Supplementary Material

# Investigation of Cation Binding and Sensing by new Crown Ether core substituted Naphthalene Diimide systems

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## 1. Materials and Methods

Chemical shifts (δ) were calibrated against the solvent peak. For $^{1}$H NMR spectra each resonance was assigned according to the following convention: chemical shift (δ) measured in parts per million (ppm), multiplicity, coupling constant (*J*), number of protons and assignment. Multiplicities are denoted as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (p) pentet, or (m) multiplet. For $^{13}$C NMR each resonance was assigned according to the following convention: chemical shift (δ) measured in parts per million (ppm) and assignment (where known).

## 2. Characterisation

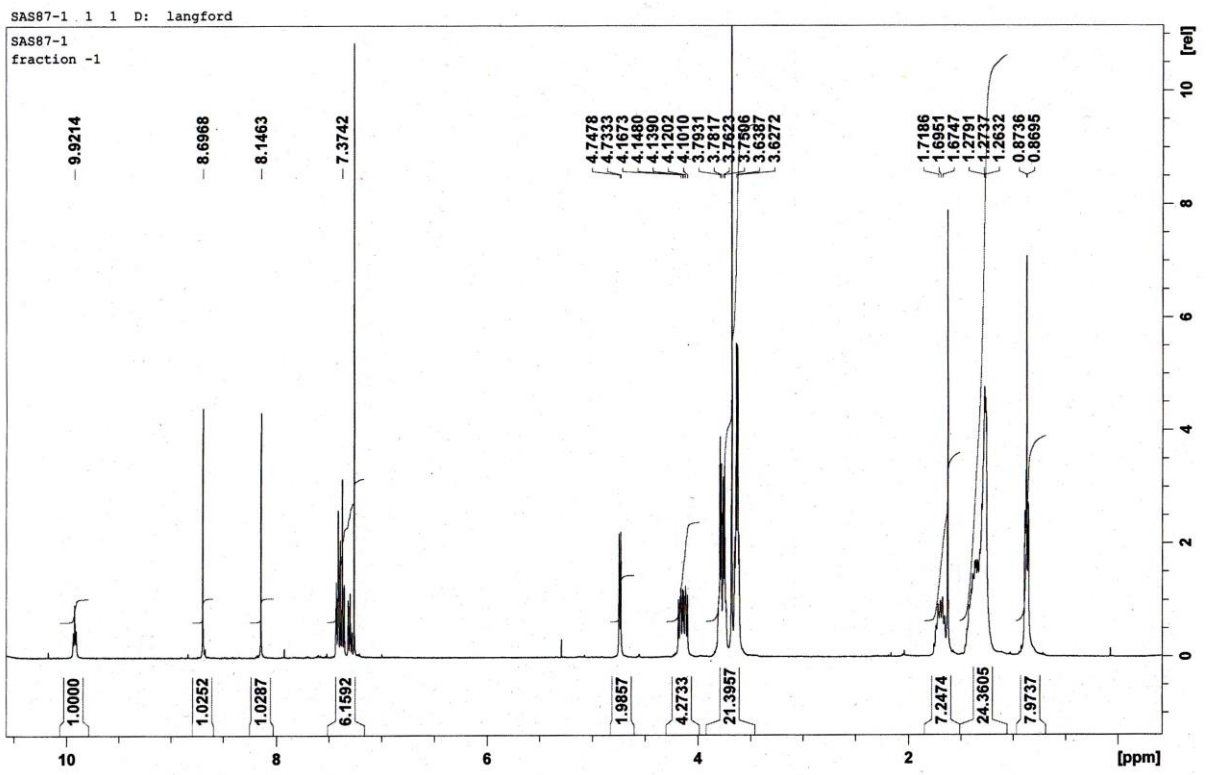



**Fig. S1** $^{1}$H NMR spectrum of **5** (300 MHz, 303 K) in $CDCl_3$.

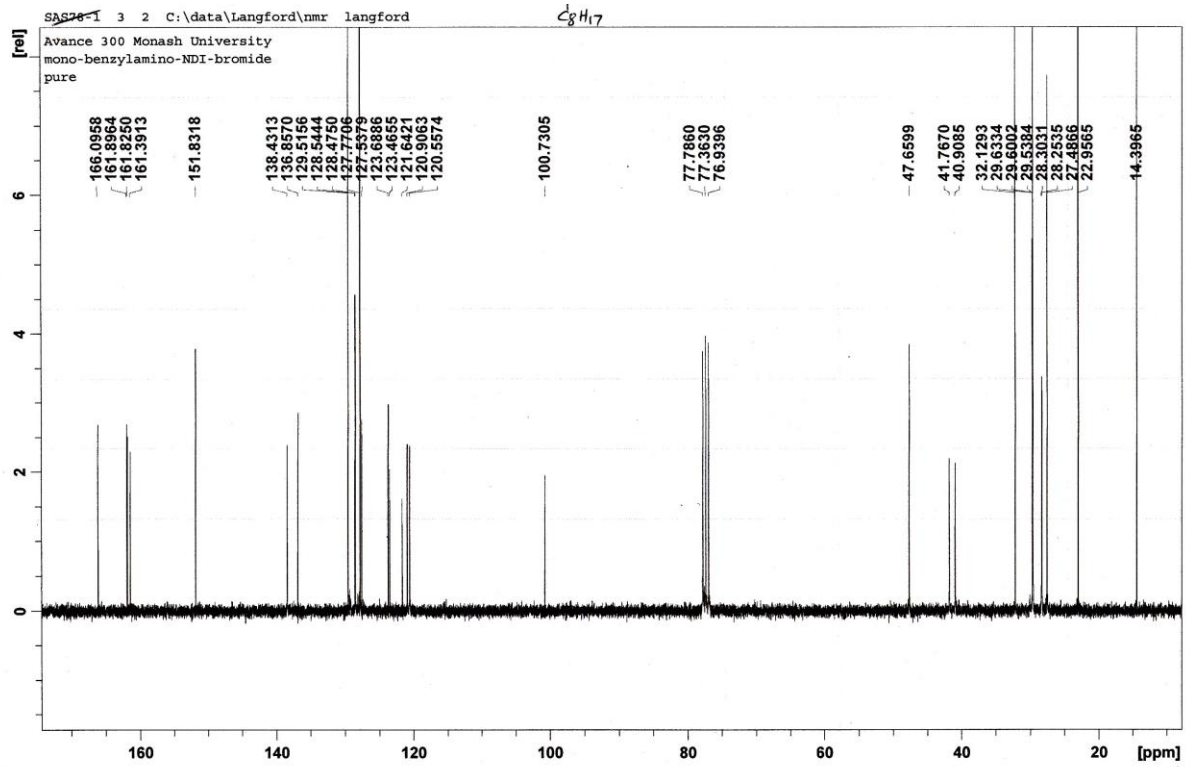



**Fig. S2** $^{13}C$ NMR spectrum of **5** (75 MHz, 303 K) in $CDCl_3$.

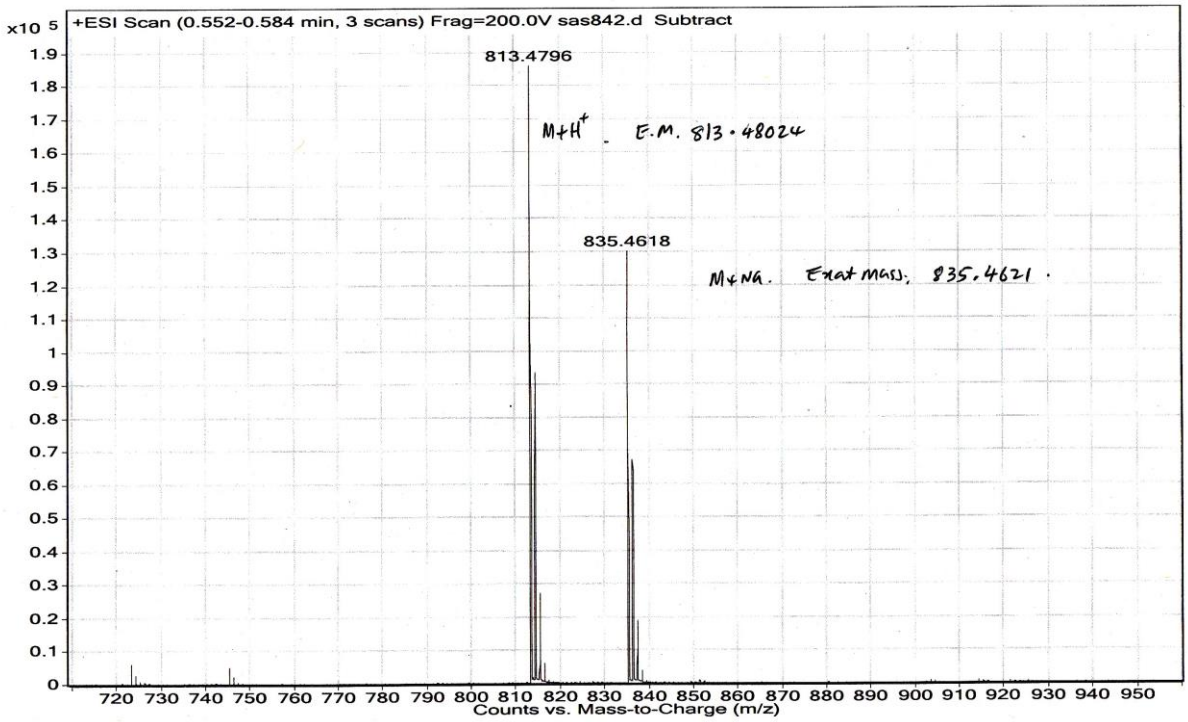



**Fig. S3** High resolution mass spectrum ($ESI^+$) of **5**.

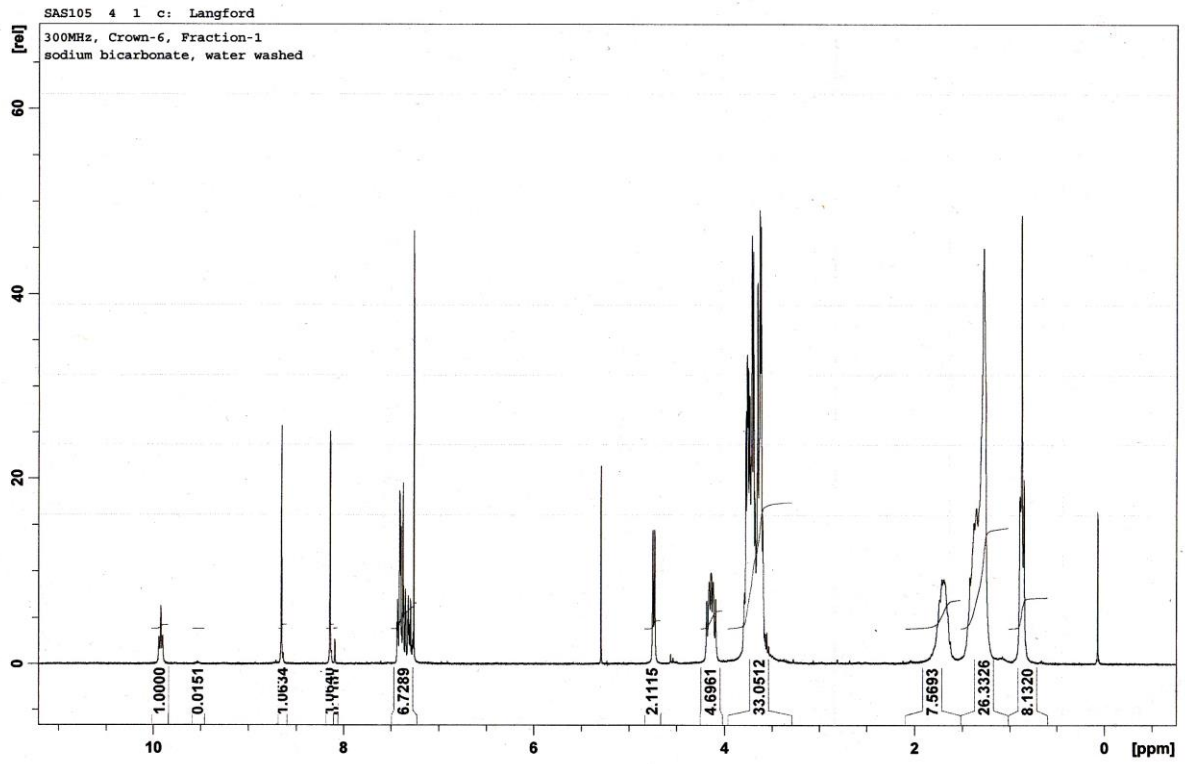



**Fig. S4** $^{1}$H NMR spectrum of **6** (300 MHz, 303 K) in $CDCl_3$.

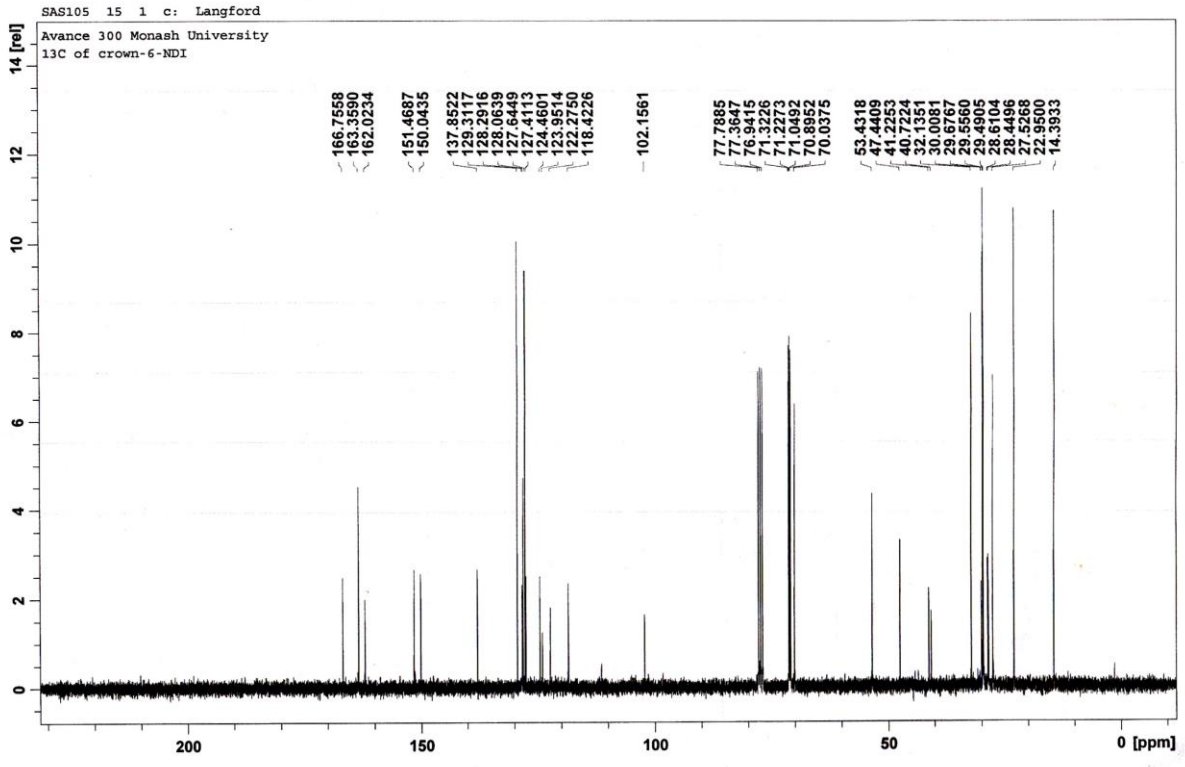



**Fig. S5** $^{13}$C NMR spectrum of **6** (75 MHz, 303 K) in $CDCl_3$.

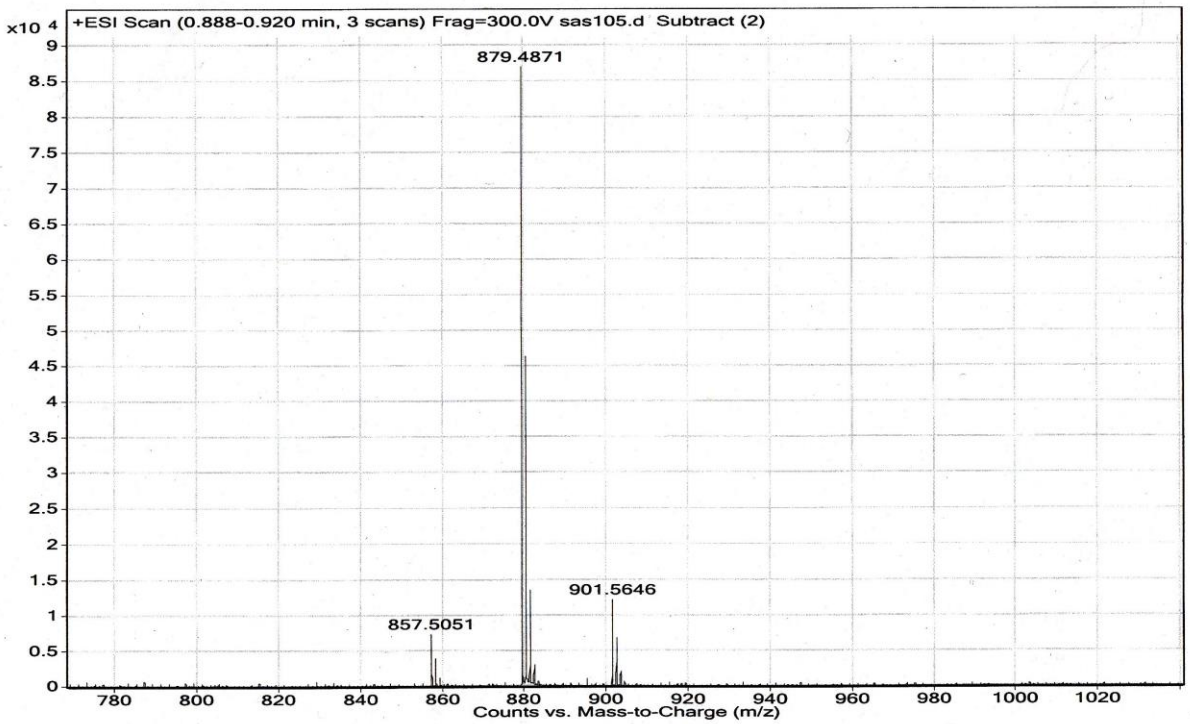



**Fig. S6** High resolution mass spectrum ($ESI^+$) of **6**.

## 3. Spectroscopic Materials and Methods

For molar absorptivity coefficient determination, 10 ml standards of concentrations ranging from 0 to 100 μmol $L^{-1}$ were prepared in ethanol in 1.0 cm pathlength quartz cuvettes. The molar extinction coefficients were determined at the absorption maximum of 600 nm and found to be 12,500 $M^{-1}cm^{-1}$ and 13,900 $M^{-1}cm^{-1}$ for sensors **5** and **6**, respectively. Samples for determination of binding via a Job's plot were prepared for concentrations of **6** from 0 to 10 μmol $L^{-1}$ every 0.5 μM with a constant total molar concentration of **6** + salt of 10 μmol $L^{-1}$. Stability constants were determined using the method of Bourson and Valeur (J. Phys. Chem., 1989, 3871-3876). Fluorescence quantum yields were determined by comparing areas under corrected emission spectra recorded under identical conditions with that of Rhodamine 101 which has a quantum yield of 1.0 in ethanol. (T. Karstens and K. Kobs, J. Phys. Chem., 1980, 84, 1871.)

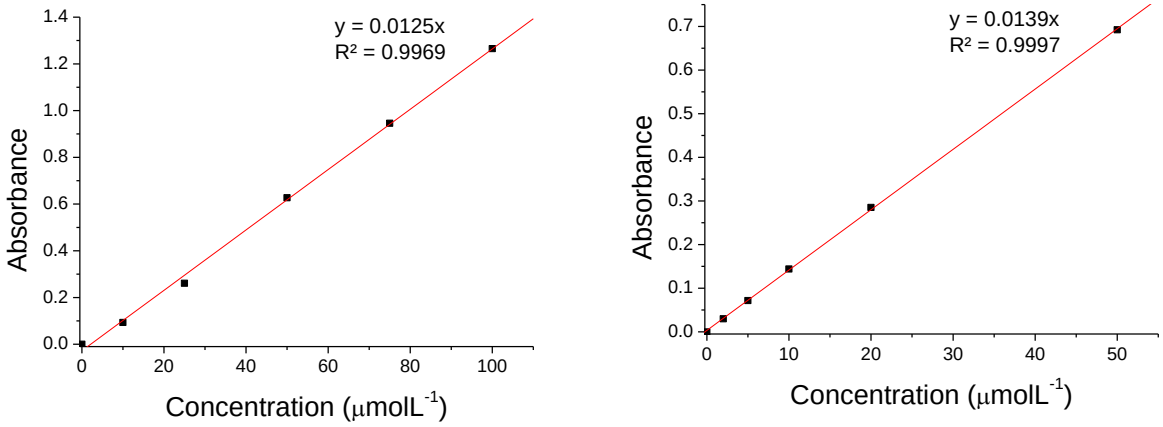



**Fig. S7** Concentration versus absorbance of **5** (left) and **6** (right) in EtOH at 600 nm.

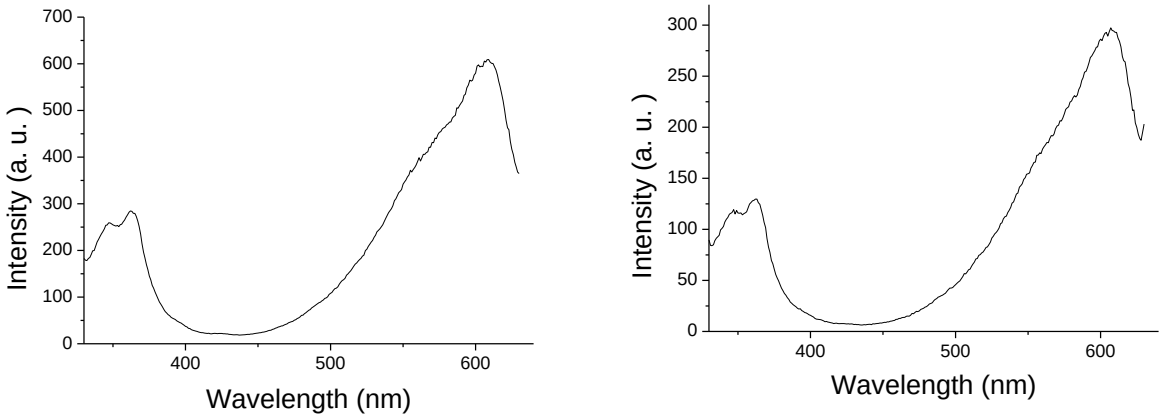



**Fig. S8** Excitation spectra of **5** (left) and **6** (right) in EtOH. Emission monitored at 640 nm.

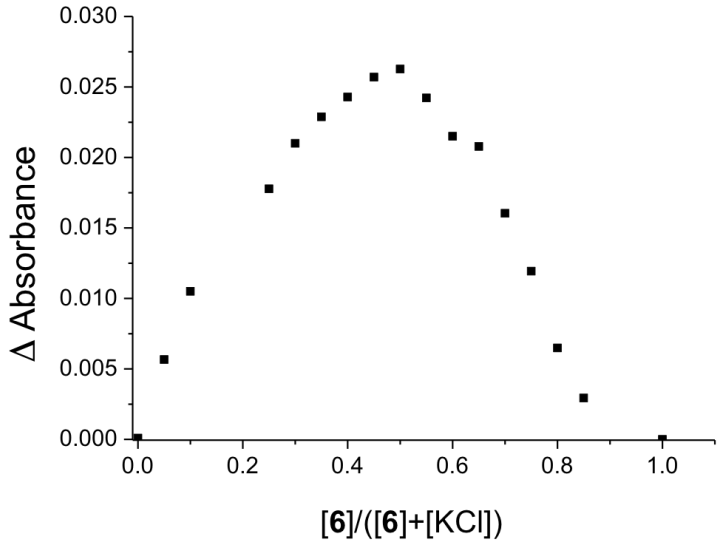



**Fig. S9** Job's plot determined over a range from 0-10 μmol $L^{-1}$ for **6** with a constant concentration of **6** + KCl = 10 μmol $L^{-1}$. Maximum ΔAbsorbance occurs at ~0.50 mole fraction of **6** indicating 1:1 binding between **6** and $K^+$. **Δ**Absorbance = measured absorbance – calculated absorbance where the calculated absorbance is [**6**/([**6**+KCl) multiplied by the measured absorbance of the 10 μmol $L^{-1}$ solution of **6**. The absorbance was taken over the range 590 – 610 nm. KCl does not absorb over this range.

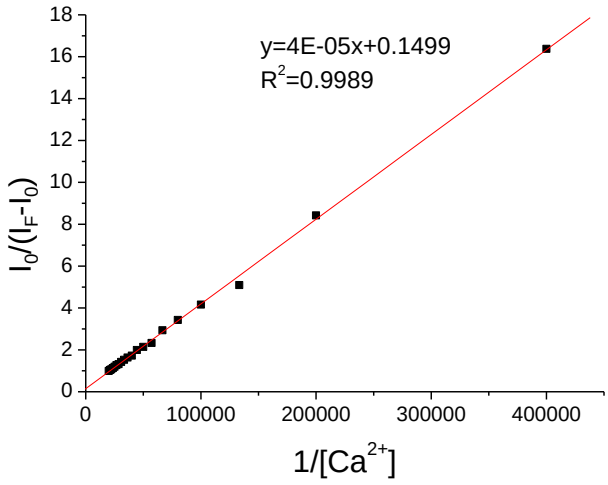



**Fig. S10** Determination of stability constant between **5** and $CaCl_2$. $I_0/(I_F-I_0)$ versus $1/[CaCl_2]$. Stability constant is determined by the ratio intercept/slope = 3748 $M^{-1}$.

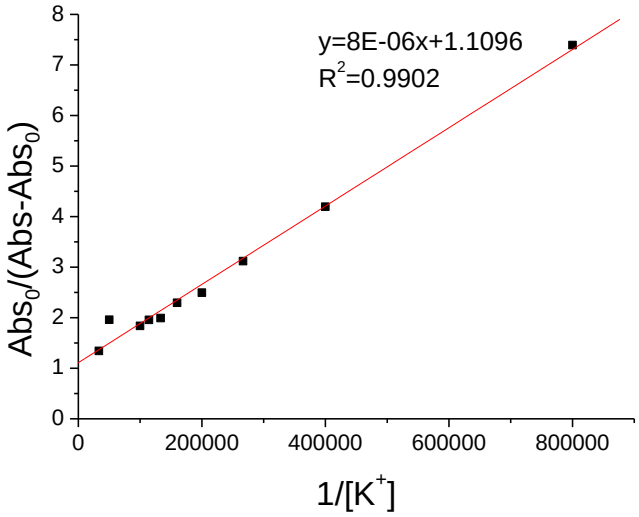



**Fig. S11** Determination of stability constant between **6** and KCl. $Abs_0/(Abs-Abs_0)$ versus 1/[KCl]. Stability constant is determined by the ratio intercept/slope = 138700 $M^{-1}$.

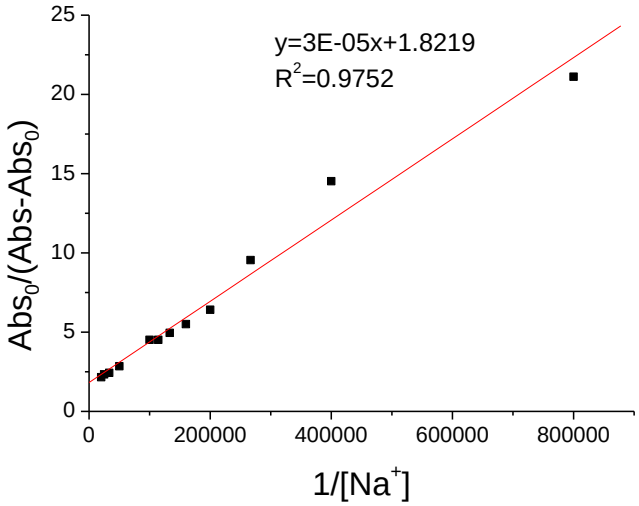



**Fig. S12** Determination of stability constant between **6** and NaCl. $Abs_0/(Abs-Abs_0)$ versus 1/[NaCl]. Stability constant is determined by the ratio intercept/slope = 60730 $M^{-1}$.

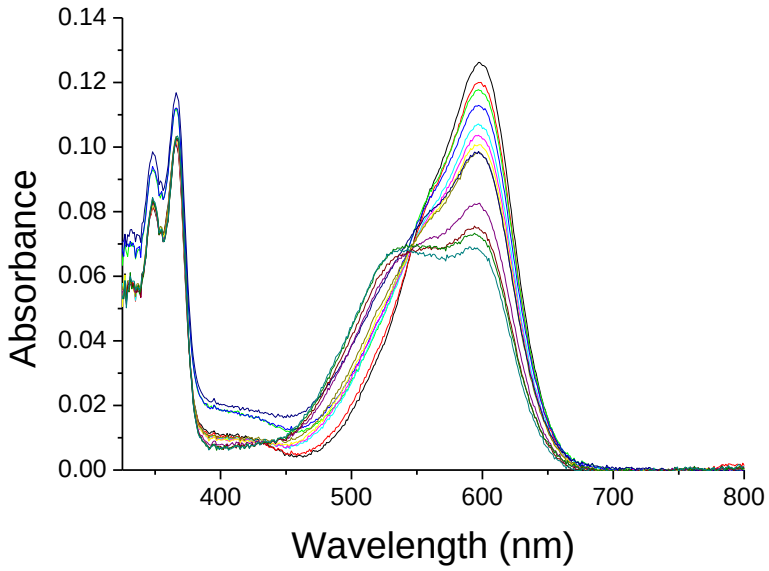



**Fig. S13** UV-Vis absorption spectra of **6** (10 μM) in EtOH on addition of 0-3 equiv. of $Na^+$ (as NaCl).

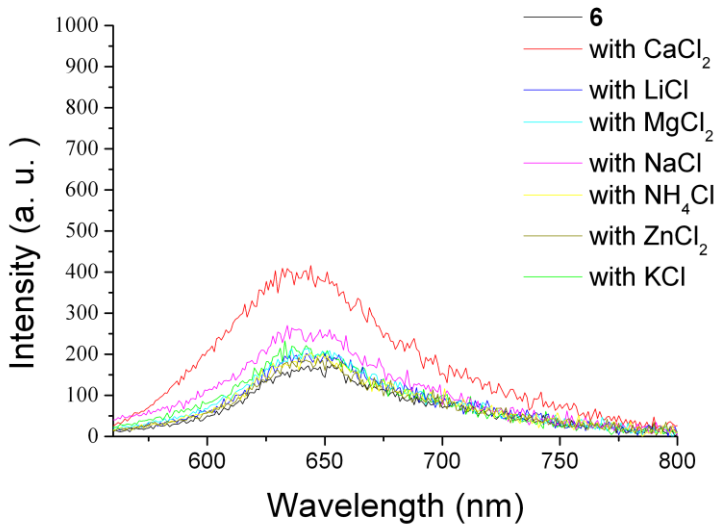



**Fig. S14** Fluorescence spectra of **6** (10 μM) in EtOH, on addition of chloride salts (50.0 equiv. of $Ca^{2+}$, $Li^+$, $Mg^{2+}$, $Na^+$, $NH_4^+$, $Zn^{2+}$ and $K^+$). Excitation at 550 nm.

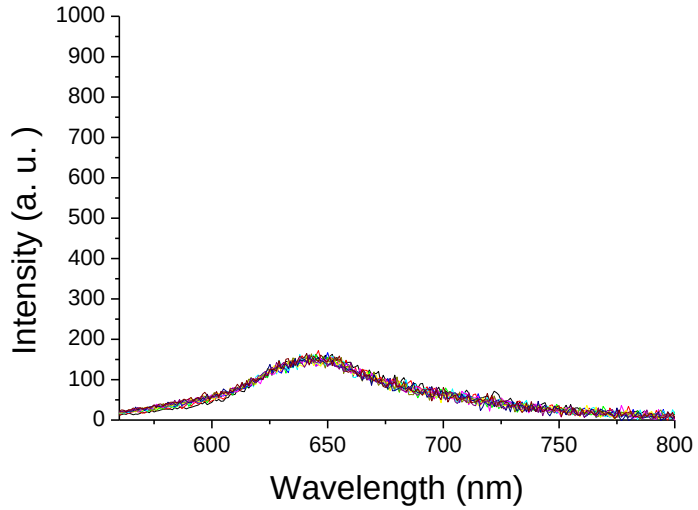



**Fig. S15** Fluorescence spectra of **6** (10 μM) in EtOH on addition of 0-5 equiv. of $K^+$ (as KCl). Excitation at 550 nm.

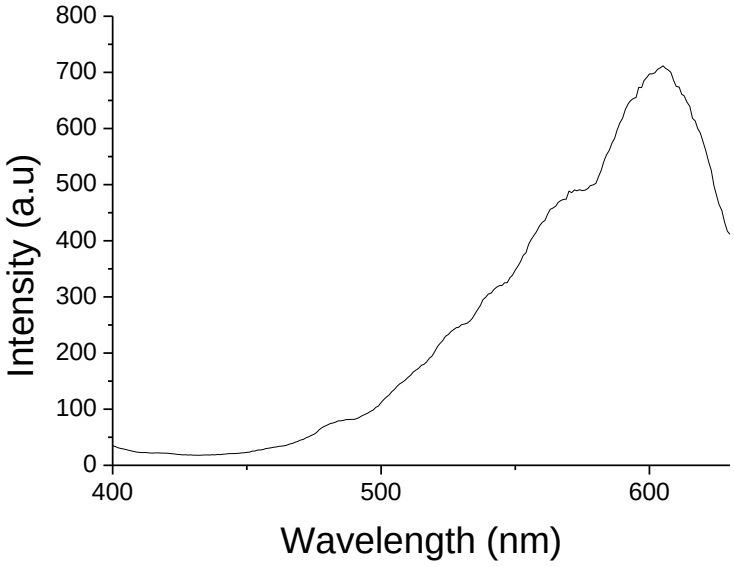



**Fig. S16** Excitation spectrum of **6**-$K^+$ in EtOH. Emission monitored at 640 nm.

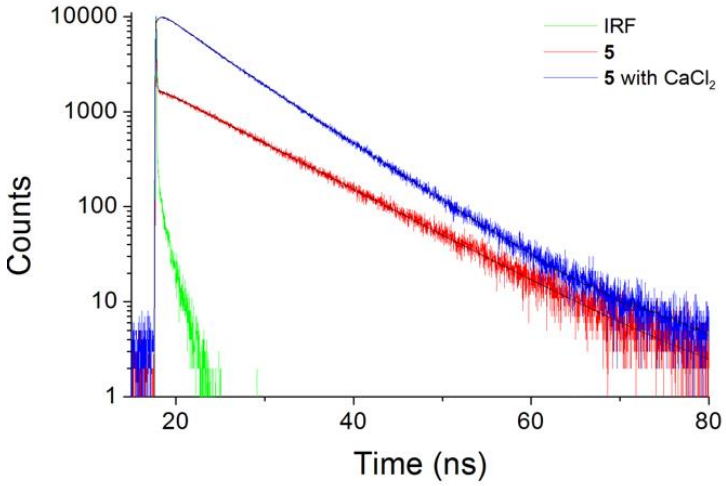



**Fig. S17** TCSPC decay profiles and fitted bi-exponential decay functions of **5** and **5** with $CaCl_2$ (10 μM in EtOH). Excitation at 532 nm, IRF = instrument response function.

**Table S1.** Time resolved data for **5** and **5** with $CaCl_2$ in EtOH.

| | $\tau_1$ (ns) | % | $\tau_2$ (ns) | % | $\chi^2$ |
|---|---|---|---|---|---|
| **5** | 0.05 | 82 | 9.00 | 18 | 1.003 |
| **5-Ca$^{2+}$** | 2.53 | 23 | 7.19 | 77 | 1.084 |

**Table S2.** M06-2X TD-DFT absorbances for **5** and **6** in the bound and unbound states.

| Structure | Cation | Unbound $\lambda_{max}$ (nm) | Bound $\lambda_{max}$ (nm) | $\Delta\lambda_{max}$ (nm) | Cation-NDI interaction energy (kJ mol$^{-1}$ z$^{-1}$) |
|---|---|---|---|---|---|
| ***Higher energy structures*** | | | | | |
| **5** | $Ca^{2+}$ | 500 | 463 | -37 | -79.6 |
| **6** | $Na^{+}$ | 499 | 506 | 7 | -30.4 |
| **6** | $K^{+}$ | 483 | 482 | -1 | -67.3 |

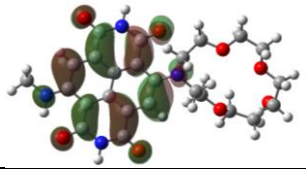
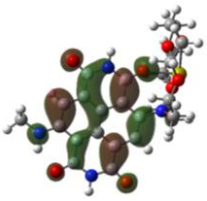
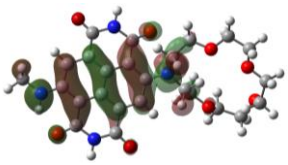
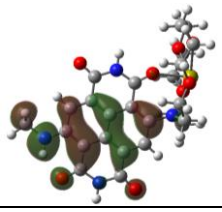
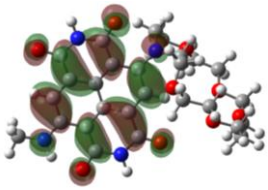
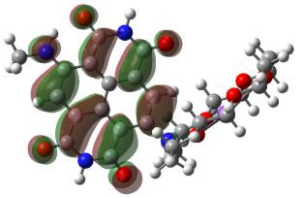
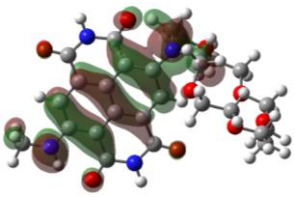
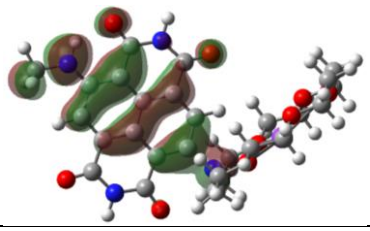
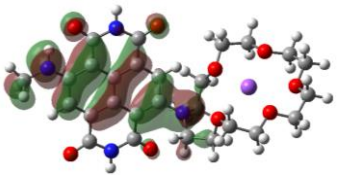
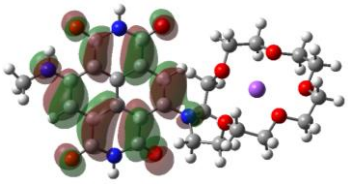
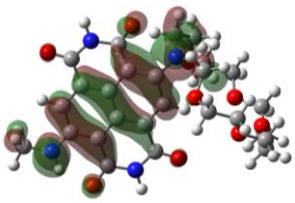
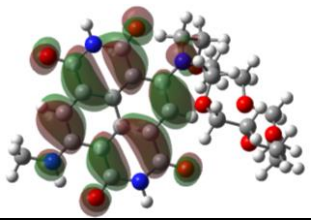
| Compound | Orbital | Unbound | Bound |
|---|---|---|---|
| **5** with $Ca^{2+}$ | **LUMO** |  |  |
| | **HOMO** |  |  |
| **6** with $K^{+}$ | **LUMO** |  |  |
| | **HOMO** |  |  |
| **6** with $Na^{+}$ | **LUMO** |  |  |
| | **HOMO** |  |  |

**Fig. S18** HOMOs and LUMOs calculated at HF/6-311++G(2d,2p) level of theory of **5** with $Ca^{2+}$ (upper panels), **6** with $K^{+}$ (centre panels) and **6** with $Na^{+}$ (lower panels)