Electronic Supplementary Information

Modulation of hydrophilicity inside the cavity of molecular rectangles self-assembled under ambient conditions

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Section S-1: General Information

Materials and methods. All chemicals and solvents used for synthesis were obtained from commercial sources and were used as received, without further purification. All reactions were carried out under aerobic conditions. The tppn, tpbn and tppen ligands were prepared by modifying the literature procedure.[15]

Caution! In this study metal perchlorates were used without any problem but special care should be taken to handle such salts which are dangerous.

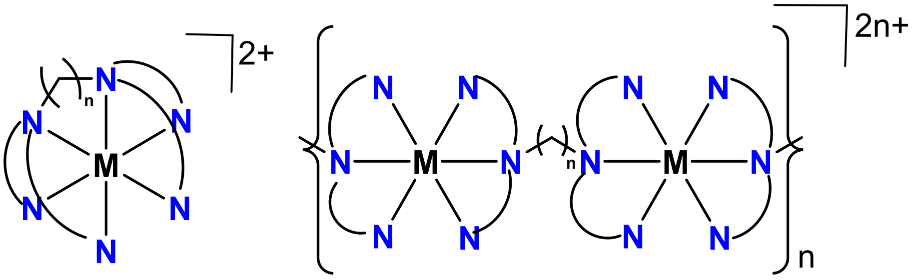
Physical measurements. *Elemental analysis* (C, H, N) was carried out using a Leco TruSpec Micro analyzer. *FTIR* spectra were measured in the 4000-400 cm^{-1} range on a Perkin-Elmer Spectrum I spectrometer with samples prepared as KBr pellets. *UV-Vis* spectra were recorded using a Cary 5000 instrument by Agilent Technology. *ESI Mass spectrometry* data were measured by Thermo Scientific LTQ XL LC-MS instrument for the 50-2000 amu range with ESI ion source. *Field Emission Scanning Electron Microscopy* (FESEM) was performed on a Zeiss EVO 40 instrument; samples were well dispersed in MeOH, drop casted in a silicon wafer, dried and coated with gold using a working distance of 4.5 to 15 mm and voltage 10 to 20 kV. *X-band EPR spectra* was collected with frozen acetonitrile solution of samples in a Bruker EMX spectrometer at 77 K.

Single crystal X-ray data collection and refinements. For manipulation, selection and mounting, crystals of each compound were transferred from mother liquor to mineral oil. Using an optical microscope, one suitable crystal was then put inside the nylon loop attached to a goniometer head which was placed under a cold stream of nitrogen gas for slow cooling to the desired temperature. Initial crystal evaluation and data collection were performed on a Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealed-tube monochromated MoKα radiation. The diffractometer was interfaced to a PC that controlled the crystal centering, unit cell determination, refinement of the cell parameters and data collection through the program APEX2.[1] By using the program SAINT[1] for the integration of the data, reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained. Data were also corrected for Lorentz and polarization effects. The subroutine XPREP[1] was used for the processing of data that included determination of space group, application of an absorption correction (SADABS)[1], merging of data and generation of files necessary for solution and refinement. Each structure was solved and refined using either SHELX 97[2] or Olex2[3] with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL programs. Several full-matrix least-squares/difference Fourier cycles were performed, locating the remainder of the non-hydrogen atoms and to have reasonable thermal parameters and converged refinement resulting in the lowest residual factors and optimum goodness of fit. Thus, the disorder in perchlorate ions and occupancy factors for water molecules were addressed accordingly, minimizing the residual electron densities. All non-hydrogen atoms, except where indicated otherwise, were refined with anisotropic displacement parameters. Hydrogen atoms were added as riding models (wherever possible) in final stage of the refinement. Hydrogen bonding parameters were generated using PLATON.[4,5]

[1] APEX2, SADABS, and SAINT; Bruker AXS inc: Madison, WI, USA, 2008.
[2] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.*, 2015, **71**, 3–8.
[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
[4] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
[5] A. L. Spek, *PLATON, Version 1.62*, University of Utrecht, 1999.

Section S-2: Possible structures for the different Metal to Ligand ratio

For a 1:1 ratio:



For a 2:1 ratio:

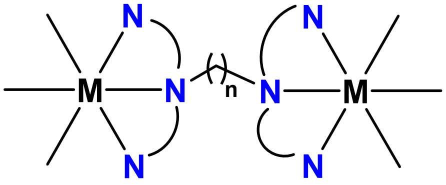


Fig. S1 Two possible structures (monomer and polymer) and one structure (desired for making coordination polymers and metal organic frameworks containing a third component) for the 1:1 and 2:1 complexes of M^{2+} ion and tpxn ligands, respectively.

Section S-3: Synthesis of 1-3

Synthesis of $[Cu_4(tppn)_2(tdc)_2(H_2O)_4](ClO_4)_4{\cdot}2.5H_2O$ (1). 46.5 mg (0.125 mmol) of $Cu(ClO_4)_2{\cdot}6H_2O$ and 27.4 mg (0.0625 mmol) of tppn were dissolved in 3 mL methanol. To this was added a clear solution of disodium thiophene dicarboxylate (Na_2tdc) [prepared by taking 11.0 mg (0.0625 mmol) of thiophene dicarboxylic acid and 5 mg (0.125 mmol) of sodium hydroxide in 1 mL of MeOH and 1 mL of water]. It immediately gave a blue precipitate. The reaction mixture was stirred for another 3.5 hours at room temperature. A blue solid was obtained via filtration using a G4 crucible, washed with methanol and vacuum dried. Yield: 50.3 mg (81%). Anal. Calcd for $C_{66}H_{77}N_{12}Cu_4Cl_4S_2O_{30.5}$ (MW 1986.51): C, 39.90; H, 3.91; N, 8.46. Found: C, 39.852; H, 3.658; N, 8.652.Selected FTIR peaks (KBr, cm^{-1}):3435, 1612vs, 1577s, 1530m, 1358vs, 1097vs, 769m, 632m. Selected Raman Peaks (cm^{-1}): 3077s, 1611w, 1573w, 1457vs, 1029s, 927m, 655m. UV-Vis: λ_{max}: 625 nm.

Synthesis of $[Cu_4(tpbn)_2(tdc)_2(H_2O)_4](ClO_4)_4{\cdot}2H_2O$ (2). It was prepared following the procedure described above for **1** except that the tpbn ligand (0.0625 mmol, 28.5 mg) was used and the reaction mixture was stirred for two hours. Yield: 47.1 mg (74.5%). Anal. Calcd for $C_{68}H_{80}N_{12}Cu_4Cl_4S_2O_{30}$ (MW 2005.55): C, 40.72; H, 4.02; N, 8.38. Found: C, 39.964; H, 3.722; N, 7.652. Selected FTIR peaks (KBr, cm^{-1}):3430, 1610vs, 1578s, 1528m, 1359vs, 1088vs, 768m, 625m. Selected Raman Peaks (cm^{-1}): 3079s, 1611w, 1571w, 1461vs, 1030s, 929m, 810, 658m, 621. UV-Vis: λ_{max}: 630 nm.

Synthesis of $[Cu_4(tppen)_2(tdc)_2(H_2O)_4](ClO_4)_4{\cdot}4H_2O$ (3). It was prepared following the procedure described above for **1** except that the tppen ligand (0.0625 mmol, 29 mg) was used and the reaction mixture was stirred for seven hours. Yield: 50.2 mg (77%). Anal. Calcd for $C_{70}H_{88}N_{12}Cu_4Cl_4S_2O_{32}$ (MW 2069.64): C, 40.62; H, 4.29; N, 8.12. Found: C, 40.09; H, 3.898; N, 8.391. Selected FTIR peaks (KBr, cm^{-1}):3438, 1611vs, 1581s, 1528m, 1356vs, 1091vs, 770m, 624m. Selected Raman Peaks (cm^{-1}): 1468vs, 1033, 931, 854. UV-Vis: λ_{max}: 614 nm.

Section S-4: Summary of crystal data and refinement parameters for 1-3

Crystal data for **1**: $C_{66}H_{75}Cl_4Cu_4N_{12}O_{29.5}S_2$, M = 1968.46, Orthorhombic, space group *Pbcn*, a = 18.0508(7) Å, b = 17.7526(7) Å, c = 24.8923(9) Å, α = β = γ = 90°, V = 7976.7(5) Å^3, Z = 4, D_c = 1.639 g cm^{-3}, μ (Mo Kα) = 1.329 mm^{-1}, T = 120(2) K, 7019 reflections collected. Refinement of 5267 reflections (534 parameters) with $I > 2\sigma(I)$ converged at a final R_1 = 0.0609, wR_2 = 0.0869, GOF = 1.045. CCDC 1994270.

Crystal data for **2**: $C_{68}H_{80}Cl_4Cu_4N_{12}O_{30}S_2$, M = 2005.52, triclinic, space group *P-1*, a = 15.352(5) Å, b = 15.546(5) Å, c = 19.838(6) Å, α = 73.309(9)°, β = 78.299(12)°, γ = 63.132(9)°, V = 4031.0(2) Å^3, Z = 2, D_c = 1.652 g cm^{-3}, μ (Mo Kα) = 1.317 mm^{-1}, T = 150(2) K, 9743 reflections collected. Refinement of 4586 reflections (959 parameters) with $I > 2\sigma(I)$ converged at a final R_1 = 0.0915, wR_2 = 0.1965, GOF = 1.011. CCDC 1994271.

Crystal data for **3**: $C_{70}H_{86}Cl_4Cu_4N_{12}O_{31}S_2$, M = 2051.58, monoclinic, space group *Pc*, a = 20.1897(12) Å, b = 13.6168(8) Å, c = 16.2901(10) Å, α = 90°, β = 108.380(3) °, γ = 90°, V = 4250.0(4) Å^3, Z = 2, D_c = 1.603 g cm^{-3}, μ (Mo Kα) = 1.252 mm^{-1}, T = 170(2) K, 12851 reflections collected. Refinement of 9995 reflections (1065 parameters) with $I > 2\sigma(I)$ converged at a final R_1 = 0.0751, wR_2 = 0.0969, GOF = 1.042. CCDC 1994272.

Table S1. Selected Bond distances and angles for **1**.

Bond distances (Å)			
Cu1-O1	2.403(4)	Cu2-O2	2.203(4)
Cu1-O3	1.957(3)	Cu2-O6$^{\#1}$	2.006(4)
Cu1-N1	1.978(5)	Cu2-N4	2.062(5)
Cu1-N2	2.033(5)	Cu2-N5	1.977(5)
Cu1-N3	1.982(5)	Cu2-N6	1.981(5)
Bond angles (°)			
O3-Cu1-N1	94.18(18)	O3-Cu1-N3	100.52(18)
N1-Cu1-N3	165.0(2)	O3-Cu1-N2	159.36(17)
N1-Cu1-N2	83.82(19)	N3-Cu1-N2	83.41(19)
O3-Cu1-O1	106.61(16)	N1-Cu1-O1	85.61(17)
N3-Cu1-O1	87.44(17)	N2-Cu1-O1	93.75(17)
N5-Cu2-N6	166.1(2)	N5-Cu2-O6$^{\#1}$	94.66(18)
N6-Cu2-O6$^{\#1}$	94.22(18)	N5-Cu2-N4	83.03(19)
N6-Cu2-N4	84.52(19)	O6$^{\#1}$-Cu2-N4	155.89(14)
N5-Cu2-O2	100.14(18)	N6-Cu2-O2	89.71(19)
O6$^{\#1}$-Cu2-O2	94.67(18)	N4-Cu2-O2	109.38(19)

#1 = -x, y, -z+1/2

Table S2. Selected Bond distances and angles for **2**.

Bond distances (Å)

Cu1-O1	2.389(9)	Cu2-O2	2.312(9)	Cu3-O7	2.273(9)	Cu4-O8	2.351(9)
Cu1-O5	1.952(10)	Cu2-O4	1.989(9)	Cu3-O12$^{\#1}$	2.010(9)	Cu4-O9	1.961(10)
Cu1-N1	2.003(12)	Cu2-N4	1.991(13)	Cu3-N7	1.974(12)	Cu4-N10	1.995 (12)
Cu1-N2	2.013(12)	Cu2-N5	2.036(11)	Cu3-N8	2.036 (11)	Cu4-N11	2.014(13)
Cu1-N3	1.980(12)	Cu2-N6	1.987(14)	Cu3-N9	2.011(13)	Cu4-N12	1.979(12)

Bond angles (°)

O5-Cu1-N3	98.1(5)	N7-Cu3-O12$^{\#1}$	98.4(5)	O5-Cu1-N1	95.0(5)	N7-Cu3-N9	164.8(5)
N3-Cu1-N1	166.6(5)	O12$^{\#1}$-Cu3-N9	95.9(5)	O5-Cu1-N2	158.7(4)	N7-Cu3-N8	83.1(5)
N3-Cu1-N2	84.7(5)	O12$^{\#1}$-Cu3-N8	163.4(4)	N1-Cu1-N2	84.1(5)	N9-Cu3-N8	81.8(5)
O5-Cu1-O1	107.4(4)	N7-Cu3-O7	93.6(4)	N3-Cu1-O1	87.7(4)	O12$^{\#1}$-Cu3-O7	88.4(4)
N1-Cu1-O1	85.9(4)	N9-Cu3-O7	91.8(4)	N2-Cu1-O1	93.8(4)	N8-Cu3-O7	108.1(4)
N6-Cu2-O4	94.1(5)	O9-Cu4-N12	98.8(5)	N6-Cu2-N4	166.6(6)	O9-Cu4-N10	96.7(5)
O4-Cu2-N4	97.9(5)	N12-Cu4-N10	164.4(5)	N6-Cu2-N5	84.5(5)	O9-Cu4-N11	155.1(4)
O4-Cu2-N5	160.8(4)	N12-Cu4-N11	82.2(5)	N4-Cu2-N5	82.2(5)	N10-Cu4-N11	83.3(5)
N6-Cu2-O2	92.8(4)	O9-Cu4-O8	109.2(4)	O4-Cu2-O2	86.3(4)	N12-Cu4-O8	87.2(4)
N4-Cu2-O2	94.1(4)	N10-Cu4-O8	88.6(4)	N5-Cu2-O2	112.9(4)	N11-Cu4-O8	95.6(4)

#1 –x+1, -y+1, z

Table S3. Selected Bond distances and angles for **3**.

Bond distances (Å)

Cu1-O1	2.409(12)	Cu2-O2	2.305(10)	Cu3-O3	2.350(9)	Cu4-O4	2.445(10)
Cu1-O5	1.937(10)	Cu2-O10	1.984(10)	Cu3-O12	1.937(11)	Cu4-O7	1.954(9)
Cu1-N1	1.997(12)	Cu2-N4	1.997(11)	Cu3-N7	2.021(13)	Cu4-N10	1.995(12)
Cu1-N2	2.036(12)	Cu2-N5	2.027(13)	Cu3-N8	2.043(13)	Cu4-N11	2.012(11)
Cu1-N3	1.960(13)	Cu2-N6	2.004(13)	Cu3-N9	1.954(14)	Cu4-N12	1.995(11)

Bond angles (°)

O5-Cu1-N3	99.5(5)	O5-Cu1-N1	94.3(4)	O12-Cu3-N9	98.7(6)	O12-Cu3-N7	95.0(5)
N3-Cu1-N1	165.9(5)	O5-Cu1-N2	164.6(4)	N9-Cu3-N7	165.4(6)	O12-Cu3-N8	167.6(5)
N3-Cu1-N2	83.7(6)	N1-Cu1-N2	83.6(5)	N9-Cu3-N8	83.9(6)	N7-Cu3-N8	81.7(5)
O5-Cu1-O1	98.5(4)	N3-Cu1-O1	86.3(5)	O12-Cu3-O3	98.5(4)	N9-Cu3-O3	88.0(5)
N1-Cu1-O1	89.1(4)	N2-Cu1-O1	96.7(4)	N7-Cu3-O3	95.2(4)	N8-Cu3-O3	93.8(4)
O10-Cu2-N4	95.7(4)	O10-Cu2-N6	99.6(5)	O7-Cu4-N10	93.7(4)	O7-Cu4-N12	99.2(4)
N4-Cu2-N6	164.6(5)	O10-Cu2-N5	166.4(5)	N10-Cu4-N12	166.7(5)	O7-Cu4-N11	165.9(4)
N4-Cu2-N5	83.3(3)	N6-Cu2-N5	81.4(5)	N10-Cu4-N11	83.9(4)	N12-Cu4-N11	84.3(5)
O10-Cu2-O2	95.9(4)	N4-Cu2-O2	93.3(4)	O7-Cu4-O4	104.2(4)	N10-Cu4-O4	86.8(4)
N6-Cu2-O2	87.1(4)	N5-Cu2-O2	97.8(5)	N12-Cu4-O4	86.9(4)	N11-Cu4-O4	89.6(4)

Table S4. Hydrogen bond parameters for **1**, **2** and **3**.

For **1**:

D-H···A	**r (D-H), Å**	**r (H···A), Å**	**r (D···A), Å**	**∠D-H···A (°)**	**Symmetry**
O(1)-H(1B)···O(5)	0.87	2.15	2.7375	124	
O(2)-H(2A)···O(4)	0.82	1.89	2.7003	170	1-x,y,1/2-z
O(2)-H(2B)···O(16)	0.82	1.94	2.693	153	1-x,y,1/2-z
O(16)-H(16A)···O(8)	0.85	1.6	2.3315	143	
O(16)-H(16A)···O(9)	0.85	2.32	3.0255	140	
O(16)-H(16B)···O(17)	0.85	1.77	2.5592	153	
O(17)-H(17A)···O(6)	0.85	2.06	2.9066	177	1-x,y,1/2-z
C(7)-H(7)···O(13)	0.95	2.47	3.2307	137	1/2+x,1/2-y,-z
C(8)-H(8)···O(12)	0.95	2.55	3.2061	127	1/2+x,1/2-y,-z
C(9)-H(9)···O(5)	0.95	2.57	3.4724	160	-1/2+x,1/2-y,-z
C(13)-H(13A)···O(10)	0.99	2.43	3.3963	165	-1/2+x,1/2-y,-z
C(13)-H(13B)···O(9)	0.99	2.57	3.362	137	1/2-x,1/2+y,z
C(16)-H(16)···O(4)	0.95	2.42	3.3335	162	1/2-x,1/2+y,z
C(17)-H(17)···O(15)	0.95	2.55	3.1637	123	1/2-x,1/2+y,z
C(18)-H(18)···O(15)	0.95	2.58	3.1891	122	1/2-x,1/2+y,z
C(19)-H(19A)···O(12)	0.99	2.59	3.4049	139	
C(20)-H(20B)···O(4)	0.99	2.48	3.3828	151	
C(26)-H(26)···O(11)	0.95	2.58	3.3357	137	1-x,y,1/2-z
C(28)-H(28B)···O(11)	0.99	2.43	3.325	151	-1/2+x,1/2+y,1/2-z

For **2**:

D-H···A	**r (D-H), Å**	**r (H···A), Å**	**r (D···A), Å**	**∠D-H···A (°)**	**Symmetry**
O(1A)-H(1B)···O(11)	0.94	1.87	2.728(15)	150	
O(1)-H(1B)···O(13)	0.94	2.01	2.89(2)	157	
O(2)-H(2A)···O(29)	0.89	2.23	2.79(2)	120	1-x,-y,1-z
O(7)-H(7A)···O(30)	0.91	1.93	2.807(18)	161	1-x,1-y,-z
O(8)-H(8A)···O(18)	0.93	2.4	3.08(2)	130	-1+x,y, z
O(8)-H(8B)···O(3)	0.93	1.83	2.722(15)	159	
O(29)-H(29C)···O(4)	0.87	2.11	2.892(17)	150	1-x,-y,1-z
O(29)-H(29D)···O(14)	0.87	2.5	3.33(3)	160	
O(30)-H(30A)···O(17)	0.87	2.16	3.00(2)	164	1-x,1-y,-z
C(7)-H(7)···O(23)	0.95	2.48	3.12(2)	125	1-x,-y,1-z
C(13)-H(13B)···O(15)	0.99	2.53	3.46(4)	157	1-x,1-y,1-z
C(18)-H(18)···O(28)	0.95	2.59	3.44(2)	150	-x,1-y,1-z
C(20)-H(20B)···O(6)	0.99	2.49	3.32(2)	141	
C(21)-H(21A)···O(24)	0.99	2.56	3.53(2)	167	

C(24)-H(24)···O(13)	0.95	2.55	3.47(3)	162	1-x,-y,1-z
C(32)-H(32)···O(11)	0.95	2.56	3.44(2)	154	-x,1-y,1-z
C(33)-H(33)···O(15)	0.95	2.5	3.38(4)	154	-1+x,y,z
C(41)-H(41)···O(22)	0.95	2.53	3.36(2)	145	x,1+y,-1+z
C(43)-H(43)···O(10)	0.95	2.49	3.37(2)	155	x,1+y,z
C(46)-H(46A)···O(19)	0.99	2.51	3.40(2)	149	x,1+y,z
C(46)-H(46B)···O(24)	0.99	2.37	3.31(2)	160	1-x,1-y,1-z
C(51)-H(51)···O(25)	0.95	2.54	3.17(2)	124	1+x,y,-1+z
C(52)-H(52)···O(25)	0.95	2.59	3.21(2)	123	1+x,y,-1+z
C(53)-H(53B)···O(10)	0.99	2.59	3.22(2)	121	1-x,-y,1-z
C(54)-H(54A)···O(24)	0.99	2.5	3.29(2)	137	1-x, 1-y, 1-z
C(55)-H(55B)···O(21)	0.99	2.54	3.48(2)	159	1-x, 1-y, 1-z
C(61)-H(61)···O(19)	0.95	2.53	3.40(3)	152	1-x,1-y,-z
C(62)-H(62)···O(30)	0.95	2.59	3.46(2)	153	
C(63)-H(63A)···O(13)	0.99	2.54	3.53(2)	174	

For **3**:

D-H···A	**r (D-H), Å**	**r (H···A), Å**	**r (D···A), Å**	**∠D-H···A (°)**	**Symmetry**
O(1)-H(1B)···O(34)	0.87	2.05	2.7387	135	x,1-y,1/2+z
O(2)-H(2B)···S(1)	0.87	2.86	3.5504	137	x,1-y,1/2+z
O(2)-H(2B)···O(7)	0.87	2.00	2.7660	147	x,1-y,1/2+z
O(3)-H(3B)···O(11)	0.87	2.25	2.7834	120	
O(4)-H(4B)···O(11)	0.87	2.41	2.9669	123	x,1+y, z
O(32)-H(32A)···O(9)	0.87	1.97	2.7824	155	x, -y, -1/2+z
O(33)-H(33A)···O(18)	0.87	2.33	2.9794	132	
O(33)-H(33B)···O(22)	0.87	2.47	2.7824	115	x,-y,1/2+z
C(10)-H(10)···O(13)	0.95	2.59	3.4485	151	x,1-y,1/2+z
C(10)-H(10)···O(16)	0.95	2.45	3.1445	130	x,1-y,1/2+z
C(12)-H(12B)···O(15)	0.99	2.51	3.4406	157	
C(13)-H(13A)···O(16)	0.99	2.39	3.2401	144	
C(17)-H(17)···O(32)	0.95	2.40	3.3312	165	
C(20)-H(20A)···O(6)	0.99	2.45	3.3335	148	
C(24)-H(24A)···O(24)	0.99	2.29	3.1799	149	x,y,1+z
C(27)-H(27)···O(6)	0.95	2.20	3.1280	167	x,-y,1/2+z
C(28)-H(28)···O(27)	0.95	2.57	3.2314	127	x,-y,1/2+z
C(52)-H(52)···O(28)	0.95	2.42	3.2331	143	
C(57)-H(57B)···O(8)	0.99	2.56	3.4502	149	
C(62)-H(62)···O(8)	0.95	2.46	3.2920	146	x,1-y,-1/2+z
C(69)-H(69)···O(29)	0.95	2.43	3.3291	158	x,1-y,1/2+z
C(70)-H(70)···O(30)	0.95	2.59	3.3354	136	x,1-y,1/2+z

Section S-5: Characterization of 1-3

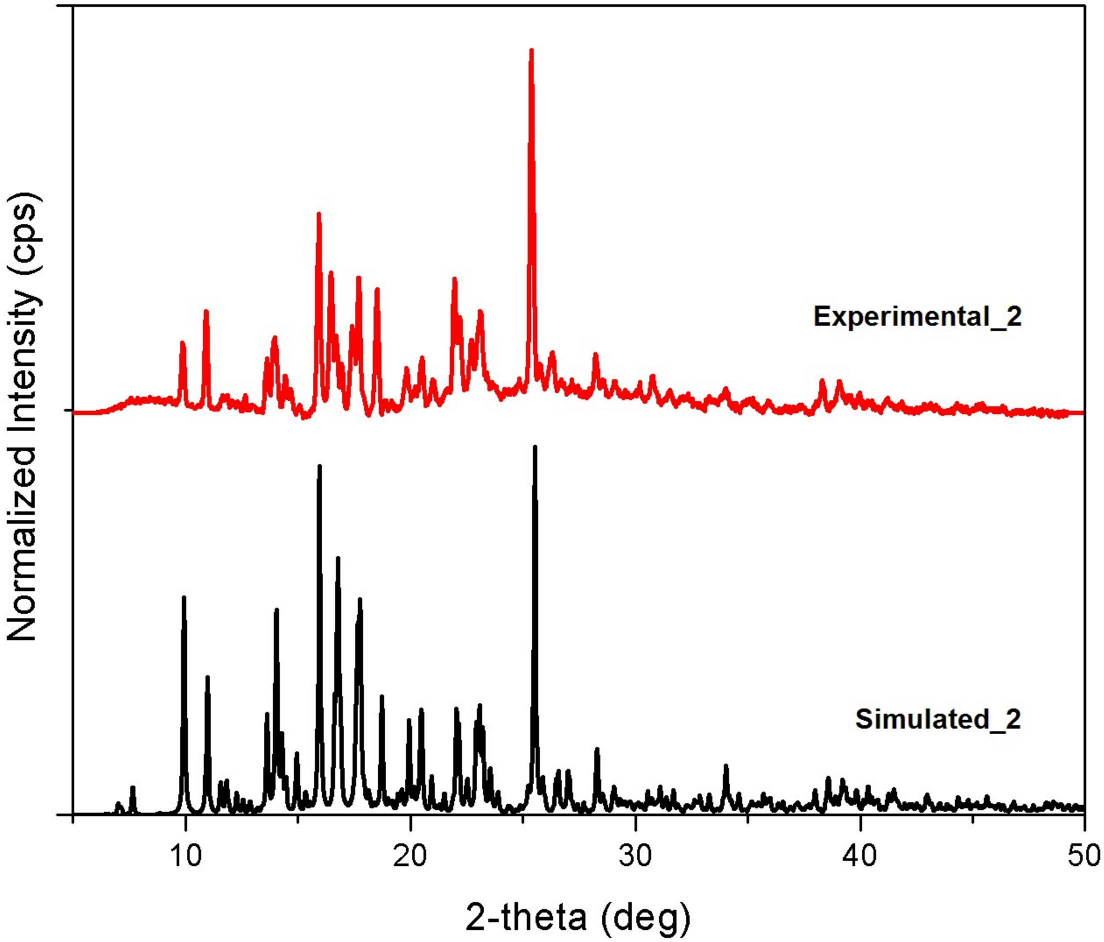


Fig. S2 Comparison of experimental and simulated (based on the single crystal data) powder X-ray diffraction for the as-isolated **2**.

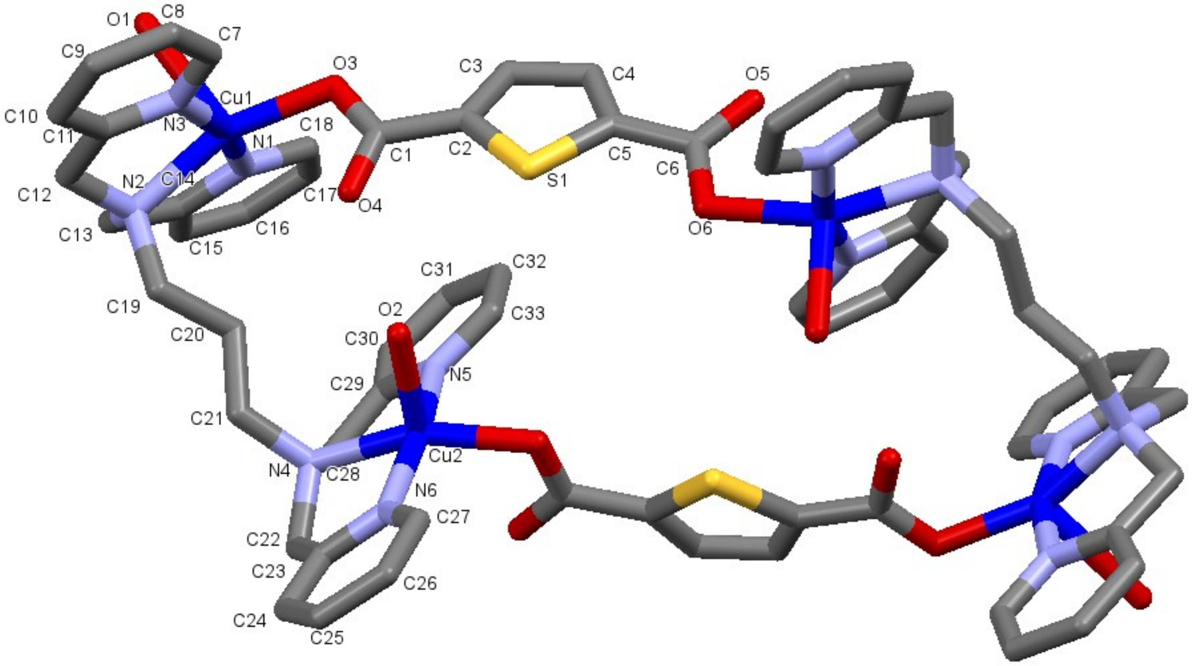


Fig. S3 Capped-stick drawing of the cation in **1** with atom labelling scheme; one half of the rectangle is in the asymmetric unit.

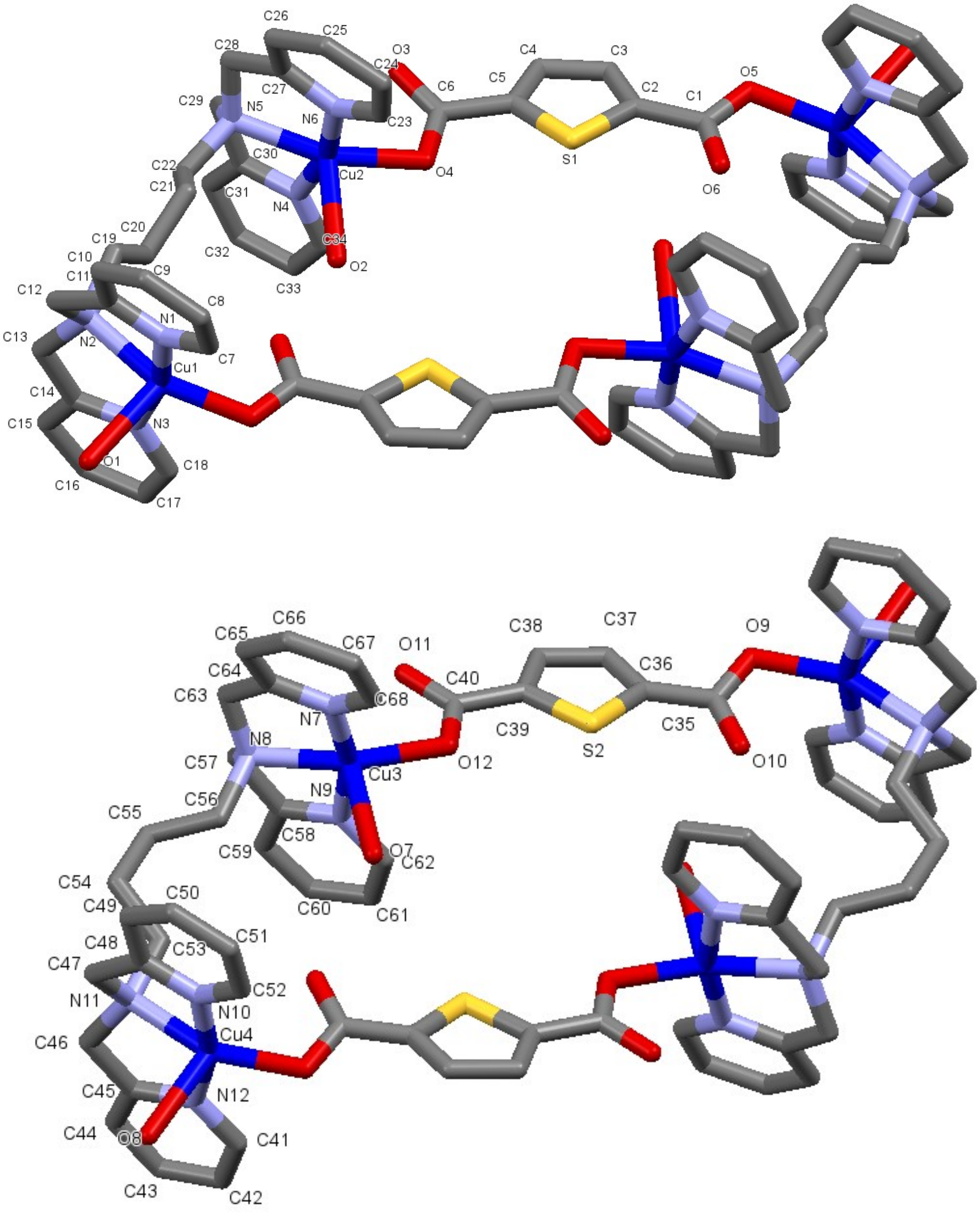


Fig. S4 Capped-stick drawing of the cation (two independent molecules) in **2** with atom labelling scheme; in each case, one half of the rectangle is in the asymmetric unit.

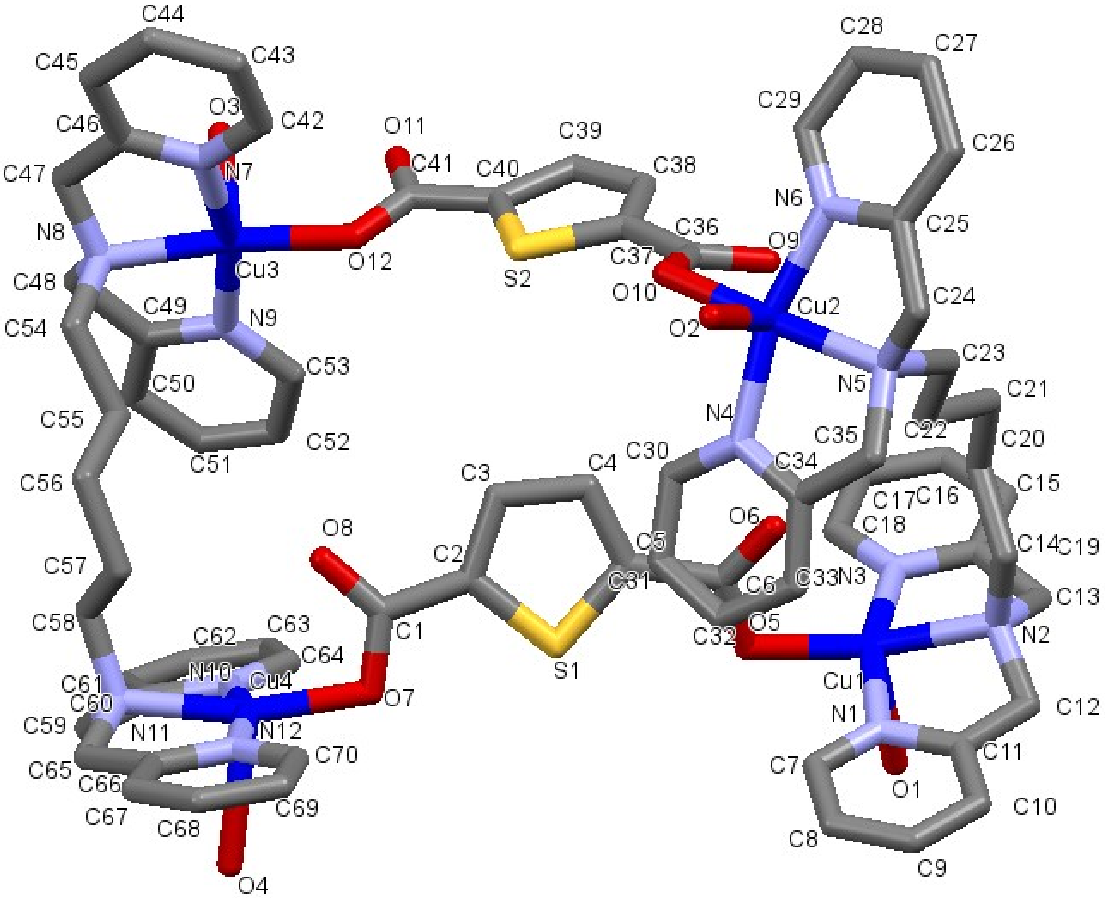


Fig. S5 Capped-stick drawing of the cation in **3** with atom labelling scheme.

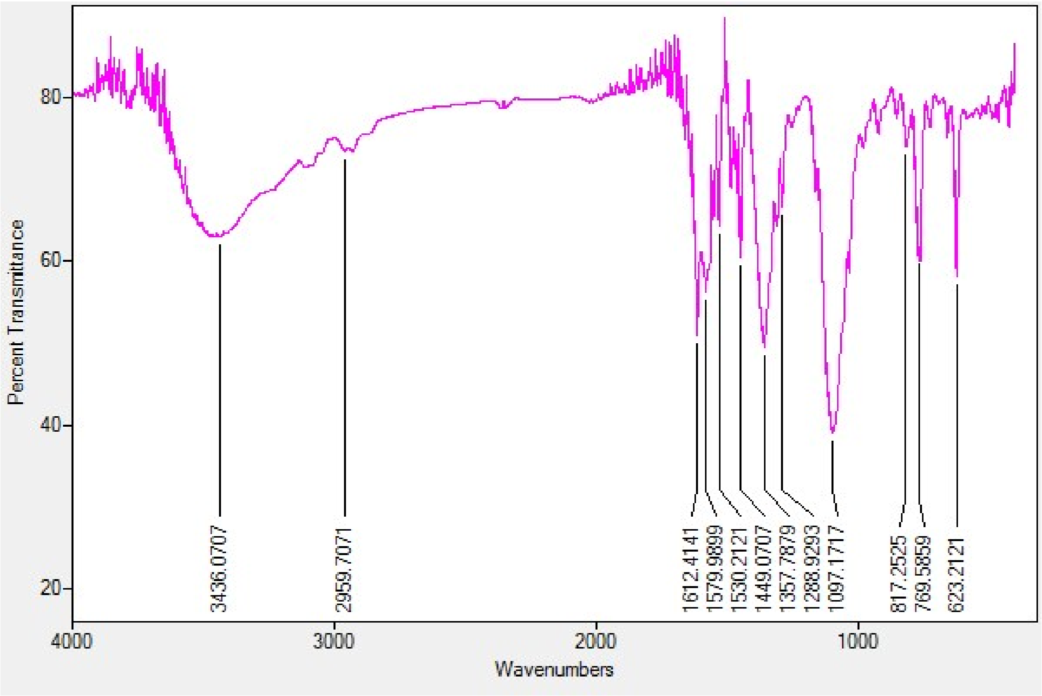


Fig. S6 FTIR spectrum of **1**.

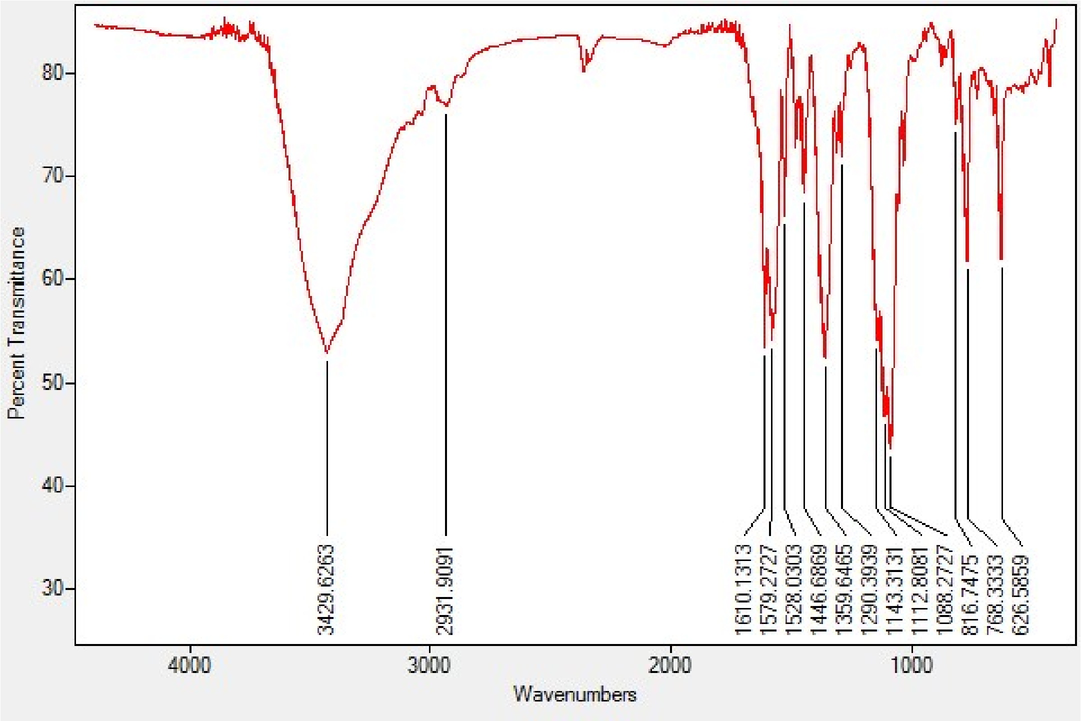


Fig. S7 FTIR spectrum of **2**.

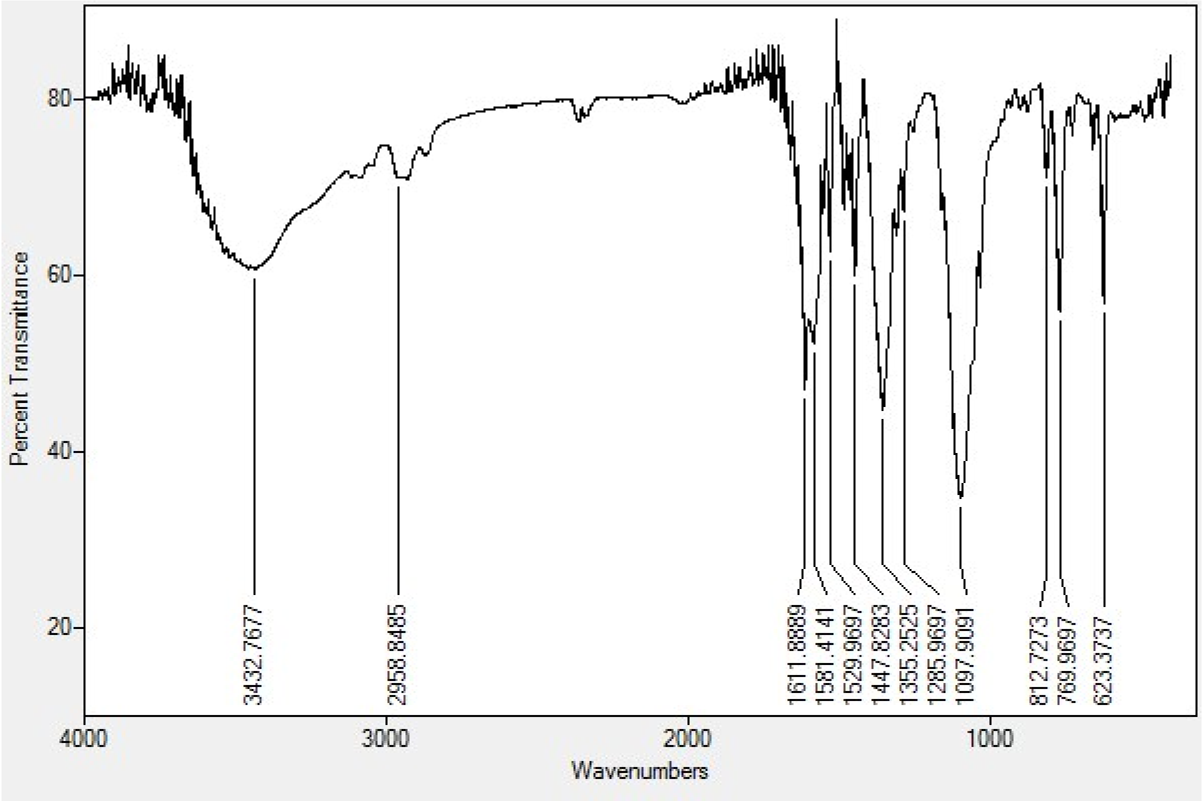


Fig. S8 FTIR spectrum of **3**.

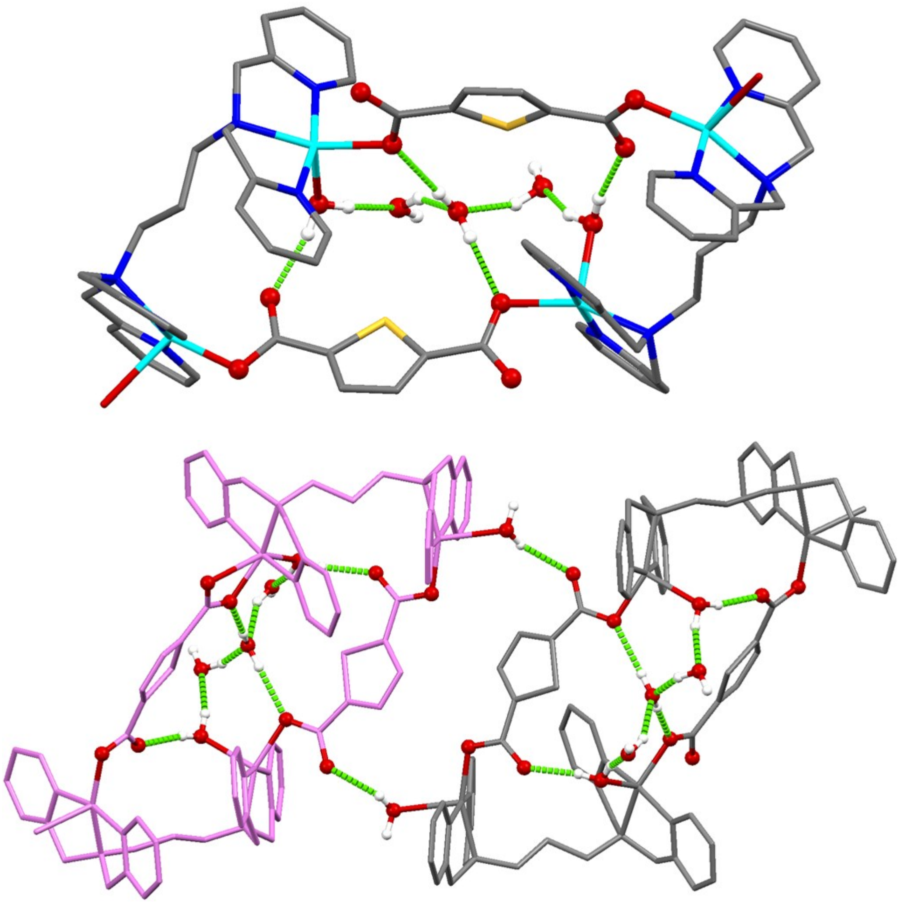


Fig. S9 Hydrogen bonding network (within and between molecular rectangles) in **1**.

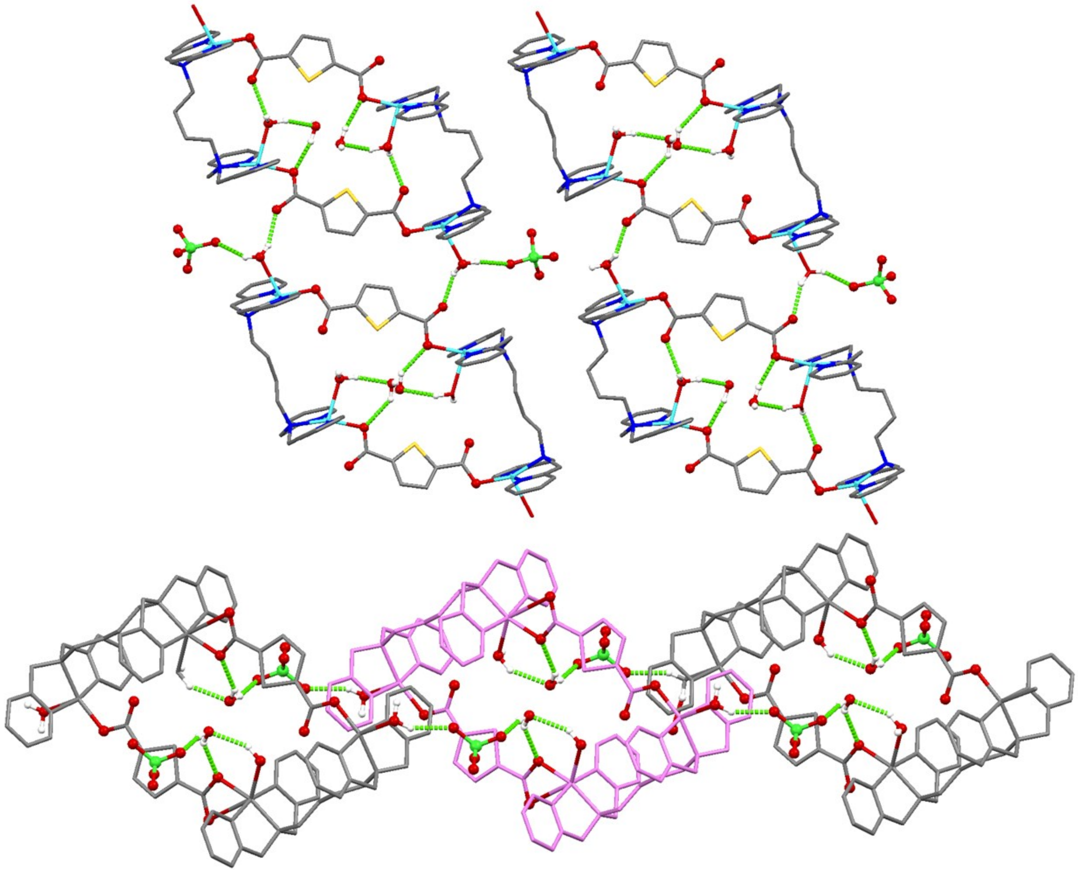


Fig. S10 Hydrogen bonding network (within and between molecular rectangles) in **2**.

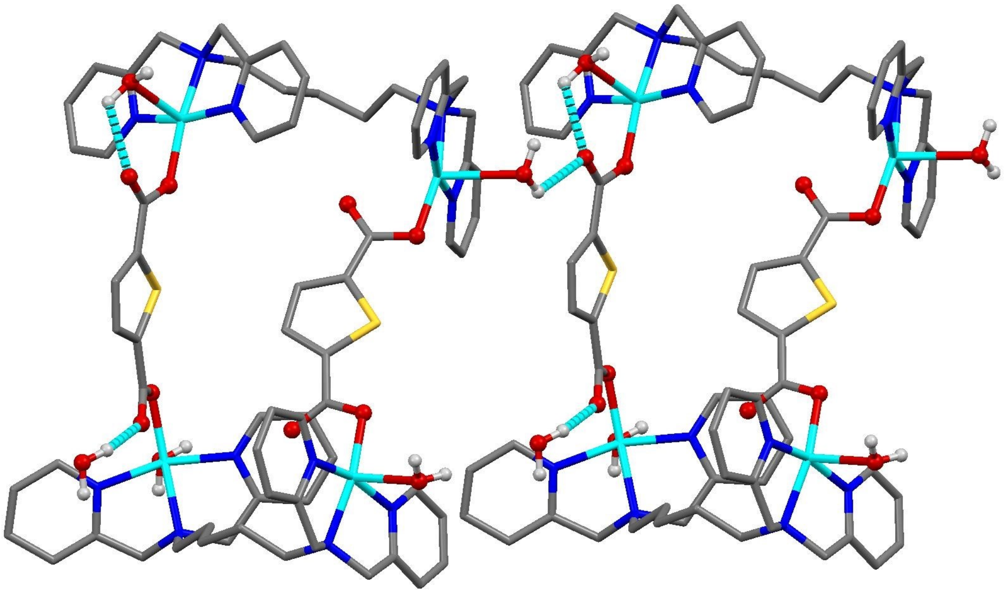


Fig. S11 Hydrogen bonding network (within and between molecular rectangles) in **3**.

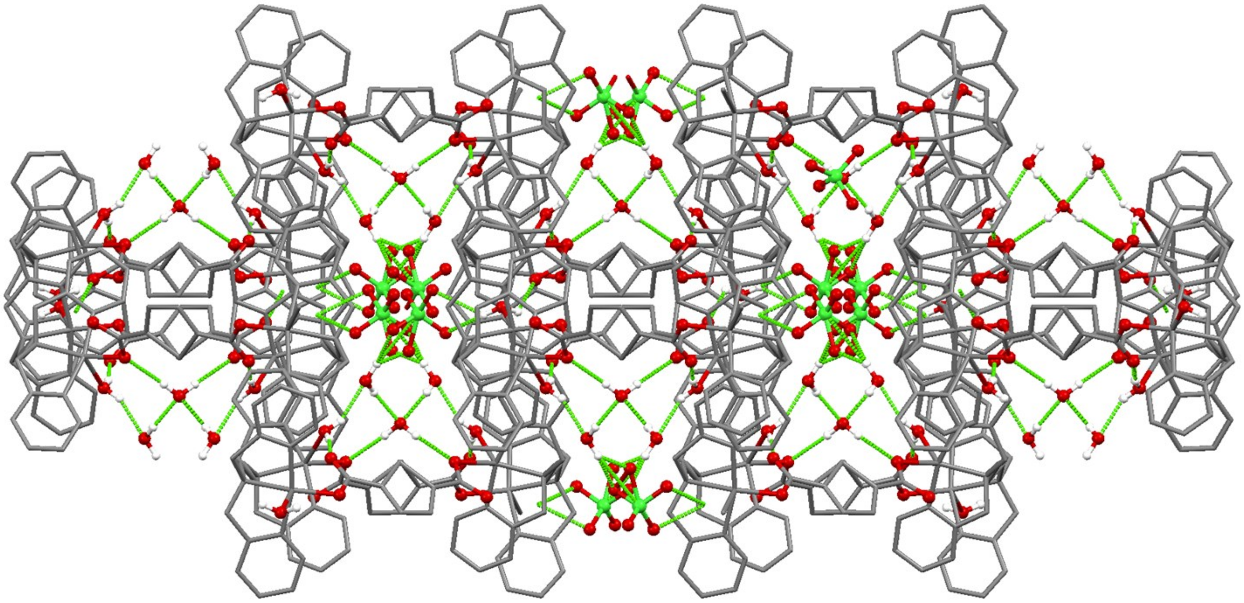


Fig. S12 Overall supramolecular assembly in **1** through hydrogen bonding interactions.

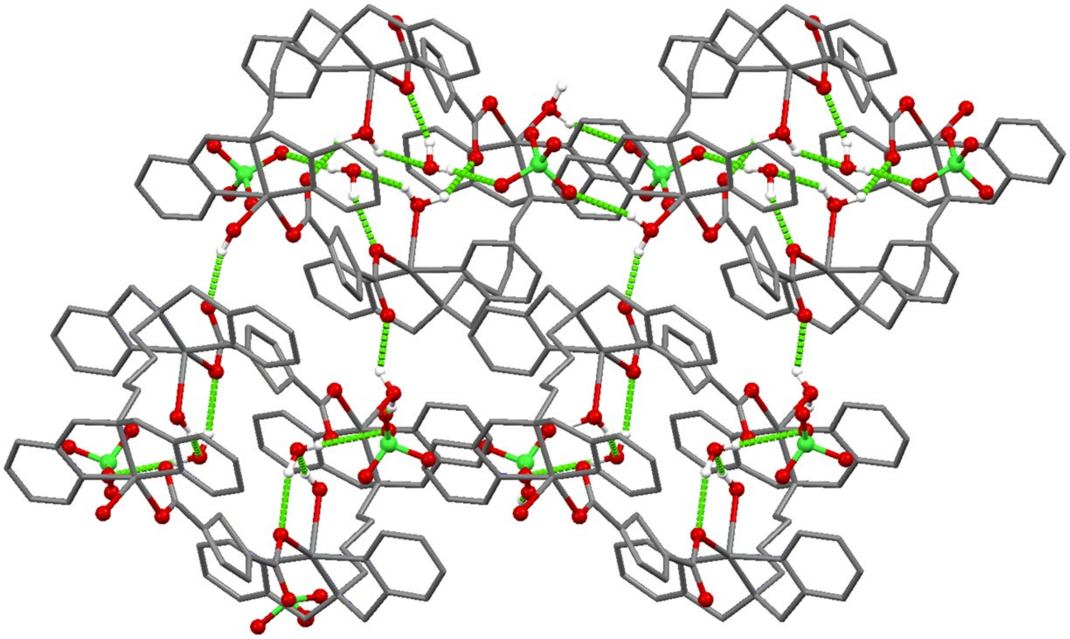


Fig. S13 Overall supramolecular assembly in **2** through hydrogen bonding interactions.

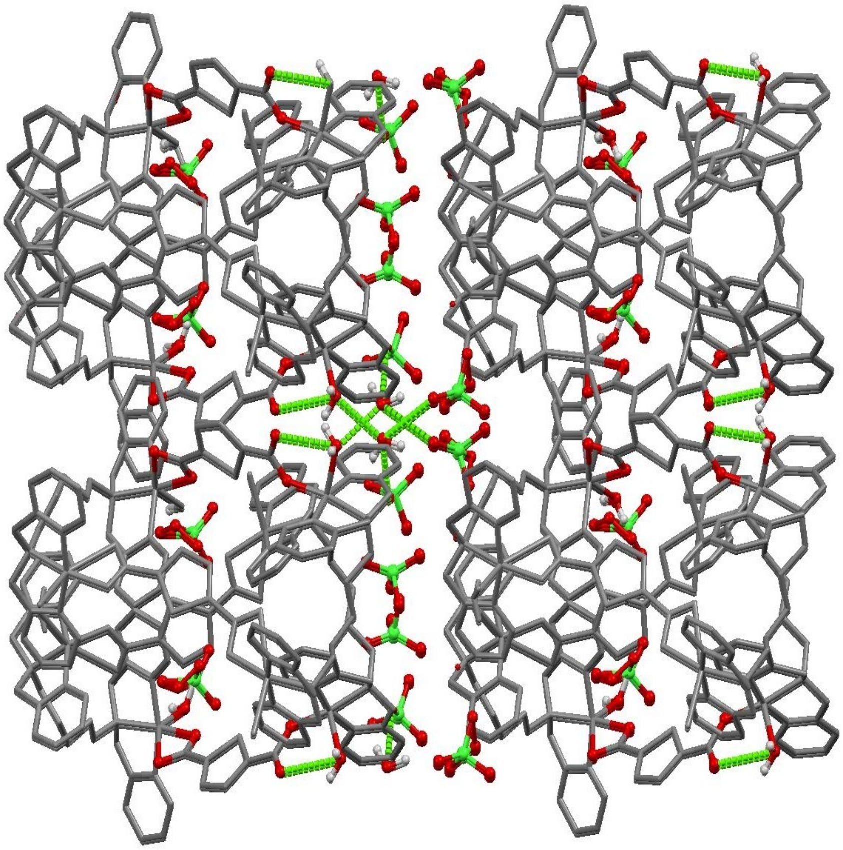


Fig. S14 Overall supramolecular assembly in **3** through hydrogen bonding interactions.

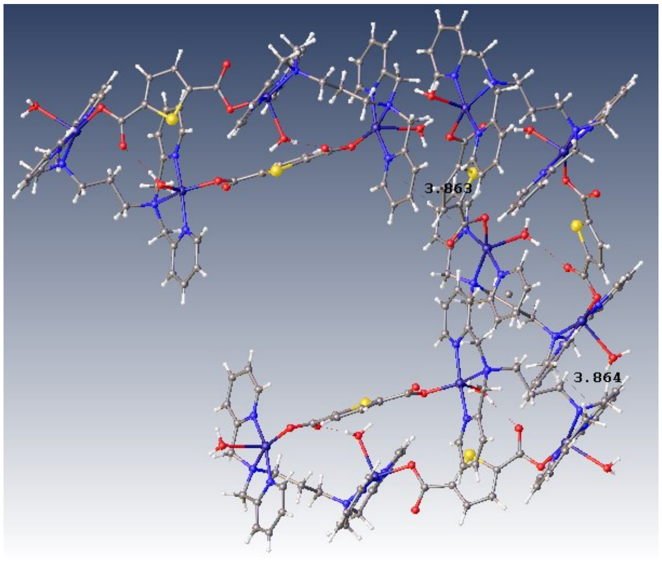


Fig. S15 Formation of supramolecular assembly via π–π interactions in **1**.

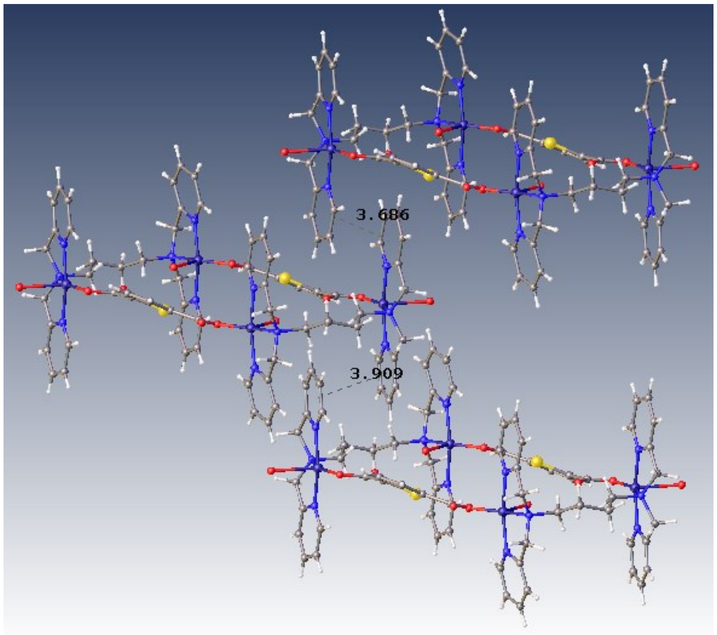


Fig. S16 Formation of supramolecular assembly via π−π interactions in **2**.

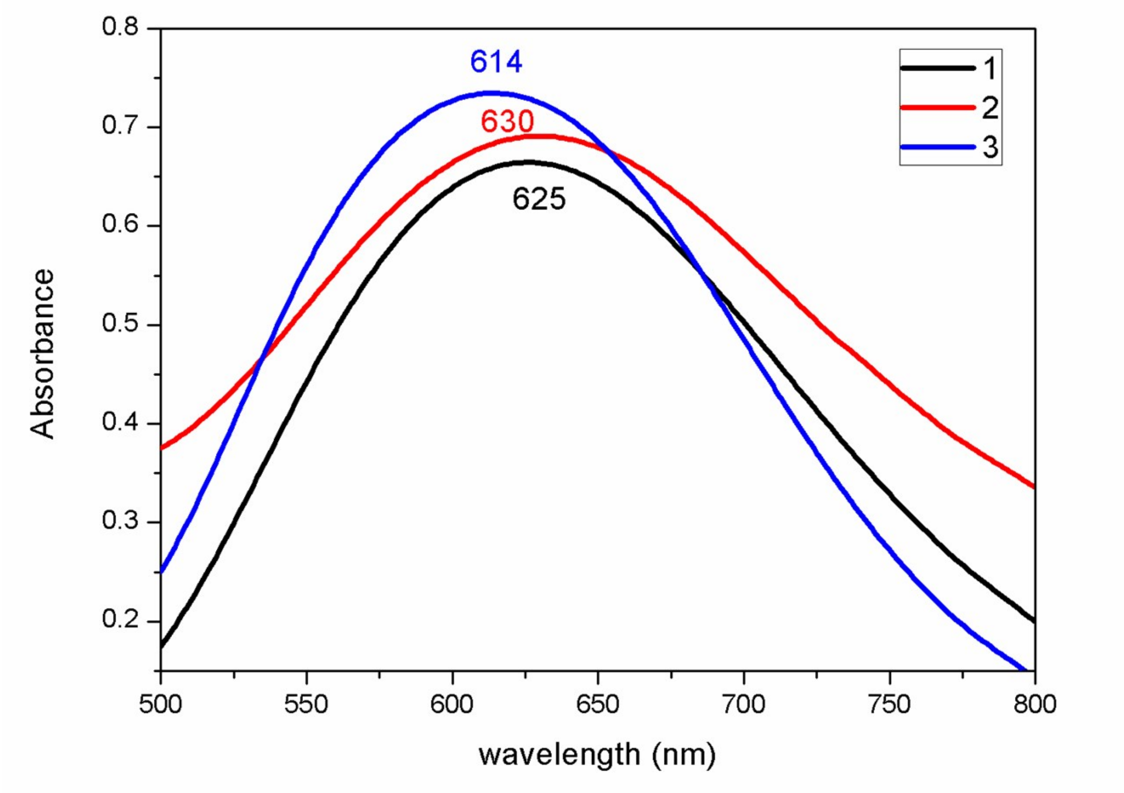


Fig. S17 UV-Vis spectra of **1**, **2** and **3**.

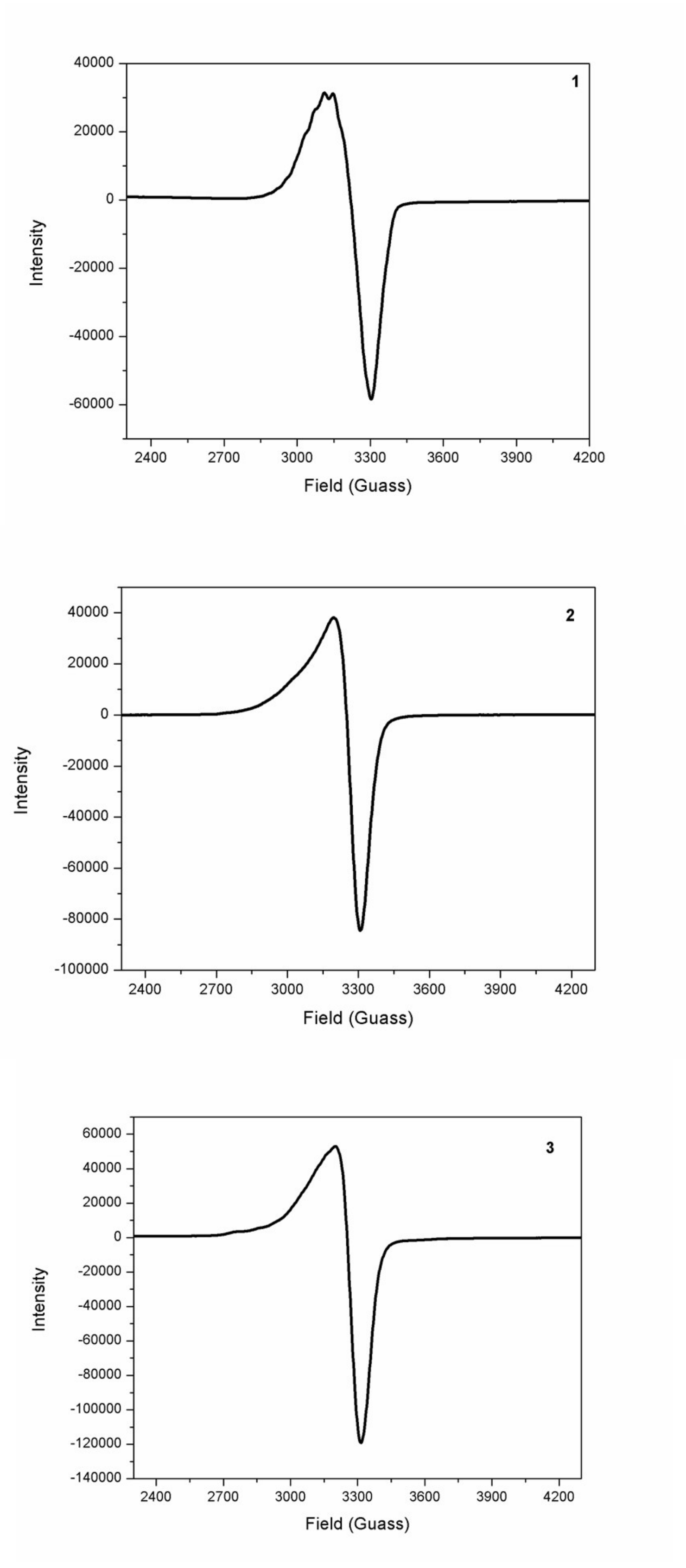


Fig. S18 EPR spectra of **1**, **2** and **3** in CH_3CN at 77 K.

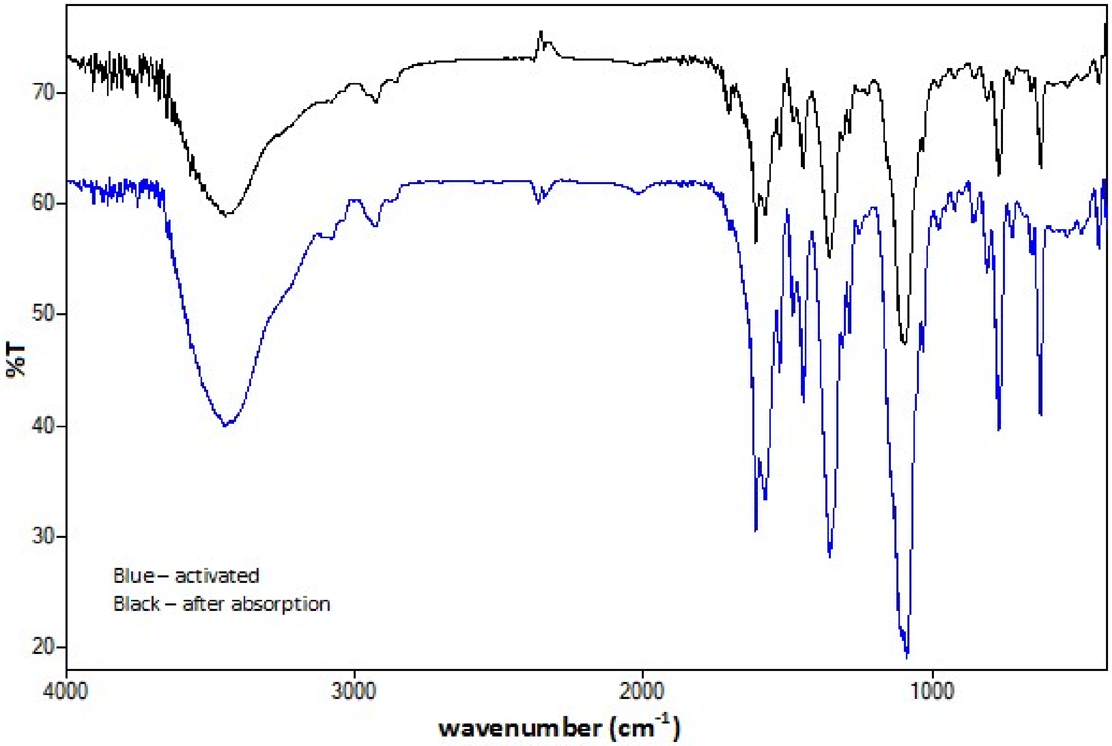


Fig. S19 Comparison of FTIR spectra of activated and after adsorption study samples of **1**.

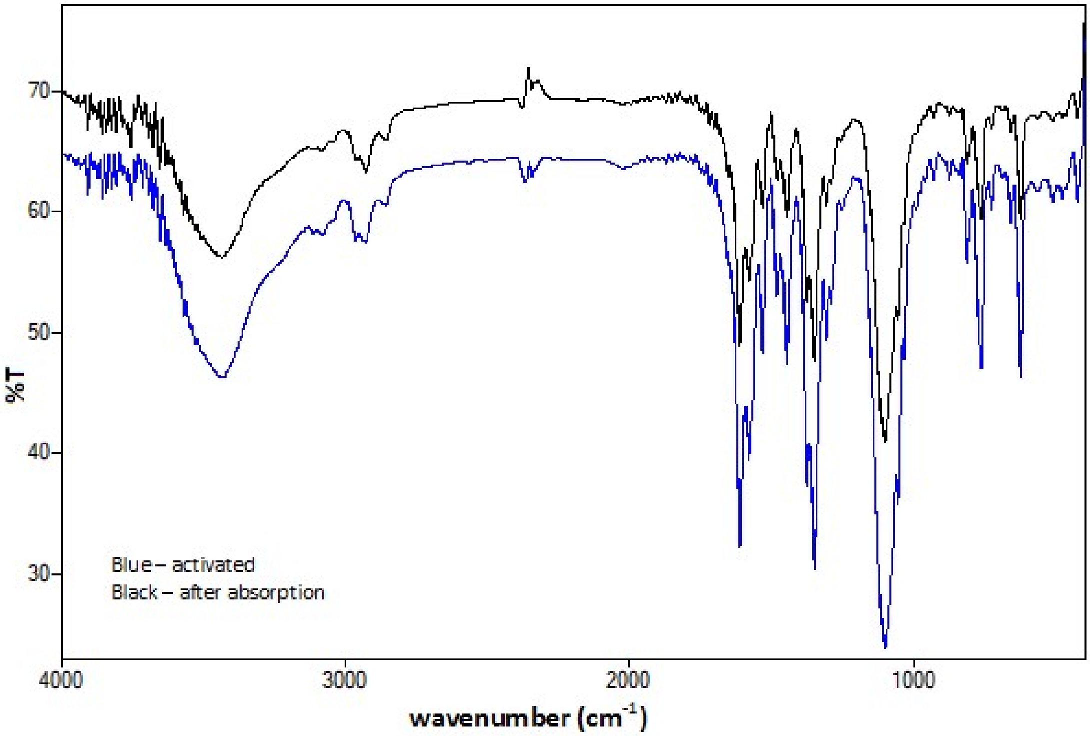


Fig. S20 Comparison of FTIR spectra of activated and after adsorption study samples of **2**.

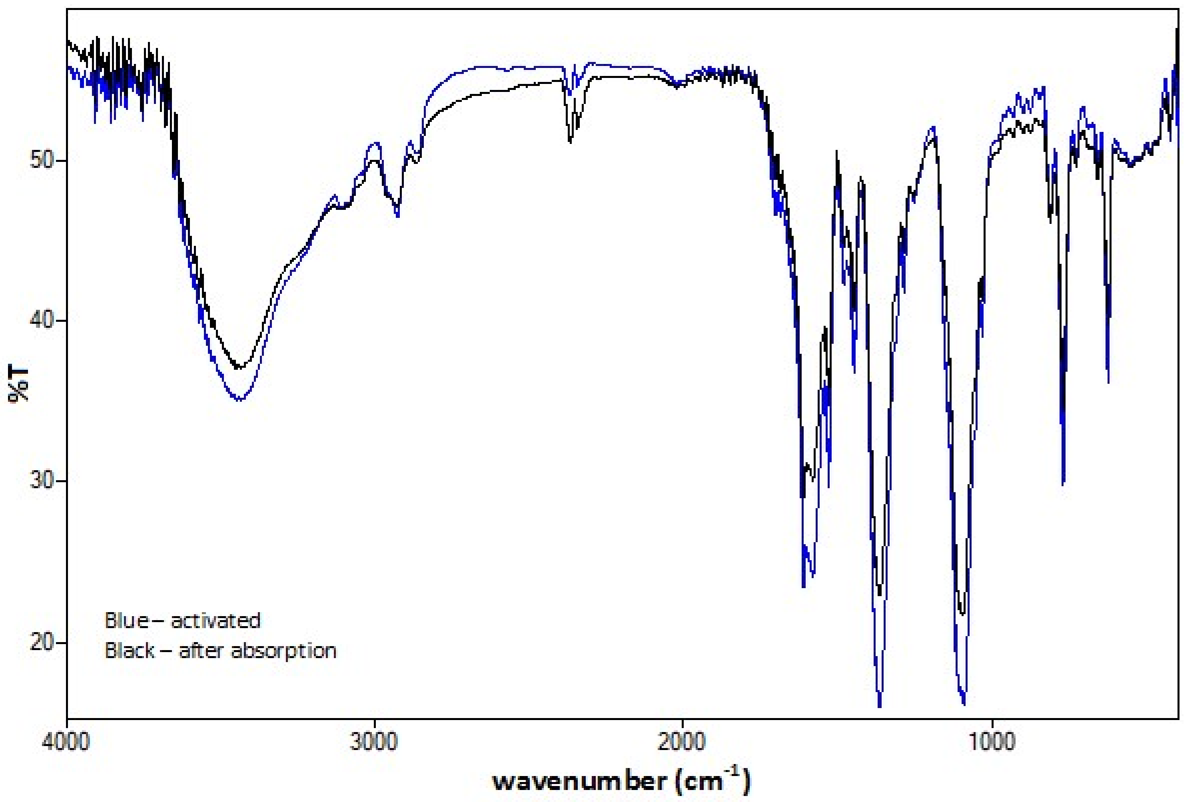


Fig. S21 Comparison of FTIR spectra of activated and after adsorption study samples of **3**.

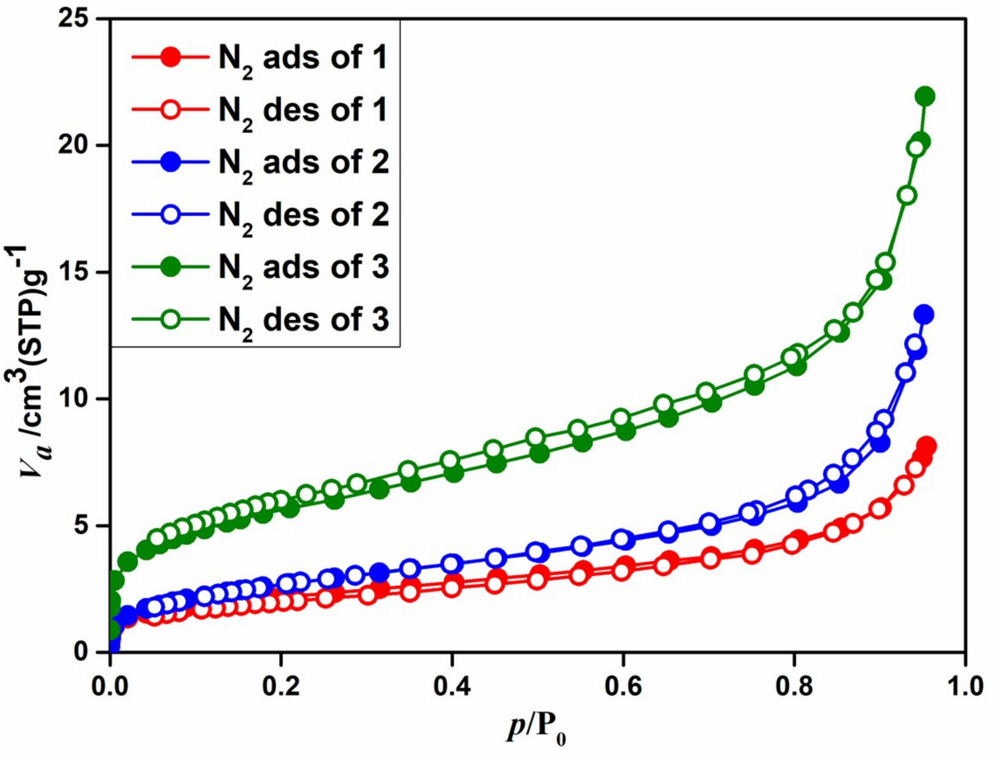


Fig. S22 N_2 isotherms of **1**, **2** and **3** at 77 K.

Table S5. Mass spectral data for **1**, **2** and **3**.

m/z values

Compound	**$[M - ClO_4^-]^+$**		**$[M - 2ClO_4^-]^{2+}$**	
	calc.	found	calc.	found
1	1769.81	1770.23	835.18	835.4
2	1797.87	1798.27	849.21	849.34
3	1825.93	1826.22	863.24	863.31