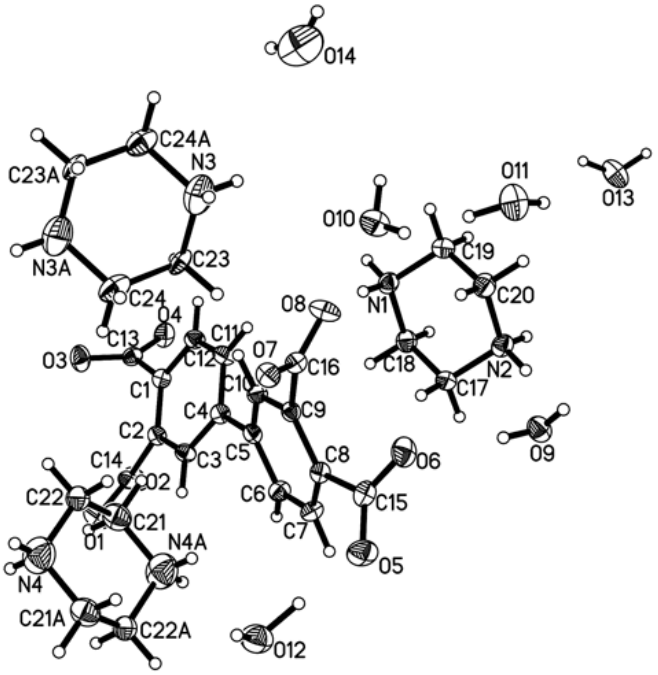
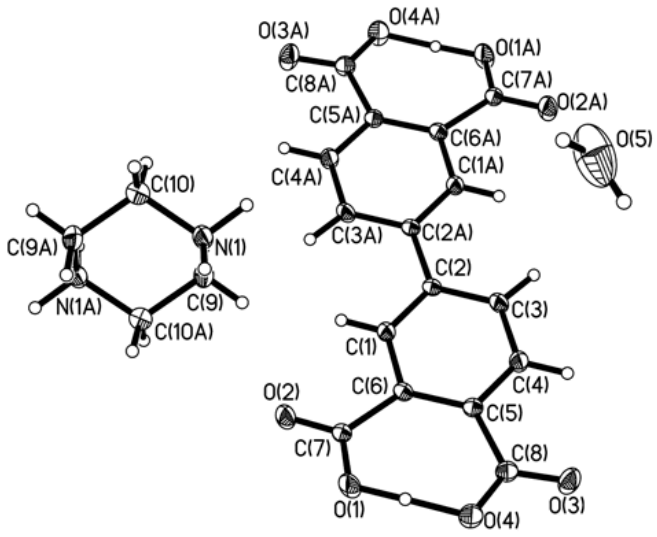
Electronic Supplementary Information

Supramolecular assembly of $[H_{(4-n)}BPTC]^{n-}$ with $pipzH_2^{2+}$: 1D negative charged rectangular tube and 2D neutral fes $4•8^2$ network

Fig. S1 Labeled diagram of **1** (a) and **2** (b) with thermal ellipsoids drawn at 30 % probability, and partial atom numbering scheme.



(a)



(b)

Fig. S2 FT-IR spectra for **1** (a) and **2** (b).

FT-IR spectra were recorded as KBr discs on a Nicolet–5700 spectrophotometer in the 4000–400 cm^{-1} regions.

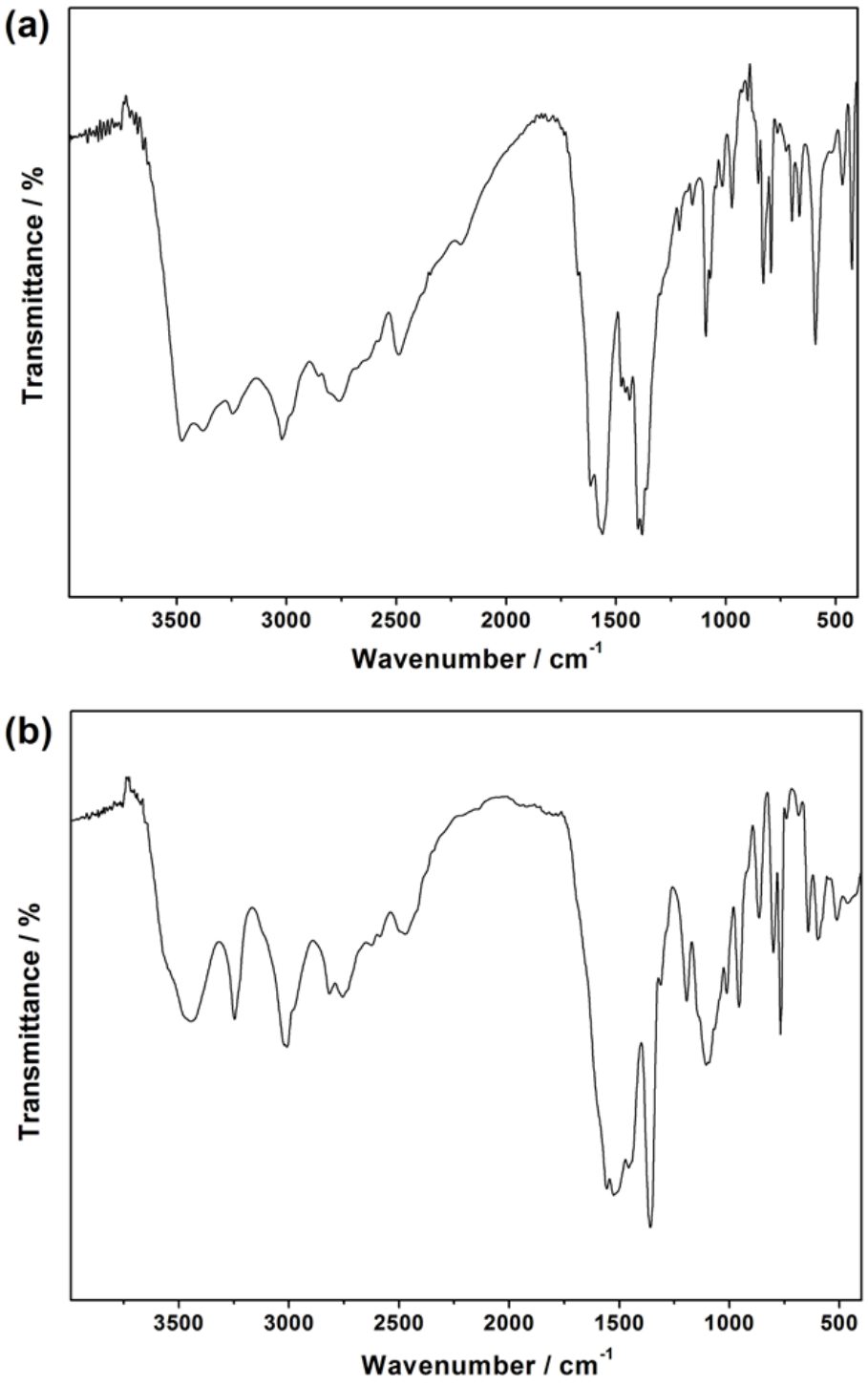


Fig. S3 PXRD patterns of **1** (A) and **2** (B): (a) simulated from single-crystal X-ray data; (b) as-synthesized; (c) dehydrated phase.

Powder X-ray diffraction (PXRD) data were collected on a D8 Advance Bruker X-ray diffractometer with monochromatized Cu Kα incident radiation. PXRD patterns were recorded from 4 to 40° with a step size of 0.02° and a step time of 2s.

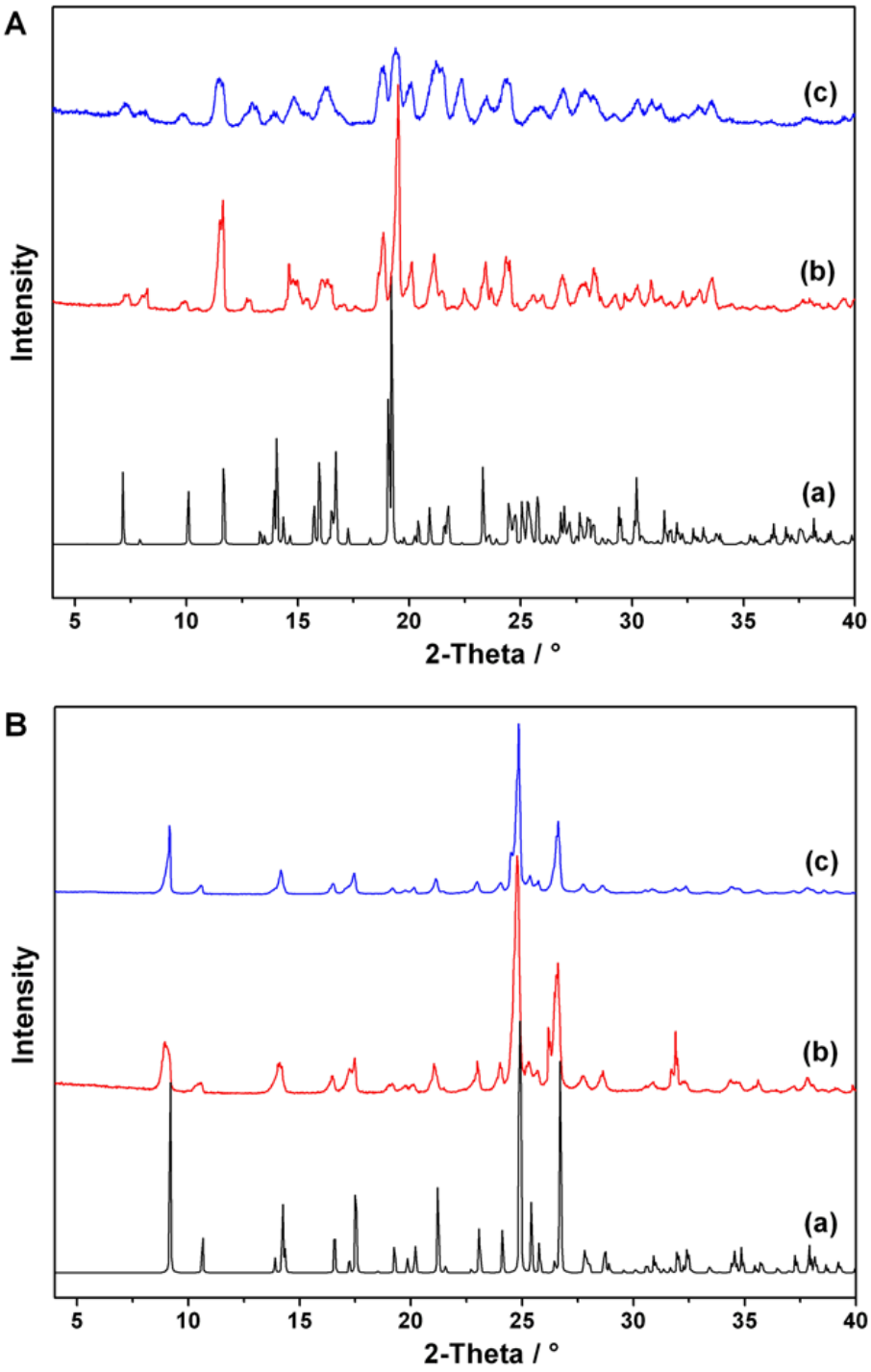
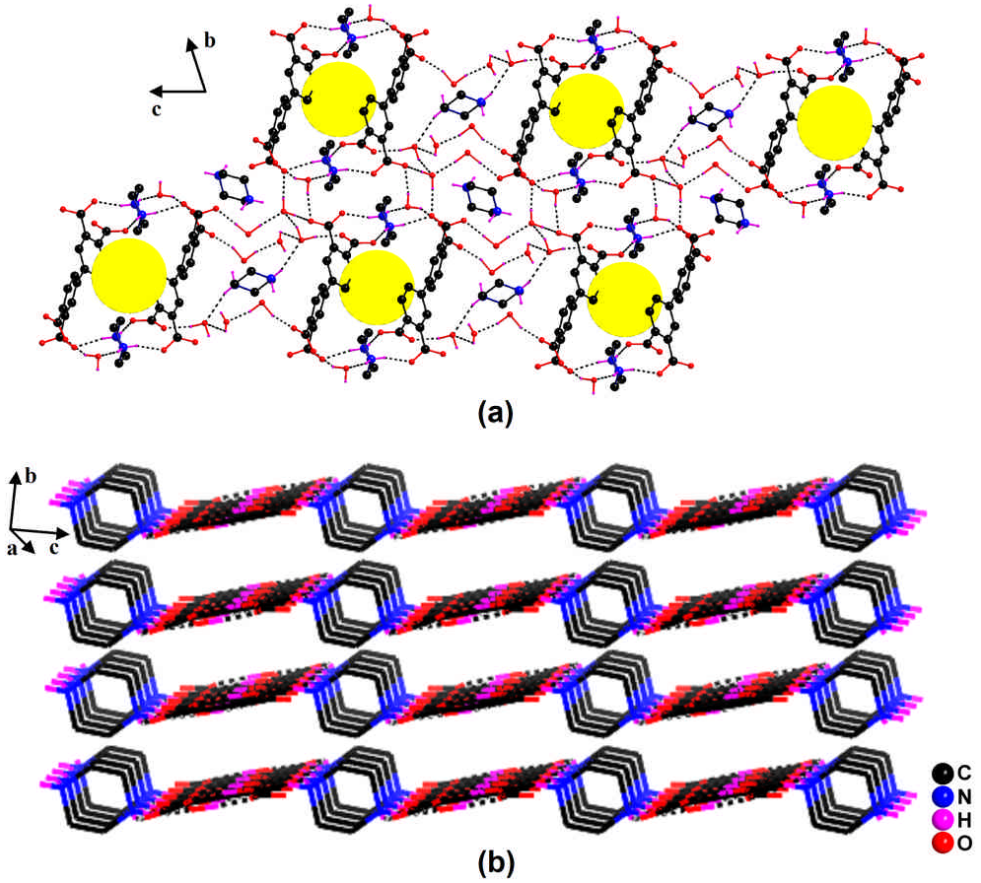


Fig. S4 Packing diagrams of the negative charged rectangular tubes in *bc* plane (a) and the fes network (b). (Dash line represents hydrogen bond and the hydrogen atoms connected to carbon atoms have been omitted for clarity).



Scheme S1 Slightly deformed H-shaped H_2BPTC^{2-}.

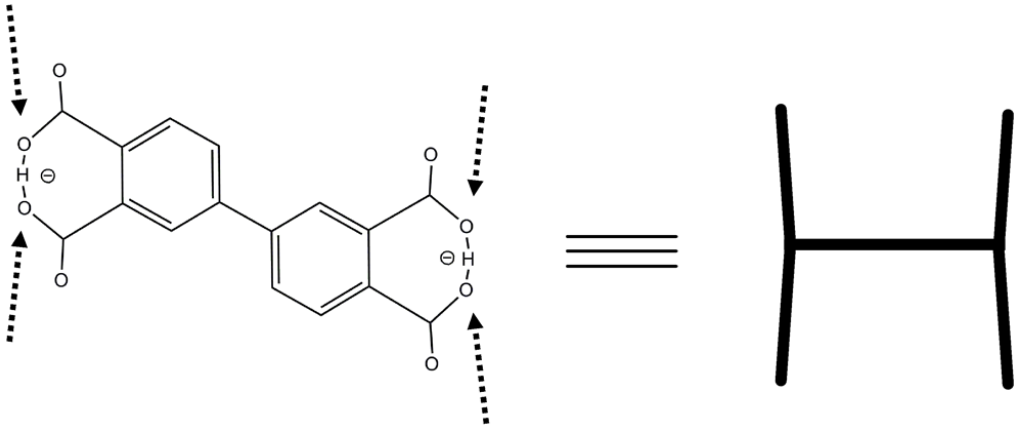


Fig. S5 TGA curves of **1** (a) and **2** (b).

Thermal analyses were performed on TG/DTA PYRIS DIAMOND instrument from room temperature to 800 °C in N_2. For **1**, the total weight loss (16.0%) between room temperature and 115 °C corresponding to the loss of H_2O molecules (17.7%) and decomposition occurs beyond 200 °C. For **2**, the weight loss (7.6%) between room temperature and 85 °C corresponds to the loss of water molecules (8.0%) and decomposition occurs beyond 245 °C. The experimental values of the two crystals are less than the expected calculated values, probably due to the slow efflorescence, which is accordance with that the eliminations of the two crystals start at temperatures lower than the room temperature. These results indicate that the single crystallinity of the two crystals will likely not be stable in dry air even at room temperature.

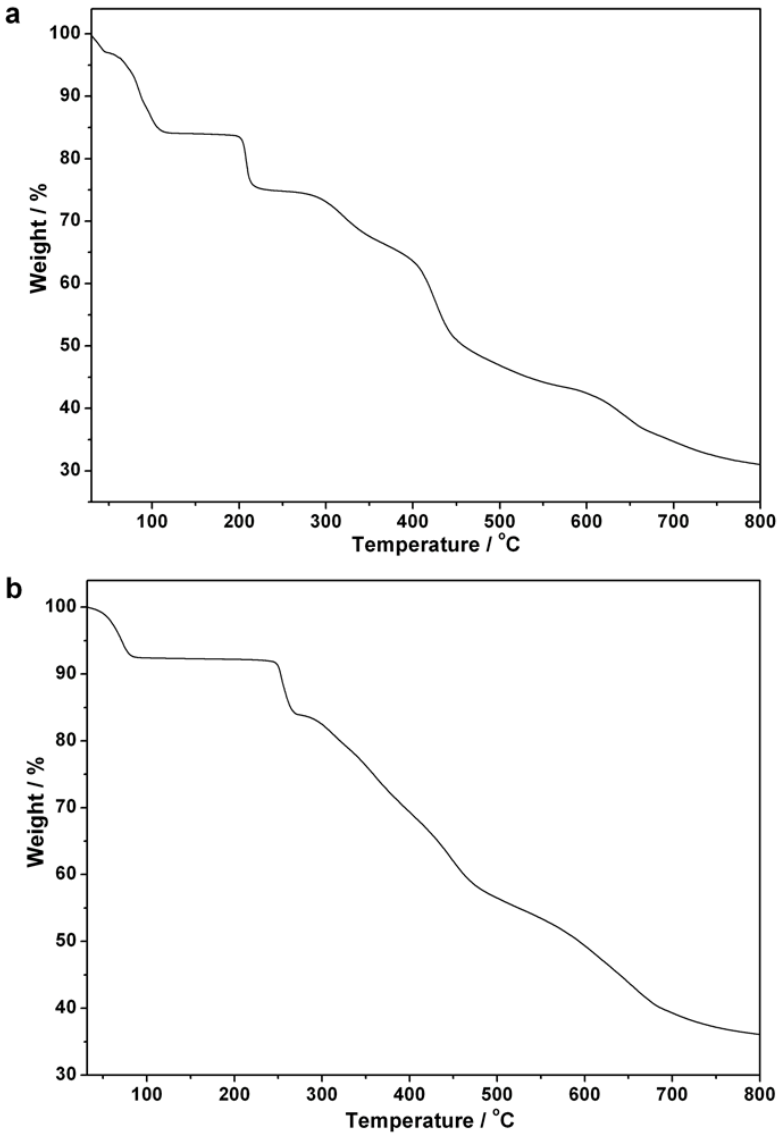


Table S1 Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
C(1)-C(12)	1.390(5)	C(14)-O(2)	1.241(5)
C(1)-C(2)	1.395(5)	C(14)-O(1)	1.259(4)
C(1)-C(13)	1.506(5)	C(15)-O(6)	1.238(5)
C(2)-C(3)	1.394(5)	C(15)-O(5)	1.247(5)
C(2)-C(14)	1.494(5)	C(16)-O(8)	1.247(5)
C(3)-C(4)	1.394(5)	C(16)-O(7)	1.252(5)
C(4)-C(11)	1.395(5)	C(17)-N(2)	1.489(5)
C(4)-C(5)	1.480(5)	C(17)-C(18)	1.504(6)
C(5)-C(6)	1.383(5)	C(18)-N(1)	1.481(5)
C(5)-C(10)	1.395(5)	C(19)-N(1)	1.463(5)
C(6)-C(7)	1.379(5)	C(19)-C(20)	1.503(6)
C(7)-C(8)	1.378(6)	C(20)-N(2)	1.486(5)
C(8)-C(9)	1.405(5)	C(21)-C(22)	1.477(6)
C(8)-C(15)	1.503(5)	C(21)-N(4)#1	1.506(7)
C(9)-C(10)	1.387(5)	C(22)-N(4)	1.478(6)
C(9)-C(16)	1.508(5)	C(23)-N(3)	1.454(6)
C(11)-C(12)	1.382(5)	C(23)-C(24)	1.485(6)
C(13)-O(3)	1.238(5)	C(24)-N(3)#2	1.523(6)
C(13)-O(4)	1.256(5)	N(4)-C(21)#1	1.506(7)
		N(3)-C(24)#2	1.523(6)
C(12)-C(1)-C(2)	119.1(3)	O(3)-C(13)-O(4)	125.4(4)
C(12)-C(1)-C(13)	116.9(3)	O(3)-C(13)-C(1)	119.6(4)
C(2)-C(1)-C(13)	124.0(4)	O(4)-C(13)-C(1)	114.9(4)
C(3)-C(2)-C(1)	118.9(4)	O(2)-C(14)-O(1)	123.2(4)
C(3)-C(2)-C(14)	118.6(3)	O(2)-C(14)-C(2)	118.7(3)
C(1)-C(2)-C(14)	122.3(3)	O(1)-C(14)-C(2)	118.0(3)
C(4)-C(3)-C(2)	122.5(3)	O(6)-C(15)-O(5)	123.6(4)
C(3)-C(4)-C(11)	117.4(3)	O(6)-C(15)-C(8)	117.4(4)
C(3)-C(4)-C(5)	121.4(3)	O(5)-C(15)-C(8)	118.9(4)
C(11)-C(4)-C(5)	121.2(4)	O(8)-C(16)-O(7)	124.3(4)
C(6)-C(5)-C(10)	118.1(4)	O(8)-C(16)-C(9)	116.7(3)
C(6)-C(5)-C(4)	121.4(3)	O(7)-C(16)-C(9)	118.9(3)
C(10)-C(5)-C(4)	120.5(3)	N(2)-C(17)-C(18)	111.3(3)
C(7)-C(6)-C(5)	120.6(4)	N(1)-C(18)-C(17)	110.1(3)
C(8)-C(7)-C(6)	121.7(4)	N(1)-C(19)-C(20)	111.7(3)
C(7)-C(8)-C(9)	118.5(3)	N(2)-C(20)-C(19)	109.4(3)
C(7)-C(8)-C(15)	119.9(3)	C(22)-C(21)-N(4)#1	110.3(4)
C(9)-C(8)-C(15)	121.4(3)	C(21)-C(22)-N(4)	111.5(4)
C(10)-C(9)-C(8)	119.4(3)	N(3)-C(23)-C(24)	112.1(3)

C(10)-C(9)-C(16)	118.0(3)	C(23)-C(24)-N(3)#2	109.4(4)
C(8)-C(9)-C(16)	122.6(3)	C(19)-N(1)-C(18)	111.4(3)
C(9)-C(10)-C(5)	121.6(3)	C(20)-N(2)-C(17)	111.5(3)
C(12)-C(11)-C(4)	120.8(4)	C(22)-N(4)-C(21)#1	110.1(4)
C(11)-C(12)-C(1)	121.2(4)	C(23)-N(3)-C(24)#2	111.8(4)

2

C(1)-C(2)	1.390(4)	C(6)-C(7)	1.514(4)
C(1)-C(6)	1.398(4)	C(7)-O(2)	1.220(4)
C(2)-C(3)	1.394(4)	C(7)-O(1)	1.281(4)
C(2)-C(2)#1	1.487(6)	C(8)-O(3)	1.231(4)
C(3)-C(4)	1.384(4)	C(8)-O(4)	1.280(4)
C(4)-C(5)	1.394(4)	C(9)-N(1)	1.486(5)
C(5)-C(6)	1.411(4)	C(9)-C(10)#2	1.501(5)
C(5)-C(8)	1.518(4)	C(10)-N(1)	1.475(4)
		C(10)-C(9)#2	1.501(5)
C(2)-C(1)-C(6)	124.2(3)	C(1)-C(6)-C(7)	113.5(3)
C(1)-C(2)-C(3)	116.9(3)	C(5)-C(6)-C(7)	128.5(3)
C(1)-C(2)-C(2)#1	121.6(3)	O(2)-C(7)-O(1)	120.3(3)
C(3)-C(2)-C(2)#1	121.5(3)	O(2)-C(7)-C(6)	120.5(3)
C(4)-C(3)-C(2)	120.2(3)	O(1)-C(7)-C(6)	119.2(3)
C(3)-C(4)-C(5)	122.8(3)	O(3)-C(8)-O(4)	120.1(3)
C(4)-C(5)-C(6)	118.0(3)	O(3)-C(8)-C(5)	119.4(3)
C(4)-C(5)-C(8)	113.7(3)	O(4)-C(8)-C(5)	120.5(3)
C(6)-C(5)-C(8)	128.3(3)	N(1)-C(9)-C(10)#2	110.5(3)
C(1)-C(6)-C(5)	117.9(3)	N(1)-C(10)-C(9)#2	110.5(3)
		C(10)-N(1)-C(9)	110.9(3)

Symmetry transformations used to generate equivalent atoms: For **1**, #1 [-x+1,-y,-z]; #2 [-x+2,-y+1,-z]. For **2**, #1 [-x+1,-y,-z+1]; #2 [-x+1,-y+1,-z+2].

Table S2 The geometries of the hydrogen bonds in **1** and **2**.

			1		
D-H	d(D-H) / (Å)	d(H···A) / (Å)	<DHA / (°)	d(D···A) / (Å)	A
N1-H1A	0.90	1.73	166	2.617(5)	O4 [2-x,-y,1-z]
N1-H1B	0.90	1.99	166	2.870(5)	O8
N2-H2A	0.90	1.87	155	2.716(4)	O9 [-1+x,y,z]
N2-H2B	0.90	1.83	164	2.703(5)	O2 [1-x,-y,1-z]
N4-H4A	0.90	2.56	124	3.152(7)	O12 [1-x,-y,-z]
N4-H4B	0.90	2.46	162	3.323(7)	O11 [1-x,1-y,-z]
O9-H91	0.90	2.02	149	2.825(5)	O6 [1+x,y,z]
O9-H92	0.87	1.91	171	2.778(4)	O1 [x,1+y,z]
O10-H101	0.87	1.82	174	2.691(4)	O8
O10-H102	0.99	1.77	173	2.760(4)	O1 [x,1+y,z]
O11-H111	0.98	1.78	163	2.730(5)	O3 [-1+x,1+y,z]
O11-H112	1.00	1.85	159	2.805(5)	O10
O12-H121	0.99	1.73	161	2.685(6)	O14 [-x,1-y,-z]
O12-H122	1.11	1.64	161	2.712(5)	O5
O13-H131	0.97	1.82	174	2.789(5)	O10 [1-x,1-y,1-z]
O13-H132	1.04	1.69	171	2.725(5)	O7 [x,y,1+z]
O14-H141	0.72	2.51	103	2.765(6)	O11
O14-H142	0.82	2.35	112	2.765(6)	O11
			2		
O1-H4	1.09(3)	1.29(3)	176(5)	2.383(4)	O4
O5-H10	1.06(4)	1.85(4)	167(3)	2.888(6)	O3 [-1+x,1+y,z]
N1-H11	0.95(4)	1.91(4)	159(4)	2.815(4)	O3 [2-x,1-y,1-z]
N1-H11	0.95(4)	2.47(4)	114(3)	2.981(4)	O4 [2-x,1-y,1-z]
N1-H12	1.03(5)	1.74(5)	165(4)	2.740(4)	O1 [-1+x,y,z]

Table S3 Crystal Data and Structure Refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{24}H_{42}N_4O_{14}$	$C_{20}H_{24}N_2O_{10}$
Formula weight	610.62	452.41
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
space group	*P-1*	*P-1*
a / b / c (Å)	7.260(3)/12.744(6)/16.409(8)	6.2017(9)/8.3441(13)/9.6508(14)
α / β / γ (°)	75.833(7)/88.378(7)/87.605(7)	91.155(2)/93.378(2)/94.221(2)
V(Å^3)	1470.4(12)	497.04(13)
Z	2	1
Calculated density (g cm^{-3})	1.379	1.511
Absorption coefficient (mm^{-1})	0.114	0.123
F(000)	652	238
Crystal size (mm)	0.3 × 0.1 × 0.1	0.2 × 0.1 × 0.1
θ range for data collection (°)	2.32 to 28.06	2.45 to 28.28
Limiting indices(h / k / l)	-9≤h≤9; -15≤k≤16; -21≤l≤21	-8≤h≤7; -11≤k≤11; -12≤l≤12
Reflections collected / unique	13657 / 6912 [R(int) = 0.0591]	4756 / 2409 [R(int) = 0.0318]
Completeness	96.8 %	97.4 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6912 / 0 / 379	2409 / 2 / 191
Goodness-of-fit on F^2	1.002	1.074
Final R indices [I>2σ(I)][a]	R_1 = 0.0804, wR_2 = 0.2197	R_1 = 0.0764, wR_2 = 0.1883
R indices (all data)	R_1 = 0.1637, wR_2 = 0.2650	R_1 = 0.1187, wR_2 = 0.2184
Largest diff. peak and hole	0.558 and -0.607 e. Å^{-3}	0.880 and -0.903 e. Å^{-3}

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[\ w\ (F_o^2-F_c^2)^2]\ /\ \sum[\ w\ (F_o^2)^2]]^{1/2}$.