Supplementary material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Calix[4]azacrown and 4-Aminophthalimide-Appended Calix[4]azacrown: Synthesis, Structure, Complexation and Fluorescence Signaling Behavior

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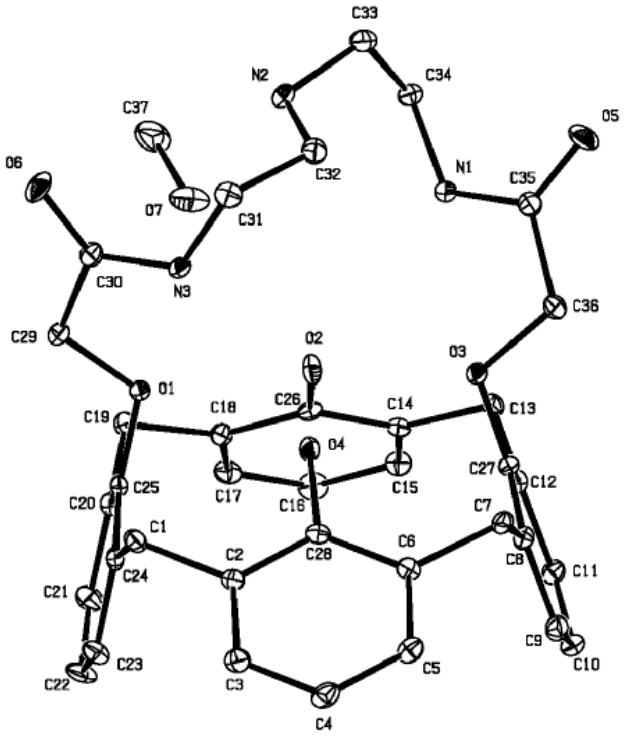

Figure S1. An ortep view of the molecular structure of **L.CH$_3$OH**, showing 10% displacement ellipsoids and the atom labeling. Hydrogen atoms are omitted for clarity.

Table S1. Crystallographic parameters for Calix[4]azacrown (**L·CH$_3$OH**):

Formula	$C_{36}H_{37}N_3O_6 \cdot CH_4O$
Formula wt	639.73
Crystal system	Monoclinic
Space group	P $2_1/n$
a (Å)	12.470(8)
b (Å)	15.549(8)
c (Å)	16.864(3)
β (°)	98.63(4)
V (Å^3)	3233(3)
Z	4
F(000)	1360
ρ_{calcd} (g cm^{-3})	1.314
Radiation (Å) (Mo-Kα)	0.71073
No. of reflections for measd	25
θ_{range} (°)	5.41-10.17
μ (mm^{-1})	0.091
Temperature (K)	293(2)
Crystal size	0.48 x 0.40 x 0.32
Color	Colorless
Diffractometer	Enraf-Nonius Mach3 four circle (CAD-4)
Data collection method	ω scans
Absorption correction	None
Total no. of reflections	5676
No. of unique reflections	5676
No. of observed reflections [I > 2σ(I)]	1765
θ_{max} (°)	24.98
hkl range	0 → 14; 0 → 18; -20 → 19
No. of parameters	429
R [$F^2 > 2\sigma(F^2)$]	0.0654
wR (F^2)	0.1298
GOF	0.96
$(\Delta/\sigma)_{max}$	0.002

$\Delta\rho_{max}$ (e/Å^3)	0.216
$\Delta\rho_{min}$ (e/Å^3)	-0.239
Extinction correction	None

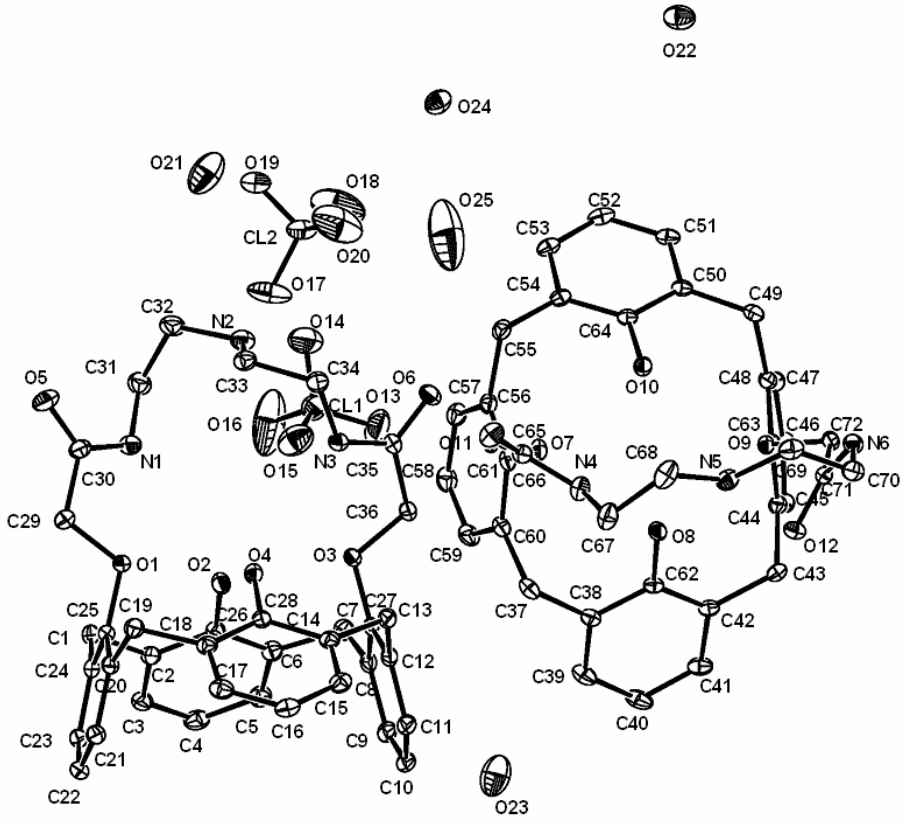

Figure S2. An ortep view of the molecular structure of **2LHClO$_4$·5H$_2$O**, showing 10% displacement ellipsoids and the atom labeling. Hydrogen atoms are omitted for clarity.

Table S2. Crystallographic parameters for **$2LHClO_4 \cdot 5H_2O$**

Formula	$2(C_{36}H_{38}N_3O_6).2(ClO_4).5(H_2O)$
Formula wt	1506.37
Crystal system	Triclinic
Space group	P-1
a (Å)	12.7722(18)
b (Å)	15.865(2)
c (Å)	20.138(3)
α (°)	78.132(2)
β (°)	71.638(2)
γ (°)	69.810(2)
V ($Å^3$)	3613.3(9)
Z	2
F(000)	1588
ρ_{calcd} (g cm^{-3})	1.385
Radiation (Å) (Mo-Kα)	0.71073
No. of reflections for measd	6704
θ_{range} (°)	2.29-21.98
μ (mm^{-1})	0.175
Temperature (K)	293(2)
Crystal size	0.29 x 0.12 x 0.04
Color	Yellow
Diffractometer	CCD area detector diffractometer
Data collection method	ϕ and ω scans
Absorption correction	Multi-scan (SADABS)
T_{min}	0.864
T_{max}	0.993
Total no. of reflections	42510
No. of unique reflections	16948
No. of observed reflections [I > 2σ(I)]	7827
θ_{max} (°)	28.32
hkl range	-16 → 16; -20 → 21; -26 → 26
No. of parameters	970

R [$F^2 > 2\sigma(F^2)$]	0.0910
wR (F^2)	0.3236
GOF	1.031
$(\Delta/\sigma)_{max}$	0.003
$\Delta\rho_{max}$ (e/Å^3)	0.802
$\Delta\rho_{min}$ (e/Å^3)	-0.510
Extinction correction	None

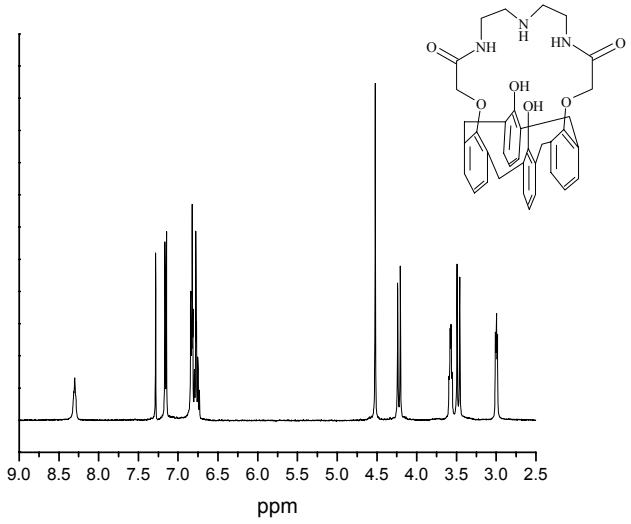

Figure S3. ^{1}H NMR spectrum of compound **L** in $CDCl_3$.

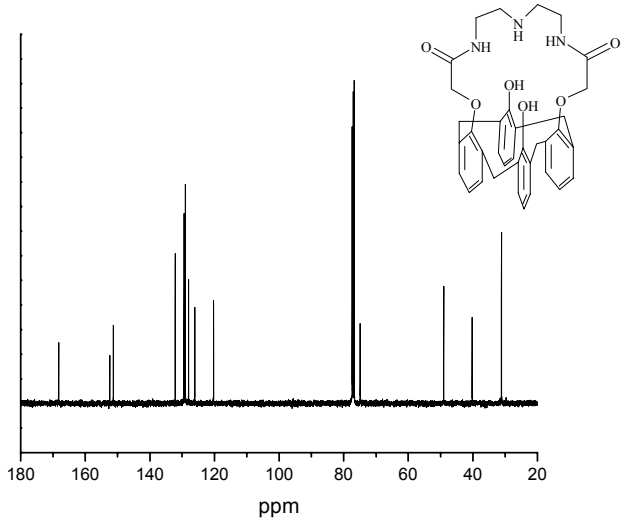

Figure S4. ^{13}C NMR spectrum of compound **L** in $CDCl_3$.

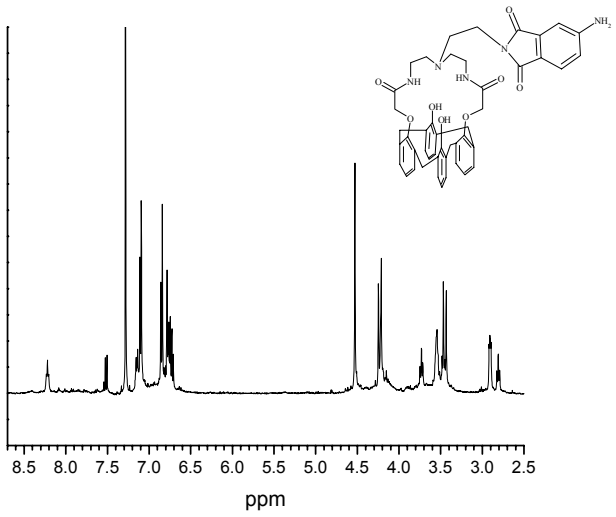

Figure S5. ^{1}H NMR spectrum of compound **APL** in $CDCl_3$.

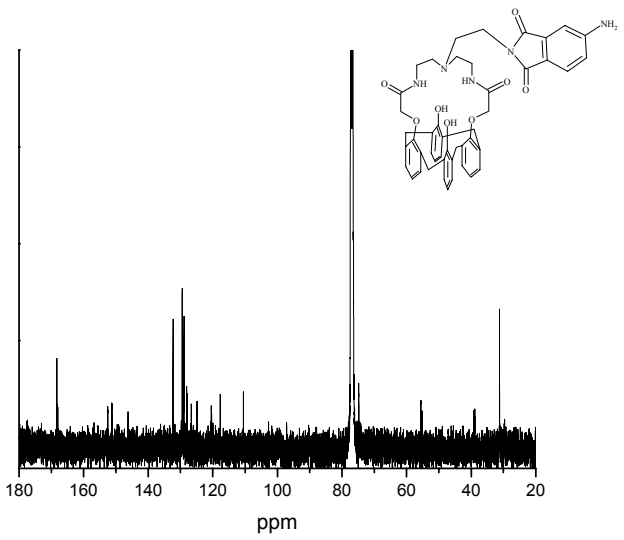

Figure S6. ^{13}C NMR spectrum of compound **APL** in $CDCl_3$.

Method S1: Procedure for the estimation of the binding constant:

Representing the 1:1 complexation of fluorosensor (F) and metal salt (M) as,

F + M === C

The equilibrium constant (K) is given by,

$$K = \frac{[C]}{([F]_0 - [C])([M]_0 - [C])} \qquad (1)$$

where, $[F]_0$ and $[M]_0$ are the initial concentration of the fluorosensor and the metal salt respectively and [C] is the equilibrium concentration of the complex.

By substituting $\Delta A/\Delta\varepsilon$ for $[C]$ (for a path length of 1 cm) the following equation can be derived,

$$\frac{[F]_0[M]_0}{\Delta A} = \left([F]_0 + [M]_0 - \frac{\Delta A}{\Delta\varepsilon}\right)\frac{1}{\Delta\varepsilon} + \frac{1}{K\Delta\varepsilon} \qquad (2)$$

where, ΔA is the change in absorbance due to the addition of metal salts, and $\Delta\varepsilon$ is the difference between the molar extinction coefficient of the complex and the fluorosensor.

A plot of $\frac{[F]_0[M]_0}{\Delta A}$ vs. $\left([F]_0 + [M]_0 - \frac{\Delta A}{\Delta\varepsilon}\right)$ would yield a straight line with slope $1/\Delta\varepsilon$ and intercept $1/K\Delta\varepsilon$. However, knowledge of the unknown quantity $\Delta\varepsilon$ is needed to make this plot.

Consequently, a tentative value of $\Delta\varepsilon$ is determined by using data from two solutions and solving equation (2) simultaneously for $\Delta\varepsilon$ and K. Using this value of $\Delta\varepsilon$ a plot is made, employing data from a series of solutions, and a new value of $\Delta\varepsilon$ is determined along with a new value of K. This procedure is repeated until a consistent set of values for both $\Delta\varepsilon$ and K have been obtained from two successive plots.