

Supplementary Materials: Inclusion of 5-Mercapto-1-Phenyl-Tetrazole into β -Cyclodextrin for Corrosion Protection of Copper and Bronze in Acidic Medium

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¹H NMR Titration

The following two solutions were prepared in D₂O: Solution A: 2.8 mM of 5-mercapto-1-phenyl-tetrazole (MPT). Solution B: 2.8 mM of MPT and 12.0 mM of β -cyclodextrin (β -CD). 0.8 mL aliquot of solution A was placed in a 5-mm NMR tube. To the NMR tube were added the amounts of solution B listed in Table S1 and spectrum recorded after each addition (Figure S1).

Table 1. Parameters related to the titration.

<i>n</i>	$\mu\text{L } \beta\text{-CD added}$	Molar fraction $[\beta\text{-CD}]/[\text{MPT}]$	[MPT]	$[\beta\text{-CD}]$
1	0	0	2,8	0
2	80	0.39	2,8	1.09
3	160	0.71	2,8	1.99
4	240	0.98	2,8	2.76
5	320	1.21	2,8	3.39
6	520	1.68	2,8	4.72
7	720	2.02	2,8	5.67
8	920	2.29	2,8	6.39

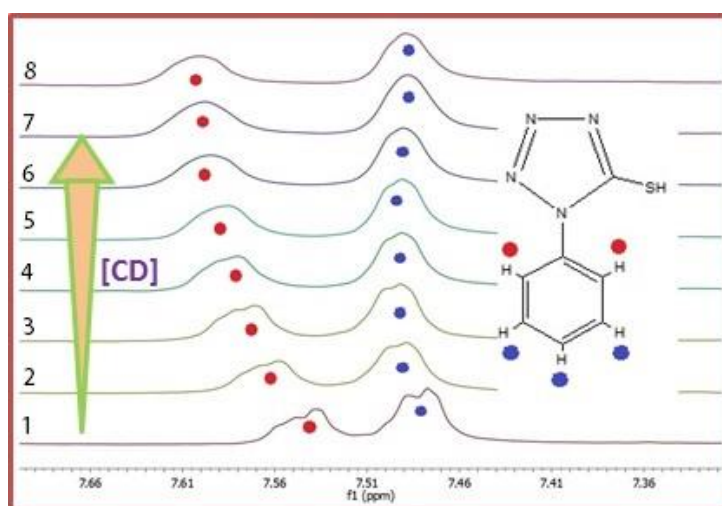
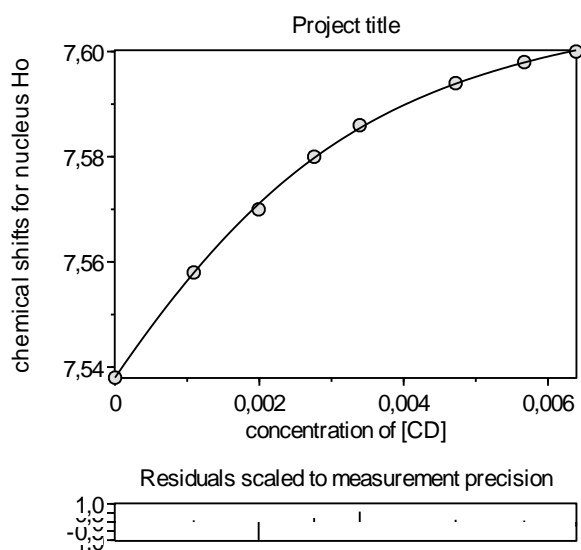


Figure S1. Variations of a portion of ¹H NMR spectrum (400 MHz) of MPT 2.8 mM during its titration with β -CD 12 mM in D₂O. The molar fractions of host are reported in Table S1.

The chemical shift variation of the ortho-phenyl protons of the MPT was collected and the binding constant (as log K) was calculated by curve fitting method [1] using the commercial HypNMR2008 program [2].

HypNMR Fitting Data Output for MPT Binding by β -CD Calculated from Ortho-Protons



HypNMR2008

Refinement concluded at 14:11:51 on 15/02/2019

Data from C:\Users\Fantin\Desktop\INCL. CYCLODEX\Titolazione MPT\MPT + CD 22-10-18 RI-RIFATTA.HQD (modified)

Project title: MPT titration with Cyclodextrin

Converged in 4 iterations with sigma = 0,504823

			standard	
	value	deviation	Comments	
1 log beta([CD][MPT])	2.9342	0.0383	2.93(4)	

DOSY Measures

Stacked plot and computational analysis of the DOSY experiments.

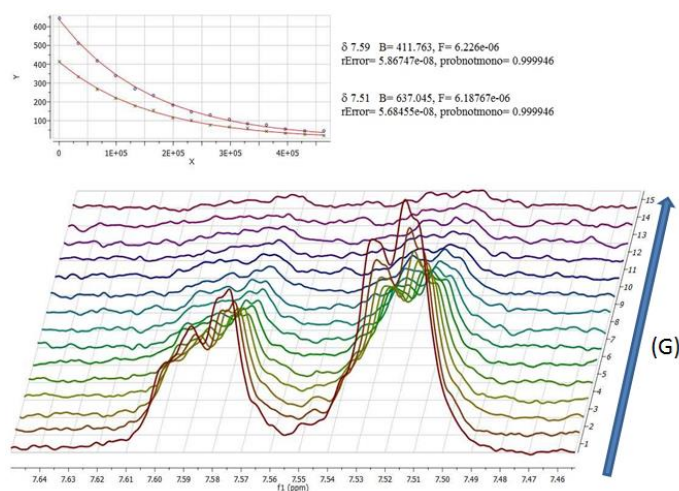


Figure S2. Stacked plot and computational analysis of the DOSY experiment of a sample containing MPT alone. MPT signal decays according to the gradients (G) together with the corresponding graphical analysis of the data. The diffusion coefficients are indicated with the letter F.

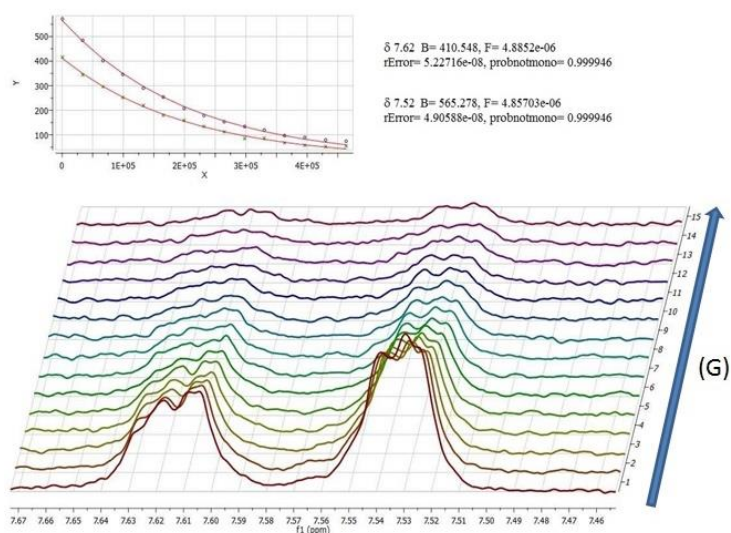


Figure S3. Stacked plot and computational analysis of the DOSY experiment of a sample containing MPT + β -CD. MPT signal decays according to the gradients (G) together with the corresponding graphical analysis of the data. The diffusion coefficients are indicated with the letter F.

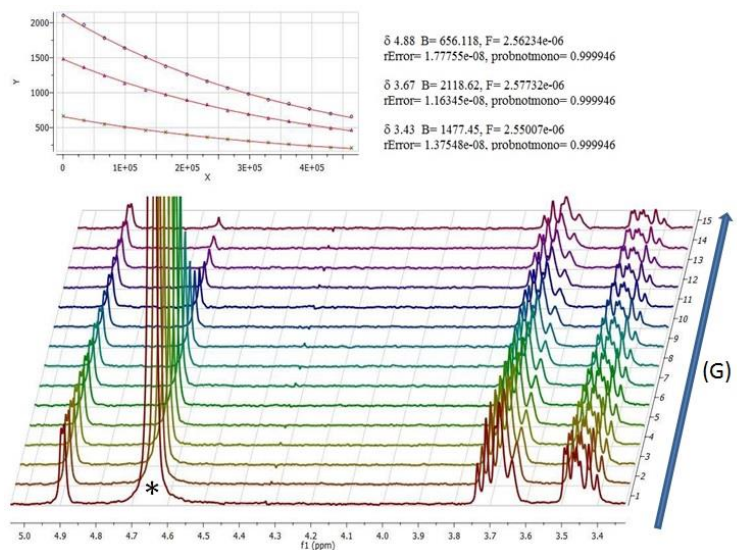


Figure S4. Stacked plot and computational analysis of the DOSY experiment of a sample containing MPT + β -CD. β -CD signal decays according to the gradients (G) together with the corresponding graphical analysis of the data.

The diffusion coefficients are indicated with the letter F; * DOH signal.

References

1. Fielding, L. Determination of Association Constants (K_a) from Solution NMR Data. *Tetrahedron* **2000**, *34*, 6151–6170.
2. Frassinetti, C.; Ghelli, S.; Gans, P.; Sabatini, A.; Moruzzi, M.S.; Vacca, A. Nuclear magnetic resonance as a tool for determining protonation constants of natural polyprotic bases in solution. *Anal. Biochem.* **1995**, *231*, 374–382.



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