Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis and photophysical evaluation of a pyridinium 4-amino-1,8-naphthalimide derivative that upon intercalation displays preference for AT-rich double stranded DNA

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The association constant, K for the binding of mononucleotide 5'-monophosphate with **1** was determined from the slope of Scatchard plot using the equation 1.[1]

$$\frac{\Delta A}{[NI][XMP]} = K\Delta\epsilon - K\frac{\Delta A}{[NI]} \qquad (1)$$

ΔA is the change in absorbance of **1** at 435 nm in the presence of mononucleotide XMP, $\Delta\varepsilon = (\varepsilon_f - \varepsilon_b)$. ε_f and ε_b are the molar extinction coefficients of free and bound naphthalimide, respectively. [NI], [XMP] refer to the total concentration of naphthalimide and mononucleotide respectively.
The binding constant for the association of **1** with GMP was also determined assuming 1:1 complex formation using equation 2.[2]

$$\frac{\Delta A}{[NI]} = \frac{K\Delta\varepsilon[GMP]}{1 + K[GMP]} \qquad (2)$$

The binding constant for the association of 1 with AMP was estimated from equation 3 assuming both 1:1 and 1:2 complex formations.[3]

$$\frac{\Delta A}{[NI]} = \frac{K_1\,\Delta\epsilon_1[AMP] + K_1K_2\Delta\epsilon_2[AMP]^2}{1 + K_1[AMP] + K_1K_2[AMP]^2} \qquad (3)$$

The absorbance change at 435 nm was analysed and fitted to the noncooperative model of McGhee and von Hippel described in equation 4 using the non-linear curve fitting algorithm in OriginPro 8 softwareto determine the binding constant, K, where *r* is the binding density and given by *r* = C_b/total DNA concentration and *n* is the average no of occupied sites, C_f and C_b are the concentrations of free and bound ligand, respectively.[4]

$$= K(1 - nr)\left[\frac{1 - nr}{1 - (n-1)r}\right]^{n-1} \qquad (4)$$

C_b and C_f were calculated from the absorbance data using the equations 5 and 6, respectively.

$$C_b = \frac{\mathrm{Af} - \mathrm{A}}{\mathrm{Af} - \mathrm{Ab}} \qquad (5)$$

$$C_f = C\text{-}C_b \qquad (6)$$

A_f and A_b are the absorbance values corresponding to free and fully bound ligand. A is the absorbance of the mixture at any point during titration and C is the total ligand concentration.

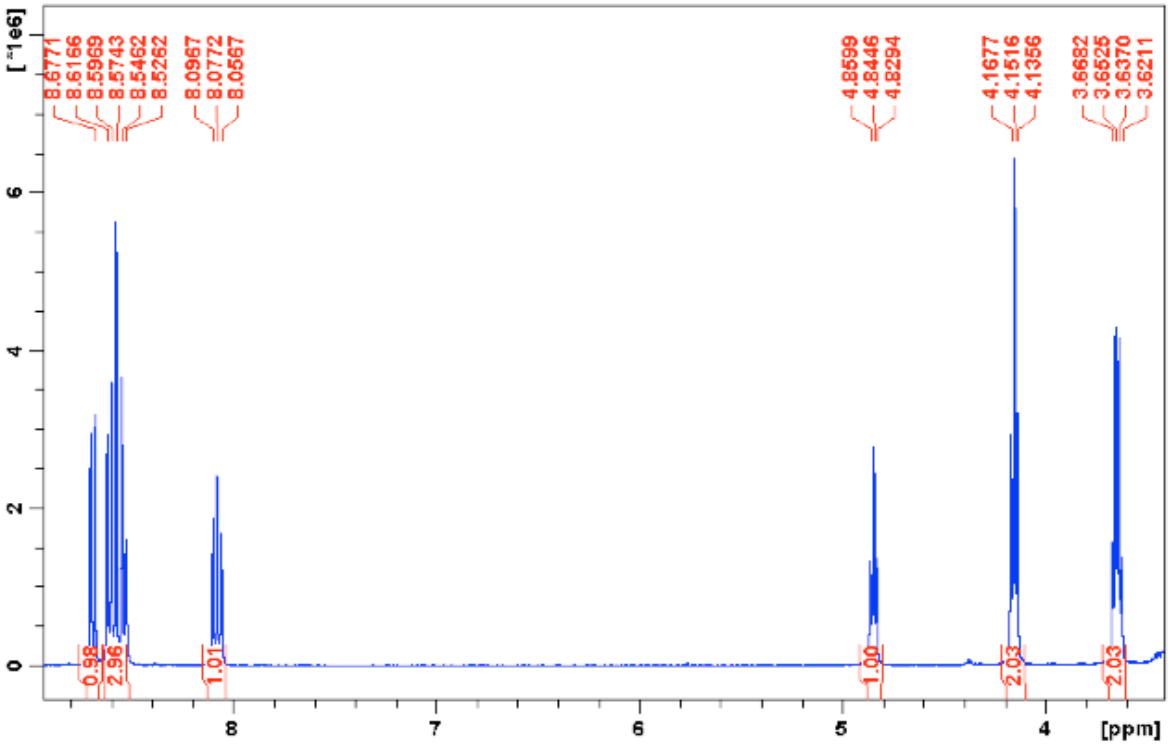


Figure ESI 1A: ^{1}H-NMR of **3** in DMSO-d6 (400 MHz)

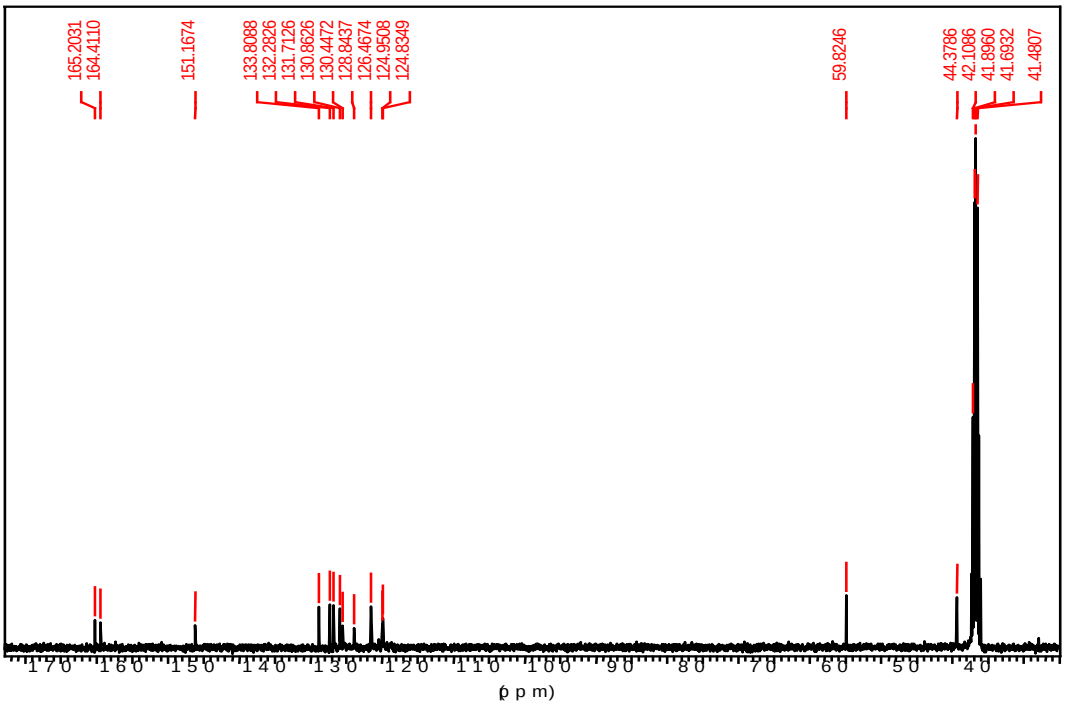


Figure ESI 1B: ^{13}C-NMR of **3** in DMSO-d6 (400 MHz)

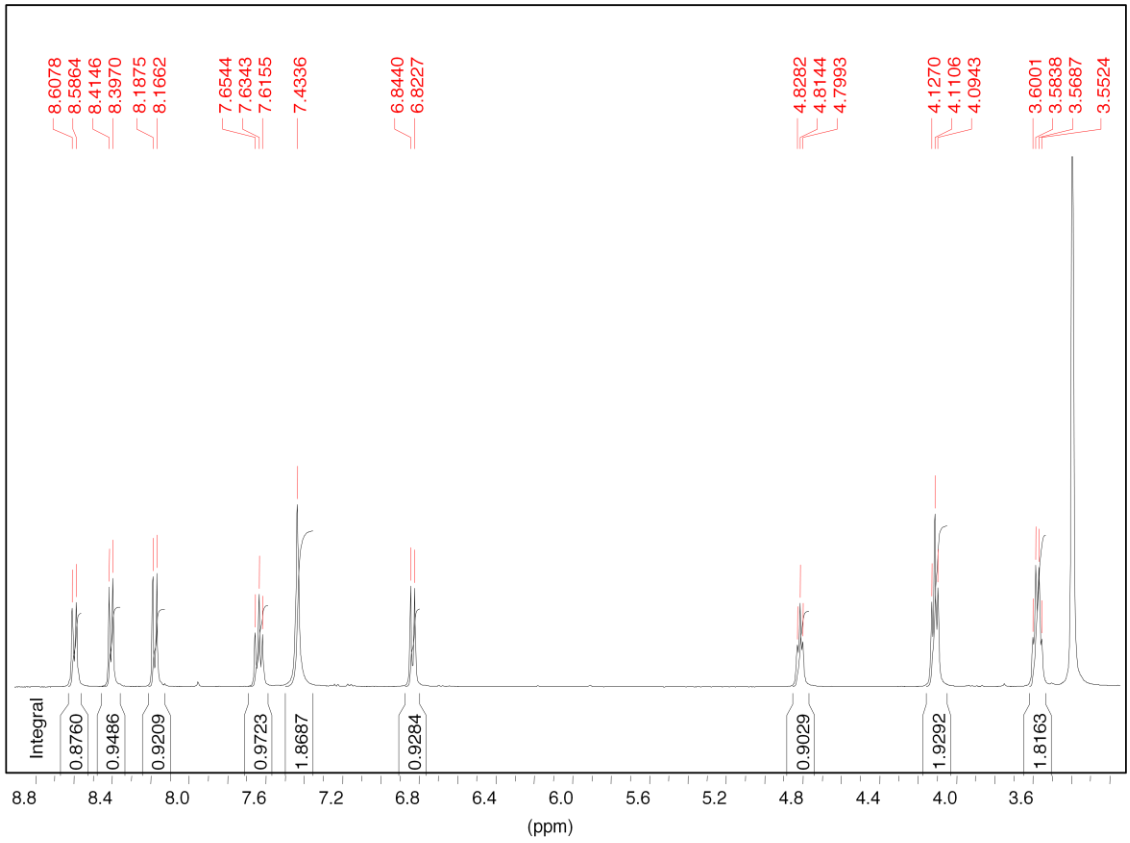


Figure ESI 1C: ^{1}H-NMR of **4** in DMSO-d6 (400 MHz)

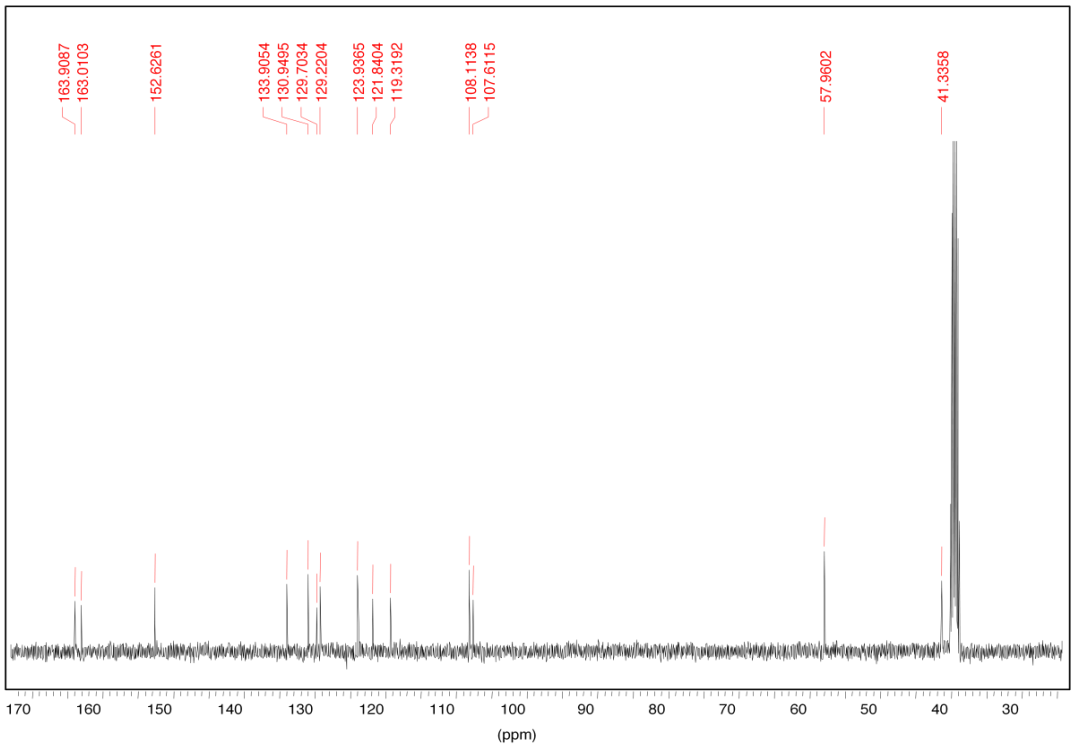


Figure ESI 1D: ^{13}C-NMR of **4** in DMSO-d6 (400 MHz)

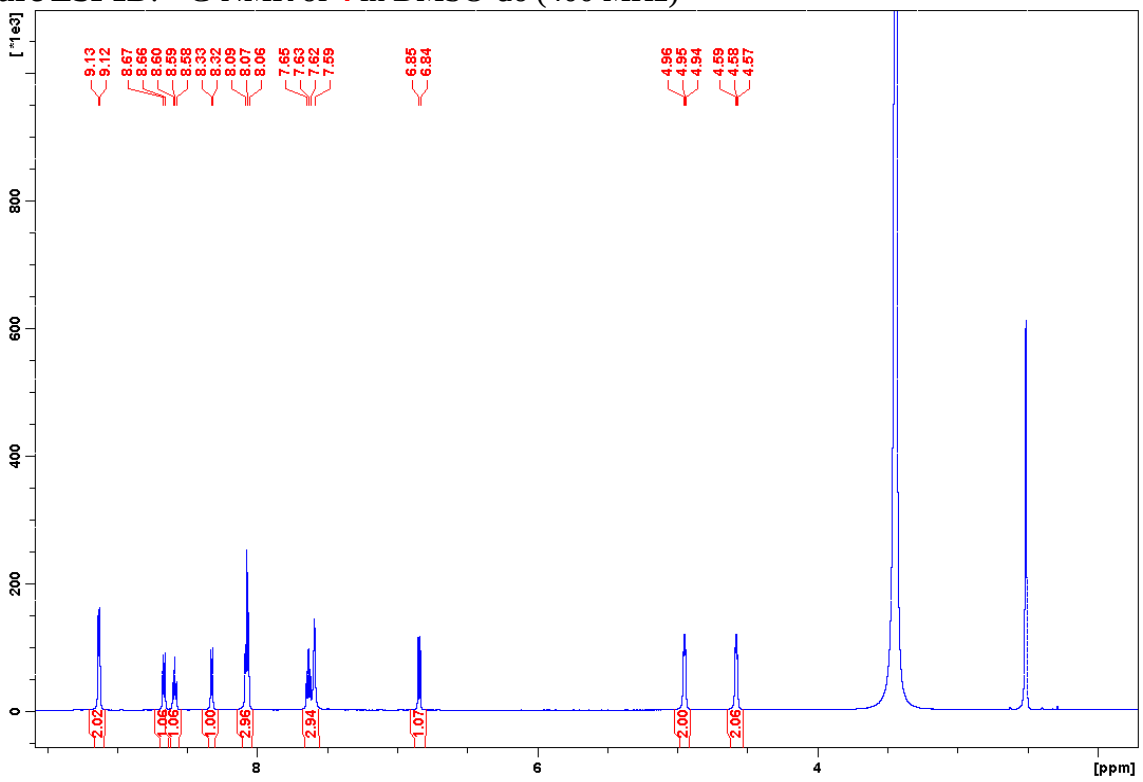


Figure ESI 1E: ^{1}H-NMR of **1** in DMSO-d6 (600 MHz)

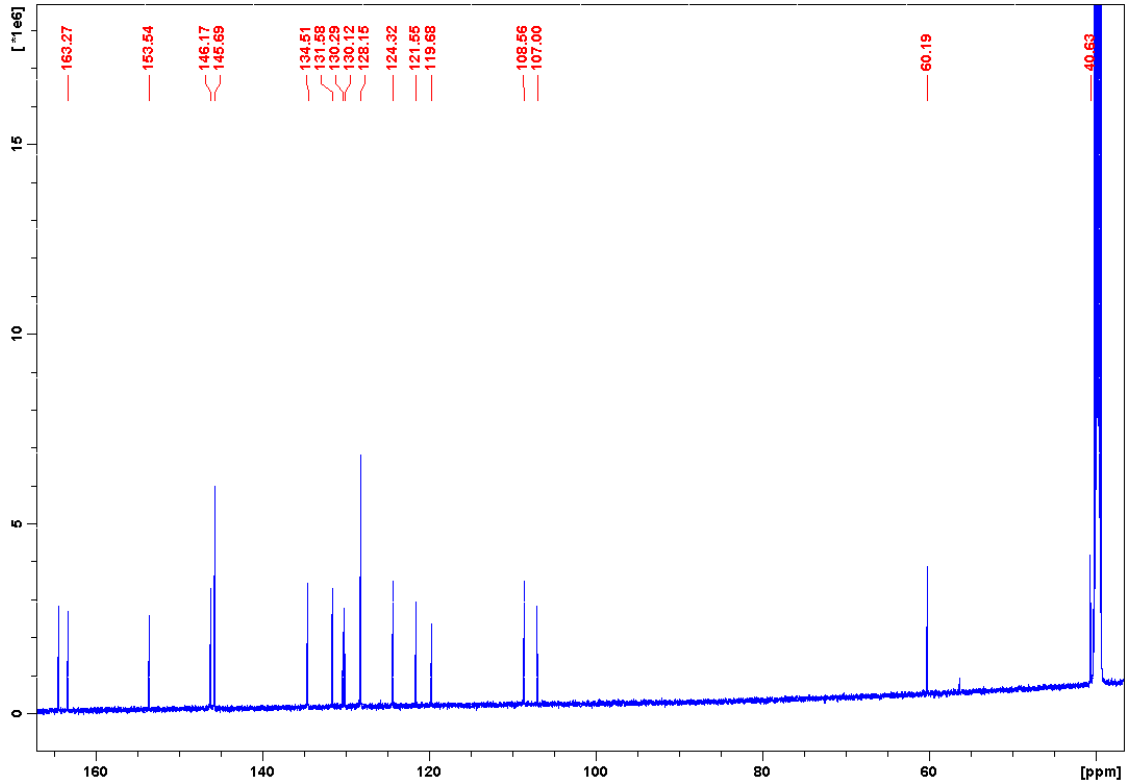


Figure ESI 1F:13-C NMR of 1 in DMSO-d6 (150 MHz)

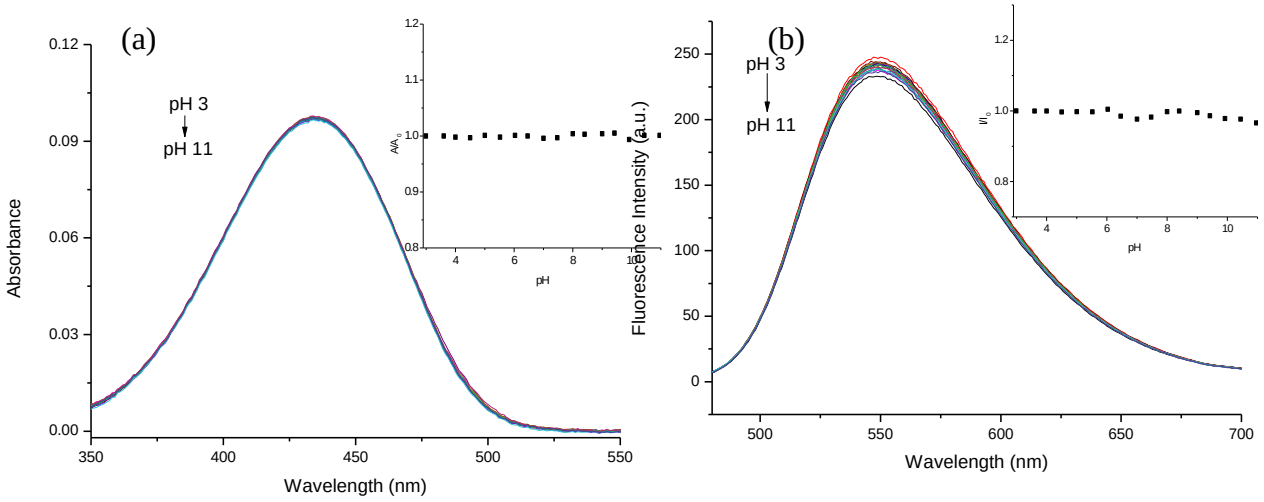


Figure ESI 2: (a) UV/vis absorption and (b) emission of **1** in water containing 10 mM NaCl as a function of pH. Insets: Normalised absorbance or fluorescence intensity as a function of pH

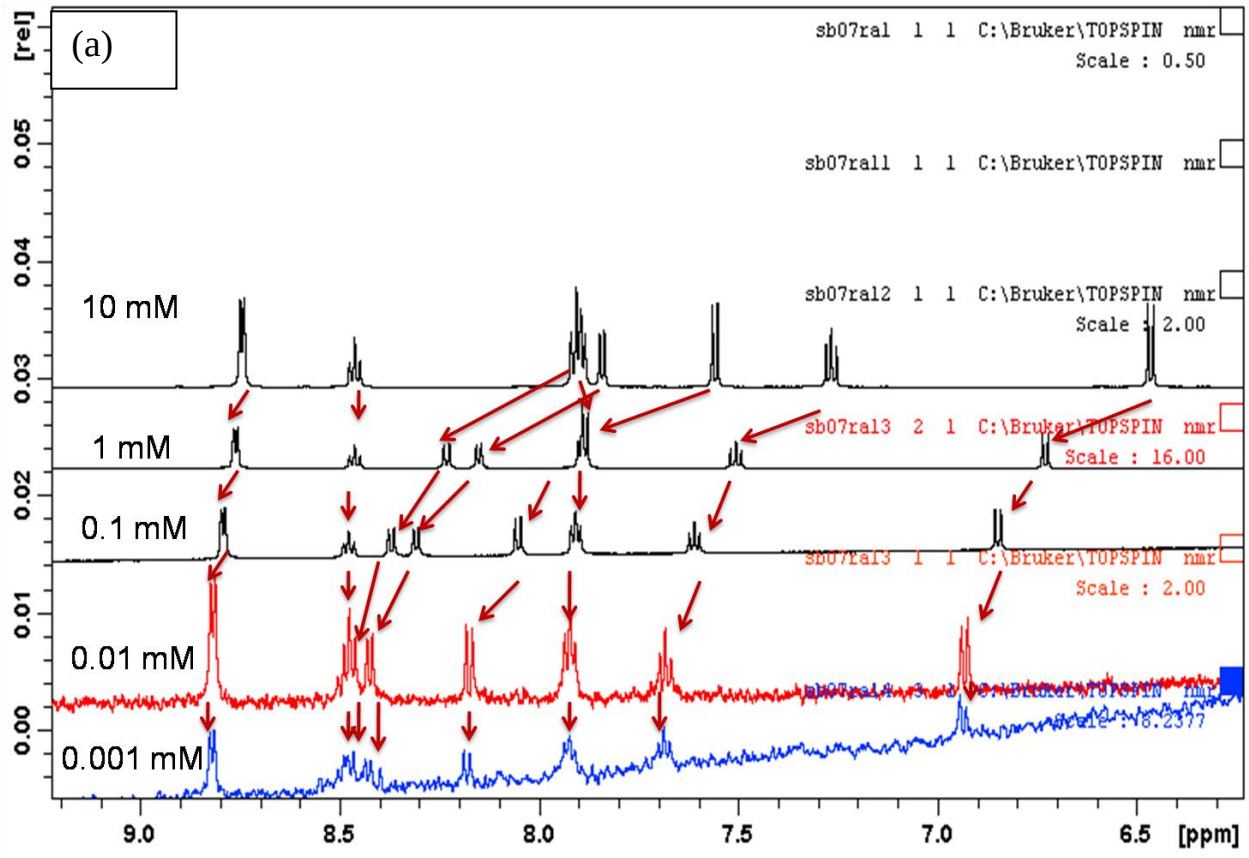
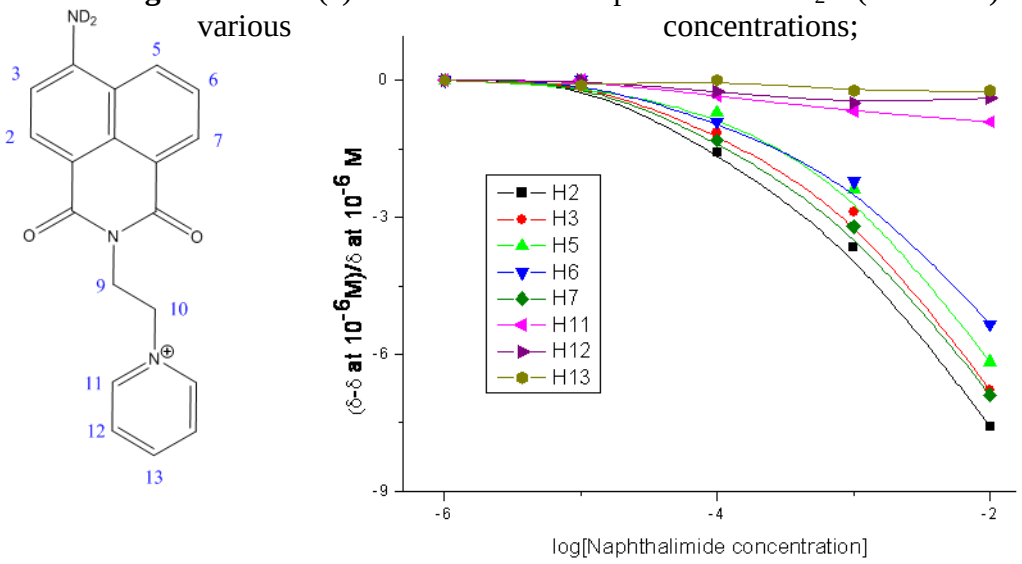


Figure ESI 3: (a) Overlaid ^{1}H-NHR spectra of **1** in D_2O (600 MHz) at various concentrations;

(b)



(b) Plot of chemical shift (δ) *vs*. log(naphthalimide concentration) (Assuming no aggregation at 0.001 M, chemical shift for each proton has been normalized using the equation (δ - δ at 0.001 M)/δ at 0.001 mM)

H	δin 10 mM	δ in 1 mM	δ in 0.1 mM	δ in 0.01 mM	δ in 0.001 mM
2	7.56	7.88	8.05	8.18	8.18
3	6.46	6.72	6.85	6.93	6.93
5	7.91	8.23	8.37	8.42	8.43
6	7.26	7.50	7.61	7.68	7.68
7	7.84	8.14	8.31	8.42	8.42
9	4.43	4.59	-	-	-
10	4.80	4.88	-	-	-
11	8.74	8.76	8.79	8.82	8.82
12	7.89	7.88	7.90	7.92	7.92
13	8.46	8.46	8.48	8.47	8.48

Table 1: Summary of chemical shifts at various concentration of **1**

Identification code	sb07	
Empirical formula	$C_{19}H_{16}F_6N_3O_2P$	
Formula weight	463.32	
Temperature	112(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.4536(19) Å	α= 90°.
	b = 9.3865(19) Å	β= 100.03(3)°.
	c = 21.293(4) Å	γ = 90°.
Volume	1860.6(7) $Å^3$	
Z	4	
Density (calculated)	1.654 Mg/m^3	
Absorption coefficient	0.230 mm^{-1}	
F(000)	944	
Crystal size	0.63 x 0.44 x 0.43 mm^3	
Theta range for data collection	2.19 to 25.00°.	
Index ranges	-11<=h<=10, -7<=k<=11, -16<=l<=25	
Reflections collected	6793	
Independent reflections	3184 [R(int) = 0.0428]	
Completeness to theta = 25.00°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5575	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3184 / 0 / 282	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1447	
R indices (all data)	R1 = 0.0600, wR2 = 0.1512	
Largest diff. peak and hole	0.721 and -0.408 $e.Å^{-3}$	

Table 2. Crystal data and structure refinement for **1**.

References

1. G. Scatchard, *Proc. New York Acad. Sci.,* 1949,**51**, 660
2. D. A. Deranleau, *J.Am. Chem. Soc.* 1969,**91**, 4044.
3. D. A. Deranleau, *J.Am. Chem. Soc.* 1969,**91**, 4050.
4. J. D. McGhee and P.H. von Hippel, *J.Mol.Biol.* 1974, **86**, 469.