

Electronic Supplementary Information

Monotopic and Heteroditopic Calix[4]arene Receptors as Hosts for Pyridinium and Viologen Ion Pairs: a Solution and Solid State Study

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Solid state studies

Table S1. Conformational parameters¹ ϕ and χ and dihedral angles δ for the complex **1** \supset NMPI

	ϕ (°)	χ (°)		δ (°)
A-B	70.3(8)	-85.3(7)	A-R	107.3(7)
B-C	88.8(7)	-72.7(8)	B-R	123.4(8)
C-D	70.8(7)	-85.5(7)	C-R	107.8(7)
D-A	87.3(8)	-72.5(8)	D-R	123.2(8)

δ represent the dihedral angles between the least-squares planes through the phenolic rings and the molecular reference plane *R* (the least-squares plane through the four CH₂ bridging groups) according to the standard rules for calixarenes.²

Table S2. Conformational parameters¹ ϕ and χ for the complex **4**₂ \supset PQ(TsO)₂

	ϕ (°)	χ (°)
A-B	96.0(4)	-84.3(5)
B-C	71.9(4)	-97.7(5)
C-D	103.4(5)	-81.0(4)
D-A	65.3(4)	-77.7(5)
E-F	80.2(4)	-73.3(4)
F-G	89.2(5)	-107.3(5)
G-H	93.7(4)	-74.9(4)
H-A	87.7(5)	-92.6(4)

¹ F. Ugozzoli and G.D. Andreotti, *J. Incl. Phen. and Mol. Rec. in Chem.*, 1992, **13**, 337

² M. Perrin and D. Oehler in *Calixarenes 2001*, Eds. Z. Asfari, V. Böhmer, J. Harrowfield and J Vicens, Kluwer Academic Publisher, Dordrecht, 2001, pp. 65-85.

NMR Studies

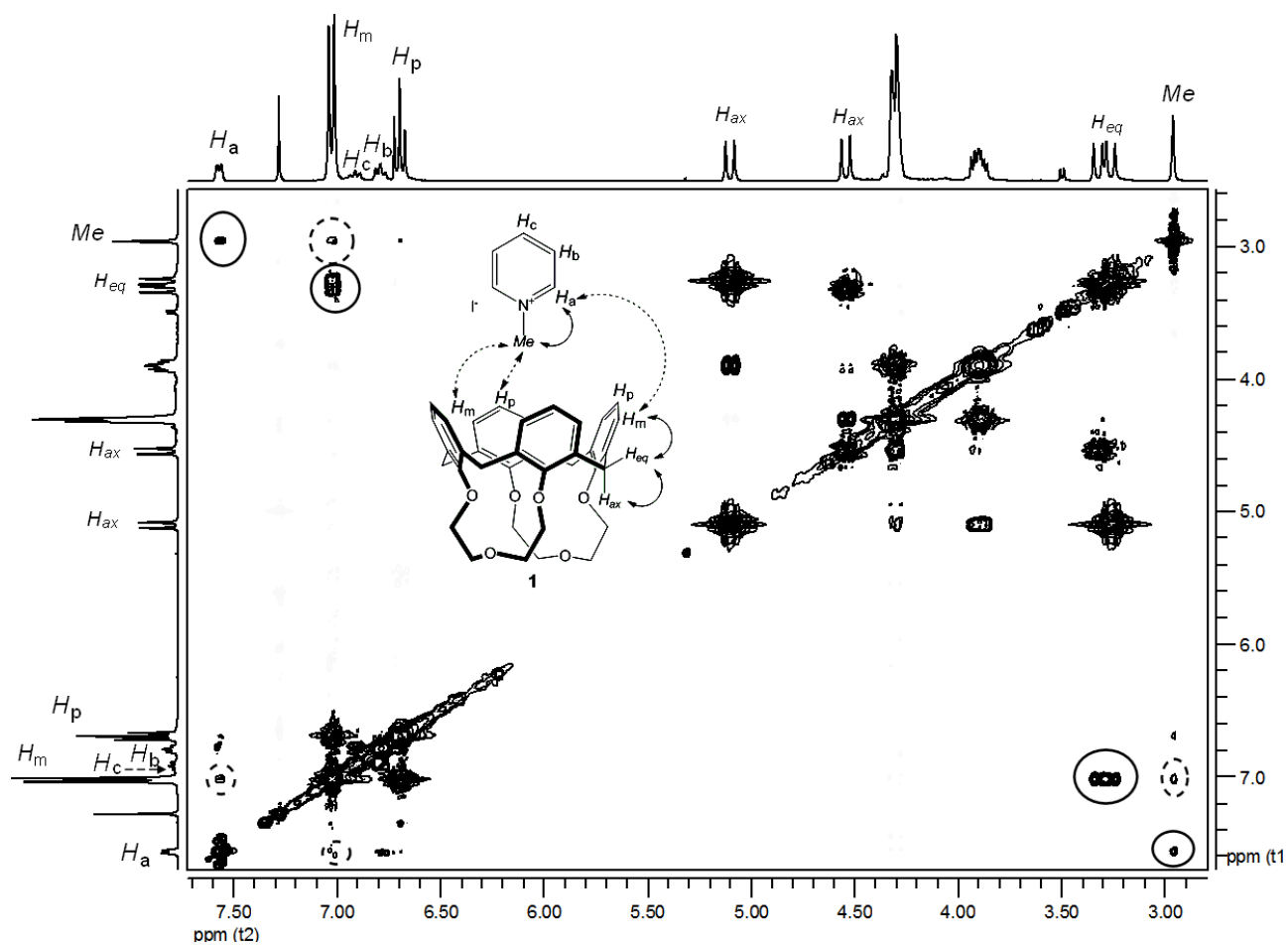


Fig S1. 2D NOESY spectrum (CDCl_3 , $T=300$ K, mixing time = 0.4 ms) of a 2:1 mixture of **1** and NMPI. Intra- and intermolecular NOE cross-peaks are represented with continuous and dashed lines.

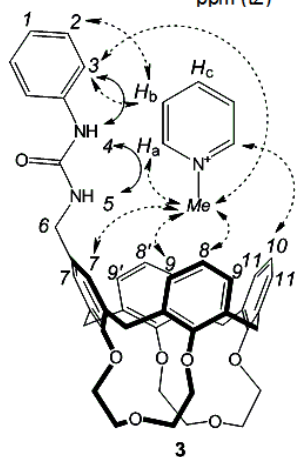
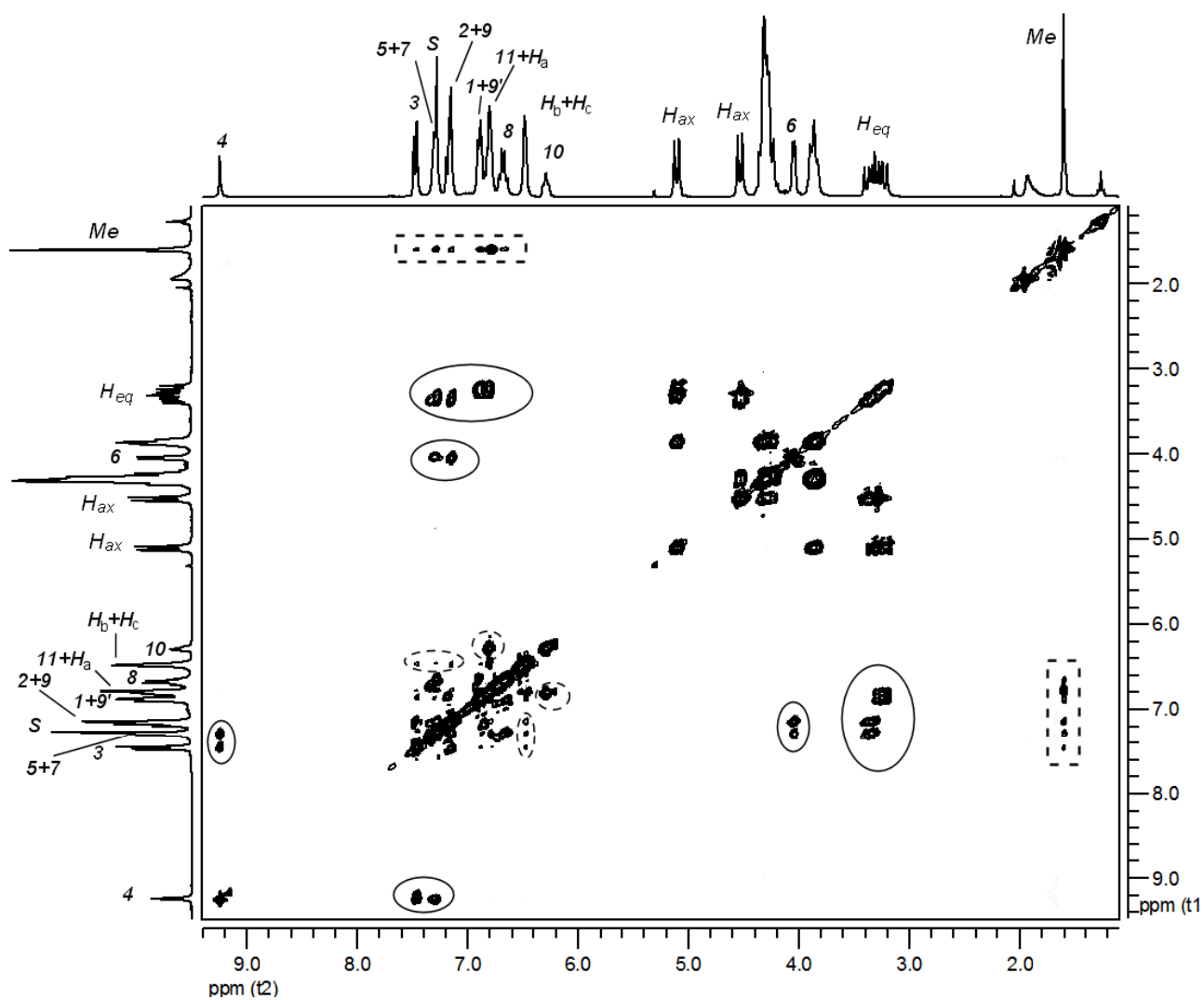


Fig. S2. 2D NOESY spectrum (CDCl_3 , $T=300\text{ K}$, mixing time = 0.4 ms) of a 1:1 mixture of **3** and NMP-Cl. Intra- and intermolecular NOE cross-peaks are represented with continuous and dashed lines.

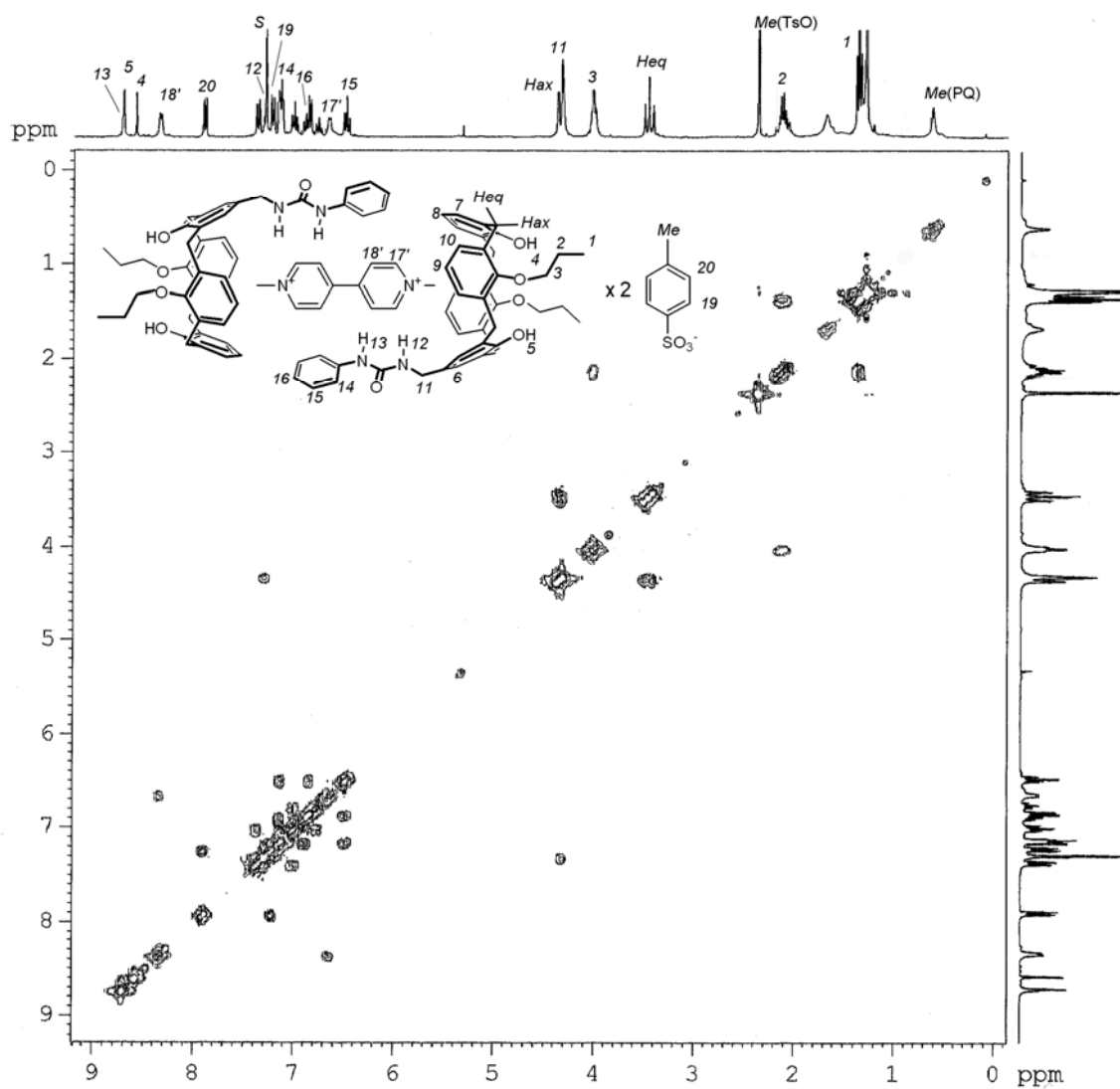


Fig. S3. 2D COSY spectrum (CDCl_3 , $T=300$ K) of the 2:1 mixture of **4** and $\text{PQ}(\text{TsO})_2$.

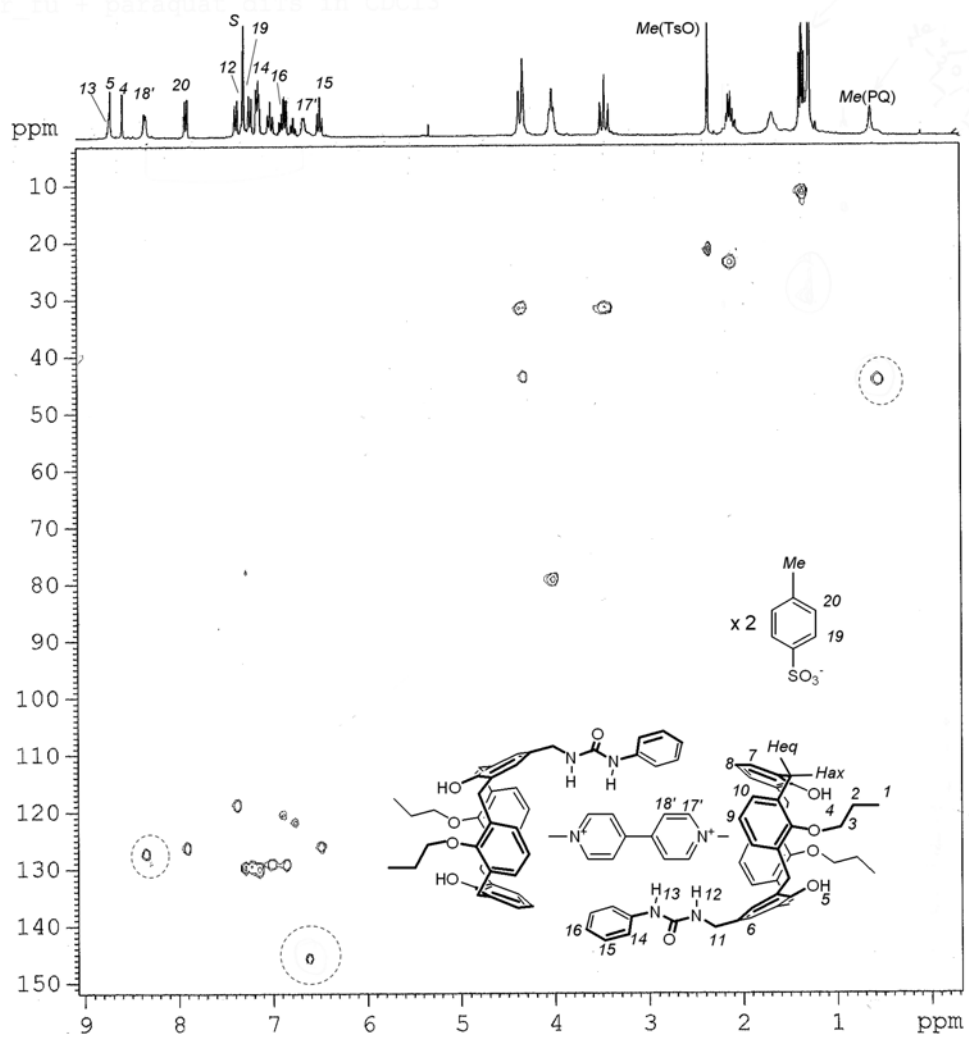


Fig. S4. 2D HMQC spectrum (CDCl₃, T=300 K) of the 2:1 mixture of **4** and PQ(TsO)₂.

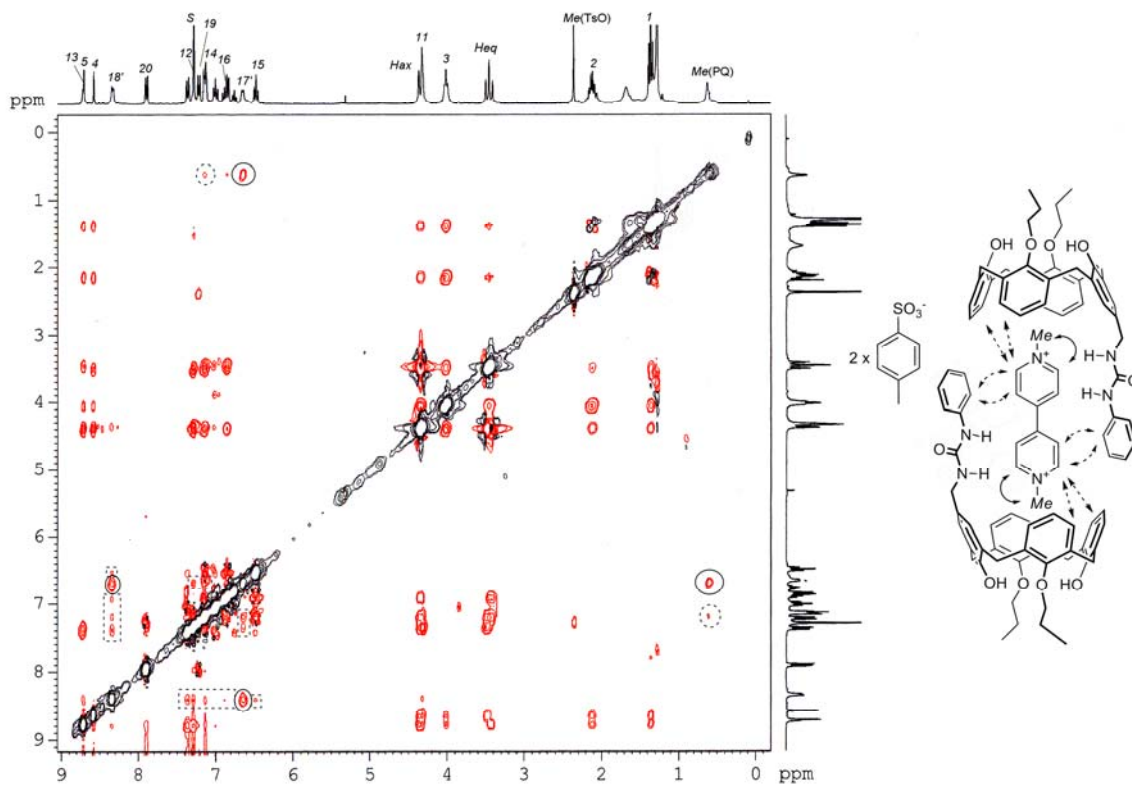


Fig. S5 2D ROESY spectrum (CDCl_3 , $T=300\text{ K}$, spin lock = 200 ms) of the 2:1 mixture of **4** and $\text{PQ}(\text{TsO})_2$. The most representative NOE cross-peaks and the corresponding intra- and intermolecular connections have been evidenced in the spectrum with continuous and dashed lines and in the schematic representation of the complex with continuous and dashed arrows, respectively.

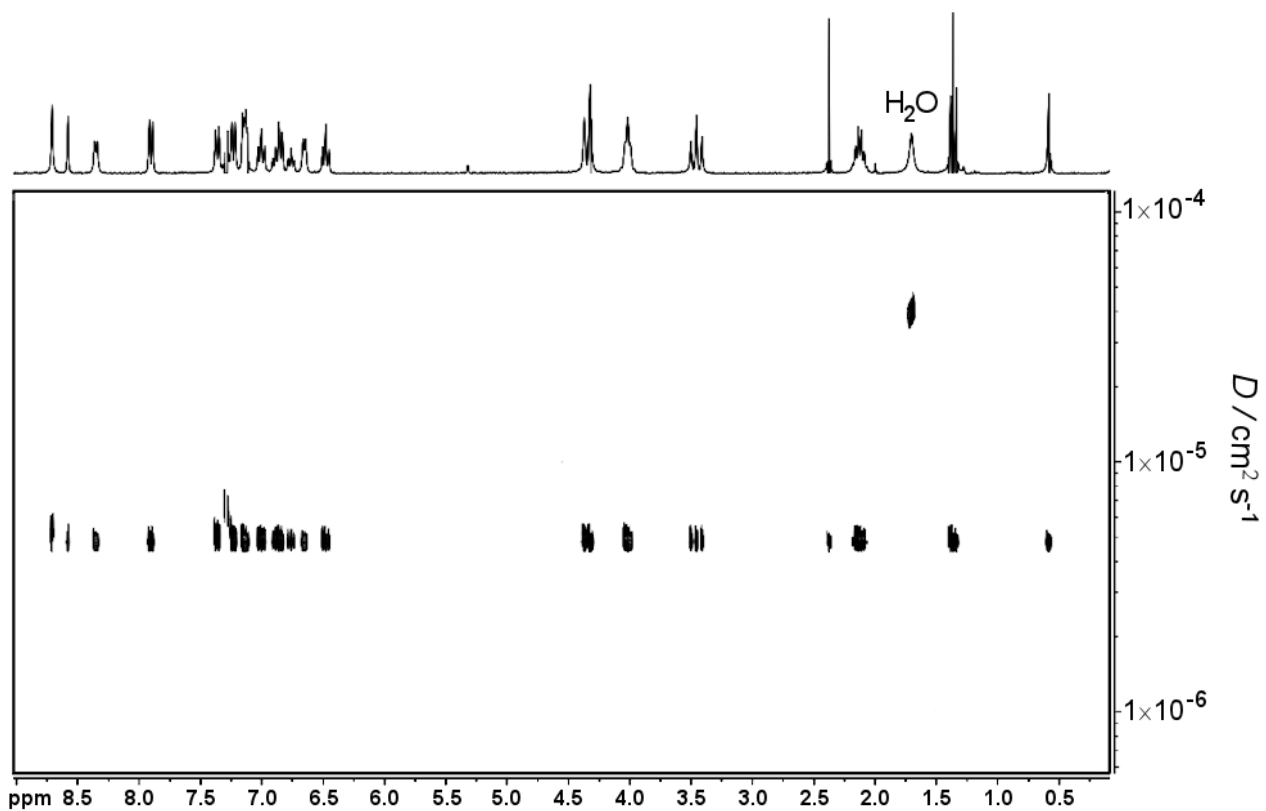


Fig. S6 2D DOSY spectrum (Experimental: $\delta = 4$ ms, $\Delta = 0.05$ s, $T = 298$ K) of the 2:1 mixture in CDCl_3 between **4** and $\text{PQ}(\text{TsO})_2$ showing the presence of a single species diffusing in solution with $D = 4.7 \pm 0.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.