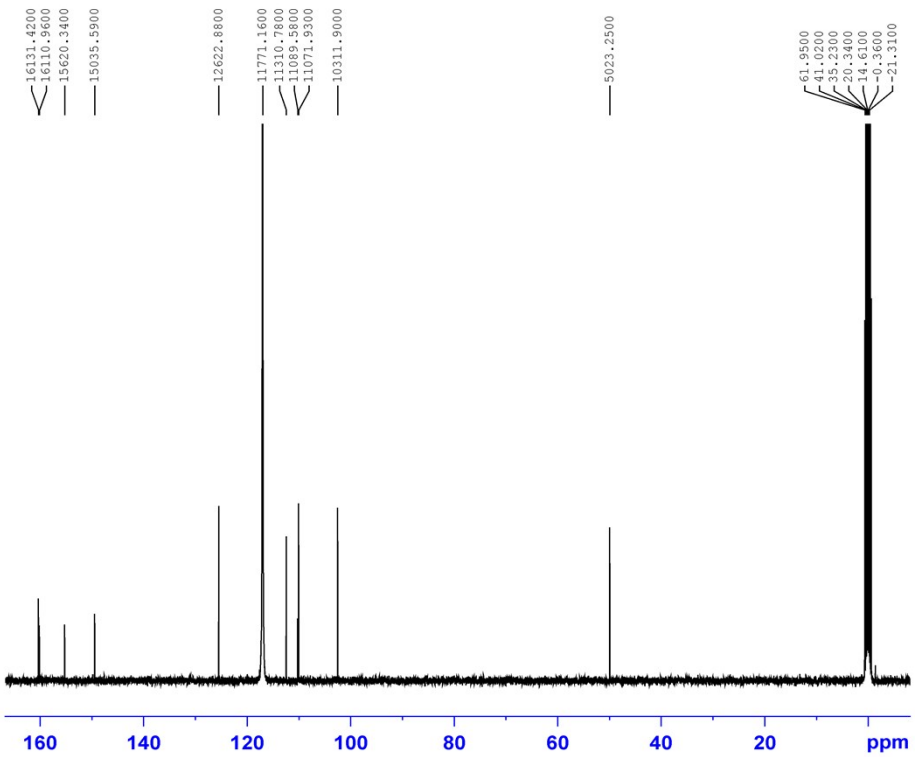
4-(Azidomethyl)-7-hydroxy-2H-chromen-2-one[10] **(2)**



Sodium azide (0.59 g, 3 eq.) was added carefully to a magnetically stirred solution of compound **13** (0.63 g, 1 eq.) in CH_3CN (10 ml) and the reaction mixture was refluxed for 10 h at 60°C. The reaction mixture was concentrated under vacuum and the residue was dissolved in EtOAc and washed with water (15 ml) and brine (15 ml). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford compound **2** as a yellow solid which was used as such without further purification. Yield 73%; ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 4.61 (2H, s, C**H**$_2$), 6.27 (1H, s, Ar**H**), 6.78 (1H, d, *J* = 2.35 Hz, Ar**H**), 6.83 (1H, dd, *J* = 6.30, 2.41 Hz, Ar**H**), 7.50 (1H, d, *J* = 8.67 Hz, Ar**H**), 7.87 (1H, br s, O**H**); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 50.2, 103.1, 110.7, 110.9, 113.1, 126.2, 150.4, 156.2, 161.1 and 161.3; MS: *m/z* 217 [M^+].

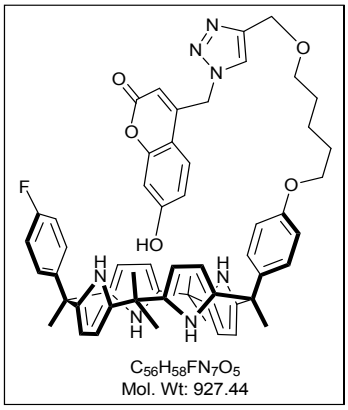


^{1}H NMR spectrum of **2**

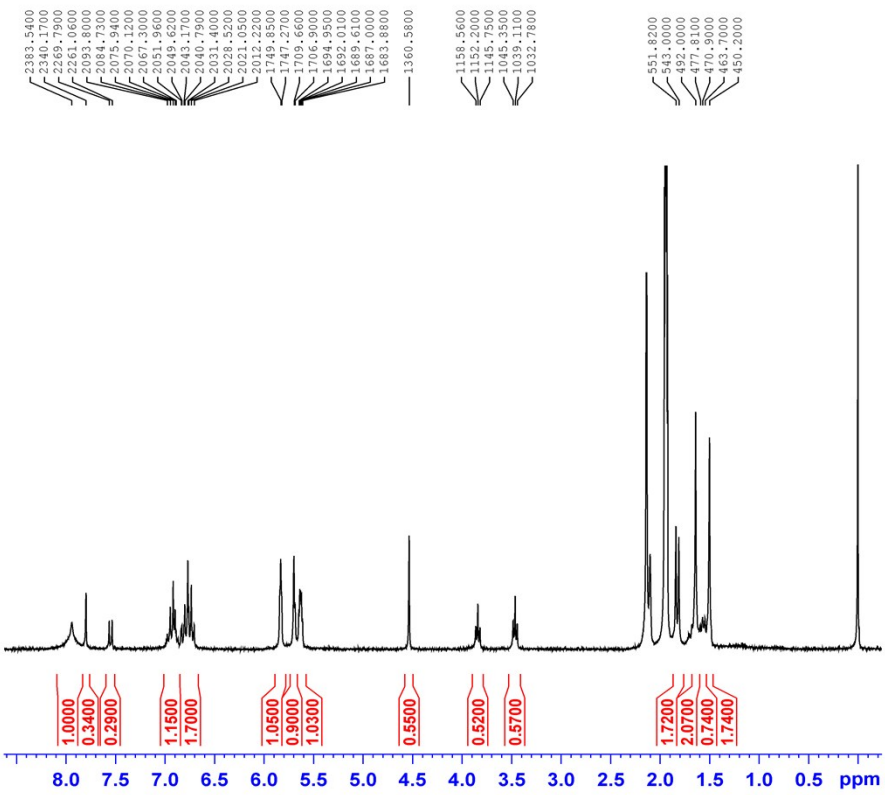


^{13}C NMR spectrum of **2**

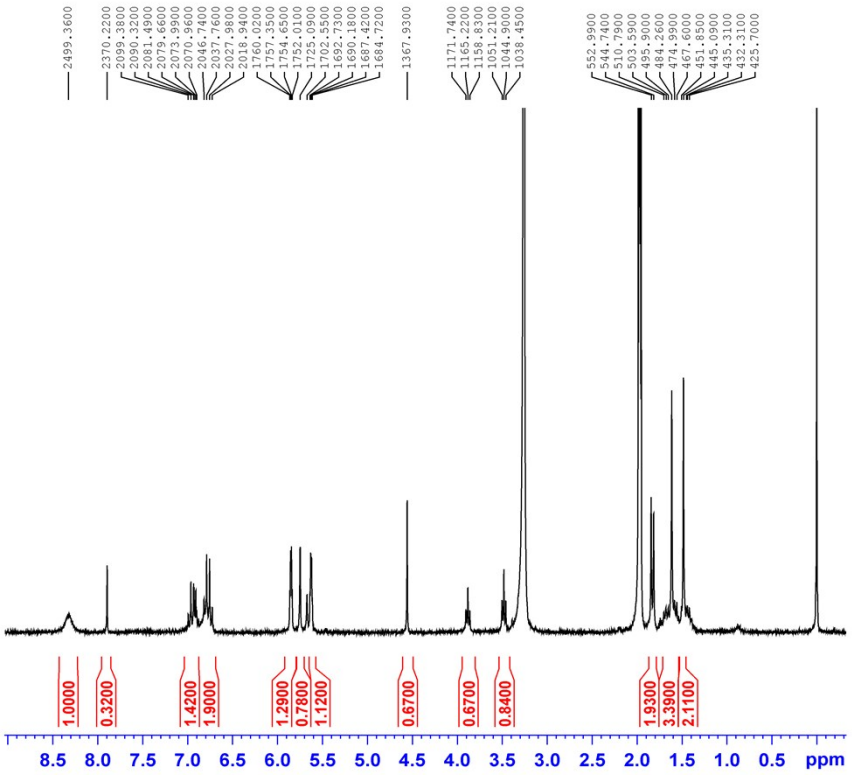
Synthesis of 3



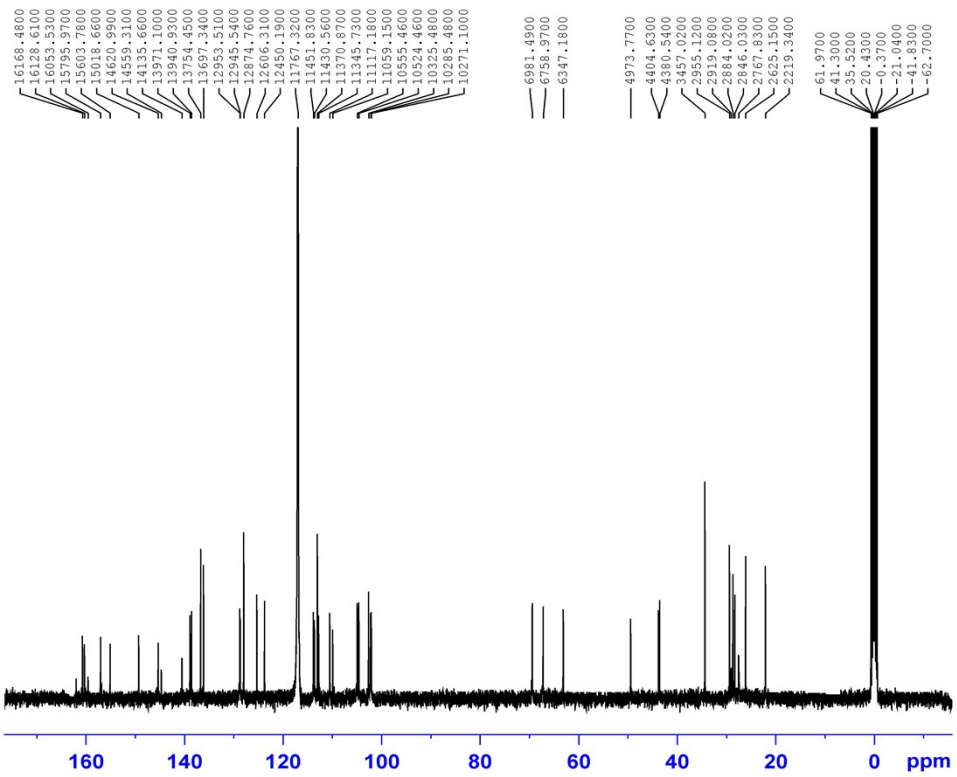
Azide **2** (0.02 g, 1 eq.) and sodium ascorbate (0.005 g, 0.3 eq.) were added to a solution of compound **1** (0.05 g, 1 eq.) in *t*-BuOH: H_2O [1: 1(*v/v*)] (6 ml) and the reaction mixture was purged with nitrogen. Nitrogen purged solution of $CuSO_4$. $5H_2O$ (0.003 g, 0.15 eq.) was added to the reaction mixture and was stirred overnight at room temperature. The reaction mixture was concentrated under vacuum and the residue was diluted with water and extracted with EtOAc (3×15 ml). The organic layer was dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The crude product was purified using column chromatography (Hex: EtOAc = 70:30) to obtain **3** as a light yellow solid. Yield: 54%; ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 1.50 (6H, s, *meso*-C**H**$_3$), 1.54-1.64 (6H, m, C**H**$_2$), 1.64 (6H, s, *meso*-C**H**$_3$), 1.82 (6H, d, *J* = 8.8 Hz, *meso*-C**H**$_3$), 3.46 (2H, t, *J* = 6.33 Hz, C**H**$_2$-O), 3.84 (2H, t, *J* = 6.44 Hz, ArO-C**H**$_2$), 4.54 (2H, s, triazole-C**H**$_2$-O), 5.61-5.65 (4H, m, pyrrolic-**H)**, 5.69 (3H, m, Cou-C**H**$_2$-triazole; Cou**H**), 5.83 (4H, m, pyrrolic-**H)**, 6.71-6.84 (6H, m, Ar**H**; Cou**H**), 6.87-6.98 (5H, m, Ar**H**; Cou**H**), 7.55 (1H, d, *J* = 8.71 Hz, O**H**), 7.80 (1H, s**,** triazole**H**), 7.94 (4H, br s, N**H**); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 22.2 (2C), 26.2, 27.7, 28.5, 28.8, 29.2, 29.6, 34.6 (4C), 43.8, 44.0, 49.7, 63.5, 67.6, 69.8, 102.7, 102.8 (2C), 103.2 (2C), 105.2 (2C), 105.6 (2C), 110.6, 111.2, 113.4, 113.7 (2C), 114.3, 114.5, 124.5, 126.1, 128.7 (2C), 129.4 (2C), 129.5, 137.0 (2C), 137.5 (2C), 139.4, 139.7, 141.4, 145.6, 146.2, 150.2, 156.0, 158.0, 160.5, 161.3 and 161.7; MS: *m/z* 926 [M^+-1].



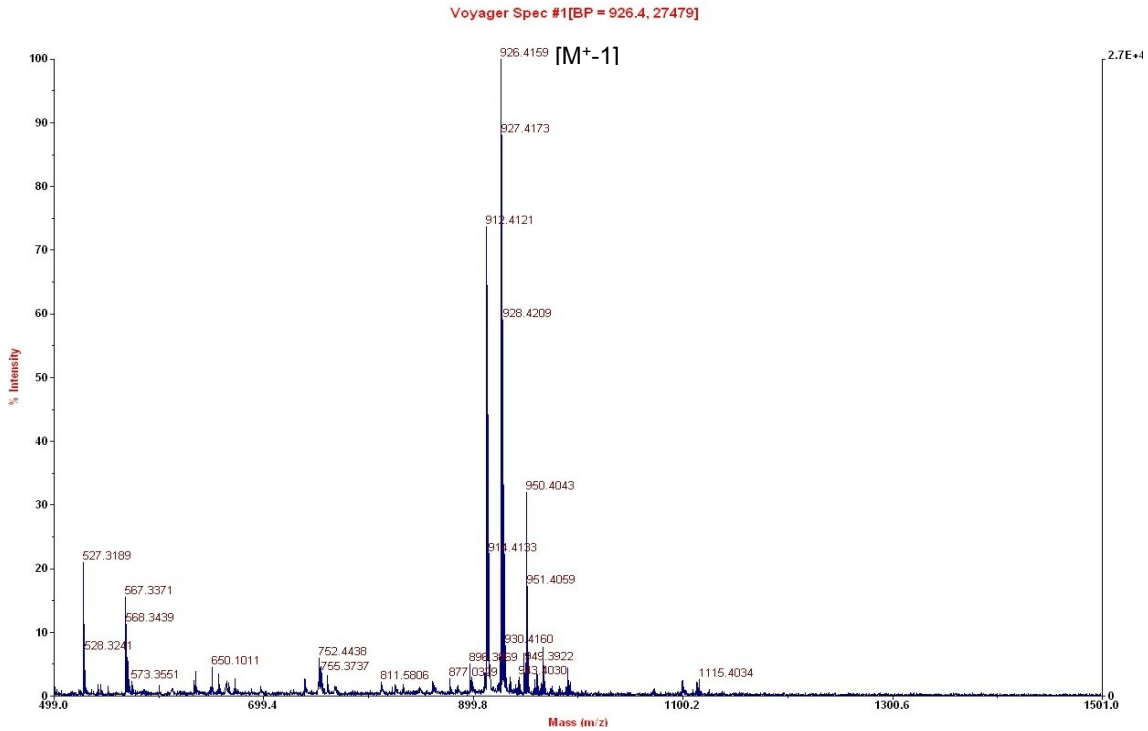
^{1}H NMR spectrum of **3**



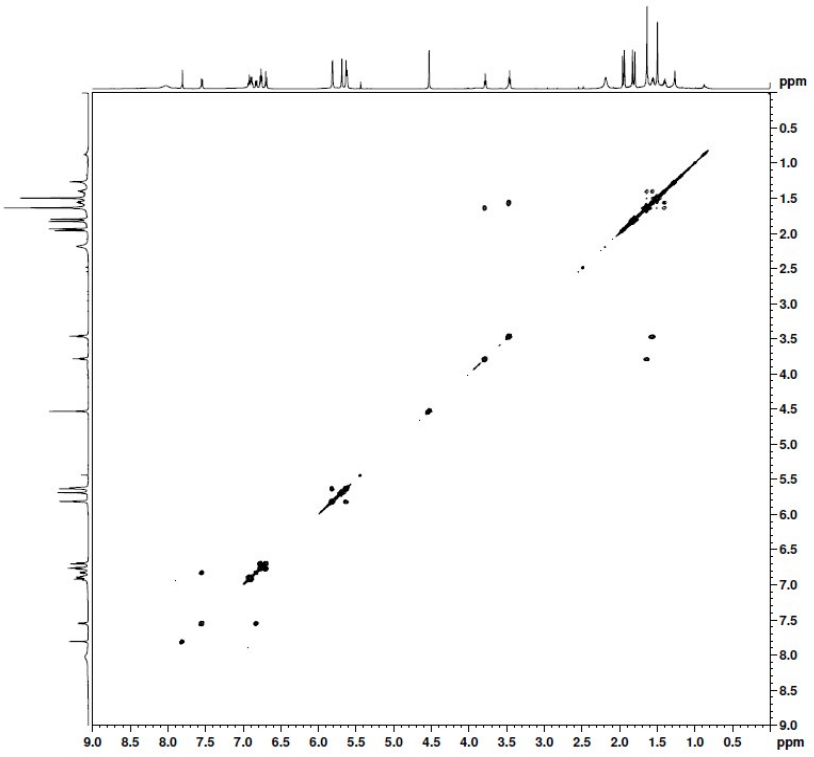
D_2O NMR spectrum of **3** (CD_3CN + D_2O)



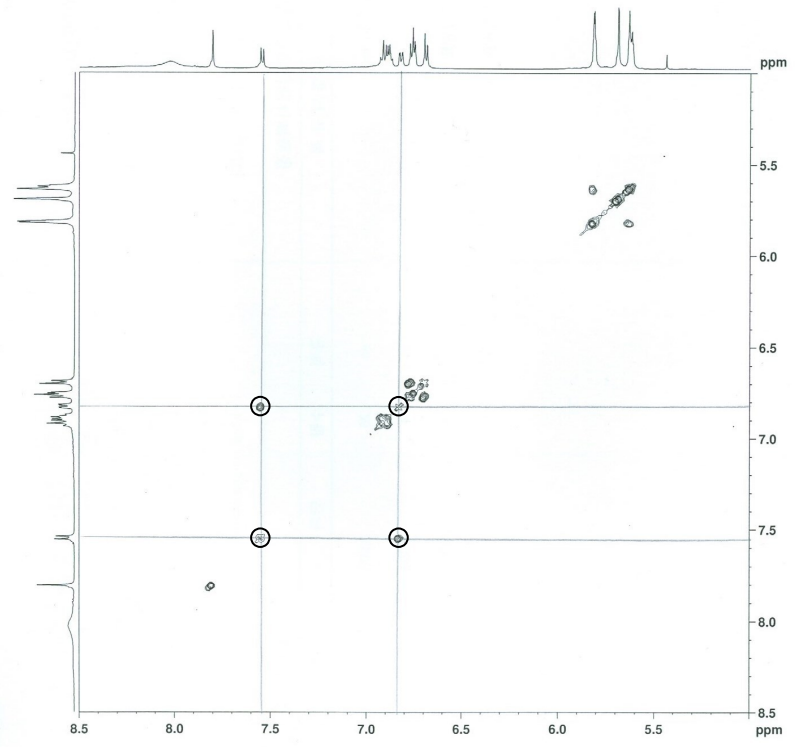
^{13}C NMR spectrum of **3**



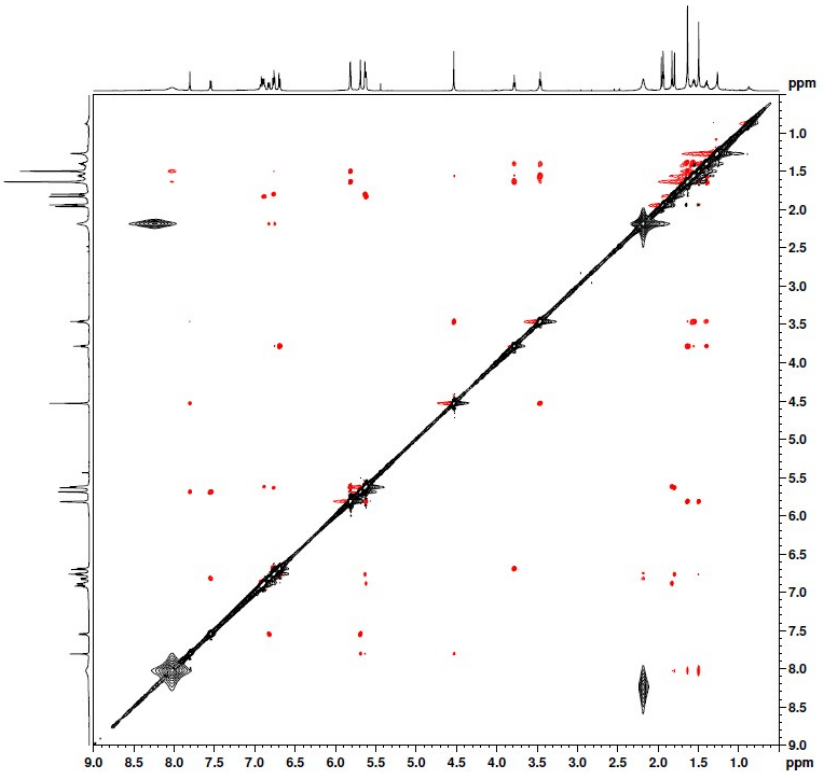
Mass spectrum of **3**



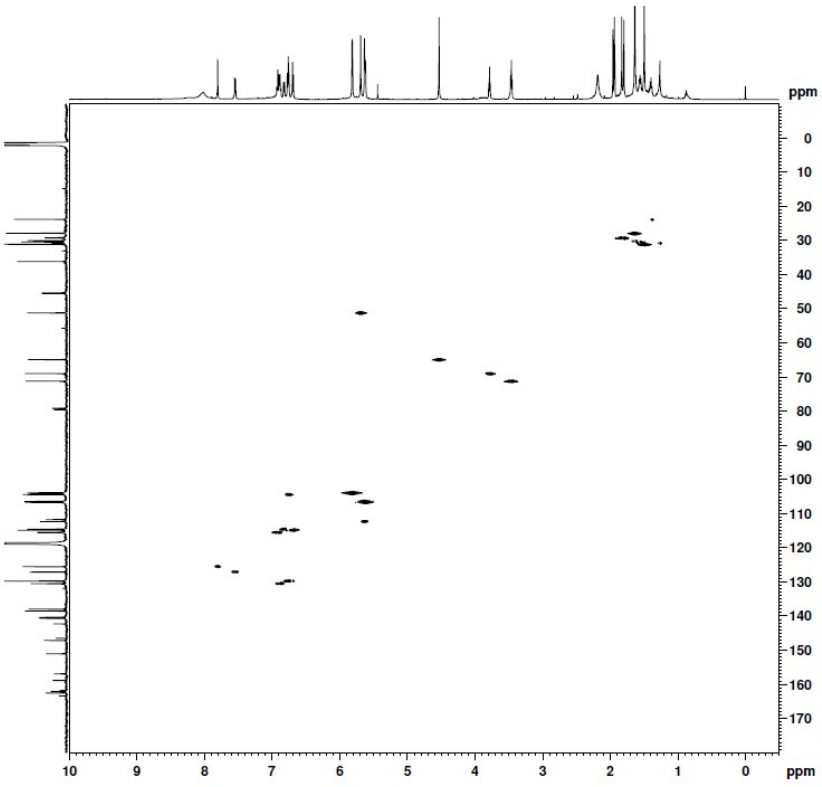
COSY NMR spectrum of **3** (CD_3CN, 600 MHz)



Expanded COSY NMR spectrum of **3** (CD_3CN, 600 MHz)



NOESY NMR spectrum of **3** (CD_3CN, 600 MHz)



HSQC NMR spectrum of **3** (CD_3CN, 600 MHz)

S3. UV-vis studies

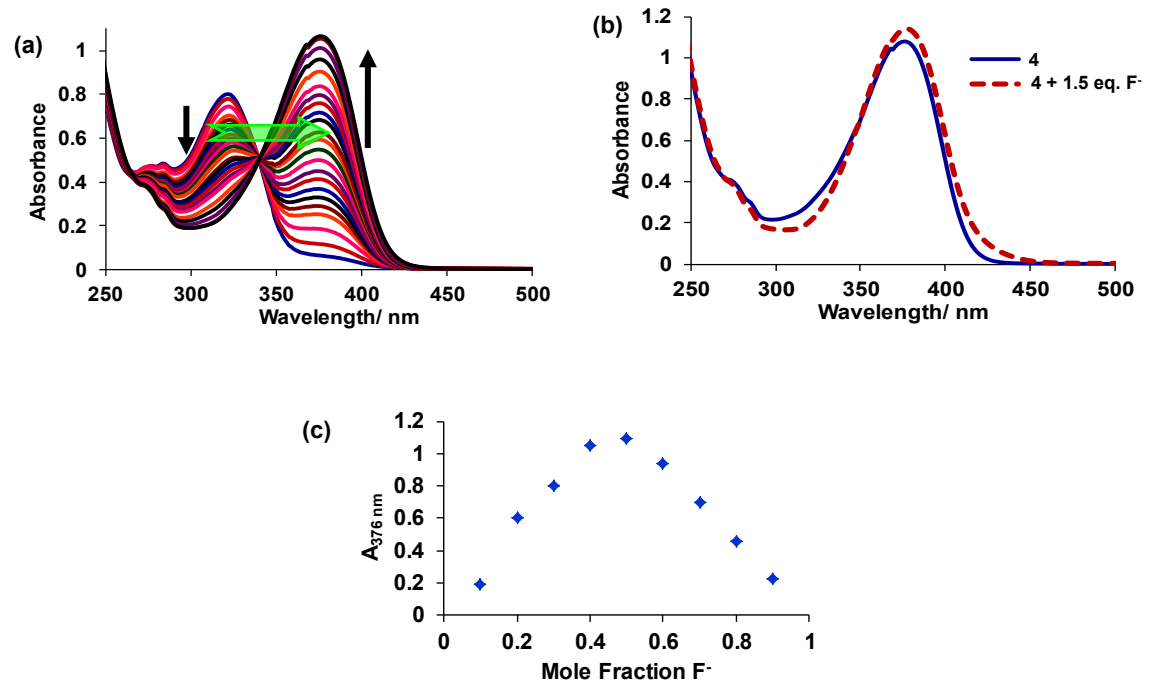


Fig. S3 (a) Changes in the absorption spectrum of **3** (50 μM, in CH_3CN) upon titration with TBAOH (1.67-51.67 μM, in CH_3CN); **(b)** Absorption spectrum of **4** (50 μM **3** + 50 μM OH^-, in CH_3CN) and upon addition of 1.5 eq. TBAF (75 μM, in CH_3CN); **(c)** Job plot for F^- ion recognition.

S4. Calculation of detection limit

The detection limit was calculated based on the fluorescence titration using the following equation:

Detection limit = 3σ/k

where σ is the standard deviation of blank signal and k is the slope of linear calibration plot.

The fluorescence emission spectrum of **4** was measured three times and σ was calculated to be 1.35. The slope was obtained by plotting emission enhancements of **4** upon fluoride addition at 475 nm as a function of fluoride ion concentrations. The emission slit width of 15 nm was employed for this experiment to permit greater sensitivity in recordings. The limit of detection was hence evaluated to be 0.40 nM.

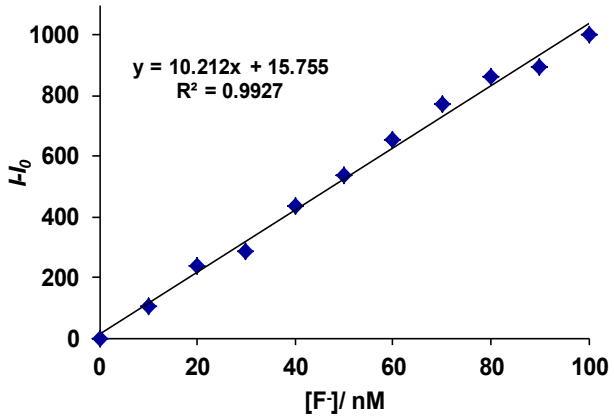


Fig. S4 Plot of fluorescence intensity enhancements of **4** (2 μM **3** + 2 μM OH^-, in CH_3CN) *vs.* F^- ion concentrations at 475 nm.

S5. Switching '*off*' of fluorescence

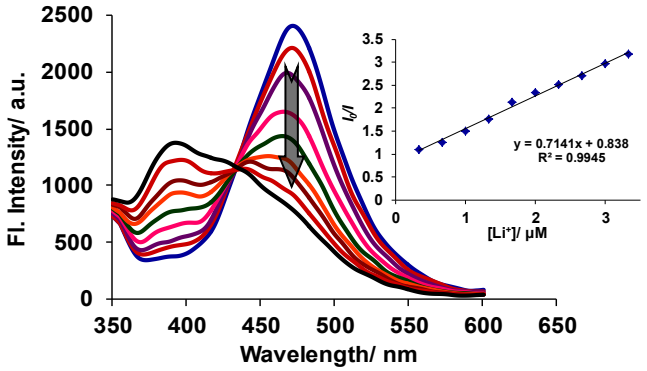


Fig. S5 Emission titration profile of **[3⁻]•F** (2 μM **3** + 2 μM OH^- + 2 μM F^-, in CH_3CN) with $LiClO_4$ (0.33-3 μM, in CH_3CN); Inset: Stern-Volmer plot for quenching.

S6. Anion selectivity

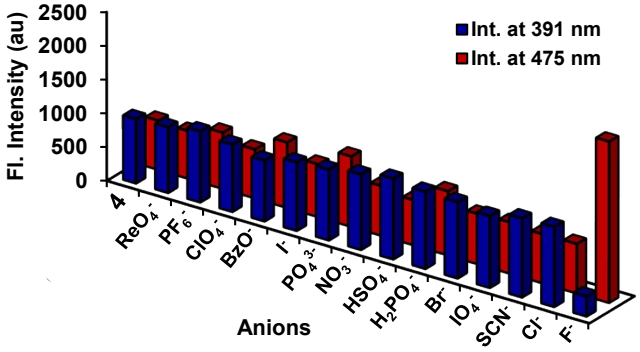


Fig. S6. Anion screening profile of **4** (2 μM **3** + 2 μM OH^-, in CH_3CN) in the presence of 1 eq. of different anions (2 μM, in CH_3CN).

S7. NMR titration data

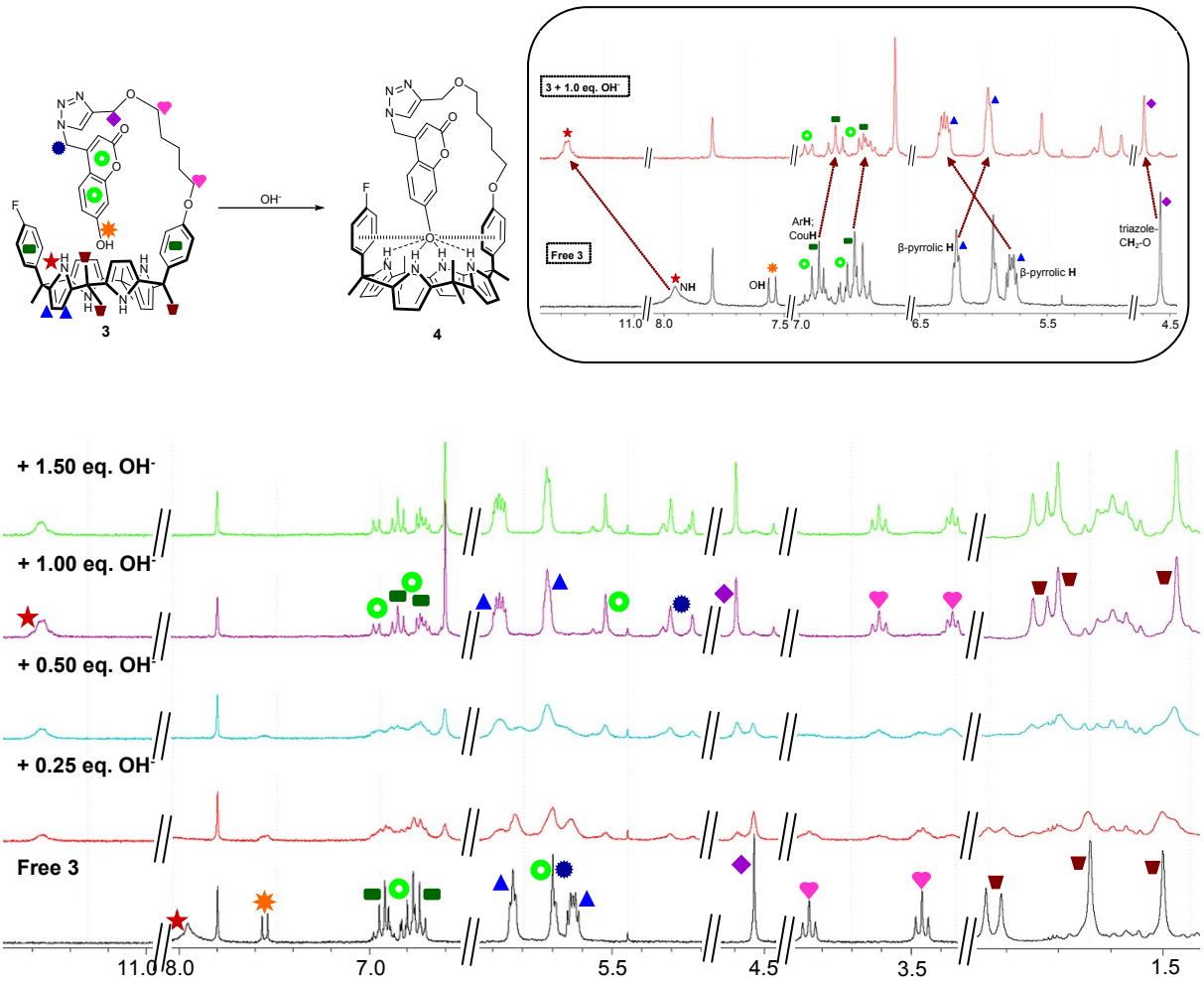


Fig. S7 (a) ^{1}H NMR titrations of **3** (3 x 10^{-3} M, in CD_3CN) with increasing concentrations of OH^- ion (as TBAOH, in CD_3CN).

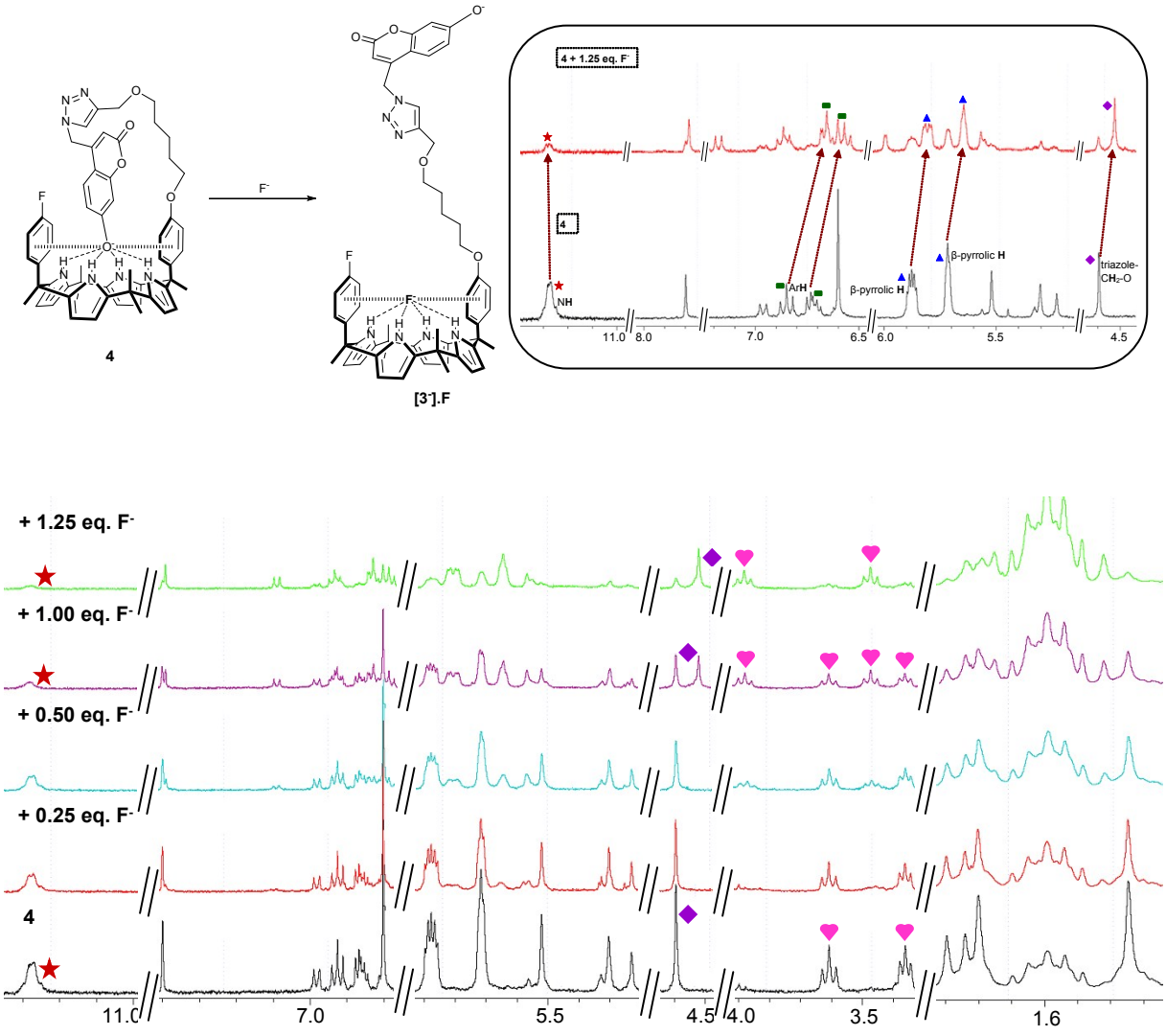


Fig. S7 (b) ^{1}H NMR titrations of **4** (3 x 10^{-3} M **3** + 1 eq. OH^-, in CD_3CN) with increasing concentrations of F^- ion (as TBAF, in CD_3CN).

S8. ITC titration data

The thermodynamic data was recorded by titrating 10^{-4} M **3** in CH_3CN with increasing concentrations of OH^- and F^- solutions at 25°C. The stock solution for both the anions was prepared as 10^{-3} M in CH_3CN.

The graph for OH^- titration has been plotted only up to addition of 1 eq. of anion (same concentration at which all other studies have been carried out) as further addition causes some auxiliary endothermic reactions which are of no significant concern to the current studies.

High [F^-]/[calixpyrrole] ratios produced changes in the ITC curves that are best interpreted in terms of an additional binding isotherm.

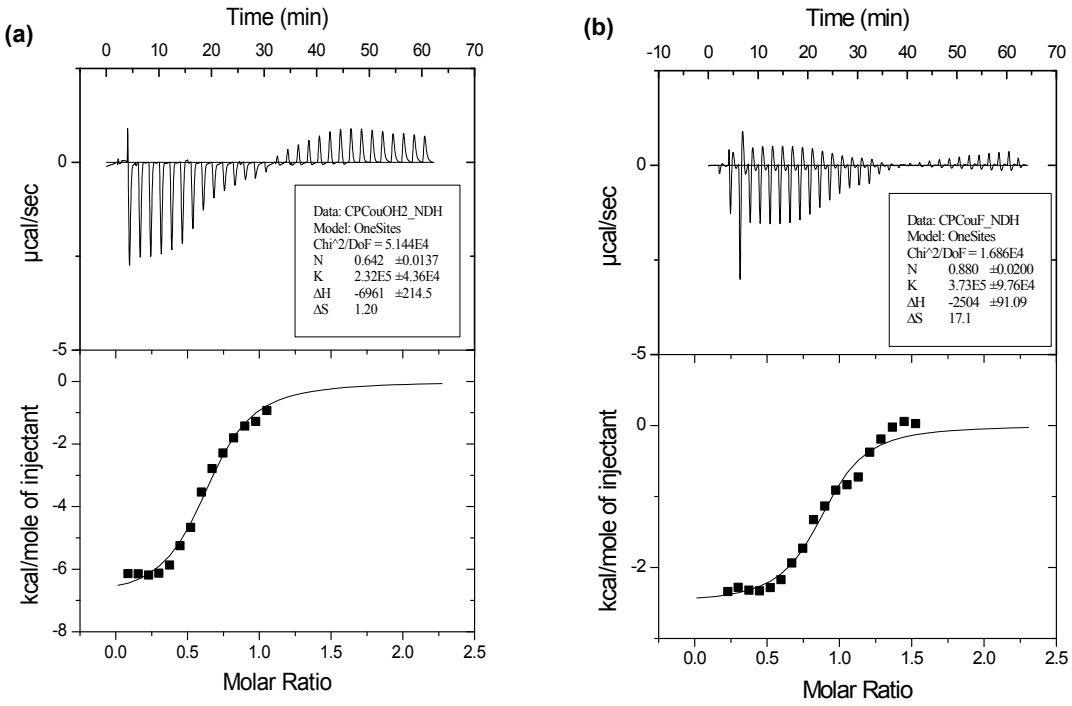
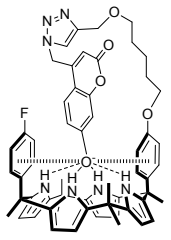
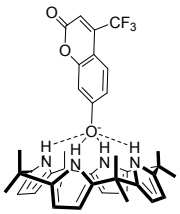
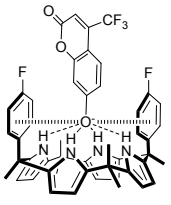
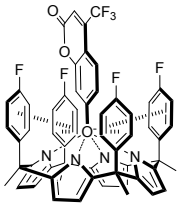


Fig. S8 ITC titration profiles of **3** (10^{-4} M, in CH_3CN) with increasing concentrations of **(a)** OH^- ion (as TBAOH, in CH_3CN); **(b)** F^- ion (as TBAF, in CH_3CN).

S9. Comparison of association constants

Table S9 Association constants for the complexation of chromenolate ion with various calix[4]pyrrole probes in CH_3CN at 298 K as determined by ITC.

	
$K_a = 2.32 \times 10^5\ M^{-1}$	$K_a = 6.66 \times 10^4\ M^{-1}$
	
[a]$K_a = 4.69 \times 10^6\ M^{-1}$	$K_a = 6.35 \times 10^6\ M^{-1}$

[a]Reference 8

S10. References

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