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Electronic Supplementary Information

Self-Assembly Supramolecular Polymer by Anti-Electrostatic Anion-Anion and Halogen Bonding Interactions

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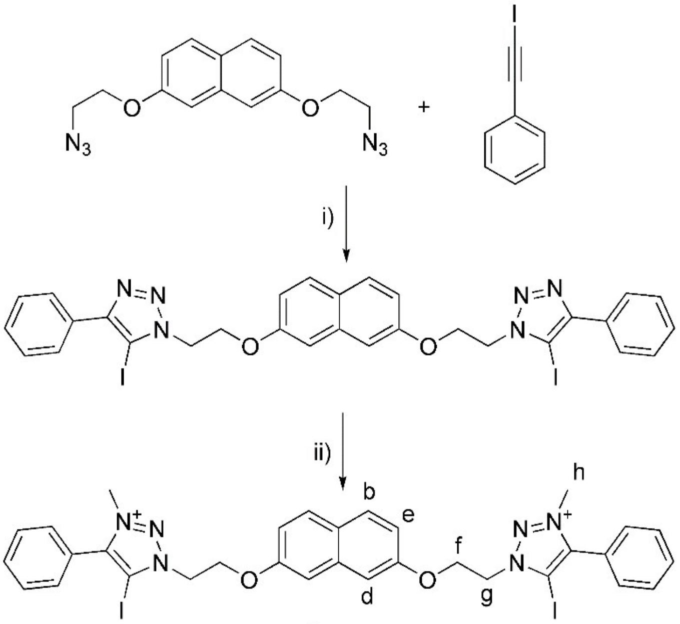
Experimental Procedures

All reactions were carried out using solvents that were dried by routine procedures. All melting points were determined by means of a Kofler hot-plate melting-point apparatus and are uncorrected. Solution ^{1}H, and ^{13}C spectra were recorded with Bruker 200, 300, 400, or 600 MHz spectrometers. The following abbreviations have been used to state the multiplicity of the signals: s (singlet), d (doublet), t (triplet) and m (multiplet). Chemical shifts (δ) in the ^{1}H and ^{13}C NMR spectra are referenced to tetramethylsilane (TMS). Diffusion NMR experiments (DOSY) were recorded with a Bruker 600 spectrometer (1H) using the LED-BPP sequence with a diffusion period (Δ) of 150 ms, field gradient pulses (δ) of 4 ms applied as half-sine profile bipolar pairs and an LED period of 5 ms. Field gradients were varied from 2-90% of maximum (53 G/cm) in 16 steps and data were analysed using Bruker TOPSPIN 2.1 software. Sample temperature was regulated at 293K.
Mass spectra were recorded with a Fisons AUTOSPEC 500 VG spectrometer and FAB+ mass spectra were carried out with 3-nitrobenzylalcohol as a matrix. Microanalyses were performed with a Carlo–Erba 1108 instrument. Dynamic Light Scattering analyses were performed using a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd, UK) at 25ºC and a 173° angle relative to the source. The hydrodynamic diameter distributions were obtained by volume using the software package of the apparatus. Each curve represents the average of 3 measurements (16 runs each). Prior to analysis, all solutions were filtered.
Scanning electron microscopy (SEM) was performed using a JSM-6100 scanning microscope instrument and the images were obtained with the INCA software (Oxford Instrument). The samples were prepared on cover glass, which was cleaned using nitric acid prior to use. The cover glass was then dropped into a polymer dissolution in CH_3CN/MeOH 9:1. The supramolecular polymer in solid state on the cover glass was obtained by the vapour diffusion of diethyl ether into a solution of the polymer. Then the cover glass was dried for 16h at 25ºC and the gold film was deposited by a SEM coating system Bio Rad Polaron Division prior to perform the analyses.
The samples for transmission electron microscopy were prepared by drop-casting one drop of the colloidal solution onto a carbon coated copper grid which was placed on a piece of filter paper to remove excess solvent. Bright field TEM micrographs were obtained on a Tecnai T12 Transmission Electron Microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. No staining of the samples was necessary.
X-Ray Structure Determinations. Intensities were registered at low temperature on a Bruker D8QUEST diffractometer using monochromated Mo $K\alpha$ radiation (λ = 0.71073Å). Absorption corrections were based on multi-scans (program SADABS). Structures were refined anisotropically using SHELXL-2016. Hydrogen atoms were included using rigid methyl groups or a riding model. *Special features and exceptions*: The iodine atoms are disordered over two positions, I1 (64:38%) and I2 (52:48%). One NO_2 ligand is disordered over two positions, 51:49%. The sulphate anion is also disordered over two positions, 69:32%.

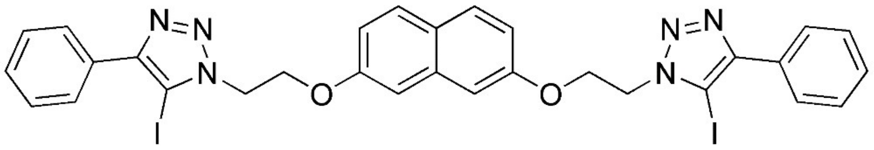
PART I: Synthesis



$1^{2+}\cdot 2BF_4^-$

Scheme 1. Synthesis of receptor **$1^{2+}\cdot 2BF_4^-$**. i) tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA), CuI, THF. ii) trime-thyloxonium tetrafluoroborate, CH_2Cl_2.

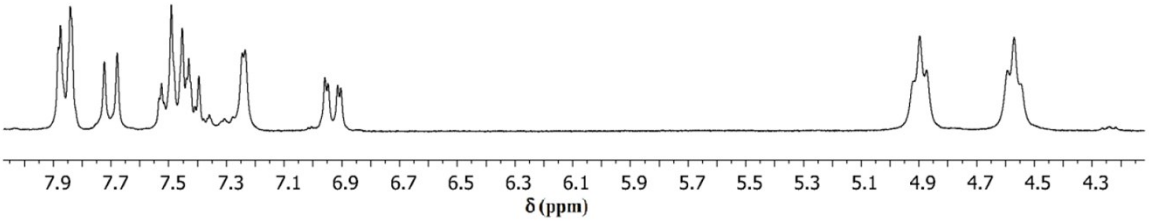
Synthesis of the bis-iodotriazole



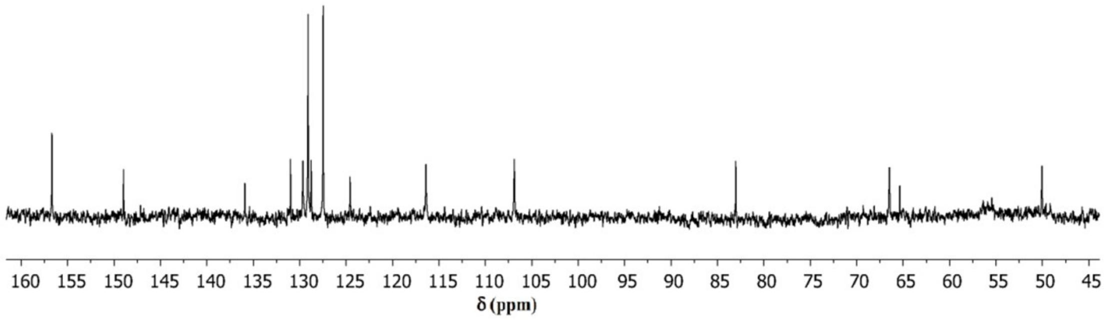
Copper iodide (0.077 g 0.4 mmol) and TBTA (0.210 g, 0.4 mmol) were stirred in dry THF (10 ml) for 20 min. The catalyst solution was added to a solution (30 ml THF) of 1-(2-iodoethynyl)benzene **2** (0.550 g, 2.4 mmol) and azide **1** (0.300 g, 1 mmol) and the reaction left to stir in the dark for 48 h at r.t. before being quenched with 10 % ammonium hydroxide solution (30 mL). The mixture is allowed to stir for 15 minutes, appearing a pale-yellow solid which is filled in vacuo. The solid is washed with more ammonium hydroxide solution (30 ml) and water (120 ml) and finally with methanol (50 ml).

Yield=(0.656 g, 87 %); **m.p.** 217ºC (decomposes); **^{1}H NMR**- δ (DMSO-d_6, 200MHz): 7.87 (dd, 4H, J = 1.5 Hz, J = 8.2 Hz), 7.70 (d, 2H, J = 8.9 Hz), 7.45 (m, 6H), 7.23 (d, 2H, J = 2.1 Hz), 6.93 (dd, 2H, J = 2.1 Hz, J = 8.9Hz), 4.89 (t, 4H, J = 4.5 Hz), 4.57 (t, 4H, J = 4.5 Hz); **^{13}C NMR**- δ (DMSO-d_6, 50MHz): 156.7, 149, 135.9, 131, 129.7, 129.2, 128.8, 127.5, 124.6, 116.4, 106.9, 83.0, 66.5, 50.1; **MS (ESI)**: *m/z* calc. for $C_{30}H_{24}I_2N_6O_2$ $[M+H]^+$ 755.01, found 755.01.

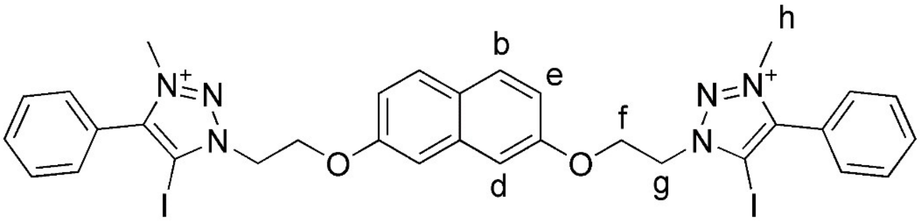
^{1}H-NMR



^{13}C-NMR



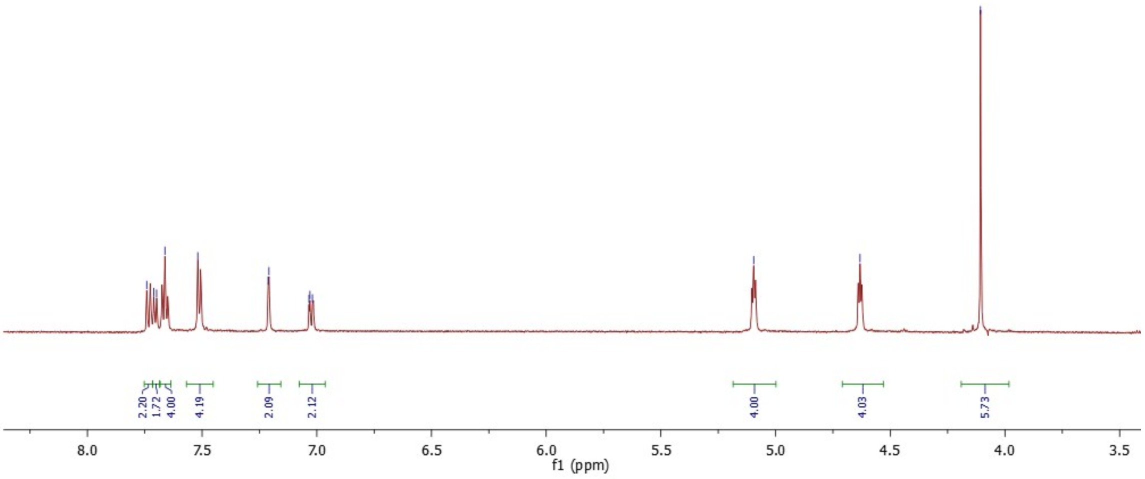
Synthesis of the monomer $1^{2+}\cdot 2BF_4^-$.



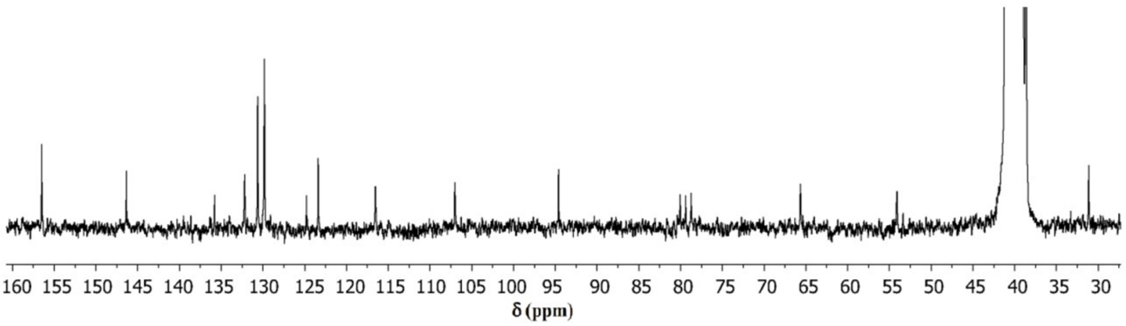
$1^{2+}\cdot 2BF_4^-$

A solution of bis-iodotriazole (0.449 g, 0.60 mmol) in dry dichloromethane (15 mL) was treated with trimethyloxonium tetrafluoroborate (0.220 g, 1.44 mmol) and the reaction mixture left to stir under N_2 for 48 h at r.t. and then all volatile components were removed in vacuo to give a yellow oil, which was purified by silica gel column chromatography (eluent CH_2Cl_2/CH_3OH 8:2) to give an yellow solid. **Yield**=(0.120 g, 21 %); **m.p.** 195 ºC (decomposes); **^{1}H NMR**- δ (CD_3CN/CD_3OD 9:1, 600MHz): 7.74 (d, 2H, J = 9 Hz), 7.71 (d, 2H, J = 7.3 Hz), 7.67 (t, 4H, J = 7.3 Hz), 7.52 (d, 4H, J = 8.2 Hz), 7.22 (d, 2H, J = 2.4 Hz), 7.03 (dd, 2H, J = 2.4 Hz, J = 8.9 Hz), 5.10 (t, 4H, J = 4.8 Hz), 4.64 (t, 4H, J = 4.8 Hz), 4.11 (s, 6H); **^{13}C NMR**- δ (CD_3CN, 100MHz): 156.4, 146.3, 135.8, 132.2, 130.6, 129.8, 124.8, 123.4, 116.5, 107, 94.6, 65.7, 54.1, 31.1; **MS (ESI)**: *m/z* calc. for $C_{32}H_{30}B_2F_8I_2N_6O_2$ [M^{2+}] 392.04, found 392.04.

^{1}H-NMR



^{13}C-NMR



PART II: ^{1}H NMR Experiments

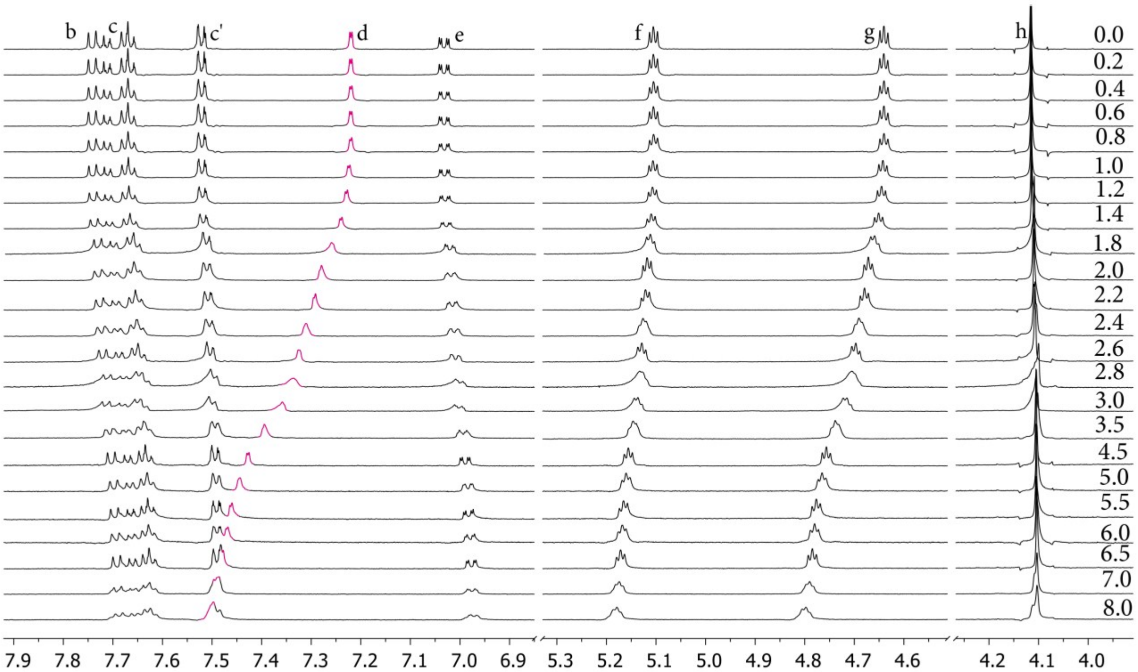


Figure SI1. ^{1}H NMR spectral changes observed in $\mathbf{1^{2+}\cdot 2BF_4^-}$ in CD_3CN/CD_3OD (9/1, v/v) during the addition of up to 8 equiv of $H_2PO_4^-$ anions.

Table SI1. Experimental NMR diffusion coefficients *D* (10^{-9} m^2s^{-1}) recorded as a function of the concentration of the bis-iodotriazolium receptor $\mathbf{1^{2+}\cdot 2BF_4^-}$ and the species $\mathbf{1^{2+}\cdot 2H_2PO_4^-}$ measured in CD_3CN/CD_3OD (9:1 v/v).

C (mM)	$\mathbf{1^{2+}\cdot 2BF_4^-}$	$\mathbf{1^{2+}\cdot 2H_2PO_4^-}$
2.5	1.083	0.817
1.25	1.081	0.848
0.625	1.075	0.913

PART III: Thermodynamic model.

In order to elaborate the thermodynamic model used to describe the formation of the heteromonomer supramolecular polymers we have used the same strategy recently applied by our research group[1]. The model is composed of one initial nucleation equilibrium followed by successive elongation steps

$$A + n\,B \rightleftarrows (AB_n), \qquad K_{\mathrm{N}} = \frac{[(AB_n)]}{[A]\,[B]^n} \ (\mathrm{M}^{-n}) \tag{1a}$$

$$(AB_n) + A + n\,B \rightleftarrows (AB_n)_2, \qquad K_{\mathrm{E}} = \frac{[(AB_n)_2]}{[(AB_n)]\,[A]\,[B]^n} \ (\mathrm{M}^{-1-n}) \tag{1b}$$

$$\vdots$$

$$(AB_n)_{i-1} + A + n\,B \rightleftarrows (AB_n)_i, \qquad K_{\mathrm{E}} = \frac{[(AB_n)_i]}{[(AB_n)_{i-1}]\,[A]\,[B]^n} \quad (\mathrm{M}^{-1-n}) \tag{1c}$$

$$\vdots$$

where A, B and $(AB_n)_i$ denote the receptor, the anion, and the supramolecular polymer of length i respectively. In the initial nucleation step (1a) an (AB_n) nucleus is formed which is subsequently elongated through the reversible addition of the monomers to post-nucleus polymer. We note that the above equations consider a polymer with general n:1 anion-receptor stoichiometry so that n is not necessarily an integer number. For instance, a 3:2 anion-receptor stoichiometry would correspond to $n = 1.5$.

From Equation (1) we can express the concentration of the polymers in terms of $[A]$ and $[B]$ as follows

$$[(AB_n)] = K_N[A][B]^n \tag{2a}$$

$$[(AB_n)_2] = K_E[(AB_n)][A][B]^n = K_N K_E[A]^2[B]^{2n} \tag{2b}$$

$$[(AB_n)_3] = K_E[(AB_n)_2][A][B]^n = K_N K_E^2[A]^3[B]^{3n} \tag{2c}$$

$$\vdots$$

$$[(AB_n)_i] = K_E[(AB_n)_{i-1}][A][B]^n = K_N K_E^{i-1}[A]^i([B]^n)^i \tag{2d}$$

The total concentration of A (C_A) is then given by

$$\begin{aligned} C_A &= [A] + [(AB_n)] + 2\,[(AB_n)_2] + 3\,[(AB_n)_3] + \ldots \\ &= [A] + \sum_{i=1}^{\infty} i\,[(AB_n)_i] \\ &= [A] + \sum_{i=1}^{\infty} i\,K_N\,K_E^{i-1}[A]^i([B]^n)^i \\ &= [A] + K_N K_E^{-1} \sum_{i=1}^{\infty} i\,(K_E[A][B]^n)^i \\ &= [A] + K_N\,\frac{[A][B]^n}{(1 - K_E\,[A][B]^n)^2} \end{aligned} \tag{3}$$

where the identity

$$\sum_{i=1}^{\infty} i\,x^i = \frac{x}{(1-x)^2}$$

was used in the last step. Following a similar procedure, we obtain

$$C_B = [B] + n\, K_N \frac{[A][B]^n}{(1 - K_E\, [A][B]^n)^2} \tag{4}$$

We note that from Equations (3) and (4) we can also derive

$$n(C_A - [A]) = C_B - [B] \tag{5}$$

which is a direct consequence from the stoichiometry of Equation (1).

Equations (3) and (4) stablish the relationship between the total concentration of A and B (C_A and C_B), quantities decided at the beginning of the experiment, and their values at equilibrium ($[A]$ and $[B]$), quantities directly related to the measurement of some experimental quantity, the NMR shift in our present study. The $[A]$ concentrations can be estimated from the measured NMR shifts, assuming that they can be evaluated using the following weighted sum

$$\delta = \frac{[A]}{C_A}\,\delta_A + \frac{C_A - [A]}{C_A}\,\delta_{\text{sp}} \tag{6}$$

where δ_A and δ_{sp} are the NMR shifts in the isolated receptor and the supramolecular polymer, respectively.

In practice we carried out two sets of fits. Firstly, the values of K_N, K_E, δ_{sp} and n are fitted using equations (3), (4) and (6) to reproduce the observed NMR shifts. This fit provides us an approximate value of the stoichiometry coefficient n that for the **$1^{2+}\cdot 2BF_4^-$ / $H_2PO_4^-$** polymer was 1.84 what points out a 2:1 stoichiometry. Then a new fit of the values of K_N, K_E, and δ_{sp} was performed fixing $n = 2$.

PART IV: SEM images.

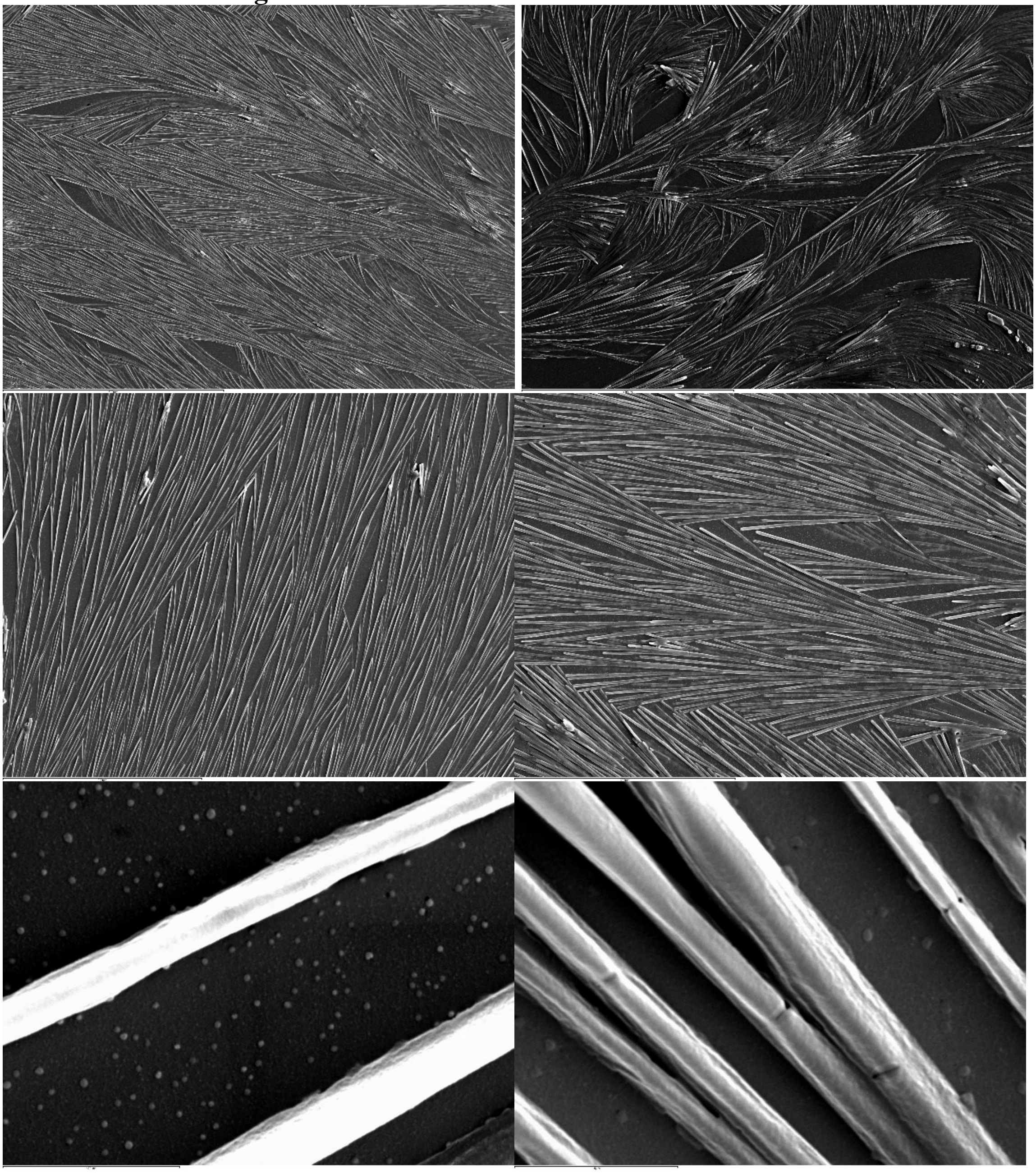


Figure SI2. Six different SEM images of the self-assembled compounds $\mathbf{1^{2+}\cdot 2H_2PO_4^-}$.

PART V: TEM images

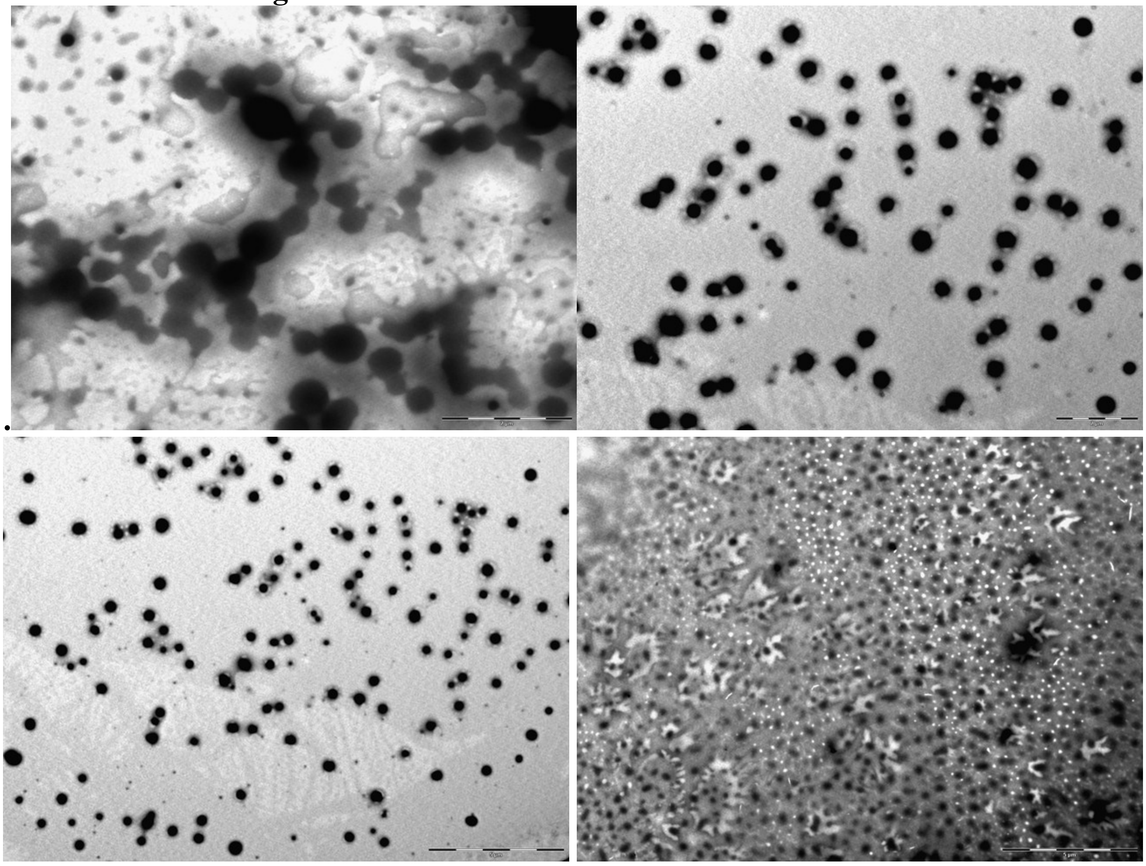


Figure SI3. Four different TEM images of the self-assembled compounds $\mathbf{1^{2+}\cdot 2H_2PO_4^-}$

PART VI: X-ray

Table 1. Crystal data and structure refinement for LG2S_0m075sp_a_sq.

Identification code	LG2S_0m075sp_a_sq	
Empirical formula	C16 H18.50 I N3 O7 P1.50	
Formula weight	538.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.2071(14) Å	α= 90°.
	b = 26.934(4) Å	β= 94.840(6)°.
	c = 21.649(3) Å	γ = 90°.
Volume	4768.5(13) Å^3	
Z	8	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	1.481 mm^{-1}	
F(000)	2136	
Crystal size	0.180 x 0.060 x 0.040 mm^3	
Theta range for data collection	1.888 to 27.102°.	
Index ranges	-10<=h<=10, -34<=k<=34, -27<=l<=27	
Reflections collected	385552	
Independent reflections	10526 [R(int) = 0.0645]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6943	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10526 / 46 / 533	
Goodness-of-fit on F^2	1.175	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1052	
R indices (all data)	R1 = 0.0547, wR2 = 0.1075	
Largest diff. peak and hole	1.436 and -1.335 e.Å^{-3}	

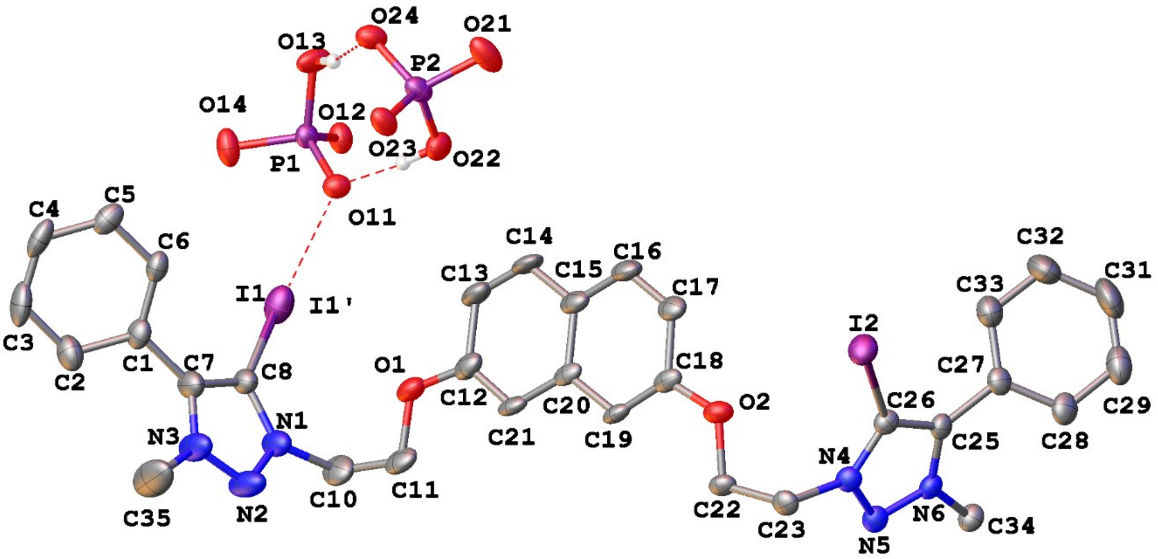


Figure SI4. X-ray structure of $\mathbf{1^{2+}\cdot 2H_2PO_4^{-}}$. Thermal ellipsoids are drawn at the 50% probability level

References

(1) Sabater, P.; Zapata, F.; Bastida, A.; Caballero, A. *Org. Biomol. Chem.*, 2020, DOI: 10.1039/d0ob00258e