SUPPLEMENTARY INFORMATION

Sodium and pH responsive Hydrogel Formation by the Supramolecular System: Calix[4]pyrrole derivative/Tetramethyl Ammonium.

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CONTENTS:

(A) Representative hydrogel formation procedures

In basic media 4.4 mg (0.006 mmol) of **1** were dissolved in 1 mL of 0.1 M aqueous NaOH in a vial. Addition of 3.7 mg (0.024 mmol) of tetramethylammonium bromide provoked the formation of a hydrogel after a few minutes.

In neutral media 4.4 mg of **1** were dissolved in 1 mL of 0.1 M aqueous NaOH in a vial. Then 0.9 mg (0.006 mmol) of tetramethylammonium bromide were added and the vial was exposed to a CO_2 atmosphere for 1 hour. Alternatively, the vial can be left exposed to the air overnight.

Table S1. Influence of tetraalkylammonium salts and alkaline hydroxide bases in the formation of hydrogels from calixpyrrole **1**[a]

Entry	Hydroxide	Ammonium species[b]	Gel formation
1	NaOH	TMA	yes
2	NaOH	TEA	no
3	NaOH	TBA	no
4	LiOH	TMA	no
5	KOH	TMA	no
6	TMAOH	-	no
7	NaOH	-	no

[a] [**1**] = 6 mM, [NR_4Cl] = 24 mM, [MOH] = 100 mM;
[b] TMA: Tetramethylammonium, TEA: tetraethylammonium, TBA: tetrabutylammonium.

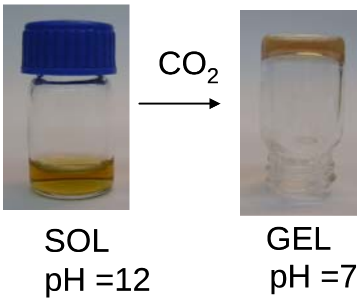

Figure S1. Vials containing an aqueous solution of compound **1** (3 mM), tetramethylammonium chloride (3 mM) and sodium hydroxide (100 mM).

(B) Acid-base thermodynamic constants of compound 1.

Potentiometric titration data revealed that the acidity of the 4 phenol units in calixpyrrole **1** is quite similar, being the molecule as a tetranion above pH 11. The cumulative protonation constants obtained are the following:

$L + 2H^+ = LH_2$ log β= 21.28; $L + 4H^+ = LH_4$ log β= 41.98.

emf Measurements. The potentiometric titrations were carried out at 298.1 ± 0.1 K using NaCl 0.15 M as supporting electrolyte. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, etc.) has been fully described elsewhere.[1] The acquisition of the emf data was performed with the computer program PASAT.[2] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as an hydrogen-ion concentration probe by titration of previously standardised amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran´s method, [3] which gives the standard potential, $E^{o\prime}$, and the ionic product of water (pKw=13.73(1)).

The computer program HYPERQUAD was used to calculate the protonation constants.[4] The pH range investigated was 2.5-10.5. The different titration curves for each system (at least two) were treated either as a single set or as separated curves without significant variations in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the final stability constants.

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[1] García-España, E.; Ballester, M.-J.; Lloret, F.; Moratal, J.-M.; Faus, J.; Bianchi, A. *J. Chem. Soc., Dalton Trans.* **1988**, 101.

[2] Fontanelli, M.; Micheloni, M. *Proceedings of the I Spanish-Italian Congress on Thermodynamics of Metal Complexes;* Diputación de Castellón, Castellón, Spain, **1990**. Program for the automatic control of the microburette and the acquisition of the electromotive force readings.

[3] Gran, G. *Analyst (London)*, **1952**, *77*, 881. Rossotti, F. J.; Rossotti, H. *J. Chem. Educ*. **1965**, *42*, 375

[4] Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739

(C) Thermal stability of hydrogels

Table S2. Influence of [NaOH] in the thermal stability of the hydrogels at basic pH.[a]

Entry	**[NaOH] / mM**	**T_{gel} / ºC**[b]
1	50	20
2	100	85
3	200	100

[a] [TMACl] = 40 mM, [**1**] = 6 mM

[b] Onset temperature for the liberation of solvent from the gel. In all the cases the formation of a white precipitate was observed.

(D) Electron microscopy

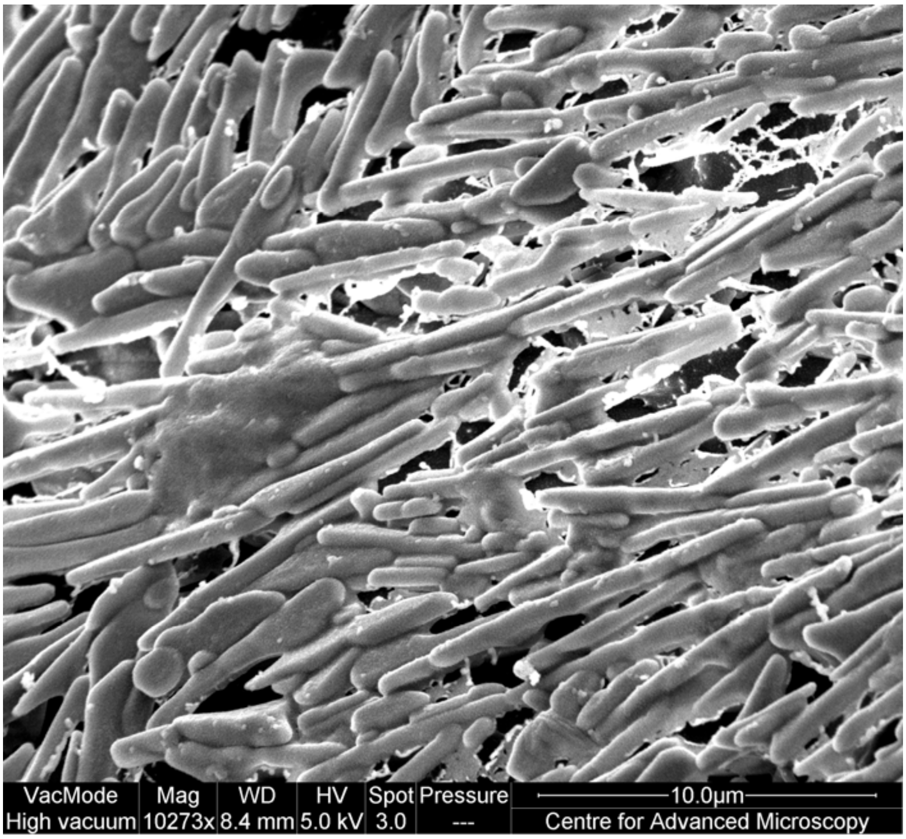

Figure S2. Cryo-SEM image obtained for a gel fromed from a 6 mM equimolecular mixture of **1** and TMABr dissolved in 100 mM NaOH and neutralized by exposure to the air overnight**.**

(E) NMR studies

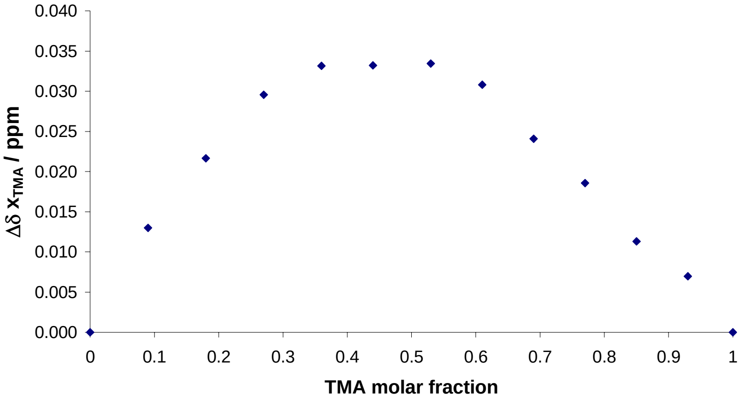

Figure S3. Job plot for the **1**-TMABr titration. The data points are derived from the ^{1}H-NMR chemical shift changes experienced by the TMA cation in different mixtures with a constant overall concentration of 3 mM.

Table S3. Comparison between total and ^{1}H-NMR observable concentration values of aqueous solutions containing calixpyrrole **1** and tetramethylammonium bromide (TMABr).

Entry	pH	[**1**]$_{total}$ / mM	[**1**]$_{obs}$ / mM	[TMA]$_{total}$ /mM	[TMA]$_{obs}$ /mM	**1**:TMA ratio^a
1	12^b	1.9	1.9	3.0	3.0	-
2	12^b	4.6	2.4	6.1	3.1	1 : 1.4
3	7^c	1.9	0	3.0	2.1	1 : 0.5
4	7^c	4.6	0	6.1	3.7	1 : 0.5

[a] For ^{1}H-NMR silent species; $[\ ]_{silent} = [\ ]_{total} - [\ ]_{obs}$.
[b] Sample prepared in 50 mM NaOH.
[c] Sample prepared in 50 mM NaOH and treated with an excess of CO_2.

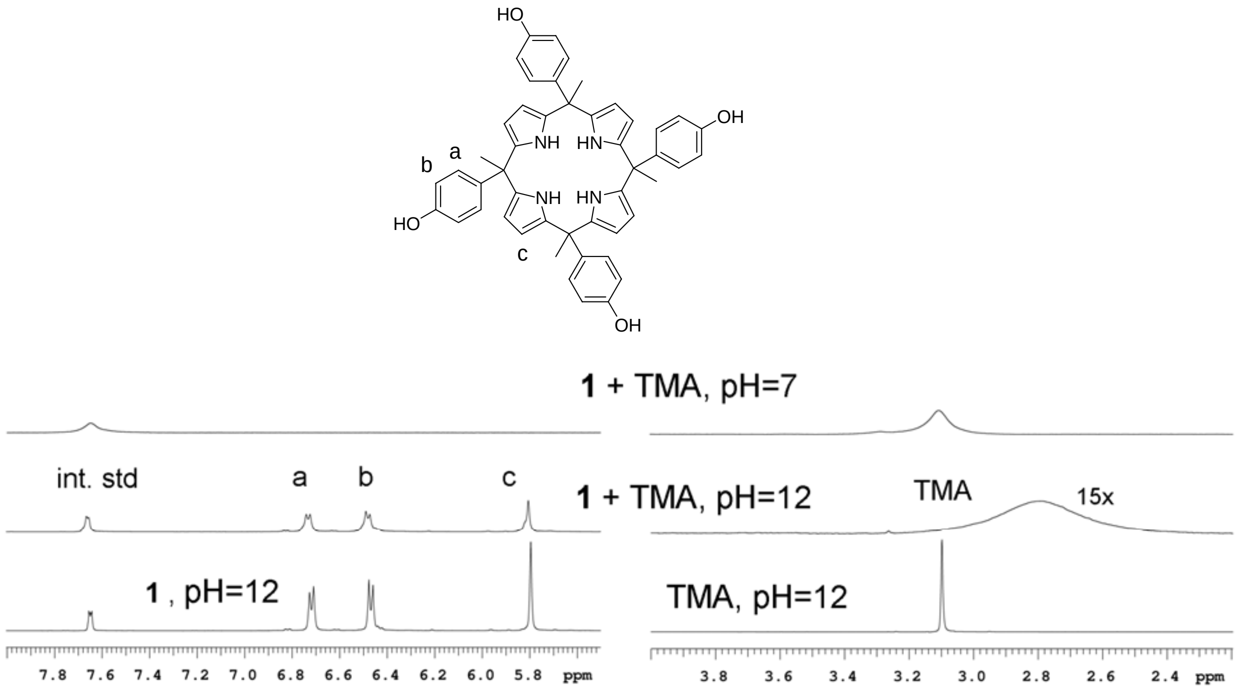

Figure S4. ^{1}H NMR spectra for the mixtures of **1,** TMABr and NaOH (100 mM) in D_2O.
Top: **1** (4.6 mM) + TMABr (6.1 mM), pH=7.
Middle : **1** (4.6 mM) + TMABr (6.1 mM), pH=12.
Bottom left: **1** (4.6 mM), pH =12.
Bottom right: TMABr (6.1 mM), pH=12.
Isonicotinic acid was used as internal standard for integration purposes.

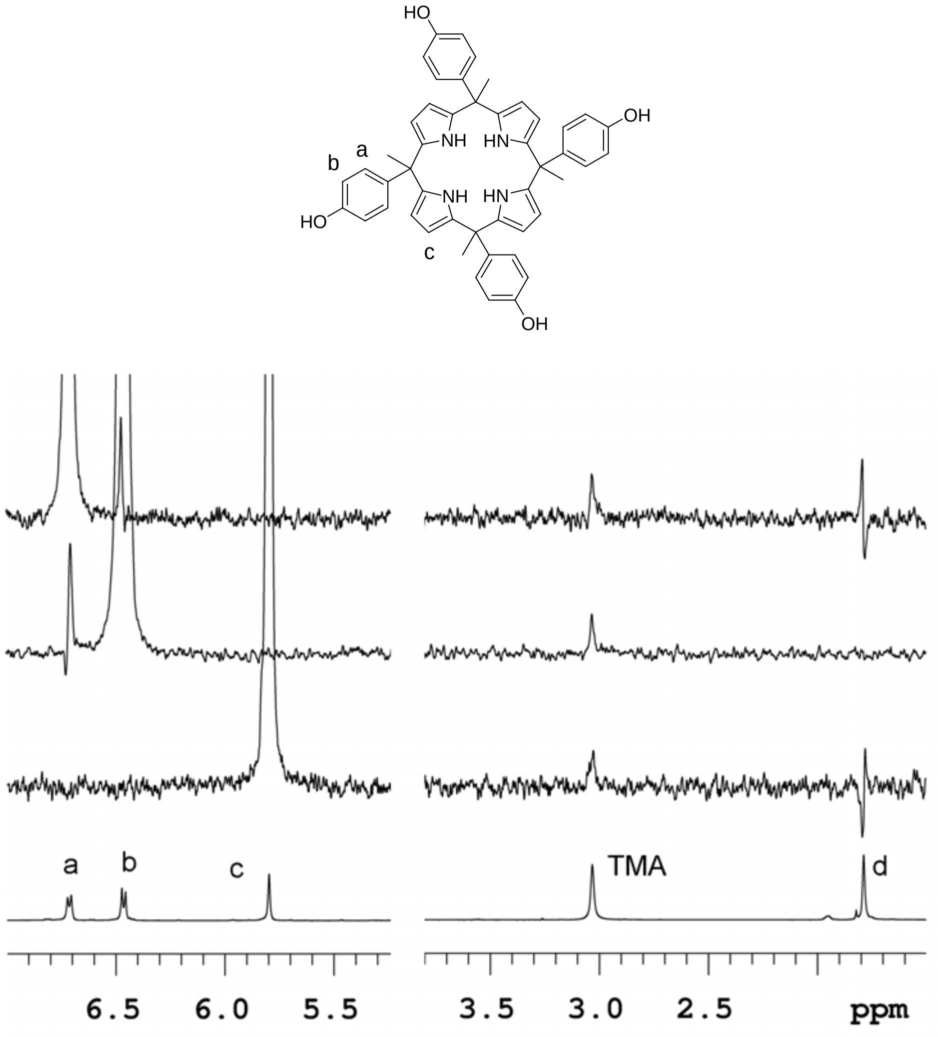

Figure S5. ^{1}H NMR NOESY-1D spectra for a solution of **1** (1.9 mM) and TMABr (3.0 mM) in D_2O. Spectra from top to bottom correspond to irradiation of signals a, b and c respectively. The ^{1}H NMR spectrum of the mixture is shown at the bottom.

(G) Crystal structure data

Crystal data for compound **1** x 2 + Cl$^-$ + TMA$^+$ + Acetone x 4: $C_{112}H_{124}Cl_1N_9O_{12}$ M = 1823.65, monoclinic, *P2/c*, *a* = 13.2426(10), *b* = 10.9831(10), *c* = 32.487(3) Å, β = 94.644(2)°; V = 4709.5(7) Å^3, Z = 2, D = 1.286 g cm^{-3}, *F*(000) = 1944 T= 100 °K; μ (Mo-K_α) = 0.111 mm $^{-1}$. 6652 independent reflections were collected on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (*T* = -173 °C). Full-sphere data collection was used with ω and φ scans. The structure was solved by direct methods and refined on F^2 using SHELXL97. Final R indices [I>2sigma(I)] R1=0.0861, wR2=0.2257. The structure presents disorder. The asymmetric unit is made up of one calixpyrrole with a disordered wall in two positions with occupation ratio 44:56, half tetramethylammonium chloride with the chloride disordered in two positions with occupation ratio 81:19 and two acetone molecules disordered in two and three positions respectively with occupations ratio 70:30 and 62:25:13. Check-cif Alert A explanation: Due to ice formation during the measurement no better completeness than 94% could be obtained. Distances between atoms O1R, O1R’ and O1R, O1R” are not relevant since O1R, O1R’ and O1R” belongs to different disordered groups from the same acetone molecule.