Supporting Information

β-Cyclodextrin Supramolecular Recognition of *bis*-Cationic Dithienylethenes

Giulio Bianchini,[a] Mattia Bazan,[a] Fabrizio Fabris,[a] Alessandro Scarso[a,*]

a) Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, via Torino 155, 30172 Mestre Venezia, Italy. E-mail: alesca@unive.it; Fax: +39-041-234-8517; Tel: +39-041-234-8569.

Experimental section.

Figure S1. Cyclodextrin recognition of photochrome 1o. **A**) 1o (7.00·10-3 M) + **β-CD** (7.00·10-3 M) in D2O; **B) β-CD** (7.00·10-3 M) in D2O; **C) 1o** (7.00·10-3 M) in D2O.

Figure S2. Cyclodextrin recognition of photochrome 1c. **A) 1c** (7.00·10-3 M) + **β-CD** (7.00·10-3 M) in D2O; **B) β-CD** (7.00·10-3 M) in D2O; **C) 1c** (7.00·10-3 M) in D2O., ^{1}H-NMR spectra.

Figure S3. Cyclodextrin recognition of photochrome 2o. **A) 2o** (7.00·10-3 M) + **β-CD** (7.00·10-3 M) in D2O; **B) β-CD** (7.00·10-3 M) in D2O; **C) 2o** (7.00·10-3 M) in D2O., ^{1}H-NMR spectra.

Figure S4. Cyclodextrin recognition of photochrome 2c. **A) 2c** (7.00·10-3 M) + **β-CD** (7.00·10-3 M) in D2O; **B) β-CD** (7.00·10-3 M) in D2O; **C) 2c** (7.00·10-3 M) in D2O., ^{1}H-NMR spectra.

Figure S5. Proton d *area* expansion of NOESY 1H-NMR ^{of} 1o **(**7.00·10-3 M) + **β-CD** (7.00·10-2 M) in D2O.

Figure S6. Proton c *area* expansion of NOESY 1H-NMR ^{of} 1o **(**7.00·10-3 M) + **β-CD** (7.00·10-2 M) in D2O.

Figure S7. Proton d' *area* expansion of NOESY 1H-NMR ^{of} 2o **(**7.00·10-3 M) + **β-CD** (7.00·10-2 M) in D2O.

Table S1**.** Diffusion coefficients for **β-CD**, **1o**, **1c** and their inclusion complexes **1o@β-CD**, **1c@β-CD** determined by ^{1}H-NMR DOSY.

Figure S8. DOSY: **1o** ($7.00\cdot10^{-3}$ M) + **β-CD** ($7.00\cdot10^{-3}$ M) diffusing at the same rate in D_2O.

Figure S9. DOSY: **1c** ($7.00\cdot10^{-3}$ M) + **β-CD** ($7.00\cdot10^{-3}$ M) diffusing at the same rate in D_2O.

Table S2. DOSY: **1c** ($7.00\cdot10^{-3}$ M) + **β-CD** ($7.00\cdot10^{-3}$ M) diffusing at the same rate in D_2O.

Figure S10. DOSY: **2o** ($7.00\cdot10^{-3}$ M) + **β-CD** ($7.00\cdot10^{-3}$ M) diffusing at the same rate in D_2O.

Figure S11. DOSY: **2c** ($7.00\cdot10^{-3}$ M) + **β-CD** ($7.00\cdot10^{-3}$ M) diffusing at the same rate in D_2O.

Figure S12. Cyclodextrin recognition of photochrome **1o** and **1c,** $^{19F\text{-}NMR.}$ A) **1o** (7.00·10-3 M) + **β-CD** (7.00·10-3 M) in D2O; **B) 1c** (7.00·10-3 M) + **β-CD** (7.00·10-3 M) in D2O; **C) 1o** (7.00·10-3 M) in D2O; **D) 1c** (7.00·10-3 M) in D2O.

Table S3. **1o@*β*-*CD*** Job's plot data and data treatment.

Table S4. **1c@*β*-*CD*** Job's plot data and data treatment.

Experimental section.

^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ^{1}H-NMR DOSY and NOESY ^{1}H-NMR were recorded at 298 K with a Bruker 400 spectrometer. ^{1}H-NMR DOSY spectra were recorded using 15 increments of gradient field strength from 2000 to 25000 G·cm^{-1}, 2 ms diffusion gradient length and 100 ms diffusion delay. NOESY ^{1}H-NMR spectra were recorded using 500 ms mixing time.

Solvents and reactants were used as purchased; otherwise, they were purified as reported in W. L. F. Armarego, C. L. L. Chai *Purification of Laboratory Chemicals*, 5rd Ed., **2003**, Elsevier, ISBN: 978-0-7506-7571-0. Compounds **1** and **2** were synthesized as reported by Lehn, J. M et al. *Chem. Eur. J.* **1995**, *5*, 275-284 and by Strukul, G. et al. *Chem. Commun.* **2013**, *49*, 5322-5324, Pace T. C. S., Müller V., S. Li, Lincoln P., Andréasson J., Enantioselective cyclization of photochromic dithienylethenes bound to DNA, *Angew. Chem. Int. Ed.* **2013**, *52*, 4393 –4396; Li Z., Davidson-Rozenfeld G., Vàzquez-Gonzàlez M., Fadeev M., Zhang J., Tian H., Willner I., Reversible Modulation of DNA-Based Hydrogel Shapes by Internal Stress Interactions, *J. Am. Chem. Soc*. 2018, *140*, 17691−17701; Yao X., Li T., Wang S., Ma X., Tian H., A photochromic supramolecular polymer based on bis-p-sulfonatocalix [4] arene recognition in aqueous solution, *Chem. Commun.* **2014**, *50*, 7166-7168.

Irradiation at 365 nm was performed with a Wood lamp, omnilux 25 W, irradiance at 365 nm 10 W/m^2 (10 cm) while irradiation at 254 nm was performed with the low-pressure Hg lamp commonly used for the visualization of TLC plates (12 W).

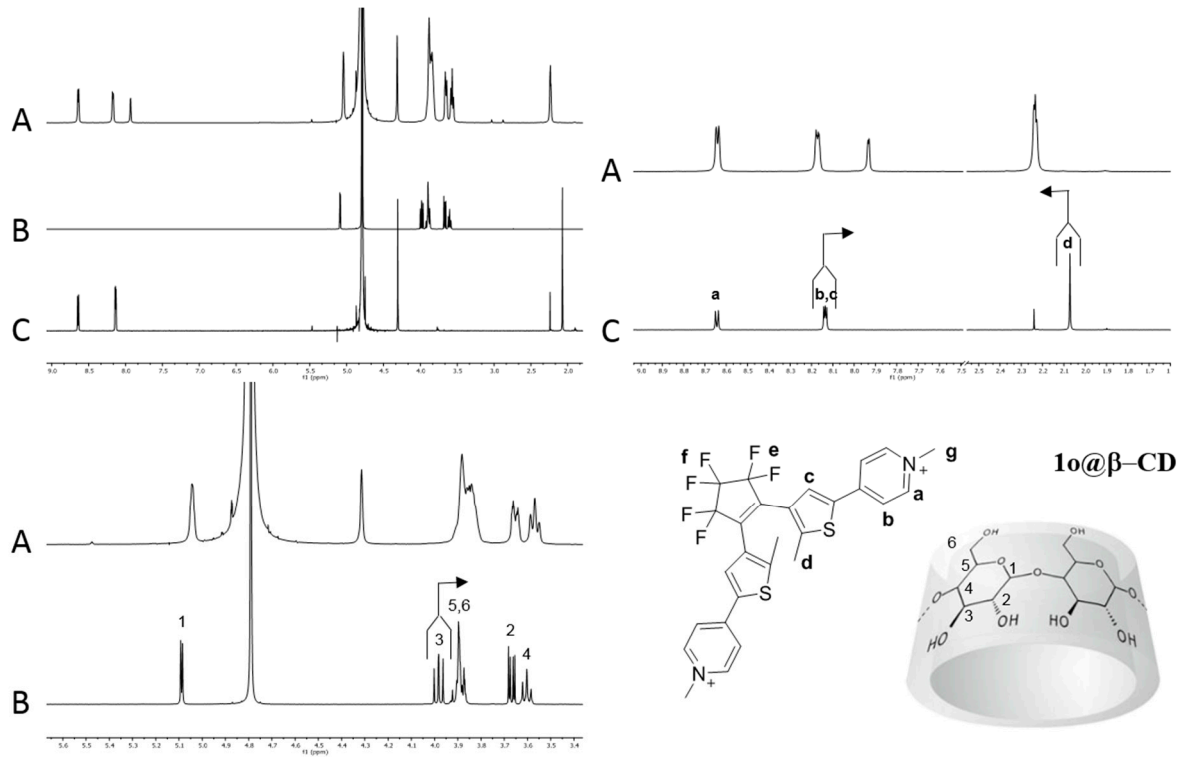

Figure S1. Cyclodextrin recognition of photochrome **1o**. **A) 1o** (7.00·10^{-3} M) + ***β*-CD** (7.00·10^{-3} M) in D_2O; **B) *β*-CD** (7.00·10^{-3} M) in D_2O; **C) 1o** (7.00·10^{-3} M) in D_2O.

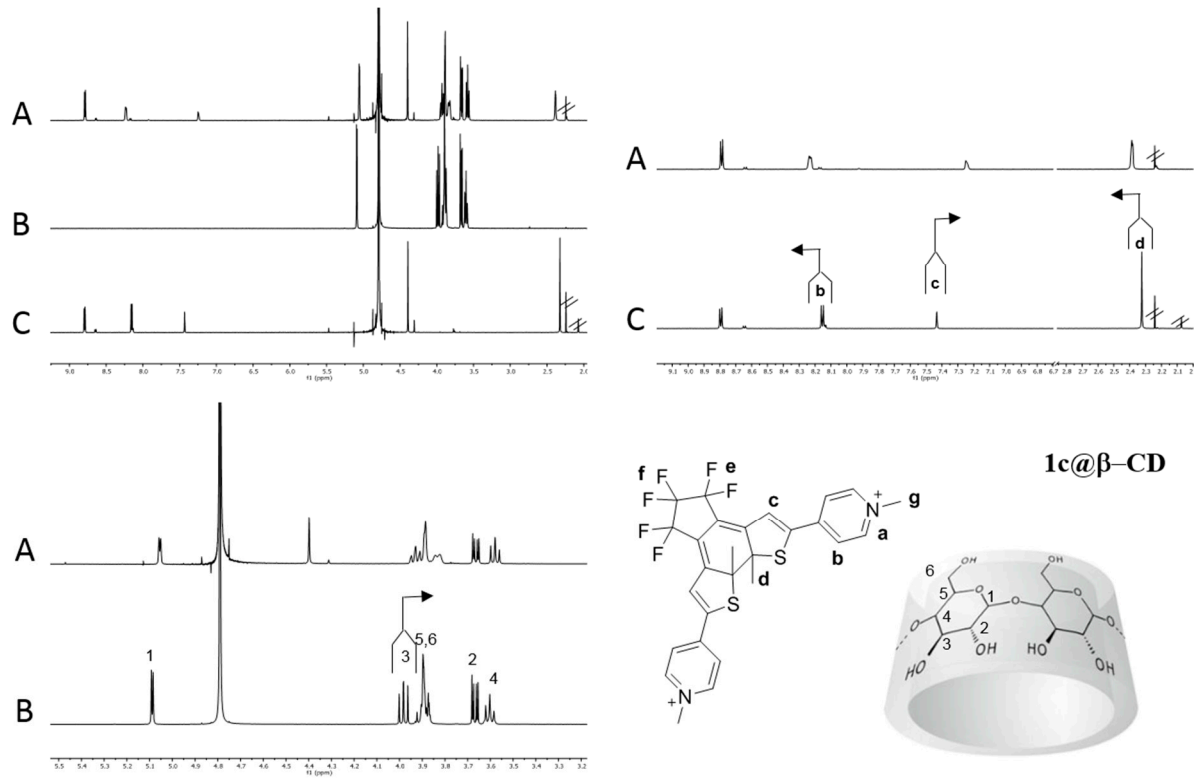

Figure S2. Cyclodextrin recognition of photochrome **1c**. **A) 1c** ($7.00 \cdot 10^{-3}$ M) + ***β*-CD** ($7.00 \cdot 10^{-3}$ M) in D_2O; **B) *β*-CD** ($7.00 \cdot 10^{-3}$ M) in D_2O; **C) 1c** ($7.00 \cdot 10^{-3}$ M) in D_2O.

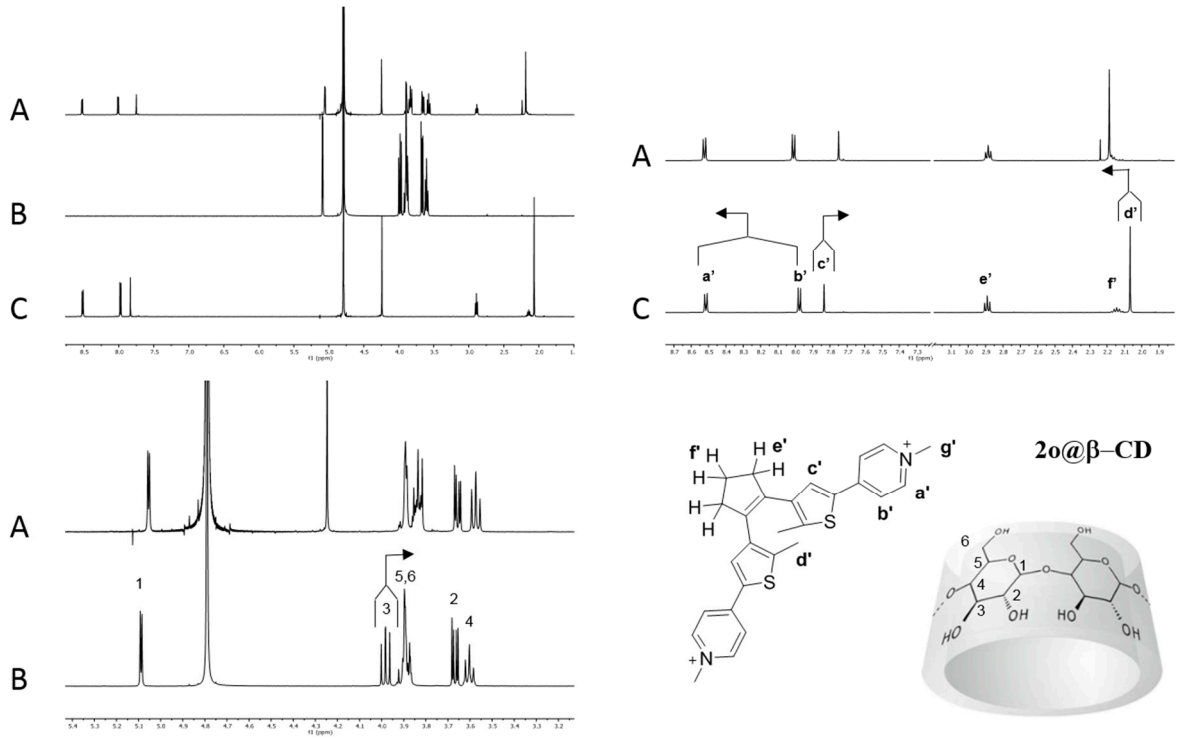

Figure S3. Cyclodextrin recognition of photochrome **2o**. **A) 2o** ($7.00 \cdot 10^{-3}$ M) + ***β*-CD** ($7.00 \cdot 10^{-3}$ M) in D_2O; **B) *β*-CD** ($7.00 \cdot 10^{-3}$ M) in D_2O; **C) 2o** ($7.00 \cdot 10^{-3}$ M) in D_2O.

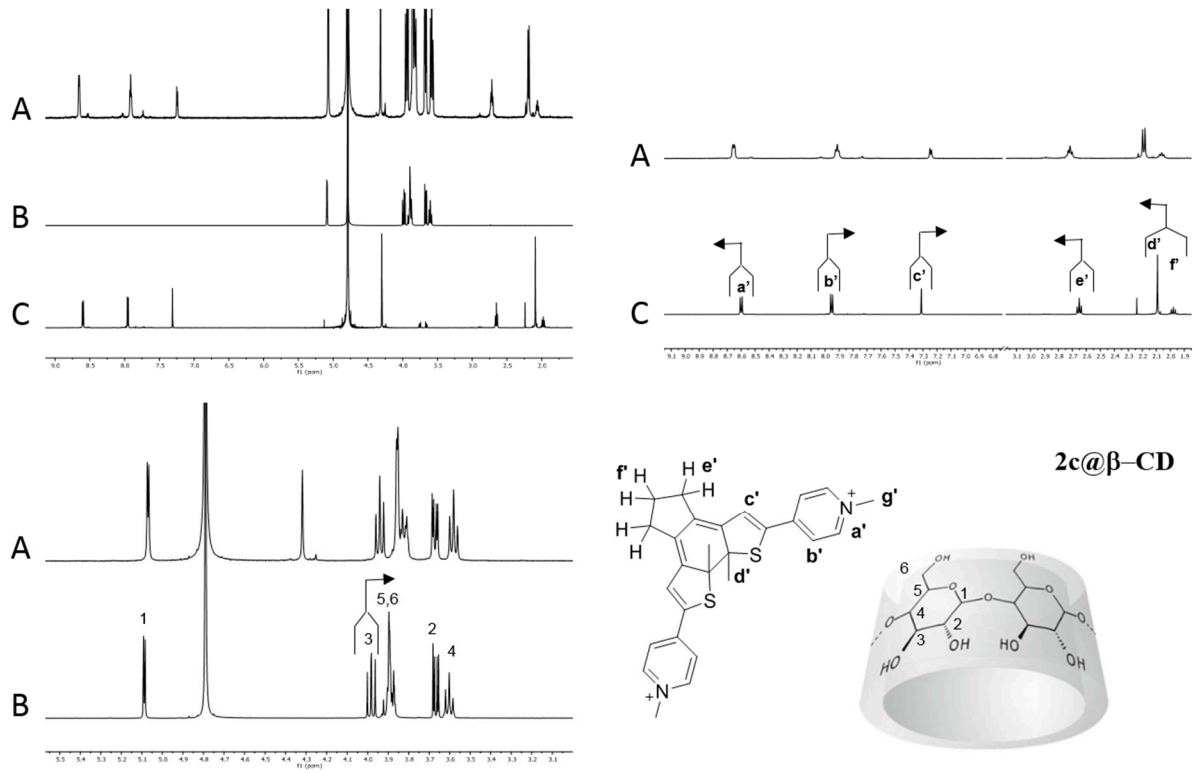

Figure S4. Cyclodextrin recognition of photochrome **2c**. **A) 2c** ($7.00\cdot10^{-3}$ M) + ***β*-CD** ($7.00\cdot10^{-3}$ M) in D_2O; **B) *β*-CD** ($7.00\cdot10^{-3}$ M) in D_2O; **C) 2c** ($7.00\cdot10^{-3}$ M) in D_2O.

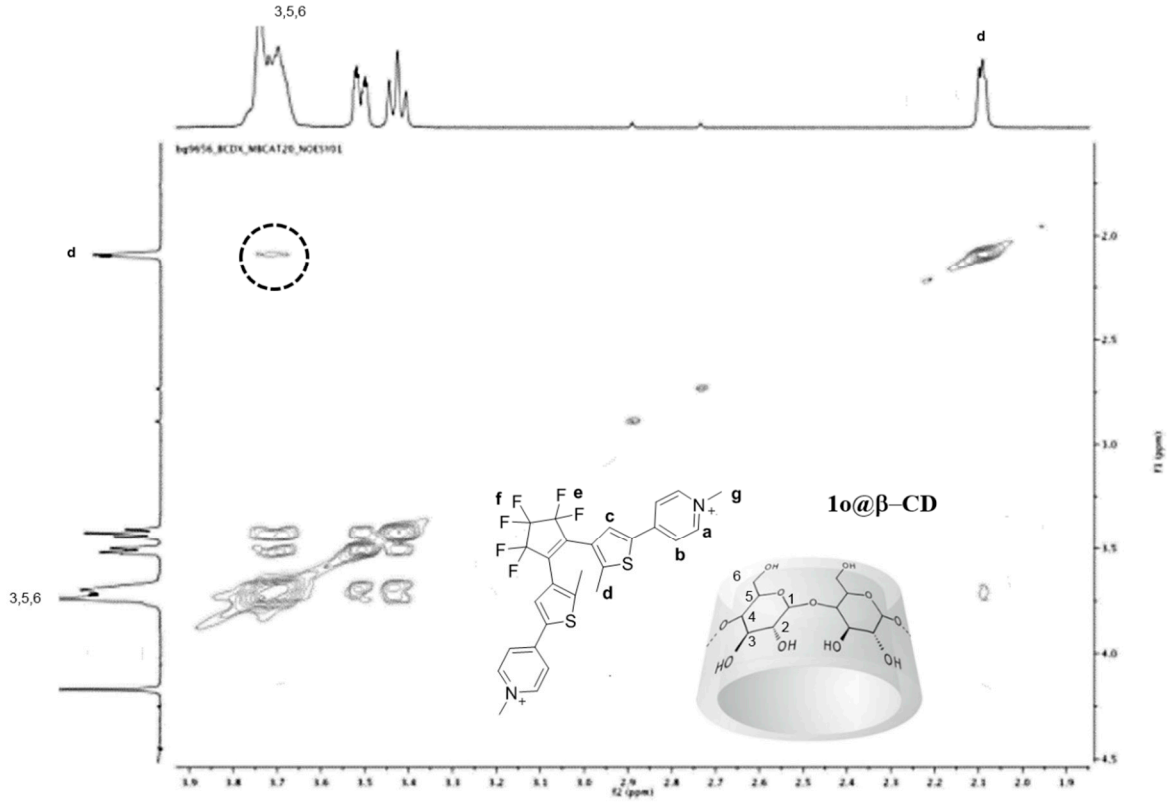

Figure S5. Proton *d* area expansion of NOESY ^{1}H-NMR of **1o** ($7.00\cdot10^{-3}$ M) + ***β*-CD** ($7.00\cdot10^{-2}$ M) in D_2O.

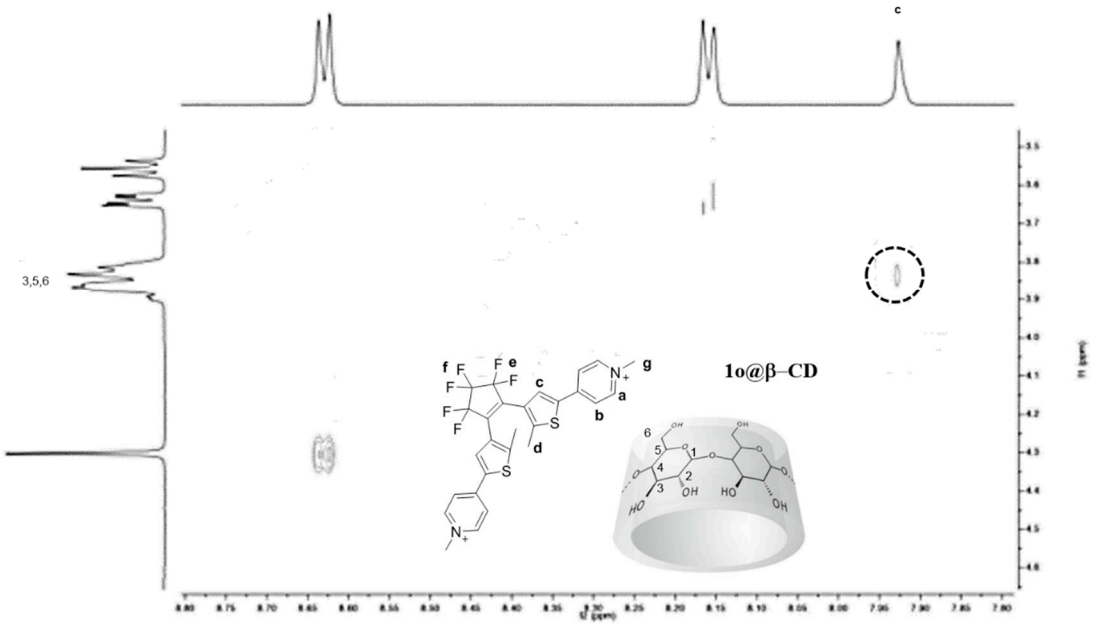

Figure S6. Proton *c* area expansion of NOESY ^{1}H-NMR of **1o** ($7.00\cdot10^{-3}$ M) + ***β*-CD** ($7.00\cdot10^{-2}$ M) in D_2O.

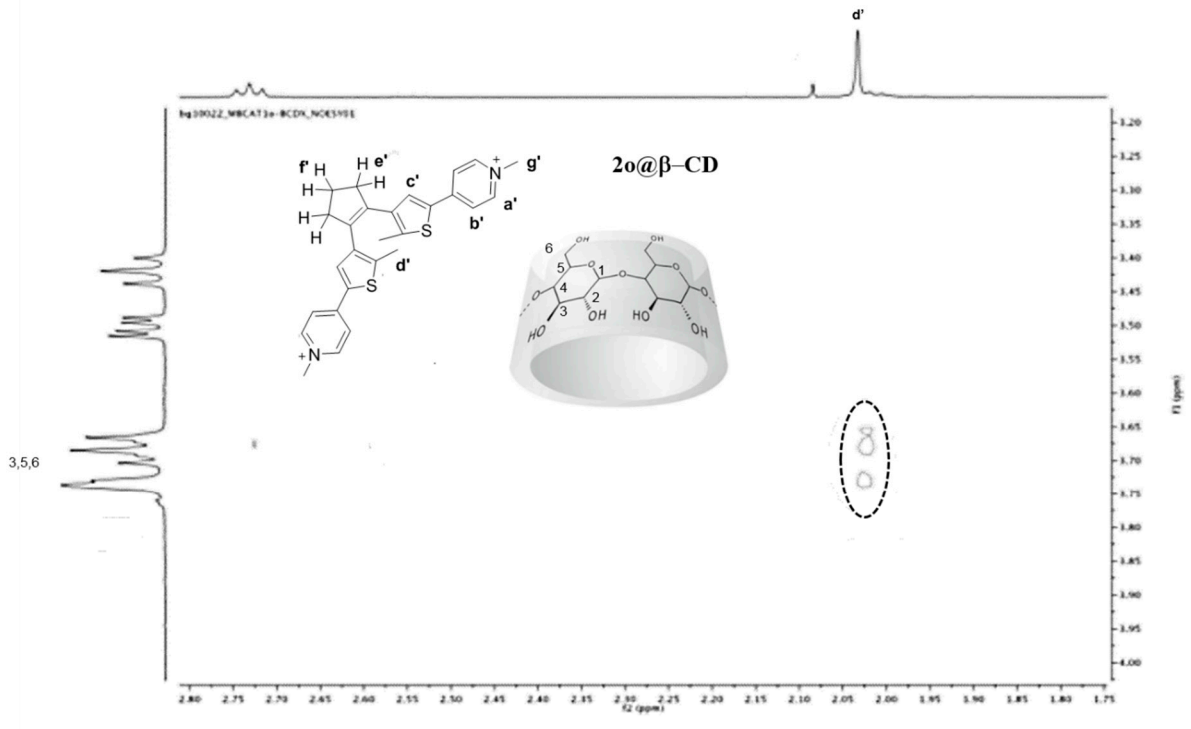

Figure S7. Proton *d'* area expansion of NOESY ^{1}H-NMR of **2o** ($7.00\cdot10^{-3}$ M) + ***β*-CD** ($7.00\cdot10^{-2}$ M) in D_2O.

Table S1. Diffusion coefficients for ***β*-CD**, **1o**, **1c** and their inclusion complexes **1o@*β*-CD**, **1c@*β*-CD** determined by ^{1}H-NMR DOSY.

#	1o D ($m^2 \cdot s^{-1}$)	1c D ($m^2 \cdot s^{-1}$)	β-CD ($m^2 \cdot s^{-1}$)
1o	$4.8 \cdot 10^{-10}$	-	-
1c	-	$4.7 \cdot 10^{-10}$	-
***β*-CD**	-	-	$3.3 \cdot 10^{-10}$
1o@*β*-CD	$3.0 \cdot 10^{-10}$	-	$3.0 \cdot 10^{-10}$
1c@*β*-CD	$3.0 \cdot 10^{-10}$	-	$3.0 \cdot 10^{-10}$

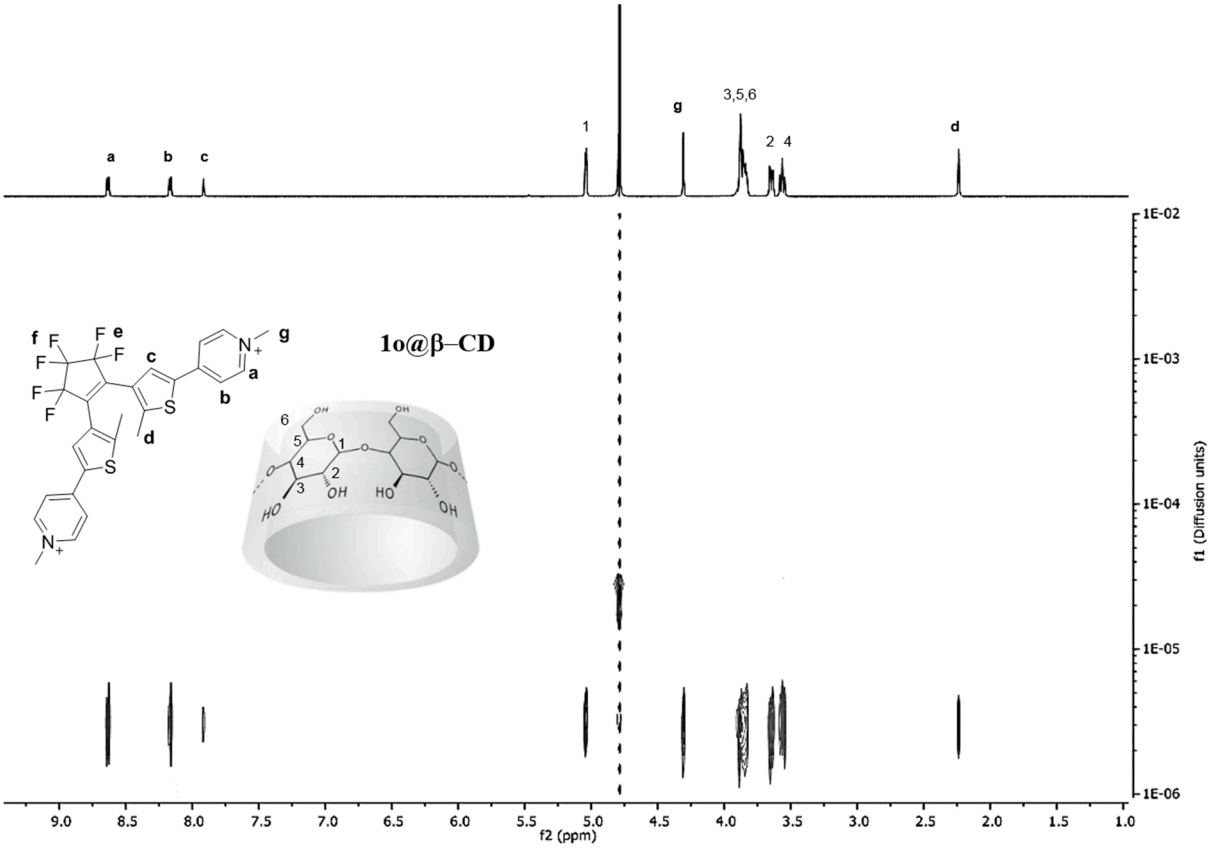

Figure S8. DOSY: 1o ($7.00 \cdot 10^{-3}$ M) + ***β*-CD** ($7.00 \cdot 10^{-3}$ M) diffusing at the same rate in D_2O.

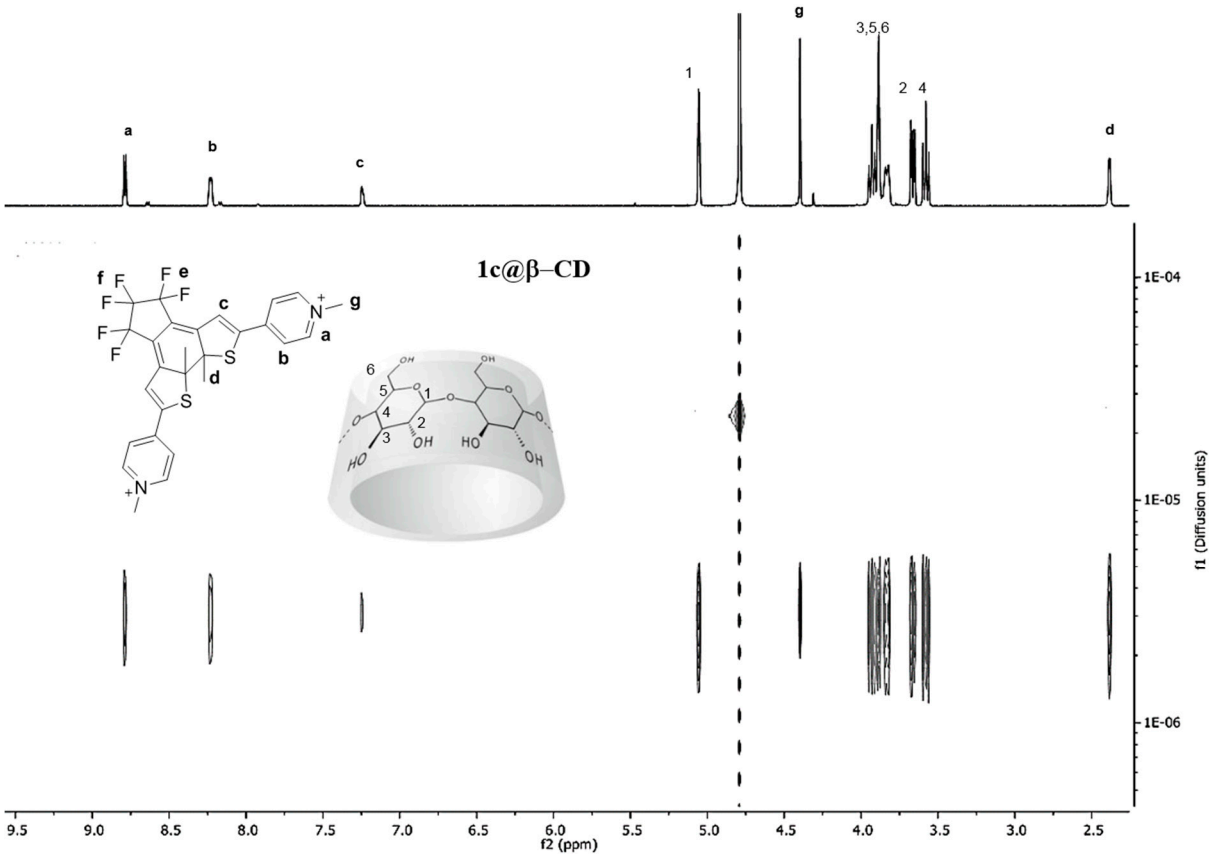

Figure S9. DOSY: 1c ($7.00 \cdot 10^{-3}$ M) + ***β*-CD** ($7.00 \cdot 10^{-3}$ M) diffusing at the same rate in D_2O.

Table S2. Diffusion coefficients for ***β*-CD**, **2o**, **2c** and their inclusion complexes **2o@*β*-CD**, **2c@*β*-CD** determined by ^{1}H-NMR DOSY.

#	2o D ($m^2 \cdot s^{-1}$)	2c D ($m^2 \cdot s^{-1}$)	β-CD ($m^2 \cdot s^{-1}$)
2o	$4.7 \cdot 10^{-10}$	-	-
2c	-	$4.9 \cdot 10^{-10}$	-
***β*-CD**	-	-	$3.3 \cdot 10^{-10}$
2o@*β*-CD	$3.0 \cdot 10^{-10}$	-	$3.1 \cdot 10^{-10}$
2c@*β*-CD	$3.0 \cdot 10^{-10}$	-	$3.1 \cdot 10^{-10}$

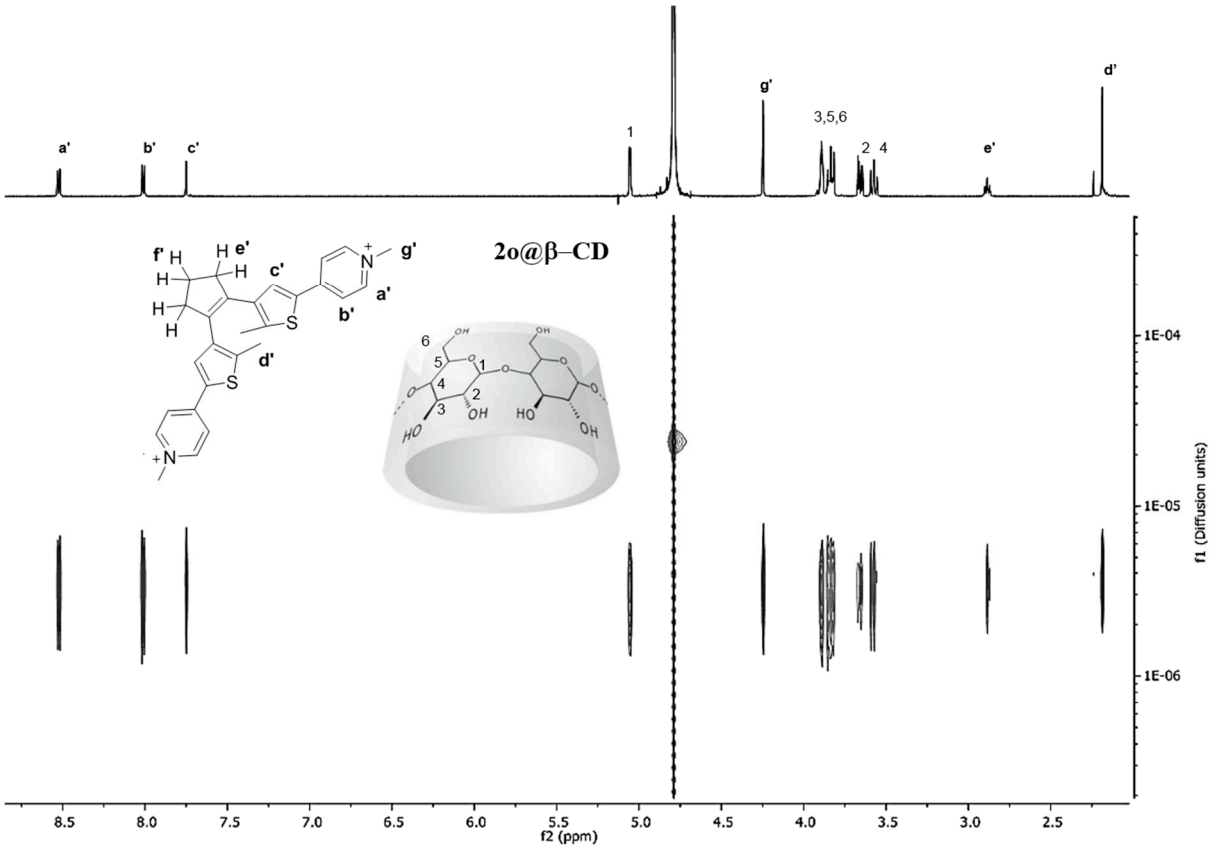

Figure S10. DOSY: 2o (7.00·10^{-3} M) + ***β*-CD** (7.00·10^{-3} M) diffusing at the same rate in D_2O.

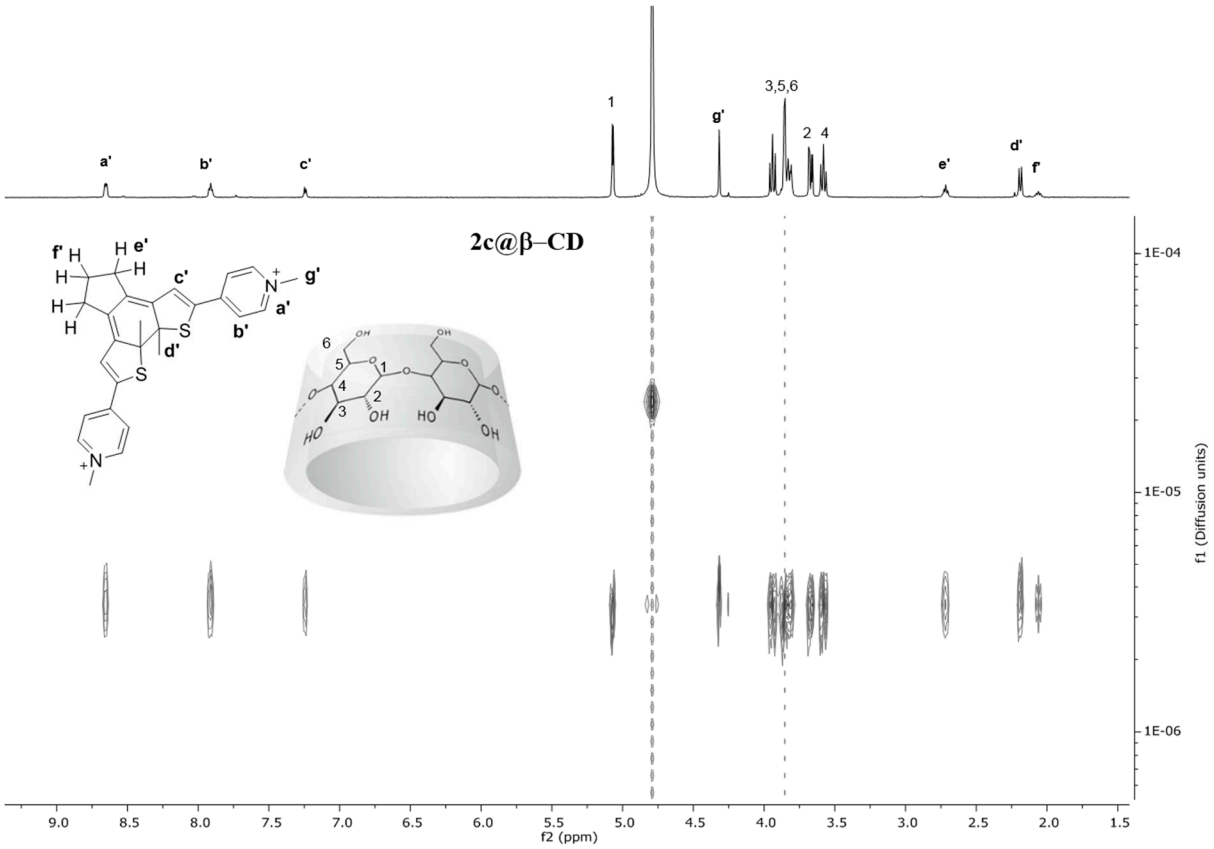

Figure S11. DOSY: 2c (7.00·10^{-3} M) + ***β*-CD** (7.00·10^{-3} M) diffusing at the same rate in D_2O.

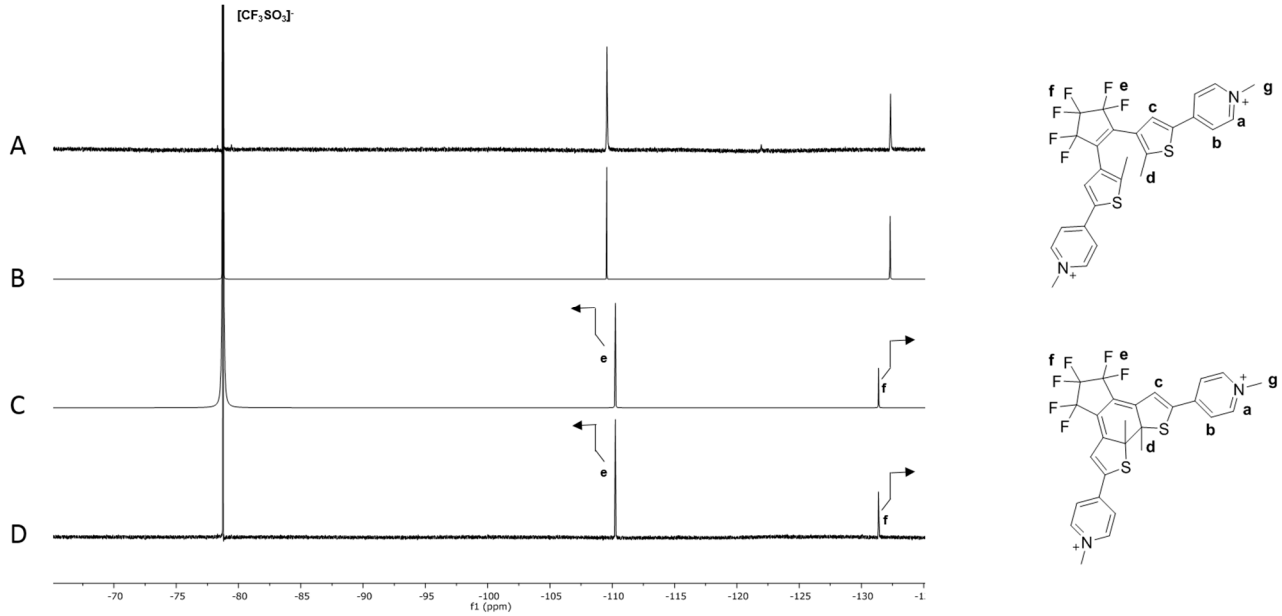

Figure S12. Cyclodextrin recognition of photochrome **1o** and **1c**, ^{19}F-NMR. **A) 1o** ($7.00\cdot10^{-3}$ M) + ***β*-CD** ($7.00\cdot10^{-3}$ M) in D_2O; **B) 1c** ($7.00\cdot10^{-3}$ M) + ***β*-CD** ($7.00\cdot10^{-3}$ M) in D_2O; **C) 1o** ($7.00\cdot10^{-3}$ M) in D_2O; **D) 1c** ($7.00\cdot10^{-3}$ M) in D_2O.

Inclusion complexes 1@*β*-CD Job's plots.

Different deuterium oxide solutions characterised by having the same final total concentration (*host* + *guest* species, $7.02\cdot10^{-2}$ M) but different amounts of β-cyclodextrin and **1o** or **1c** were prepared and analysed by ^{1}H-NMR. In Table S3 are reported the different combinations and the data used for the Job's plot of **1o@*β*-CD.** The ordinate in the modified Job plot is proportional to the concentration of the inclusion complex ([1@β-CD]; the ratio between the association constants can be expressed by the following equation:

$$\frac{K_{1o@\beta CD}}{K_{1c@\beta CD}} = \frac{[1o@\beta CD]}{[1c@\beta CD]} \cdot \frac{([1o]_0 - [1c@\beta CD])^2}{([1o]_0 - [1o@\beta CD])^2}$$

Table S3. 1o@β-CD Job's plot data and data treatment.

[1o] (M)	[*β*-CD] (M)	χ_{1o}[a]	$\chi_{\beta\text{-CD}}$[b]	δ(ppm)[c]	$\Delta\delta$(ppm)[d]	$\Delta\delta$[1o]
0.00	$7.02\cdot10^{-4}$	0.00	1.00	0.000	0.000	0.00
$8.77\cdot10^{-5}$	$6.14\cdot10^{-4}$	0.13	0.88	2.223	0.151	$1.32\cdot10^{-5}$
$1.75\cdot10^{-4}$	$5.26\cdot10^{-4}$	0.25	0.75	2.208	0.136	$2.38\cdot10^{-5}$
$2.63\cdot10^{-4}$	$4.39\cdot10^{-4}$	0.38	0.63	2.192	0.120	$3.16\cdot10^{-5}$
$3.51\cdot10^{-4}$	$3.51\cdot10^{-4}$	0.50	0.50	2.173	0.101	$3.55\cdot10^{-5}$
$4.39\cdot10^{-4}$	$2.63\cdot10^{-4}$	0.63	0.38	2.148	0.076	$3.34\cdot10^{-5}$
$5.26\cdot10^{-4}$	$1.75\cdot10^{-4}$	0.75	0.25	2.121	0.049	$2.58\cdot10^{-5}$
$6.14\cdot10^{-4}$	$8.77\cdot10^{-5}$	0.88	0.13	2.095	0.023	$1.41\cdot10^{-5}$
$7.02\cdot10^{-4}$	0.00	1.00	0.00	2.072	0.000	0.00

a) **1o** molar fraction; b) ***β*-CD** molar fraction; c) chemical shift of the methyl unit attached to the thiophene ring (*d*); d) chemical shift difference with respect β-cyclodextrin free sample.

Table S4. 1c@β-CD Job's plot data and data treatment.

[1c] (M)	[*β*-CD] (M)	χ_{1c}[a]	$\chi_{\beta\text{-CD}}$[b]	δ(ppm)[c]	$\Delta\delta$(ppm)[d]	$\Delta\delta$[1c]

0.00	$7.02\cdot10^{-4}$	0.00	1.00	0.000	0.000	0.00
$8.77\cdot10^{-5}$	$6.14\cdot10^{-4}$	0.13	0.88	2.368	0.041	$3.60\cdot10^{-6}$
$1.75\cdot10^{-4}$	$5.26\cdot10^{-4}$	0.25	0.75	2.363	0.036	$6.30\cdot10^{-6}$
$2.63\cdot10^{-4}$	$4.39\cdot10^{-4}$	0.38	0.63	2.354	0.027	$7.10\cdot10^{-6}$
$3.51\cdot10^{-4}$	$3.51\cdot10^{-4}$	0.50	0.50	2.351	0.024	$8.42\cdot10^{-6}$
$4.39\cdot10^{-4}$	$2.63\cdot10^{-4}$	0.63	0.38	2.345	0.018	$7.90\cdot10^{-6}$
$5.26\cdot10^{-4}$	$1.75\cdot10^{-4}$	0.75	0.25	2.338	0.011	$5.79\cdot10^{-6}$
$6.14\cdot10^{-4}$	$8.77\cdot10^{-5}$	0.88	0.13	2.334	0.007	$4.30\cdot10^{-6}$
$7.02\cdot10^{-4}$	0.00	1.00	0.00	2.327	0.000	0.00

a) **1c** molar fraction; b) ***β*-CD** molar fraction; c) chemical shift of the methyl unit attached to the thiophene ring (*d*); d) chemical shift difference with respect β-cyclodextrin free sample.

Inclusion complexes 2@*β*-CD Job's plots.

Different deuterium oxide solutions characterised by having the same final total concentration (*host* + *guest* species, $7.02\cdot10^{-2}$ M) but different amounts of β-cyclodextrin and **2o** or **2c** were prepared and analysed by ^{1}H-NMR. In **Error! Reference source not found.** are reported the different combinations and the data used for the Job's plot of **2o@*β*-CD.**

Table S5. **2o@*β*-CD** Job's plot data and data treatment.

[2o] (M)	[*β*-CD] (M)	χ_{2o}[a]	$\chi_{\beta\text{-CD}}$[b]	δ(ppm)[c]	$\Delta\delta$(ppm)[d]	$\Delta\delta$[2o]
0.00	$7.02\cdot10^{-4}$	0.00	1.00	0.000	0.000	0.00
$8.77\cdot10^{-5}$	$6.14\cdot10^{-4}$	0.13	0.88	2.138	0.084	$7.37\cdot10^{-6}$
$1.75\cdot10^{-4}$	$5.26\cdot10^{-4}$	0.25	0.75	2.128	0.074	$1.30\cdot10^{-5}$
$2.63\cdot10^{-4}$	$4.39\cdot10^{-4}$	0.38	0.63	2.118	0.064	$1.68\cdot10^{-5}$
$3.51\cdot10^{-4}$	$3.51\cdot10^{-4}$	0.50	0.50	2.103	0.049	$1.72\cdot10^{-5}$
$4.39\cdot10^{-4}$	$2.63\cdot10^{-4}$	0.63	0.38	2.090	0.036	$1.58\cdot10^{-5}$
$5.26\cdot10^{-4}$	$1.75\cdot10^{-4}$	0.75	0.25	2.073	0.019	$1.00\cdot10^{-5}$
$6.14\cdot10^{-4}$	$8.77\cdot10^{-5}$	0.88	0.13	2.066	0.012	$7.37\cdot10^{-6}$
$7.02\cdot10^{-4}$	0.00	1.00	0.00	2.054	0.000	0.00

a) **2o** molar fraction; b) ***β*-CD** molar fraction; c) chemical shift of the methyl unit attached to the thiophene ring (*d*); d) chemical shift difference with respect β-cyclodextrin free sample.

Table S6. **2c@*β*-CD** Job's plot data and data treatment.

[2c] (M)	[*β*-CD] (M)	χ_{2c}[a]	$\chi_{\beta\text{-CD}}$[b]	δ(ppm)[c]	$\Delta\delta$(ppm)[d]	$\Delta\delta$[2c]
0.00	$7.02\cdot10^{-4}$	0.00	1.00	0.000	0.000	0.00
$8.77\cdot10^{-5}$	$6.14\cdot10^{-4}$	0.13	0.88	2.028	0.048	$4.21\cdot10^{-6}$
$1.75\cdot10^{-4}$	$5.26\cdot10^{-4}$	0.25	0.75	2.018	0.038	$6.67\cdot10^{-6}$
$2.63\cdot10^{-4}$	$4.39\cdot10^{-4}$	0.38	0.63	2.016	0.036	$9.47\cdot10^{-6}$
$3.51\cdot10^{-4}$	$3.51\cdot10^{-4}$	0.50	0.50	2.007	0.027	$9.47\cdot10^{-6}$
$4.39\cdot10^{-4}$	$2.63\cdot10^{-4}$	0.63	0.38	1.999	0.019	$8.33\cdot10^{-6}$
$5.26\cdot10^{-4}$	$1.75\cdot10^{-4}$	0.75	0.25	1.992	0.012	$6.31\cdot10^{-6}$
$6.14\cdot10^{-4}$	$8.77\cdot10^{-5}$	0.88	0.13	1.988	0.008	$4.91\cdot10^{-6}$
$7.02\cdot10^{-4}$	0.00	1.00	0.00	1.980	0.000	0.00

a) **2c** molar fraction; b) ***β*-CD** molar fraction; c) chemical shift of the methyl unit attached to the thiophene ring (*d*); d) chemical shift difference with respect β-cyclodextrin free sample.

Determination of 1@*β*-CD association constants (K_{Ass})

1o and **1c** deuterium oxide solutions ($2.35\cdot10^{-3}$ M) have been titrated with increasing amounts of β-cyclodextrin till no variation of chemical shift was observed in ^{1}H-NMR spectra. In Table

S7 are reported the data obtained and later used for the determination of the K_{Ass} of **1o@*β*-CD** by means of the non-linear least-squares method.

Table S7. Data from **1o** titration with *β*-CD.

[*β*-CD] (M)	δ(ppm)[a]	$\Delta\delta$(ppm)[b]
0.00	2.068	0.000
$1.22\cdot10^{-3}$	2.163	0.095
$2.44\cdot10^{-3}$	2.222	0.154
$3.80\cdot10^{-3}$	2.245	0.177
$5.15\cdot10^{-3}$	2.254	0.186
$6.51\cdot10^{-3}$	2.260	0.192
$7.73\cdot10^{-3}$	2.262	0.194
$9.08\cdot10^{-3}$	2.263	0.195
$1.27\cdot10^{-2}$	2.265	0.197
$1.97\cdot10^{-2}$	2.265	0.197
$2.66\cdot10^{-2}$	2.265	0.197

a) chemical shift of the methyl unit attached to the thiophene ring (*d*); b) chemical shift difference with respect β-cyclodextrin free sample.

In Table S8 are reported the data obtained and later used for the determination of the K_{Ass} of **1c@*β*-CD** by means of the non-linear least-squares method.

Table S8. Data from **1c** titration with *β*-CD

[*β*-CD] (M)	δ(ppm)[a]	$\Delta\delta$(ppm)[b]
0.00	2.320	0.000
$1.22\cdot10^{-3}$	2.361	0.041
$2.44\cdot10^{-3}$	2.392	0.072
$4.20\cdot10^{-3}$	2.409	0.089
$5.69\cdot10^{-3}$	2.418	0.098
$6.78\cdot10^{-3}$	2.420	0.100
$8.00\cdot10^{-3}$	2.423	0.103
$9.62\cdot10^{-3}$	2.427	0.107
$1.36\cdot10^{-2}$	2.429	0.109
$1.05\cdot10^{-2}$	2.431	0.111
$2.72\cdot10^{-2}$	2.432	0.112

a) chemical shift of the methyl unit attached to the thiophene ring (*d*); b) chemical shift difference with respect β-cyclodextrin free sample.

Determination of 2@*β*-CD association constants (K_{Ass})

2o and **2c** deuterium oxide solutions ($2.15\cdot10^{-3}$ M) have been titrated with increasing amounts of β-cyclodextrin till no variation of chemical shift was observed in ^{1}H-NMR spectra. In Table S9 are reported the data obtained and later used for the determination of the K_{Ass} of **2o@*β*-CD** by means of the non-linear least-squares method.

Table S9. Data from **2o** titration with *β*-cyclodextrin

[*β*-CD] (M)	δ(ppm)[a]	$\Delta\delta$(ppm)[b]
0.00	1.961	0.000
$1.36\cdot10^{-3}$	2.061	0.100
$2.71\cdot10^{-3}$	2.100	0.139
$4.07\cdot10^{-3}$	2.133	0.172

$5.42 \cdot 10^{-3}$	2.157	0.196
$6.78 \cdot 10^{-3}$	2.176	0.215
$8.13 \cdot 10^{-3}$	2.185	0.224
$9.49 \cdot 10^{-3}$	2.191	0.230
$1.36 \cdot 10^{-2}$	2.204	0.243
$2.03 \cdot 10^{-2}$	2.209	0.248
$2.71 \cdot 10^{-2}$	2.211	0.250

a) chemical shift of the methyl unit attached to the thiophene ring (*d*); b) chemical shift difference with respect β-cyclodextrin free sample.

In Table S10 are reported the data obtained and later used for the determination of the K_{Ass} of **2c@*β*-CD** by means of the non-linear least-squares method.

Table S10. Data from **2c** titration with *β*-cyclodextrin

[*β*-CD] (M)	**δ(ppm)[a]**	**$\Delta\delta$(ppm)[b]**
0.00	2.001	0.000
$1.36 \cdot 10^{-3}$	2.057	0.056
$2.71 \cdot 10^{-3}$	2.086	0.085
$4.07 \cdot 10^{-3}$	2.097	0.096
$5.42 \cdot 10^{-3}$	2.106	0.105
$6.78 \cdot 10^{-3}$	2.120	0.119
$8.13 \cdot 10^{-3}$	2.130	0.129
$9.49 \cdot 10^{-3}$	2.135	0.134
$1.36 \cdot 10^{-2}$	2.142	0.141
$2.03 \cdot 10^{-2}$	2.142	0.141
$2.71 \cdot 10^{-2}$	2.144	0.143

a) chemical shift of the methyl unit attached to the thiophene ring (*d*); b) chemical shift difference with respect β-cyclodextrin free sample.