

## *Supporting Information*

### **Molecular Inclusion of Organometallic Sandwich Complexes within Hybrid Cavitand-resorcin[4]arene Receptors**

María Ángeles Sarmentero<sup>a</sup> and Pablo Ballester,<sup>a,b\*</sup>

<sup>a</sup>Institute of Chemical Research of Catalonia (ICIQ), 43007 Tarragona (Spain).

<sup>b</sup>Institució Catalana de Recerca i Estudis Avançats (ICREA), Pg. Lluís Companys  
23, 08010 Barcelona (Spain).

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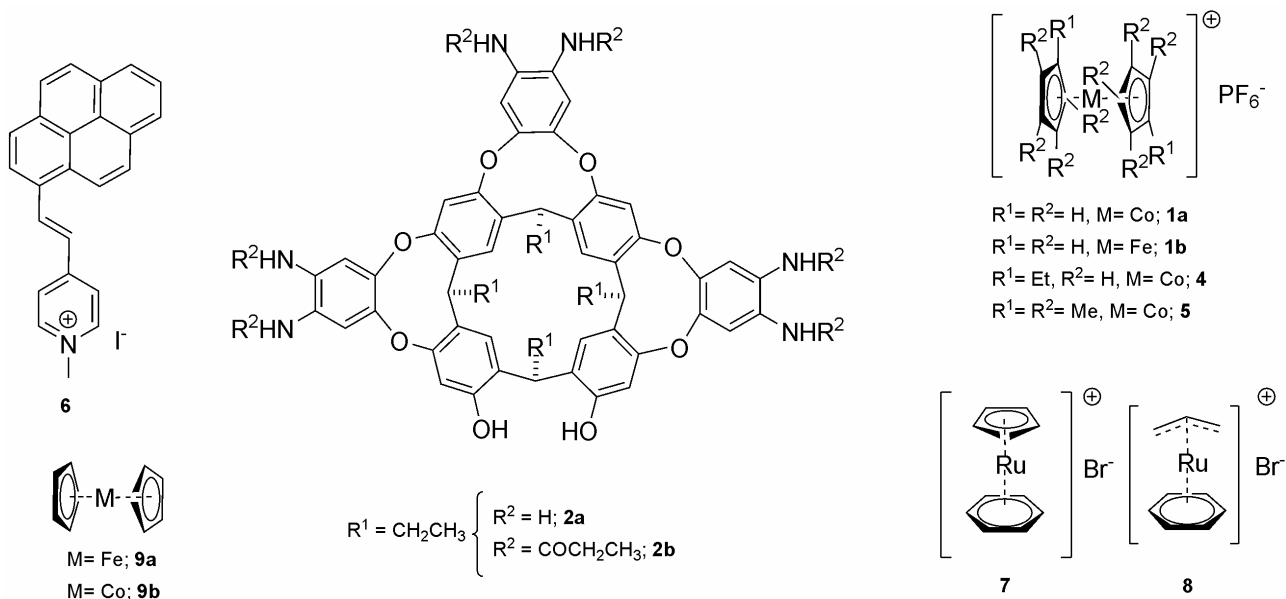
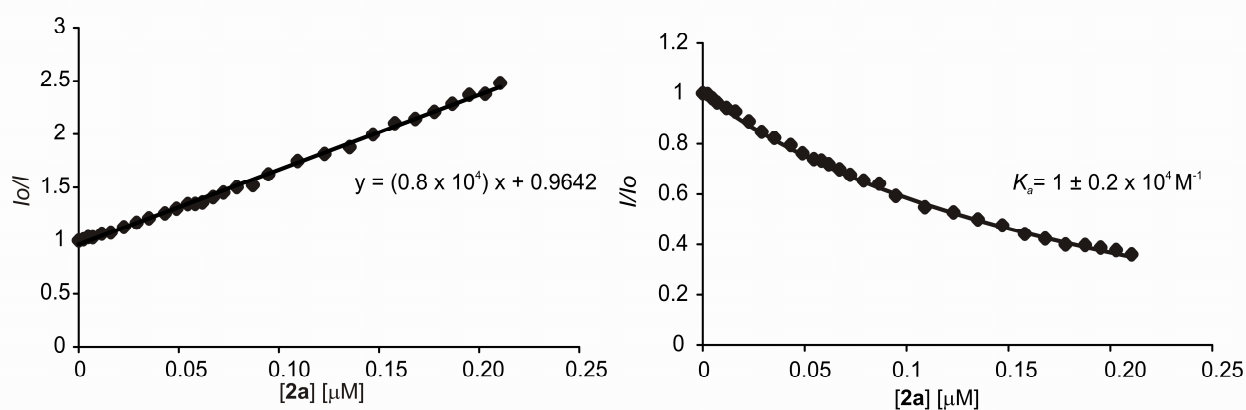
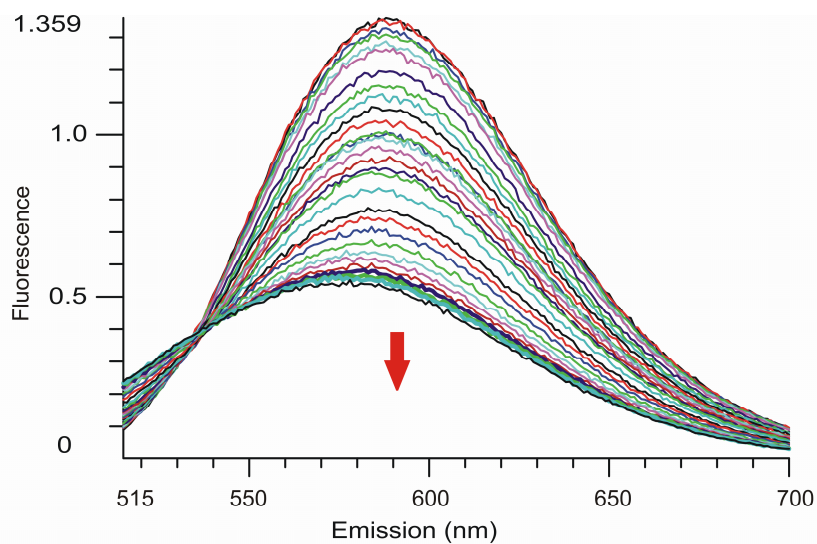
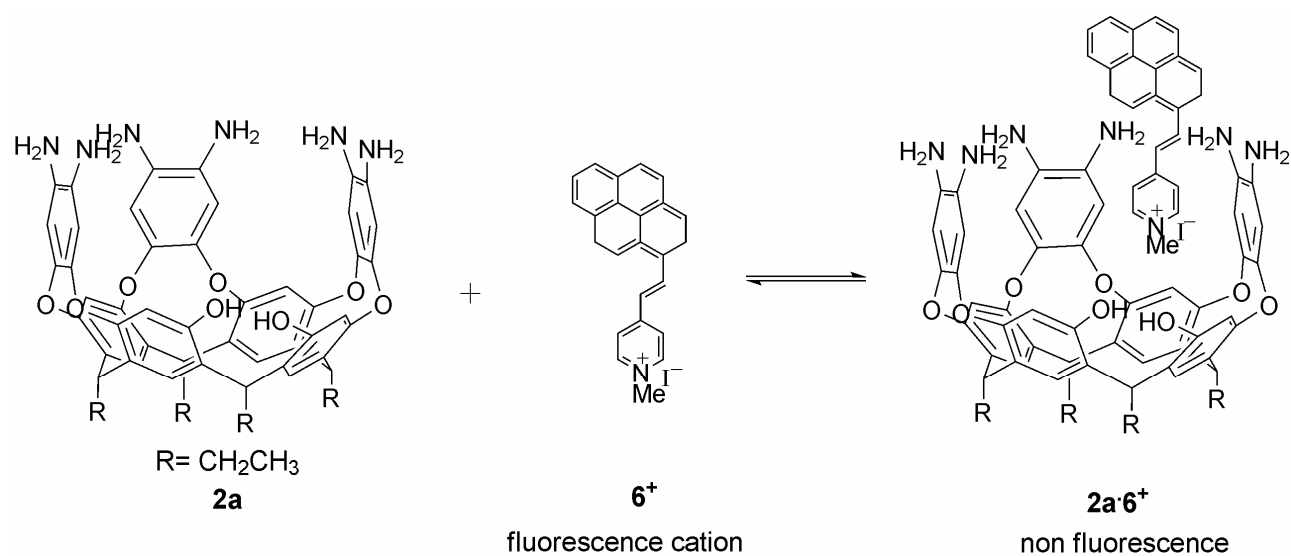
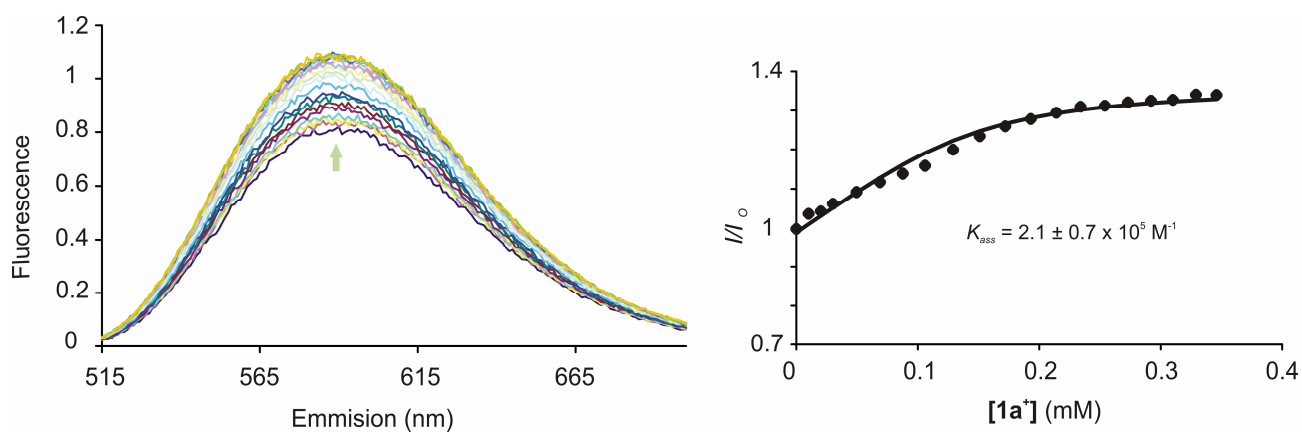
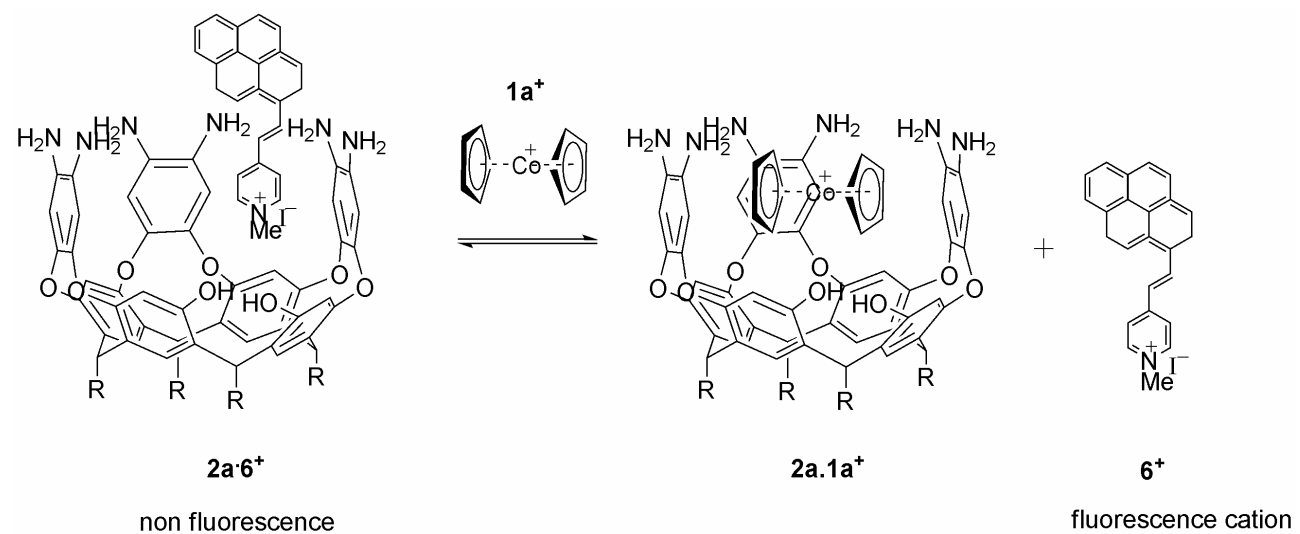


Figure S1. Structure of substrates and the receptors **2a-b**.

## Fluorescence titrations

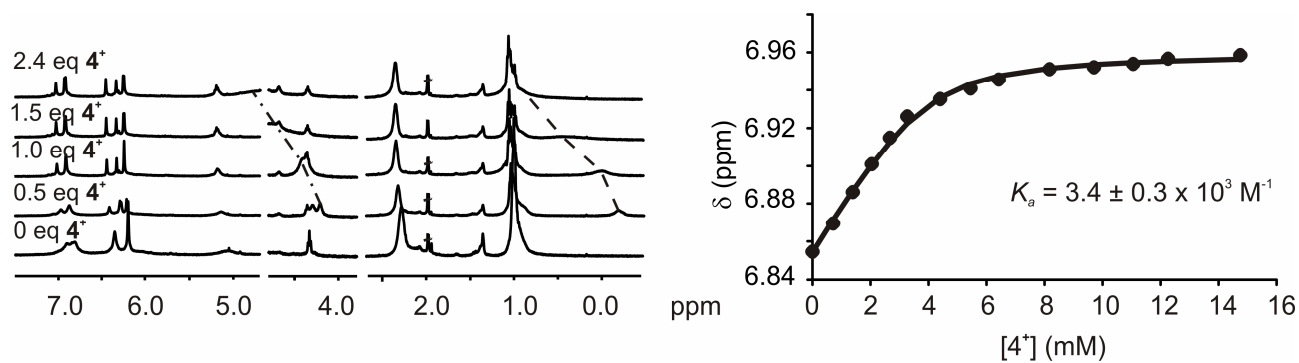


**Figure S2.** : Fluorescence titration of **6<sup>+</sup>** ( $8.25 \times 10^{-6} \text{ M}$ ) in MeOH upon addition of incremental amounts of **2a**.



**Figure S3.** : Fluorescence titrations of  $6^+$  (0.24 mM) in MeOH in the presence of  $2a$  (0.15 mM) and upon addition of incremental amounts of  $1a^+$ .

### $^1H$ NMR titrations



**Figure S4.** : NMR titration of  $2a$  ( $[2a]= 4.48$  mM) with  $4^+$  in MeOH- $d_4$ .

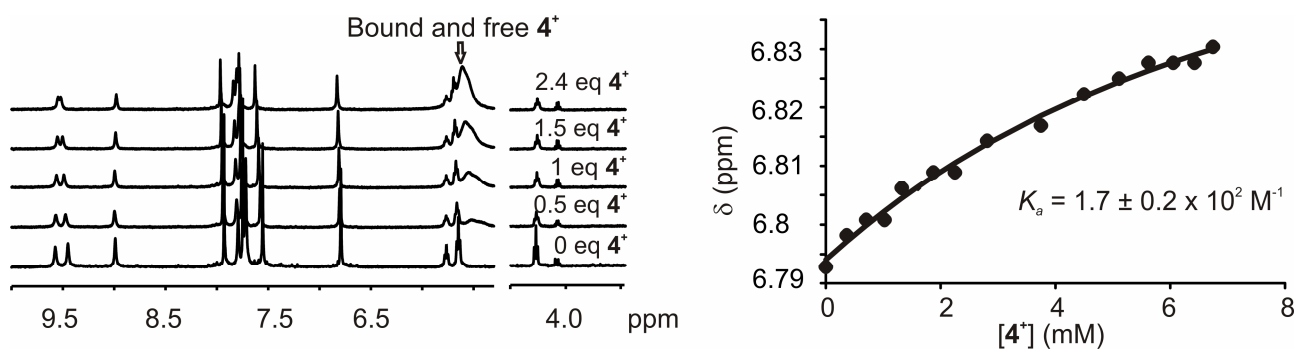


Figure S5. : NMR titration of **2b** ( $[2b]=2.80 \text{ mM}$ ) with  $4^+$  in acetone- $d_6$ .

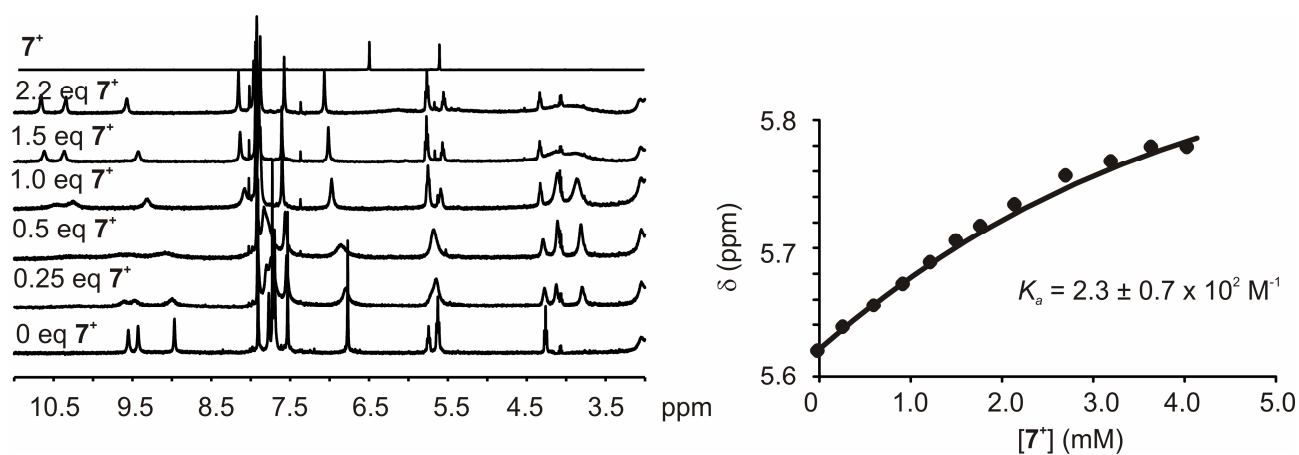


Figure S6. : NMR titration of **2b** ( $[2b]=2.64 \text{ mM}$ ) with  $7^+$  in acetone- $d_6$ .

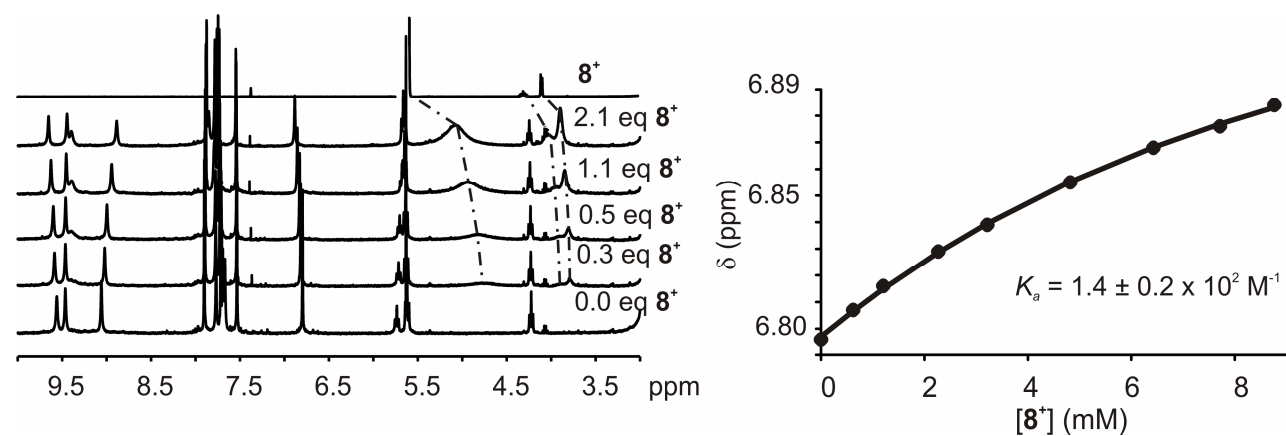
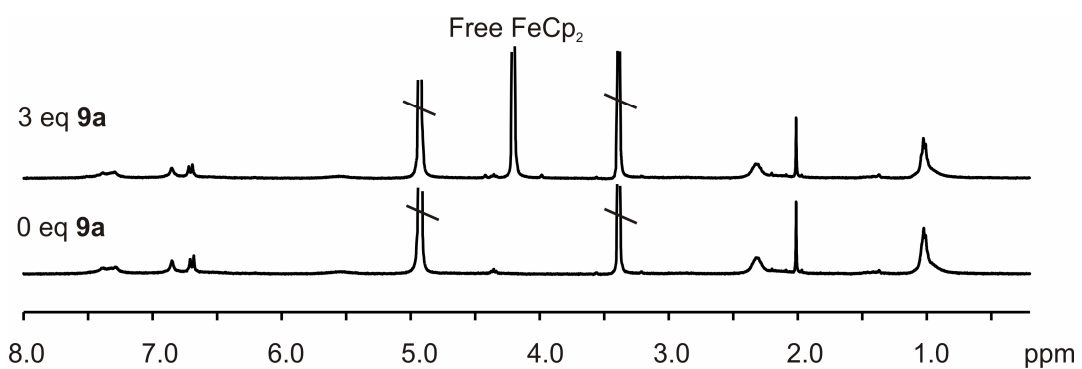
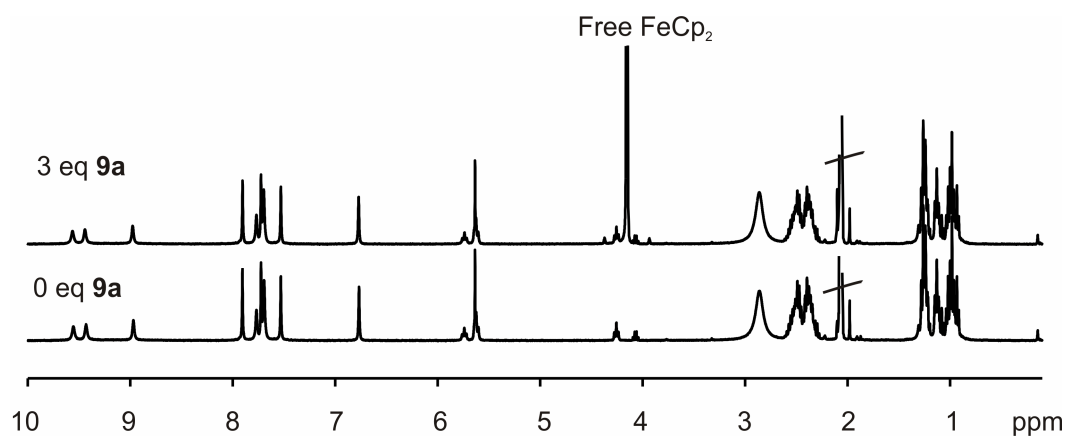


Figure S7. : NMR titration of **2b** ( $[2b]=4.20 \text{ mM}$ ) with  $8^+$  in acetone- $d_6$ .

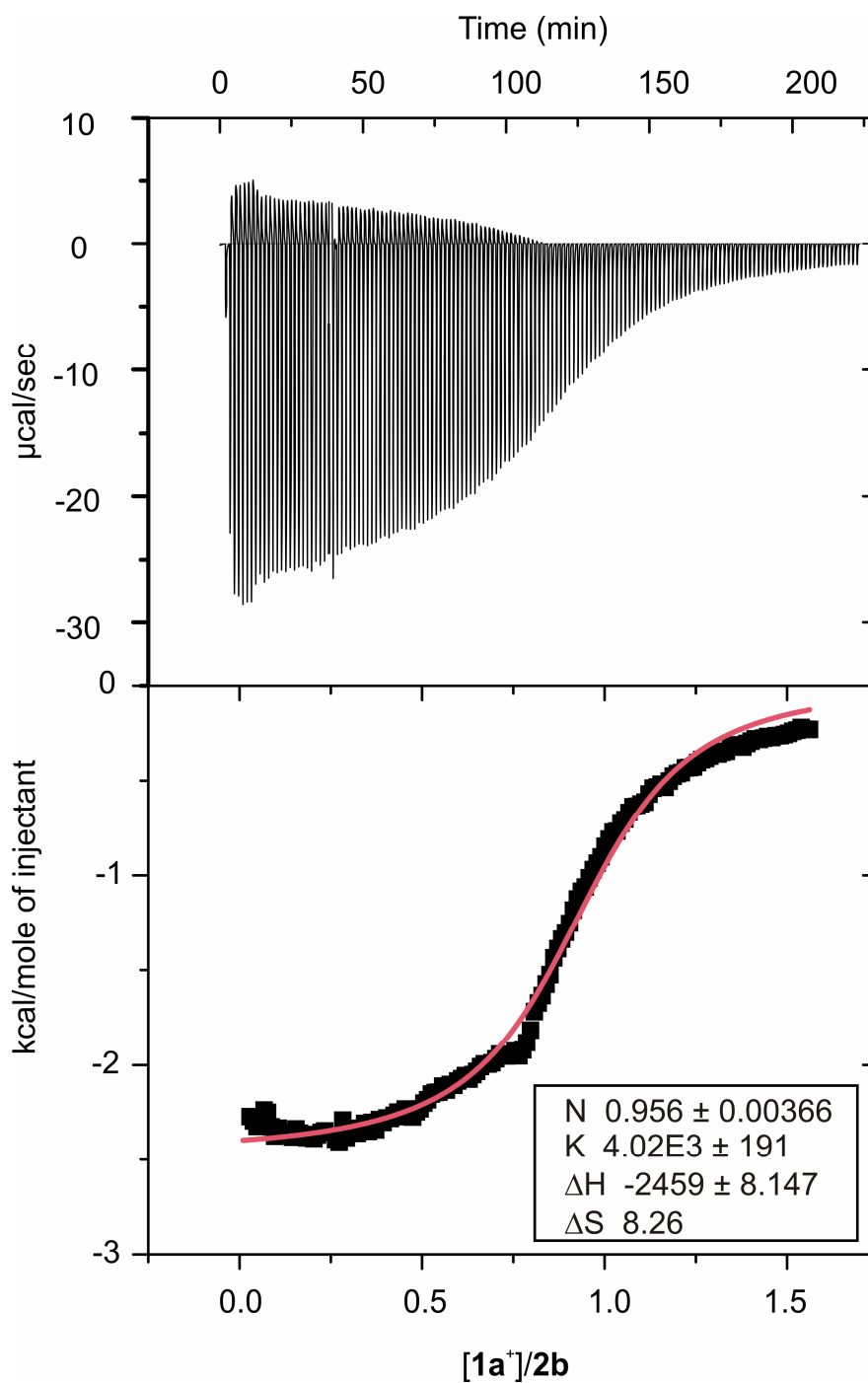


**Figure S8.** : NMR spectra of **2a** ( $[\mathbf{2a}] = 2.50 \text{ mM}$ ) and **2a** with 3 equivalents of **9a** in  $\text{MeOH-}d_4$ .



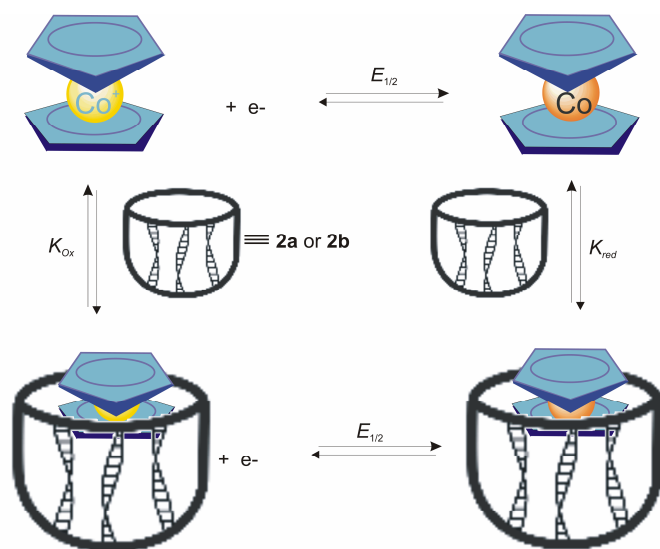
**Figure S9.** : NMR spectra of **2b** ( $[\mathbf{2b}] = 4.50 \text{ mM}$ ) and **2b** with 3 equivalents of **9a** in  $\text{acetone-}d_6$ .

### ITC titration.

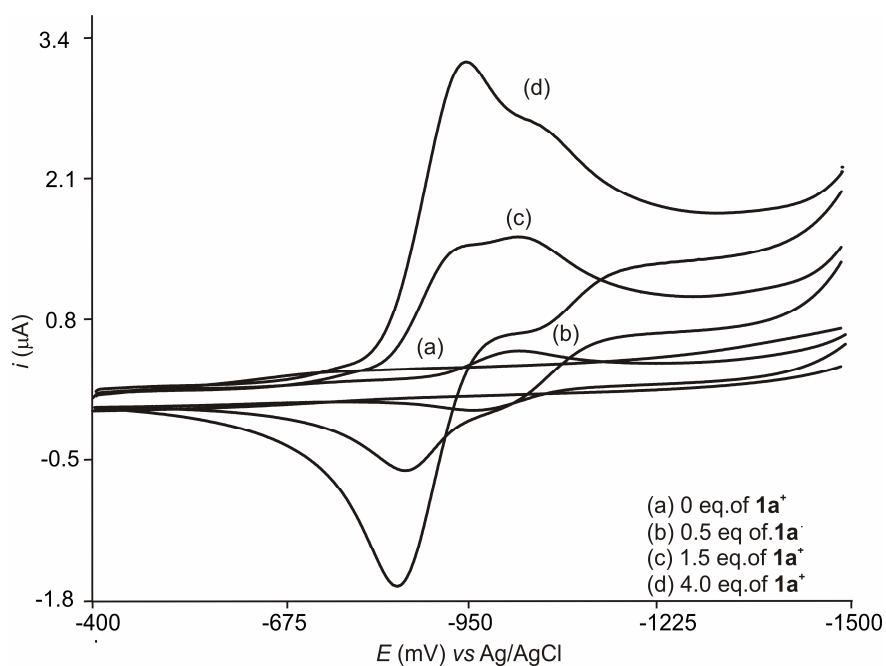


**Figure S10:** Calorimetric titration between the receptor or **2b** ( $[\mathbf{2b}] = 10 \text{ mM}$  in acetone) and  $\mathbf{1a}^+$  seven times more concentrated than the corresponding receptor.

## Cyclic voltammetry



**Scheme S1:** Coupled electrochemical and chemical equilibria for the cobaltocenium  $1a^+$  forming supramolecular complexes with non-electroactive hosts  $2a$  or  $2b$ .



**Figure S11.** : Cyclic voltammetric behavior on glass carbon ( $0.071 \text{ cm}^2$ ) of 1.0 mM  $2b$  in acetone also containing 0.1 M tetraoctylammonium bromide (a) and after each addition ( (b) 0.5 (c) 1.5 (d), 4.0 eq) of cobaltocenium  $1a^+$ . Scan rate 100 mV/s.



## Diffusion coefficients

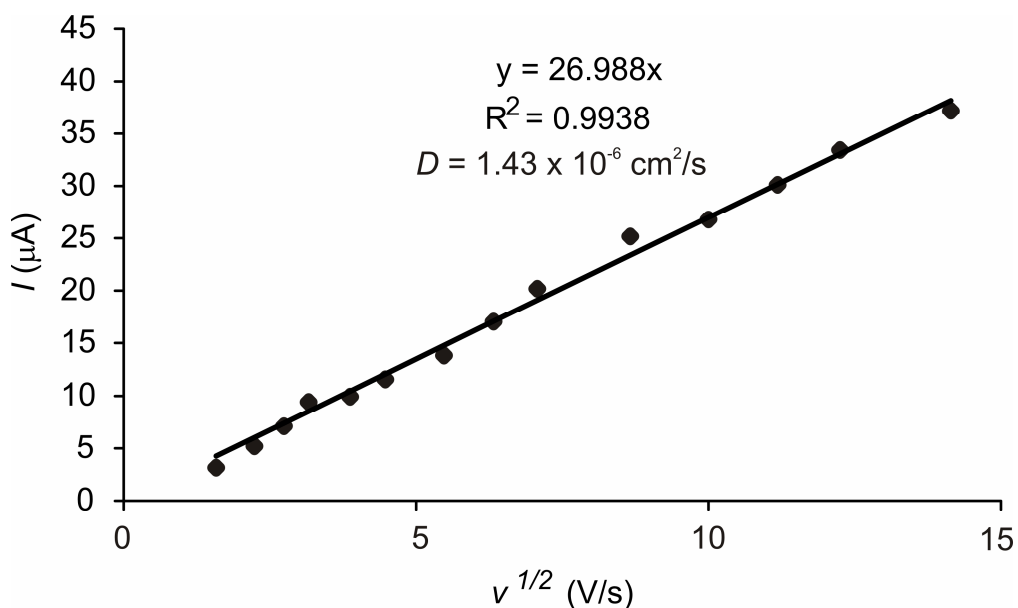


Figure S12: Representation of  $I$  vs  $v^{1/2}$  of a 1.0 mM solution of  $1\text{a}^+$ .

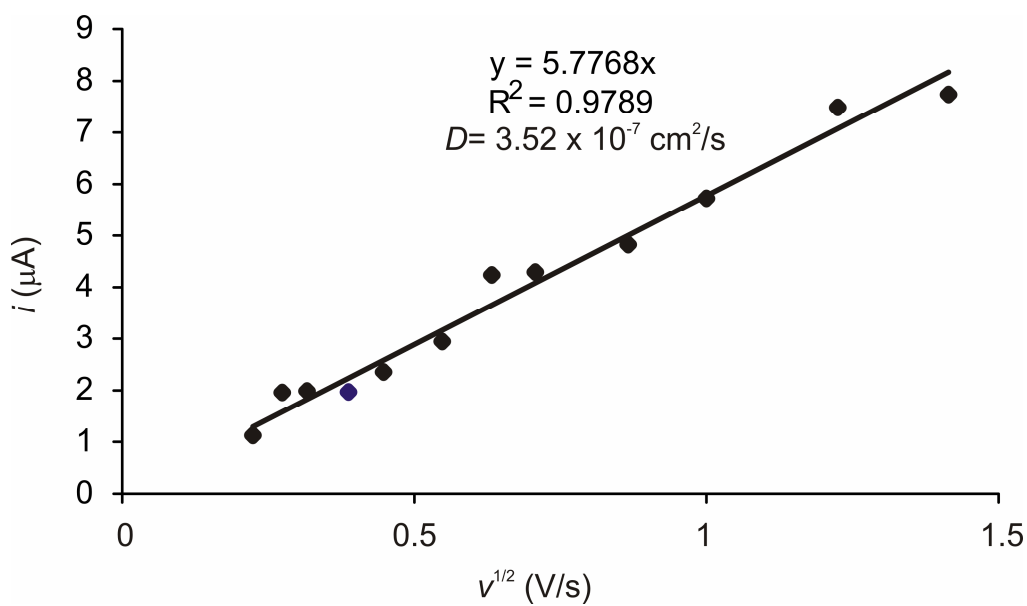


Figure S13: Representation of  $I$  vs  $v^{1/2}$  of a 1.0 mM solution of  $1\text{a}^+$  with 2 equivalents of  $2\text{a}$ .