SUPPLEMENTARY INFORMATION

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Synthesis and evaluation of a novel ionophore based on a thiacalix[4]arene derivative bearing imidazole units†

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General description for the computational study:

To better understand the binding properties of 1,3-*alternate*-**4** with Ag^+, and in the absence of being able to obtain suitable crystals for X-ray crystallographic confirmation, a computation study was carried out. The individual structures in the gas-phase were fully geometry-optimized using Gaussian 09[1] with the B3LYP level of DFT and the lanl2dz basis set. Significant conformational changes were observed for the imidazole ring protons of **4** in its Ag^+ complexes. The conformation changes for **4** upon complexation with Ag^+ ion (1:1 and 2:1 complex) can be seen in Fig. S1-S4. Fig. S1 shows the structure (*right*) 1:1 complexation of **4** with Ag^+. The N---N distance between one pair of the "top" 1,3-distally-located imidazole nitrogen atoms decreases from 7.765 to 4.143 (Å) for N_{41}-N_{142}. That is, these nitrogen atoms move inwards upon complexing with the Ag^+ and this strongly supports experimental evidence obtained for the 1:1 complexation of **4** with Ag^+ occurred. All four bridge sulphur atoms are roughly the same distance from the Ag^+ and presumably take an equal part in the coordination bonding. Fig. S3 further shows the structure (*right*) of the 2:1 complex i.e. $Ag^+\subset$**4**$\supset Ag^+$ which formed upon addition of a second Ag^+ ion to the 1:1 **4**$\supset Ag^+$ complex (Fig. S3 and Fig. S4). The distance between the opposite pair of imidazole nitrogen atoms (of the "bottom" 1,3-distally-located imidazoles) decreases from 7.923 to 4.139 (Å) for N_{69}-N_{1115} and this also strongly supports the experimental evidence obtained for the formation of a 2:1 ($Ag^+\subset$**4**$\supset Ag^+$) complex. The calculated complexation energies (ΔE kJ/mole) for the Ag^+ complexes **4**$\supset Ag^+$ and $Ag^+\subset$**4**$\supset Ag^+$ are -483.675 and -811.239 kJ/mole respectively, in agreement with the trend observed for the observed complexation data obtained by ^1H NMR titration experiments.

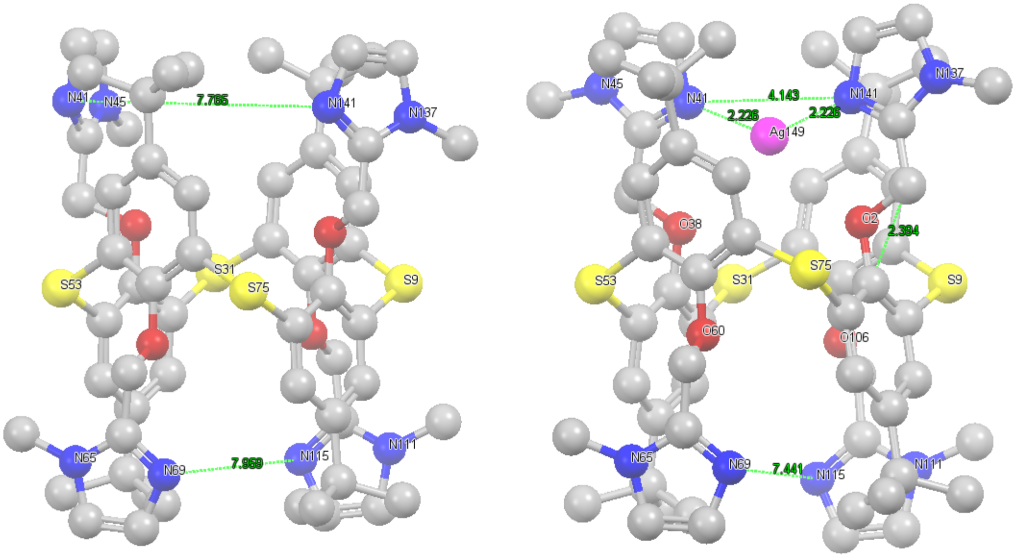

Fig. S1. Geometry-optimized (ball-and-stick) structures of: *Left*: **4** and *Right*: **4**⊃Ag$^+$ complex. Colour code: Ag$^+$ = magenta, imidazole nitrogen = blue, sulphur = yellow and oxygen atom = red. Hydrogen atoms have been omitted for clarity.

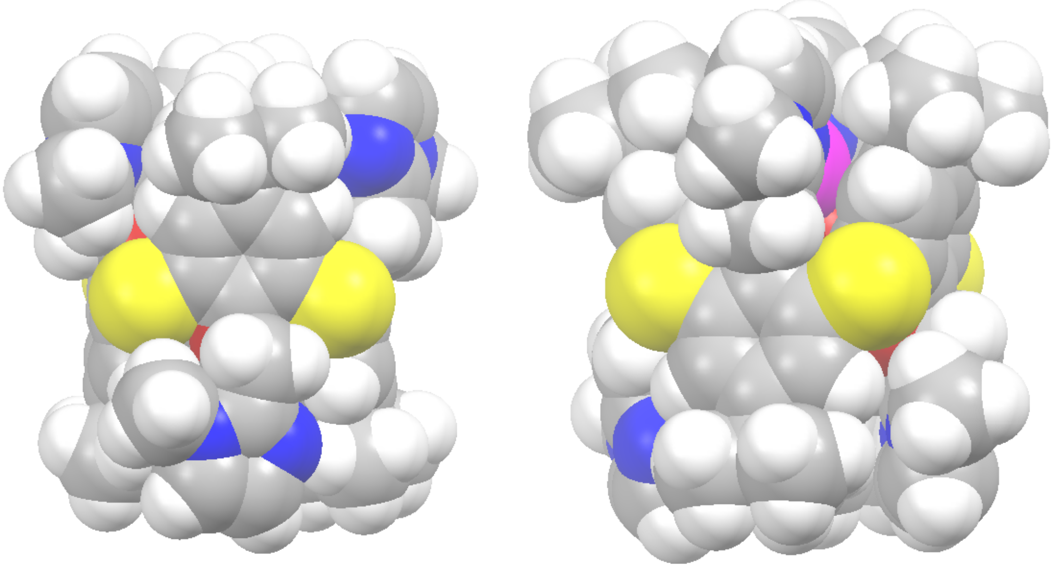

Fig. S2. Geometry-optimized (space fill) structures of: *Left*: **4** and *Right*: **4**⊃Ag$^+$ complex. Colour code: Ag$^+$ = magenta, imidazole nitrogen = blue, sulphur = yellow and oxygen atom = red. Hydrogen atoms have been omitted for clarity.

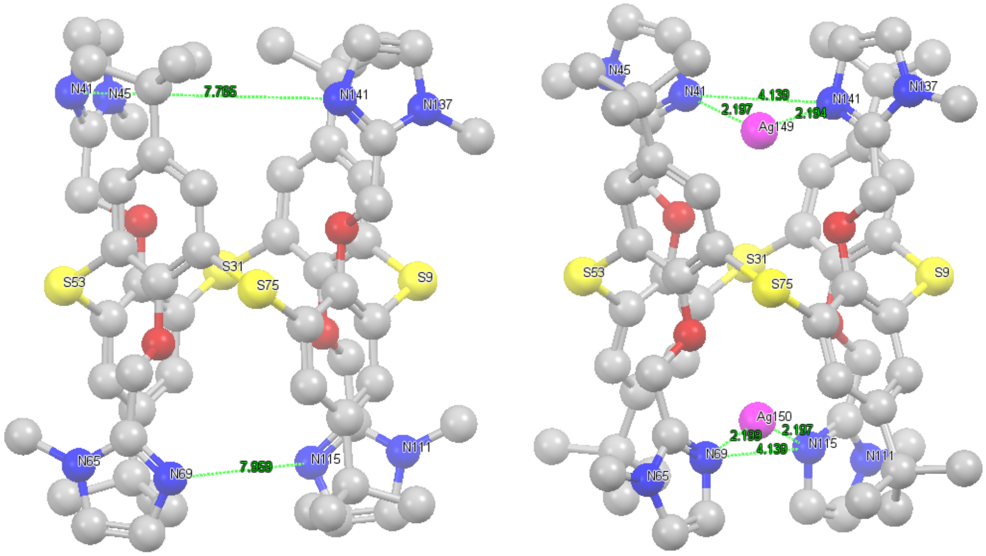

Fig. S3. Geometry-optimized (ball-and-stick) structures of: *Left*: **4** and *Right*: Ag$^+\subset$**4**$\supset$Ag$^+$ complex. Colour code: Ag$^+$ = magenta, imidazole nitrogen = blue, sulphur = yellow and oxygen atom = red. Hydrogen atoms have been omitted for clarity.

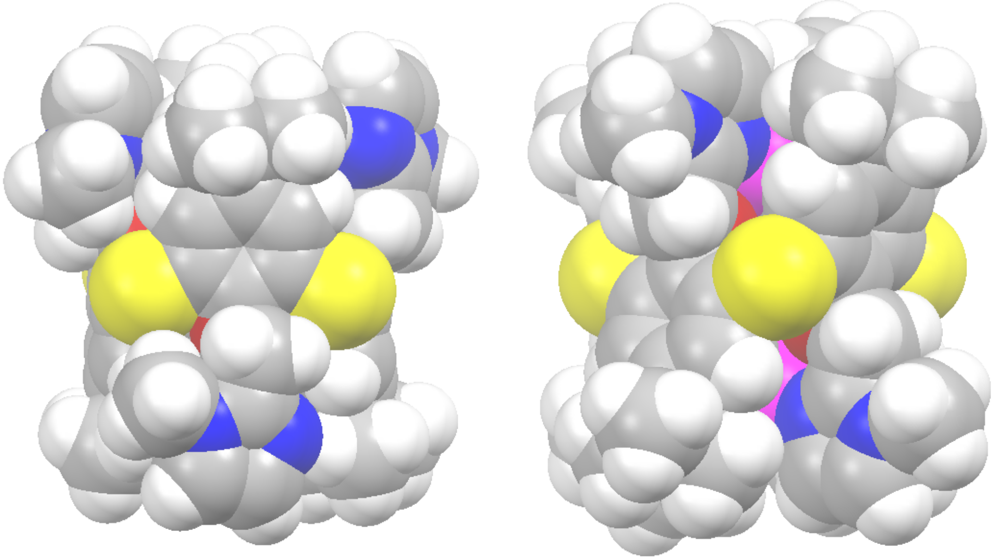

Fig. S4. Geometry-optimized (space fill) structures of: *Left*: **4** and *Right*: Ag$^+\subset$**4**$\supset$Ag$^+$ complex. Colour code: Ag$^+$ = magenta, imidazole nitrogen = blue, sulphur = yellow and oxygen atom = red. Hydrogen atoms have been omitted for clarity.

Table S1 The calculated distance for selected parameters for the backbones of the 1,3-*alternate*-**4** and complexes with Ag$^+$ optimized at B3LYP/ lanl2dz level(Distance in Å).

Parameter	**4 (**Å)	**4**$\supset$Ag$^+$ (Å)	Ag$^+$$\subset$**4**$\supset$Ag$^+$ (Å)
N$_{41}$-N$_{142}$	7.765	4.143	4.139
N$_{69}$-N$_{115}$	7.959	7.441	4.139
N$_{41}$-S$_{9}$	8.946	7.095	7.105
N$_{41}$-S$_{75}$	5.907	6.85	6.912
N$_{142}$-S$_{31}$	8.145	6.85	6.904
N$_{142}$-S$_{53}$	4.714	7.096	7.091
N$_{69}$-S$_{9}$	8.098	7.887	6.917
N$_{69}$-S$_{31}$	8.933	8.706	7.102
N$_{115}$-S$_{53}$	8.06	7.887	6.894
N$_{115}$-S$_{75}$	8.891	8.706	7.085
N$_{41}$-Ag$^+$(149)	-	2.226	2.197
N$_{141}$-Ag$^+$(149)	-	2.226	2.194
N$_{69}$-Ag$^+$(150)	-	-	2.199
N$_{115}$-Ag$^+$(150)	-	-	2.197
S$_{9}$-Ag$^+$(149)	-	5.223	5.255
S$_{31}$-Ag$^+$(149)	-	5.101	5.234
S$_{53}$-Ag$^+$(149)	-	5.222	5.255
S$_{75}$-Ag$^+$(149)	-	5.100	5.249
S$_{9}$-Ag$^+$(150)	-	-	5.248
S$_{31}$-Ag$^+$(150)	-	-	5.248
S$_{53}$-Ag$^+$(150)	-	-	5.225
S$_{75}$-Ag$^+$(150)	-	-	5.243

Calculated binding energies

The DFT B3LYP/ lanl2dz basis set-calculated binding energies (ΔE) of the Ag^+ complexes of 1,3-*alternate*-**4** ($L_{free} + Ag^+_{free} \rightarrow L{:}Ag^+_{complex}$) formed between the Ag^+ ion and the free 1,3-*alternate*-**4** in the gas phase at 298 K are based on the equation (1), are listed in Table S2.

For this system, the binding energy ΔE can be express as follows:

$$\Delta E = E_{(L:Ag+complex)} - E_{(Lfree)} - E_{(Ag+free)} \qquad (1)$$

Table S2 Calculated binding energies for the 1,3-*alternate*-**4** with Ag^+.

Parameter	**4** $\supset Ag^+$(1:1) ΔE (KJ/mole)	$Ag^+ \subset$ **4** $\supset Ag^+$(1:2) ΔE (KJ/mole)
1,3-alternate-**4** with $\mathbf{Ag^+}$	**-483.675**	**-811.239**

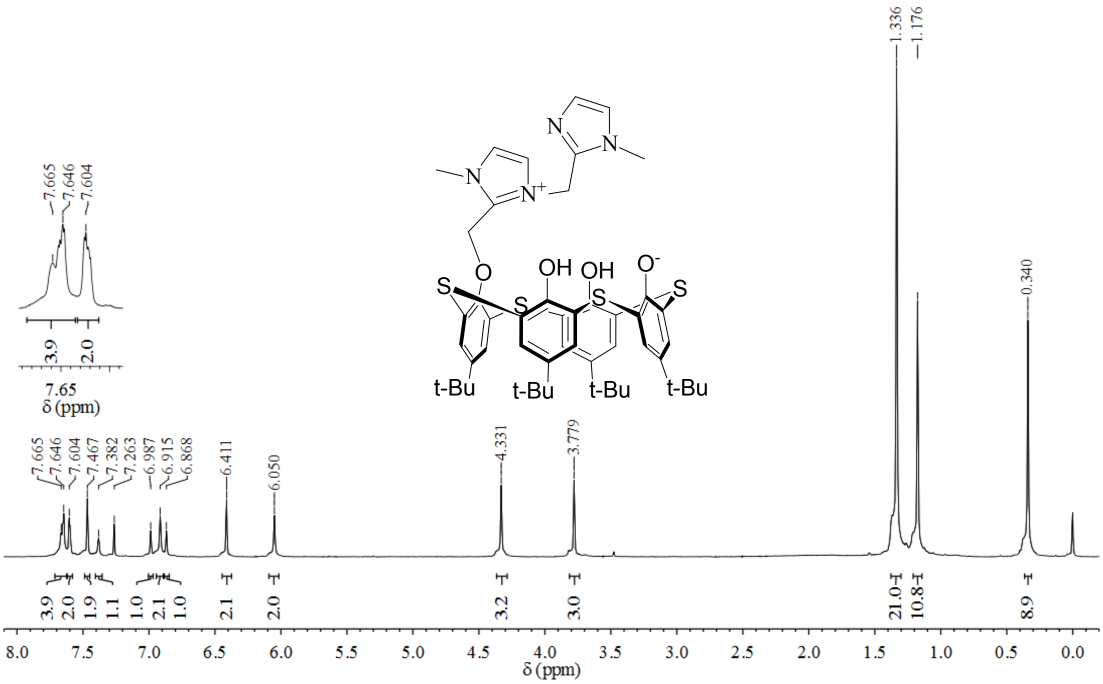

Fig. S5. ^{1}H–NMR spectrum of compound **3** (400 MHz, CDCl$_3$, 293 K).

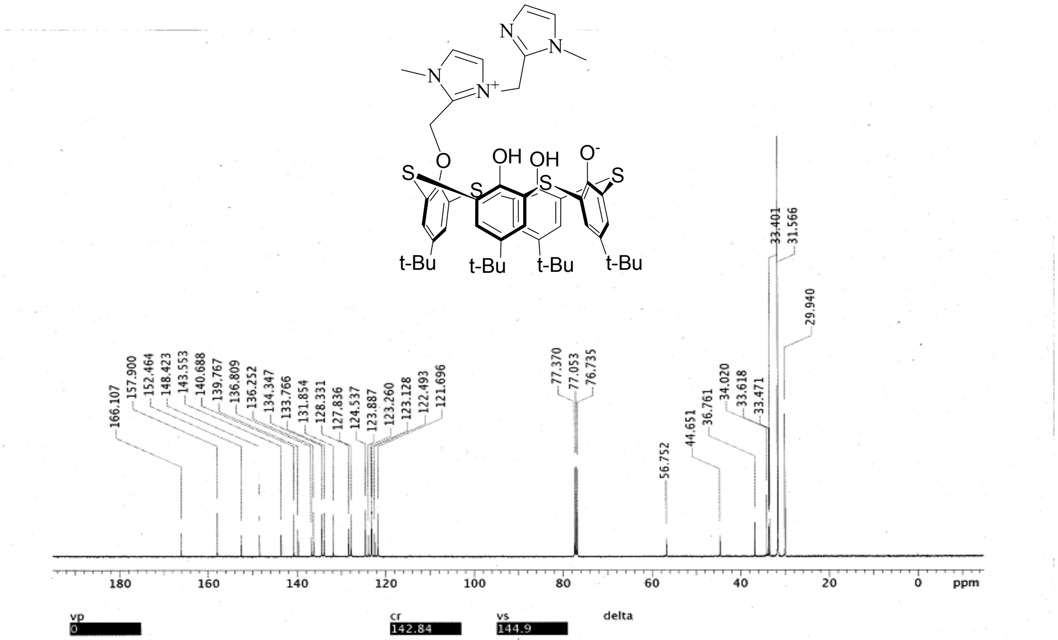

Fig. S6. ^{13}C–NMR spectrum of compound **3** (100 MHz, CDCl$_3$, 293 K).

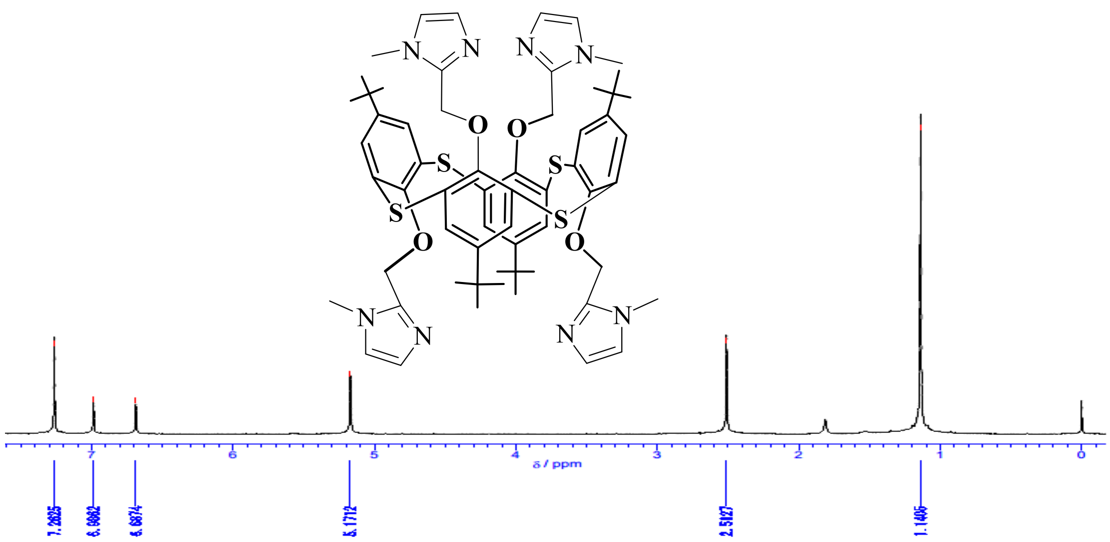

Fig. S7. ^{1}H–NMR spectrum of *1,3-alternate*-**4** (300 MHz, $CDCl_3$, 293 K).

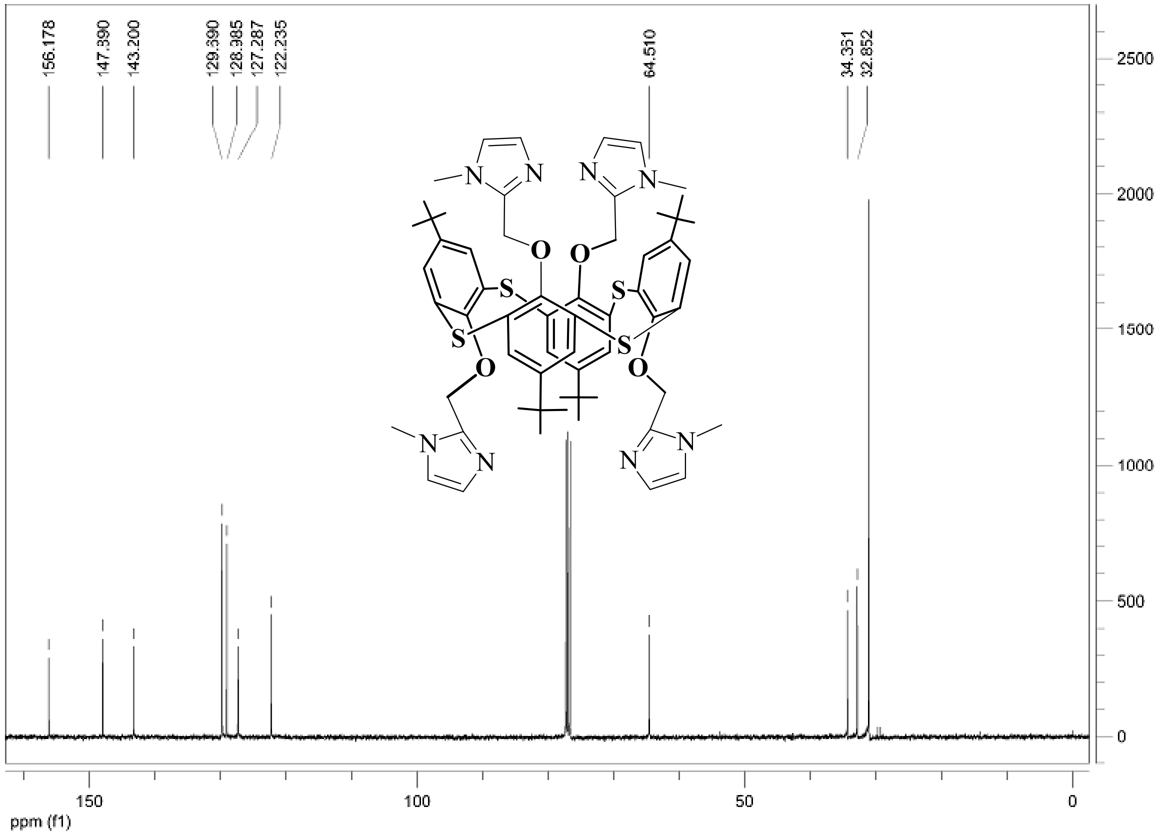

Fig. S8. ^{13}C–NMR spectrum of *1,3-alternate*-**4** (100 MHz, $CDCl_3$, 293 K).

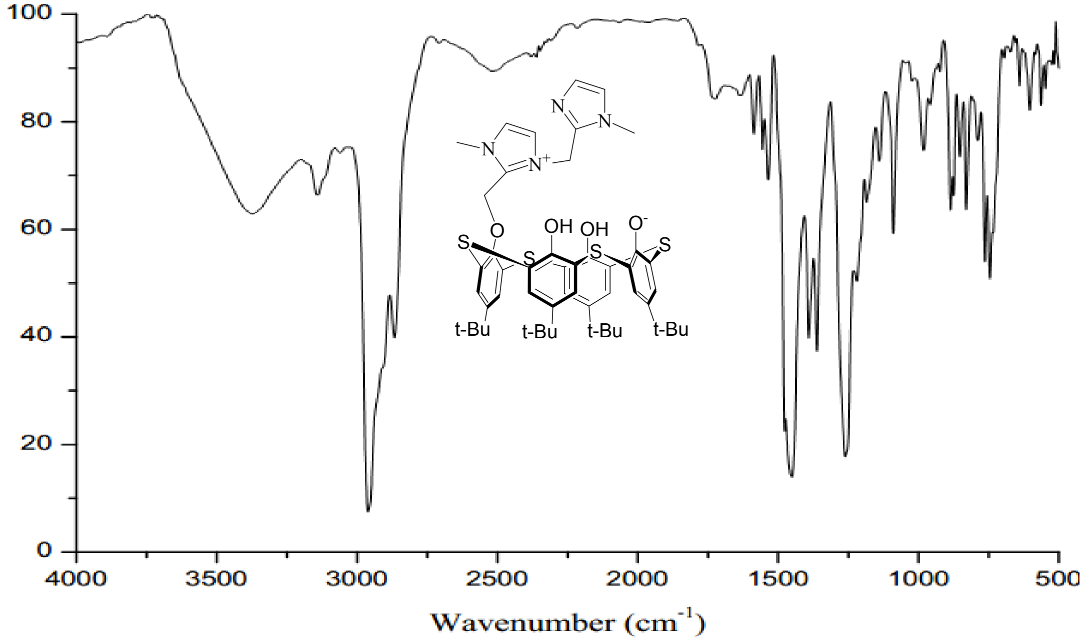

Fig. S9. IR spectrum of compound **3.**

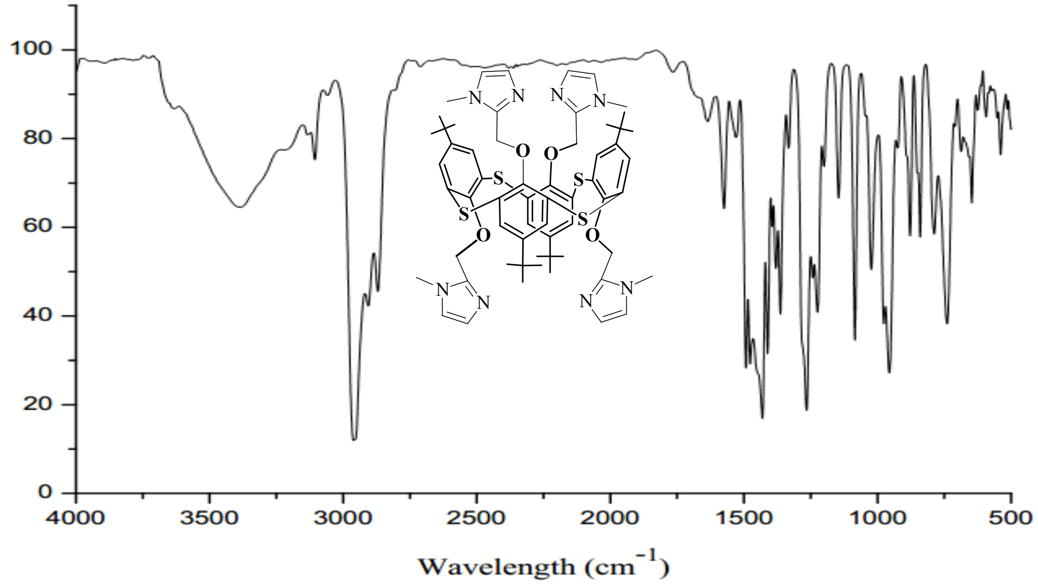

Fig. S10. IR spectrum of *1,3-alternate*-**4.**

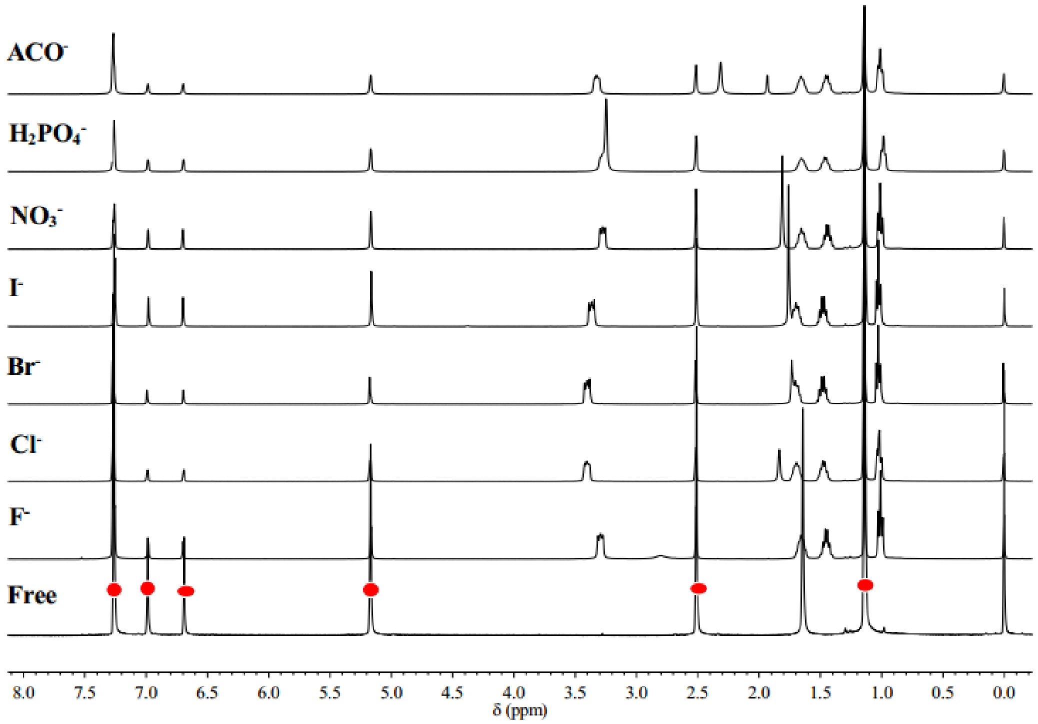

Fig. S11. ^{1}H NMR spectra of 1,3-*alternate*-**4**/guest (**4**/G = 1:3); free 1,3-*alternate*-**4** and in the presence of 3 equiv. of Bu_4NX (X = F, Cl, Br, I, AcO, NO_3, H_2PO_4), respectively. 1,3-*alternate*-**4** concentration was 4 mM. Solvent: $CDCl_3$. 400 MHz at 298 K. ● Denoted the 1,3-*alternate*-**4** peaks.

Reference

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