

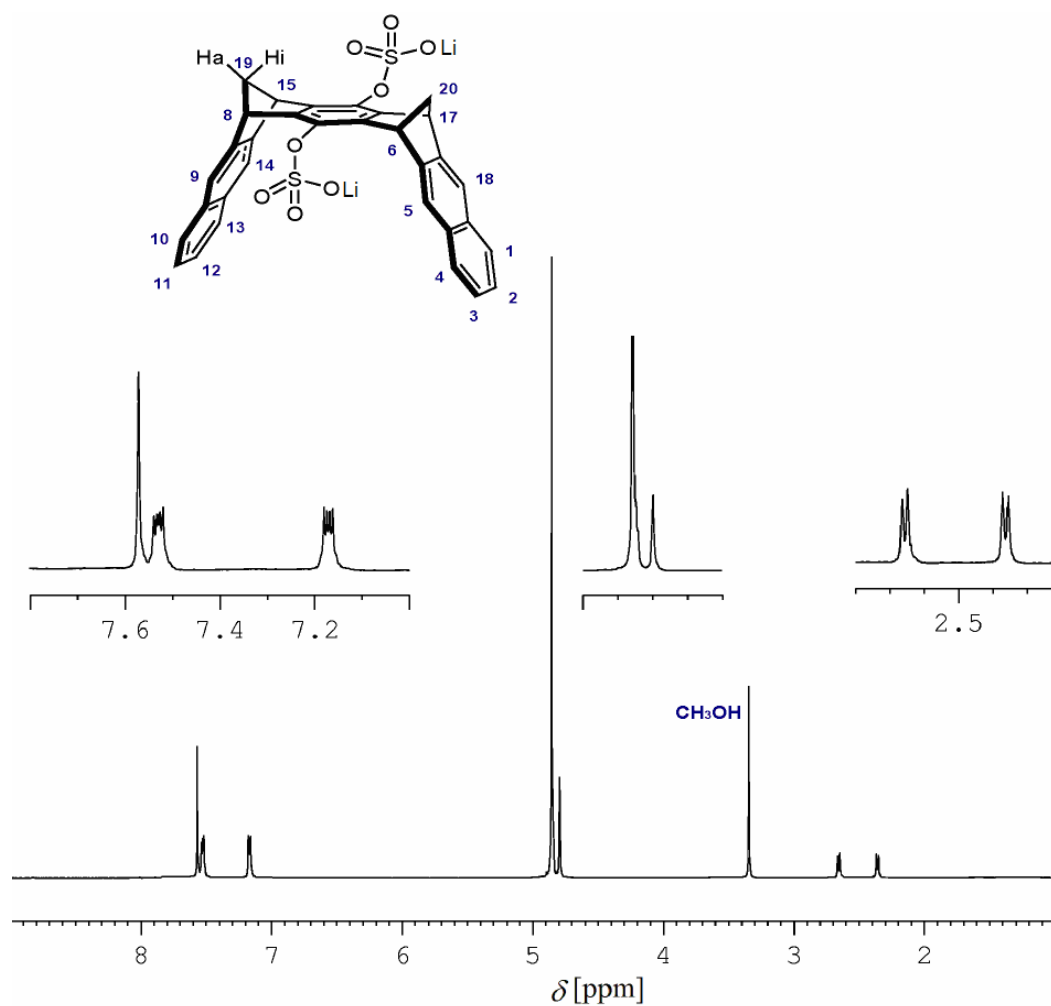
## Fluorescent water-soluble molecular clips. Self-association and formation of adducts in aqueous and methanol solution.

Barbara Branchi,<sup>a</sup> Paola Ceroni,<sup>a\*</sup> Vincenzo Balzani,<sup>a</sup> Marçal Casas Cartagena<sup>b</sup>, Frank-Gerrit Klärner<sup>b\*</sup>, Fritz Vögtle<sup>c\*</sup>

<sup>a</sup>Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, Italy. Tel: +39 051 2099535; Fax: +39 051 2099456; E-mail: [paola.ceroni@unibo.it](mailto:paola.ceroni@unibo.it)

<sup>b</sup>Institut für Organische Chemie der Universität Duisburg-Essen, Campus Essen, Universitätsstr. 5, 45117 Essen, Germany; E-mail: [frank.klaerner@uni-duisburg-essen.de](mailto:frank.klaerner@uni-duisburg-essen.de)

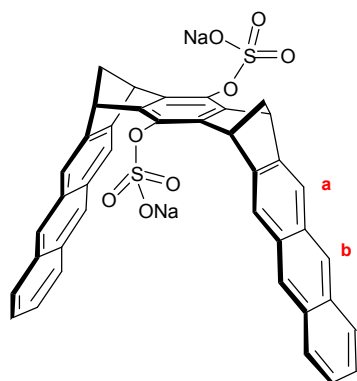
### Supporting Information



**Figure S1:** <sup>1</sup>H NMR spectrum of the naphthalene clip NC.

## Self-association of the anthracene clip AC at different temperatures

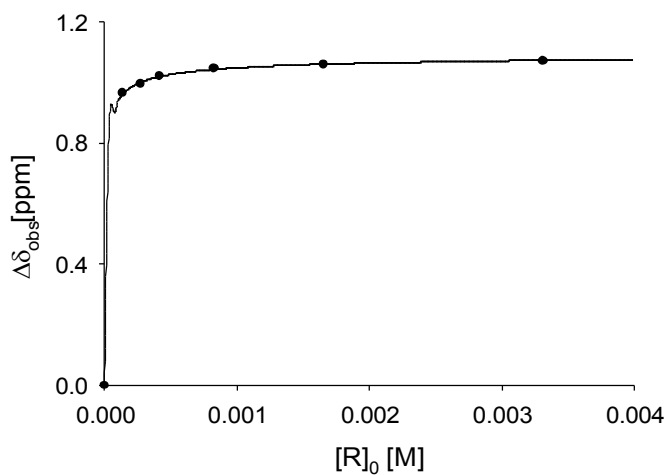
Receptor:	AC	$M_R$ [g/mol]:	742.72
Solvent:	D <sub>2</sub> O	$m_R$ [mg]:	3.69
$T$ [°C]:	25	$V_0$ [mL]:	1.50
Substrat:	Itself (self-association)	$[R]_0$ [mM]:	3.31



$$\delta_0 (H_a) \text{ [ppm]} = 7.7140$$

$$\delta_0 (H_b) \text{ [ppm]} = 8.0915$$

$[R]_0$ [M]	$\delta_{\text{obs}} (H_a)$ [ppm]	$\Delta\delta_{\text{obs}} (H_a)$ [ppm]	$\Delta\delta_{\text{calc}} (H_a)$ [ppm]
0.00331214	6.6431	1.0709	1.0729
0.00165607	6.6535	1.0605	1.0606
0.00082803	6.6669	1.0471	1.0434
0.00041402	6.6914	1.0226	1.0195
0.00027601	6.7189	0.9951	1.0016
0.00013801	6.7500	0.9640	0.9623



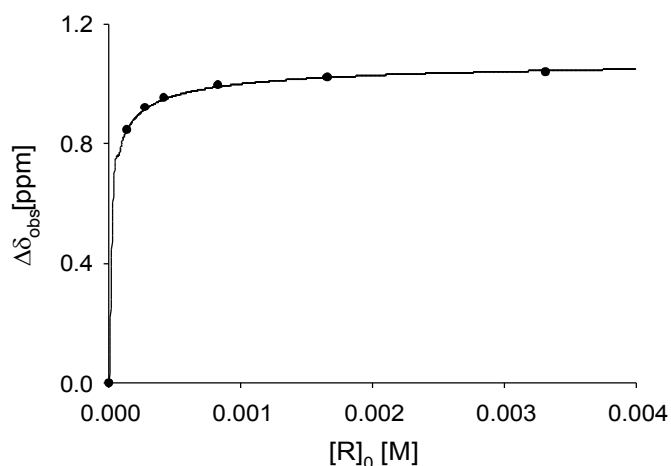
$$K_{\text{dim}} [\text{M}^{-1}] = (1.94 \pm 0.2) \cdot 10^5$$

$$\Delta\delta_{\text{max}} (H_a) \text{ [ppm]} = 1.10$$

$$\Delta\delta_{\text{max}} (H_b) \text{ [ppm]} = 2.26$$

$T$  [°C]: 45

$[R]_0$ [M]	$\delta_{\text{obs}} (H_a)$ [ppm]	$\Delta\delta_{\text{obs}} (H_a)$ [ppm]	$\Delta\delta_{\text{calc}} (H_a)$ [ppm]
0.00331214	6.6756	1.0384	1.0437
0.00165607	6.6936	1.0204	1.0212
0.00082803	6.7197	0.9943	0.9902
0.00041402	6.7621	0.9519	0.9480
0.00027601	6.7936	0.9204	0.9168
0.00013801	6.8692	0.8448	0.8505



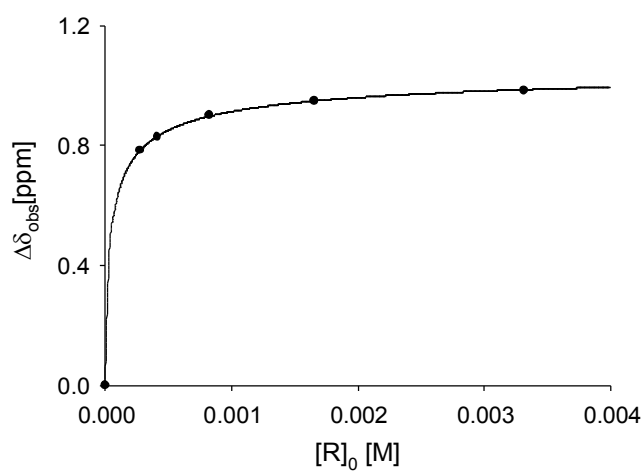
$$K_{\text{dim}} [\text{M}^{-1}] = (5.44 \pm 0.5) \cdot 10^4$$

$$\Delta\delta_{\text{max}} (\text{H}_a) [\text{ppm}] = 1.10$$

$$\Delta\delta_{\text{max}} (\text{H}_b) [\text{ppm}] = 2.33$$

$T [^{\circ}\text{C}]$ : 65

$[\text{R}]_0 [\text{M}]$	$\delta_{\text{obs}} (\text{H}_a) [\text{ppm}]$	$\Delta\delta_{\text{obs}} (\text{H}_a) [\text{ppm}]$	$\Delta\delta_{\text{calc}} (\text{H}_a) [\text{ppm}]$
0.00331214	6.7289	0.9851	0.9864
0.00165607	6.7650	0.9490	0.9488
0.00082803	6.8125	0.9015	0.8982
0.00041402	6.8858	0.8282	0.8313
0.00027601	6.9295	0.7845	0.7836
0.00331214	6.7289	0.9851	0.9864



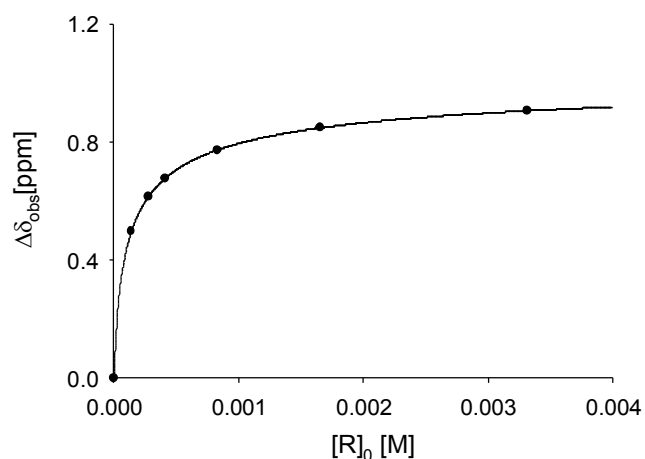
$$K_{\text{dim}} [\text{M}^{-1}] = (1.71 \pm 0.2) \cdot 10^4$$

$$\Delta\delta_{\text{max}} (\text{H}_a) [\text{ppm}] = 1.08$$

$$\Delta\delta_{\text{max}} (\text{H}_b) [\text{ppm}] = 2.34$$

$T [^{\circ}\text{C}]$ : 85

$[\text{R}]_0 [\text{M}]$	$\delta_{\text{obs}} (\text{H}_a) [\text{ppm}]$	$\Delta\delta_{\text{obs}} (\text{H}_a) [\text{ppm}]$	$\Delta\delta_{\text{calc}} (\text{H}_a) [\text{ppm}]$
0.00331214	6.8072	0.9068	0.9066
0.00165607	6.8642	0.8498	0.8489
0.00082803	6.9406	0.7734	0.7737
0.00041402	7.0364	0.6776	0.6794
0.00027601	7.0986	0.6154	0.6157



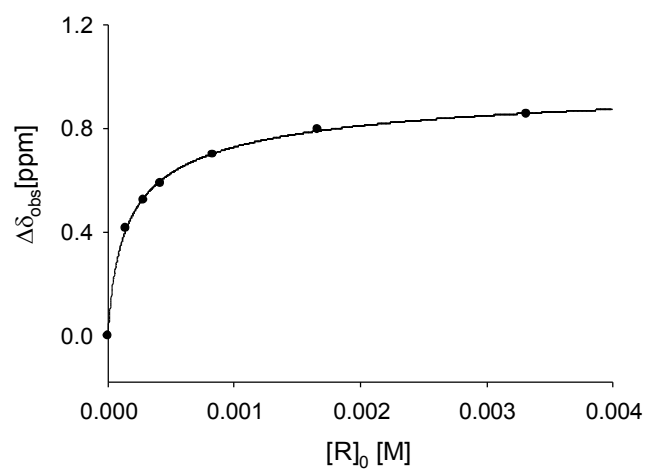
$$K_{\text{dim}} [\text{M}^{-1}] = (5.91 \pm 0.6) \cdot 10^3$$

$$\Delta\delta_{\text{max}} (\text{H}_a) [\text{ppm}] = 1.06$$

$$\Delta\delta_{\text{max}} (\text{H}_b) [\text{ppm}] = 2.32$$

$T$  [°C]: 95

$[R]_0$ [M]	$\delta_{\text{obs}} (\text{H}_a)$ [ppm]	$\Delta\delta_{\text{obs}} (\text{H}_a)$ [ppm]	$\Delta\delta_{\text{calc}} (\text{H}_a)$ [ppm]
0.00331214	6.8588	0.8552	0.8565
0.00165607	6.9179	0.7961	0.7882
0.00082803	7.0147	0.6993	0.7014
0.00041402	7.1260	0.5880	0.5962
0.00027601	7.1915	0.5225	0.5275



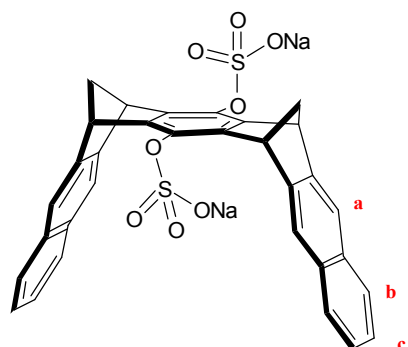
$$K_{\text{dim}} [\text{M}^{-1}] = (3.70 \pm 0.4) \cdot 10^3$$

$$\Delta\delta_{\text{max}} (\text{H}_a) [\text{ppm}] = 1.05$$

$$\Delta\delta_{\text{max}} (\text{H}_b) [\text{ppm}] = 2.31$$

## Self-association of the naphthalene clip NC at 25°C

Receptor:	NC	$M_R$ [g/mol]:	642.61
Solvent:	D <sub>2</sub> O	$m_R$ [mg]:	9.70
$T$ [°C]:	25	$V_0$ [mL]:	1.50
Substrat:	Itself (self-association)	$[R]_0$ [mM]:	10.07

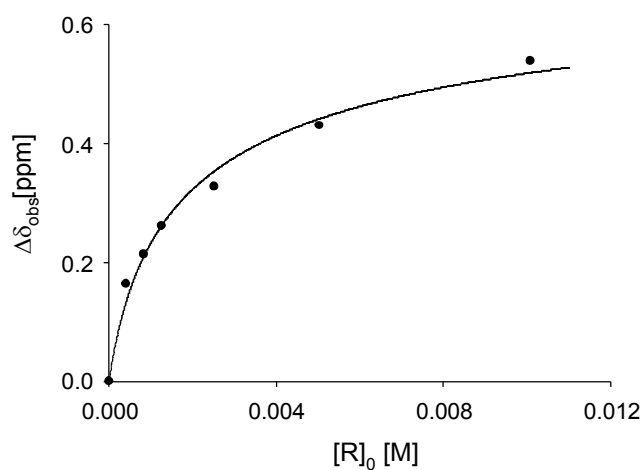


$$\delta_0(\text{H}_a) [\text{ppm}] = 7.8132$$

$$\delta_0(\text{H}_b) [\text{ppm}] = 7.7919$$

$$\delta_0(\text{H}_c) [\text{ppm}] = 7.4324$$

$[R]_0$ [M]	$\delta_{\text{obs}}(\text{H}_b)$ [ppm]	$\Delta\delta_{\text{obs}}(\text{H}_b)$ [ppm]	$\Delta\delta_{\text{calc}}(\text{H}_b)$ [ppm]
0.01475	7.2525	0.5394	0.5195
0.007377	7.3612	0.4307	0.4421
0.003688	7.4640	0.3279	0.3541
0.001844	7.5303	0.2616	0.2626
0.000922	7.5777	0.2142	0.2117
0.0004611	7.6630	0.1502	0.1170



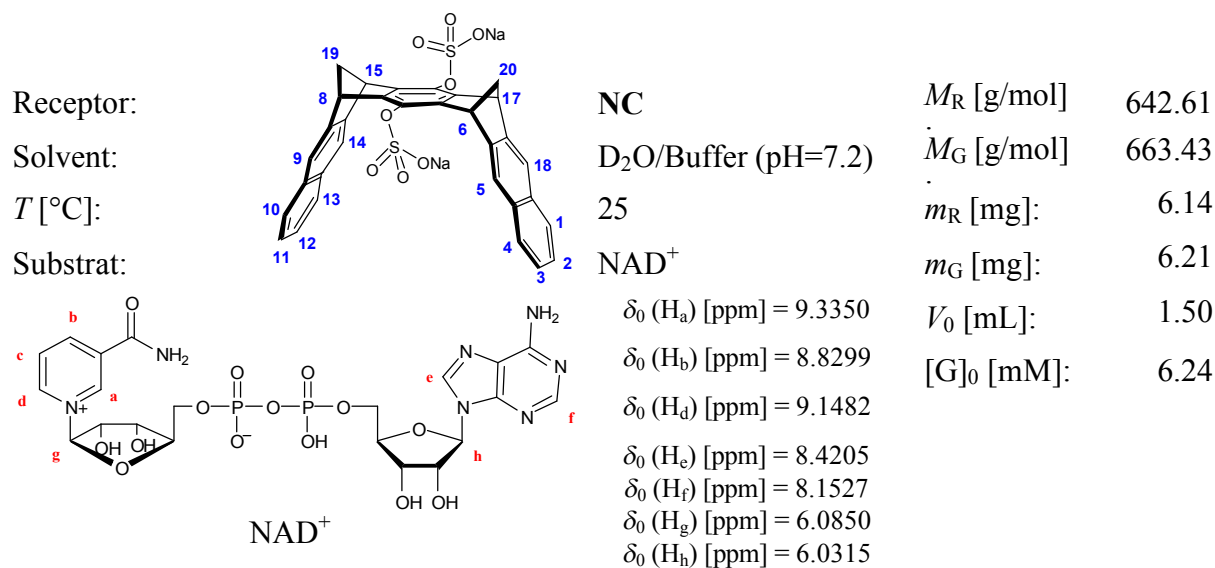
$$K_{\text{dim}} [\text{M}^{-1}] = 310 \pm 30$$

$$\Delta\delta_{\text{max}}(\text{H}_a) [\text{ppm}] = 0.60$$

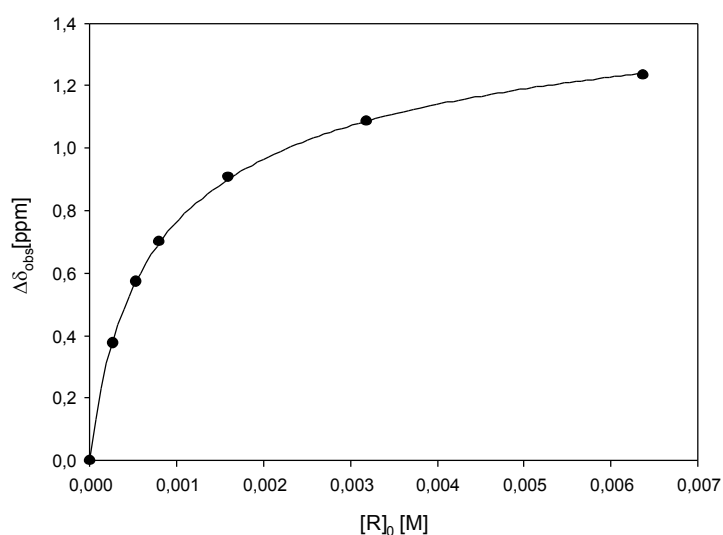
$$\Delta\delta_{\text{max}}(\text{H}_b) [\text{ppm}] = 0.77$$

$$\Delta\delta_{\text{max}}(\text{H}_c) [\text{ppm}] = 0.63$$

## Binding of NAD<sup>+</sup> by the naphthalene clip NC at 25°C



[R] <sub>0</sub> [M]	[G] <sub>0</sub> [M]	$\delta_{\text{obs}}$ (H <sub>b</sub> ) [ppm]	$\Delta\delta_{\text{obs}}$ (H <sub>b</sub> ) [ppm]	$\Delta\delta_{\text{calc}}$ (H <sub>b</sub> ) [ppm]
0.006370	0.00842	7.5960	1.2339	1,2386
0.003185	0.00470	7.7440	1.0859	1,0859
0.001592	0.00235	7.9224	0.9075	0,9004
0.000796	0.00118	8.1292	0.7007	0,6951
0.000531	0.00079	8.2566	0.5733	0,5747
0.000265	0.00039	8.4536	0.3763	0,3860



$K_a$  [M<sup>-1</sup>] = 1200 ± 30  
 $\Delta\delta_{\text{max}}$  (H<sub>a</sub>) [ppm] = 0.95  
 $\Delta\delta_{\text{max}}$  (H<sub>b</sub>) [ppm] = 2.06  
 $\Delta\delta_{\text{max}}$  (H<sub>c</sub>) [ppm] = 2.89  
 $\Delta\delta_{\text{max}}$  (H<sub>d</sub>) [ppm] = 1.55  
 $\Delta\delta_{\text{max}}$  (H<sub>e</sub>) [ppm] = 0.22  
 $\Delta\delta_{\text{max}}$  (H<sub>f</sub>) [ppm] = 0.36  
 $\Delta\delta_{\text{max}}$  (H<sub>g</sub>) [ppm] = 0.22  
 $\Delta\delta_{\text{max}}$  (H<sub>h</sub>) [ppm] = 0.37

NAD<sup>+</sup>•NC <sup>1</sup>H NMR (500MHz, D<sub>2</sub>O/Buffer)  $\delta$ [ppm]: 2.47 (dd, 2H, H-19a+H-20a), 2.70 (d, 2H, H-19i+H-20i), 4.74 (s, 4H, H-6+H-8+H-15+H-17), 5.66 (d, 1H, NAD<sup>+</sup>, H<sub>h</sub>), 5.87 (d, 1H, NAD<sup>+</sup>, H<sub>g</sub>), 6.91 (dd, 4H, H-2+H-3+H-12+H-11), 7.08 (dd, 4H, H-1+H-4+H-10+H-13), 6.77 (d, 1H, NAD<sup>+</sup>, H<sub>b</sub>), 7.30 (s, 4H, H-5+H-9+H-14+H-18), 7.79 (s, 1H, NAD<sup>+</sup>, H<sub>f</sub>), 7.60 (d, 1H, NAD<sup>+</sup>, H<sub>d</sub>), 8.18 (s, 1H, NAD<sup>+</sup>, H<sub>e</sub>), 8.38 (s, 1H, NAD<sup>+</sup>, H<sub>a</sub>)