Electronic Supporting Information

for the

Manuscript entitled

Two–dimensional {Co^{3+}– Zn^{2+}} and {Co^{3+}– Cd^{2+}} networks and their applications in heterogeneous and solvent–free ring opening reactions†

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Amit Pratap Singh, Girijesh Kumar and Rajeev Gupta*

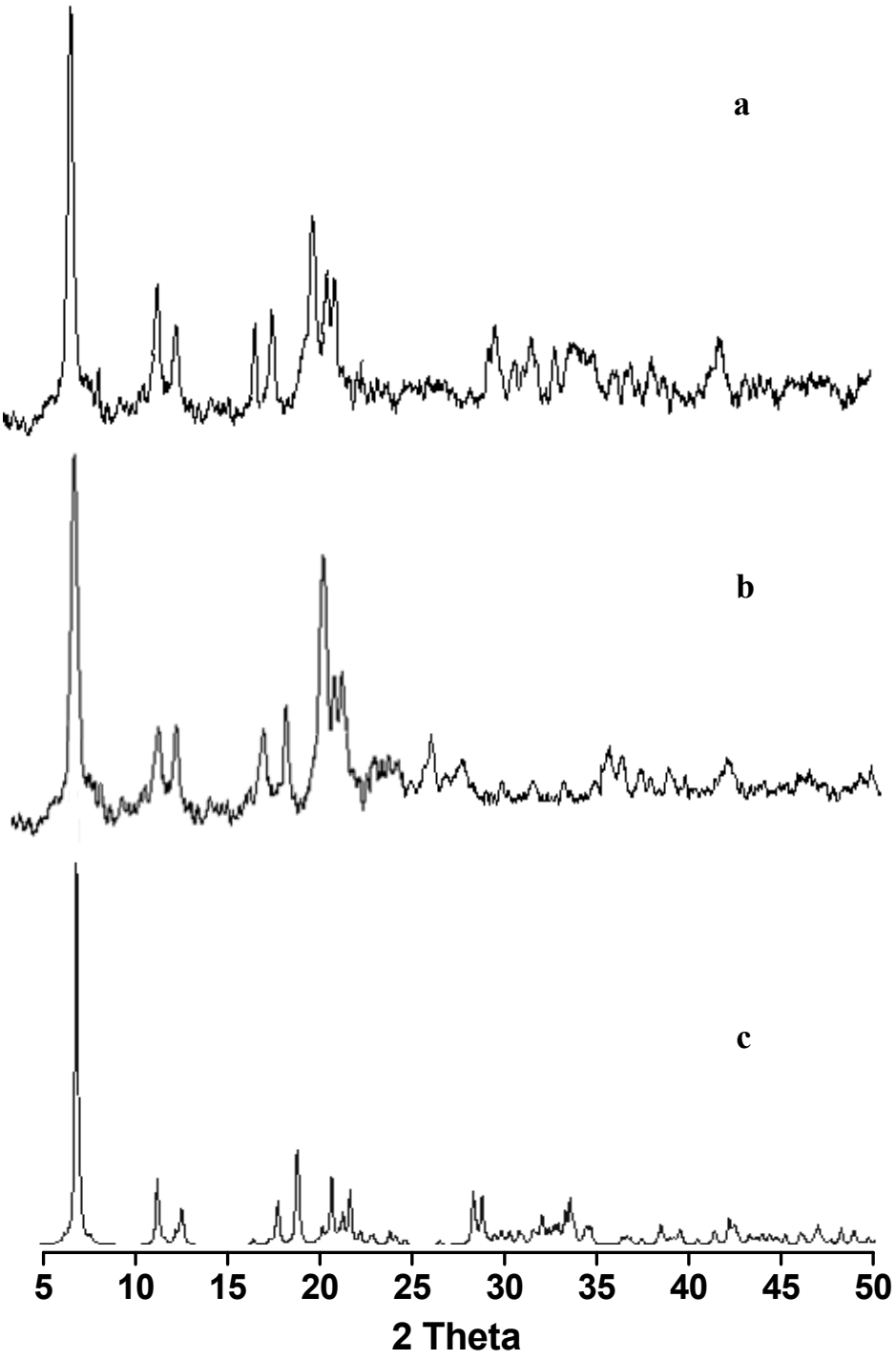

Figure S1. XRPD patterns for network **2a**; bulk sample (**a**), after catalysis (**b**) and the one simulated from the single crystal structural analysis (**c**) using Mercury 2.3.

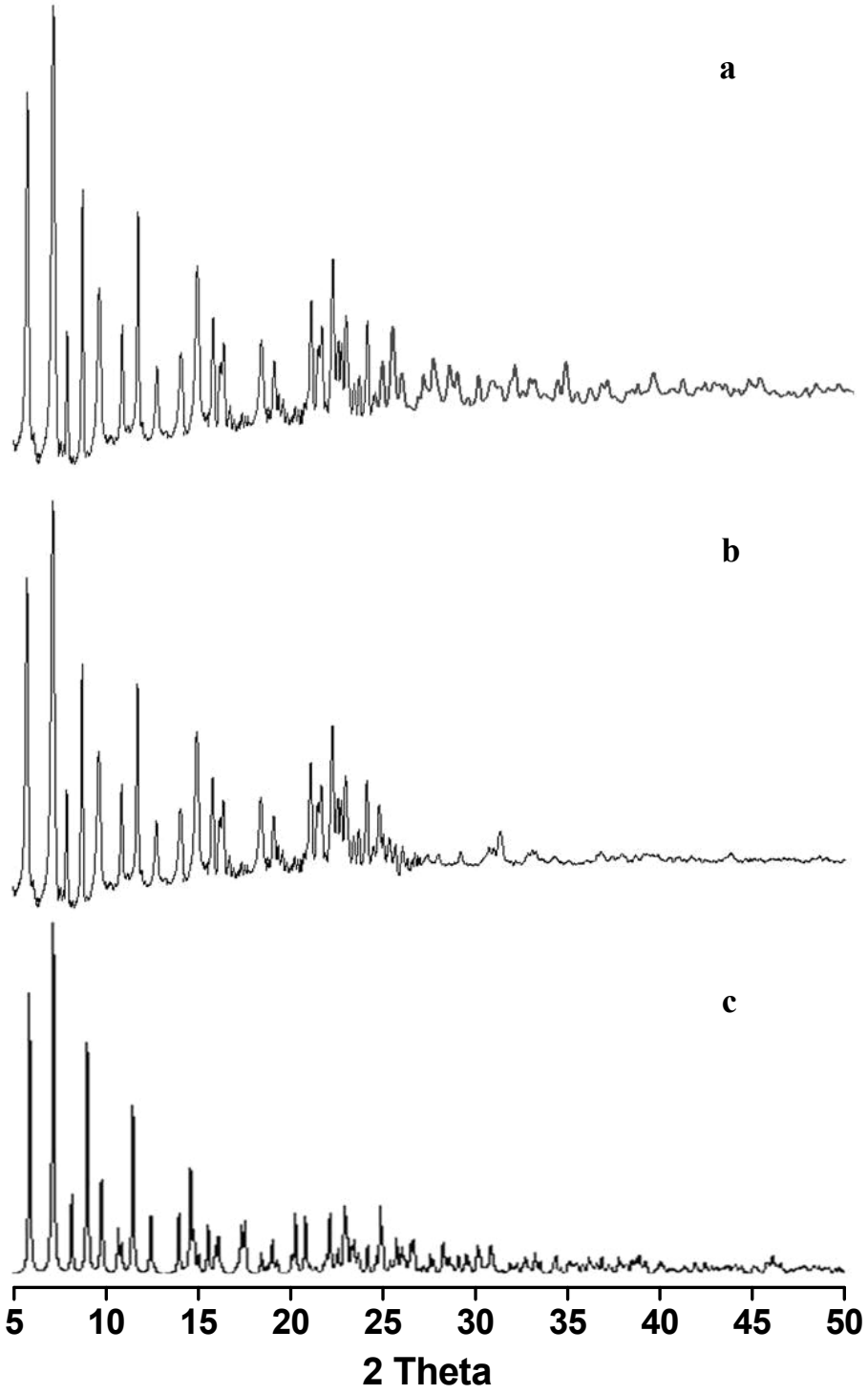

Figure S2. XRPD patterns for network **2b**; bulk sample (**a**), after catalysis (**b**) and the one simulated from the single crystal structural analysis (**c**) using Mercury 2.3.

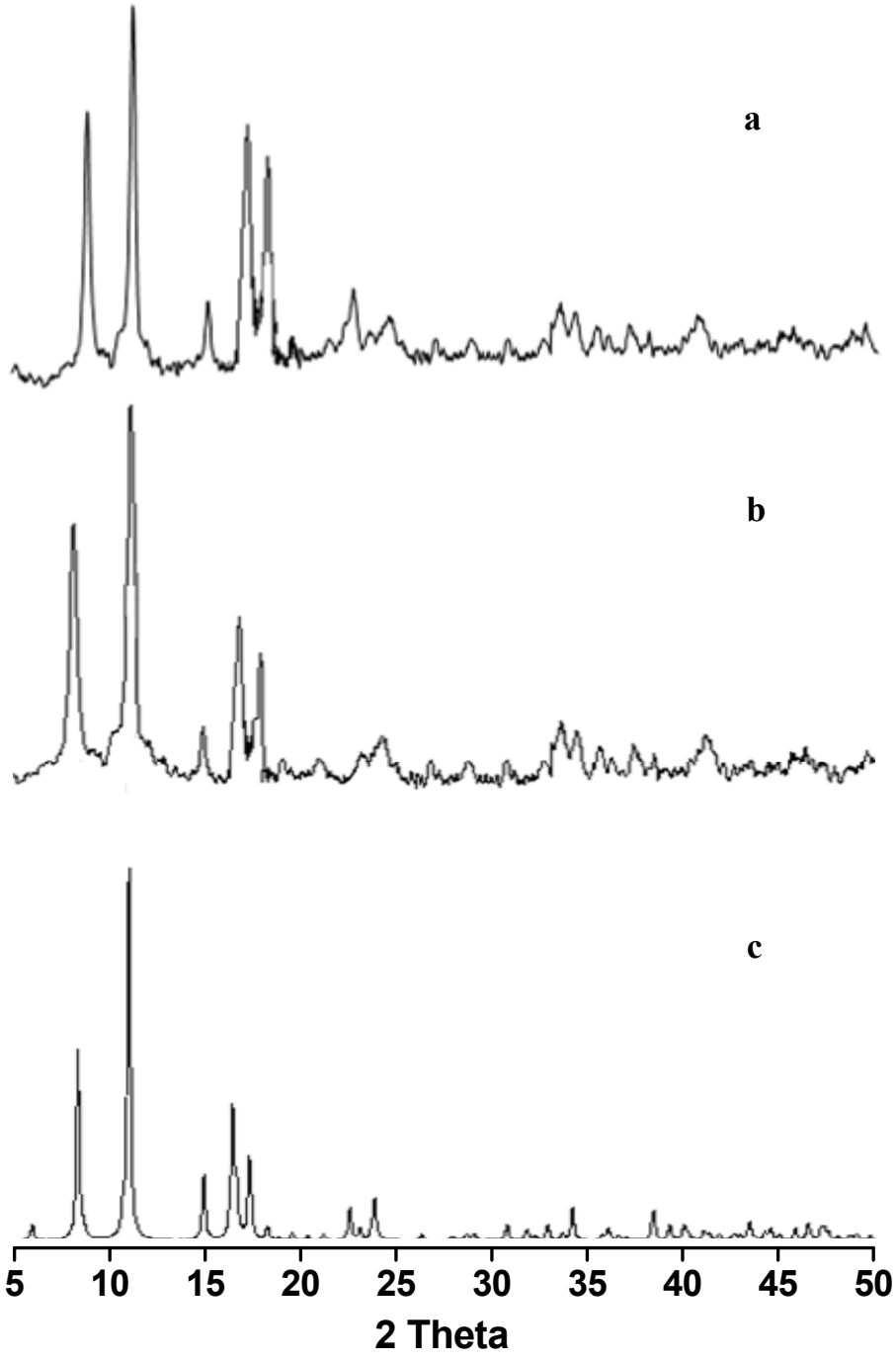

Figure S3. XRPD patterns for network **3a**; bulk sample (**a**), after catalysis (**b**) and the one simulated from the single crystal structural analysis (**c**) using Mercury 2.3.

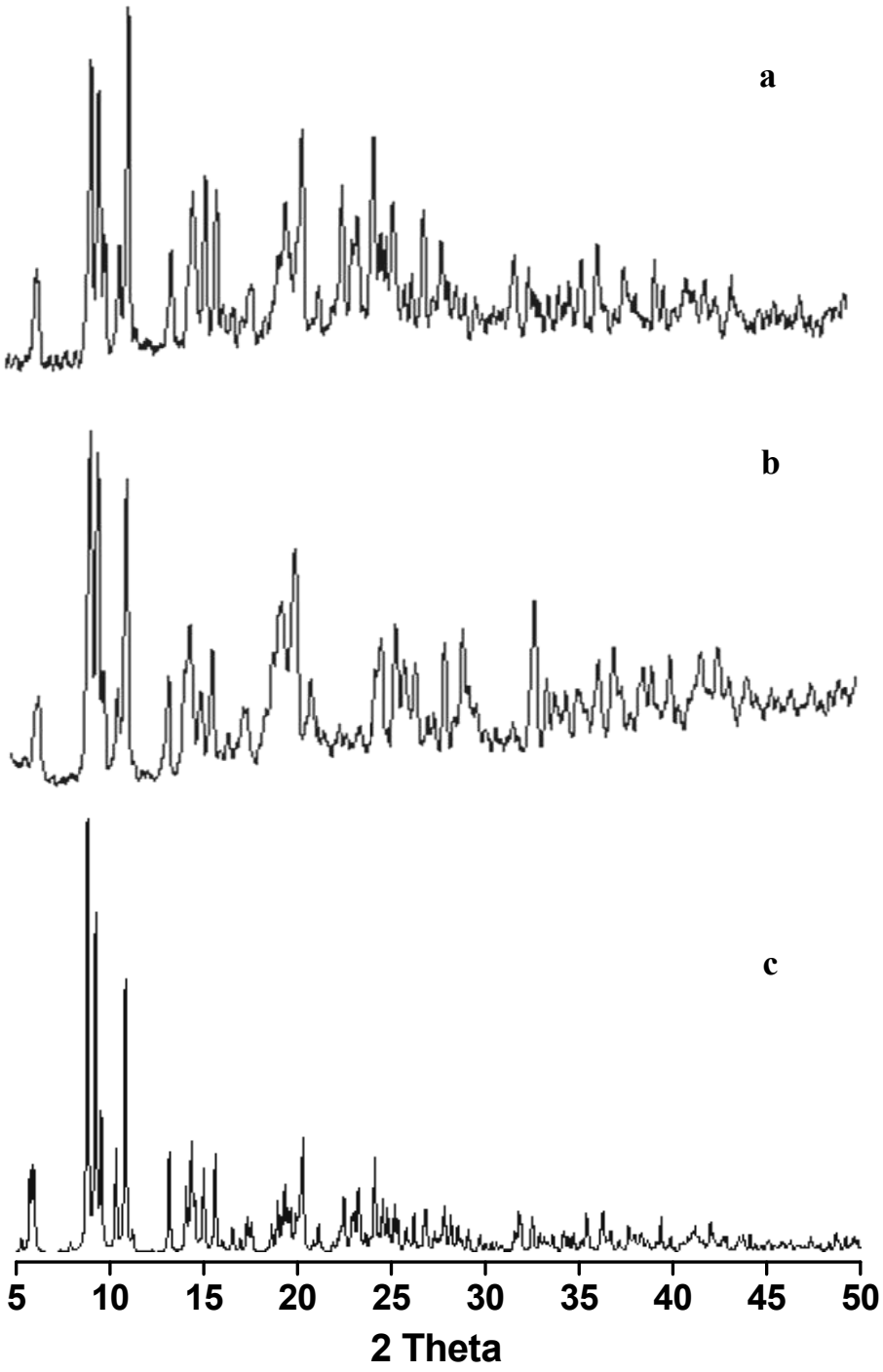

Figure S4. XRPD patterns for network **3b**; bulk sample (**a**), after catalysis (**b**) and the one simulated from the single crystal structural analysis (**c**) using Mercury 2.3.

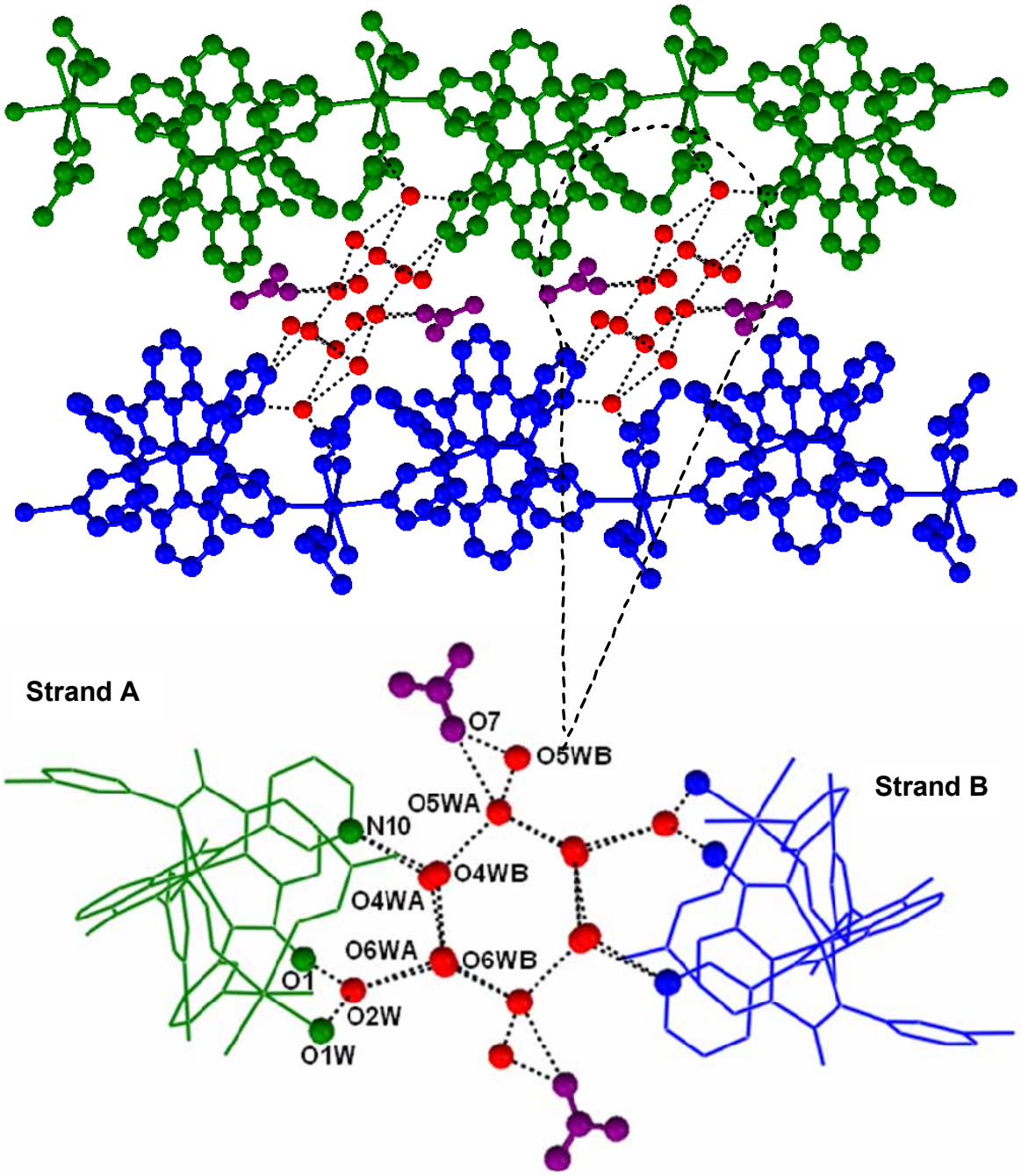

Figure S5. Views of network **2b** with partial numbering scheme showing that strands **A** and **B** are connected to each other via hydrogen – bonding between uncoordinated water molecules (shown in red), N10 atom of the uncoordinated pyridine, amide oxygen atom O1, and coordinated water molecule O1W. Hydrogen atoms have been omitted for clarity.

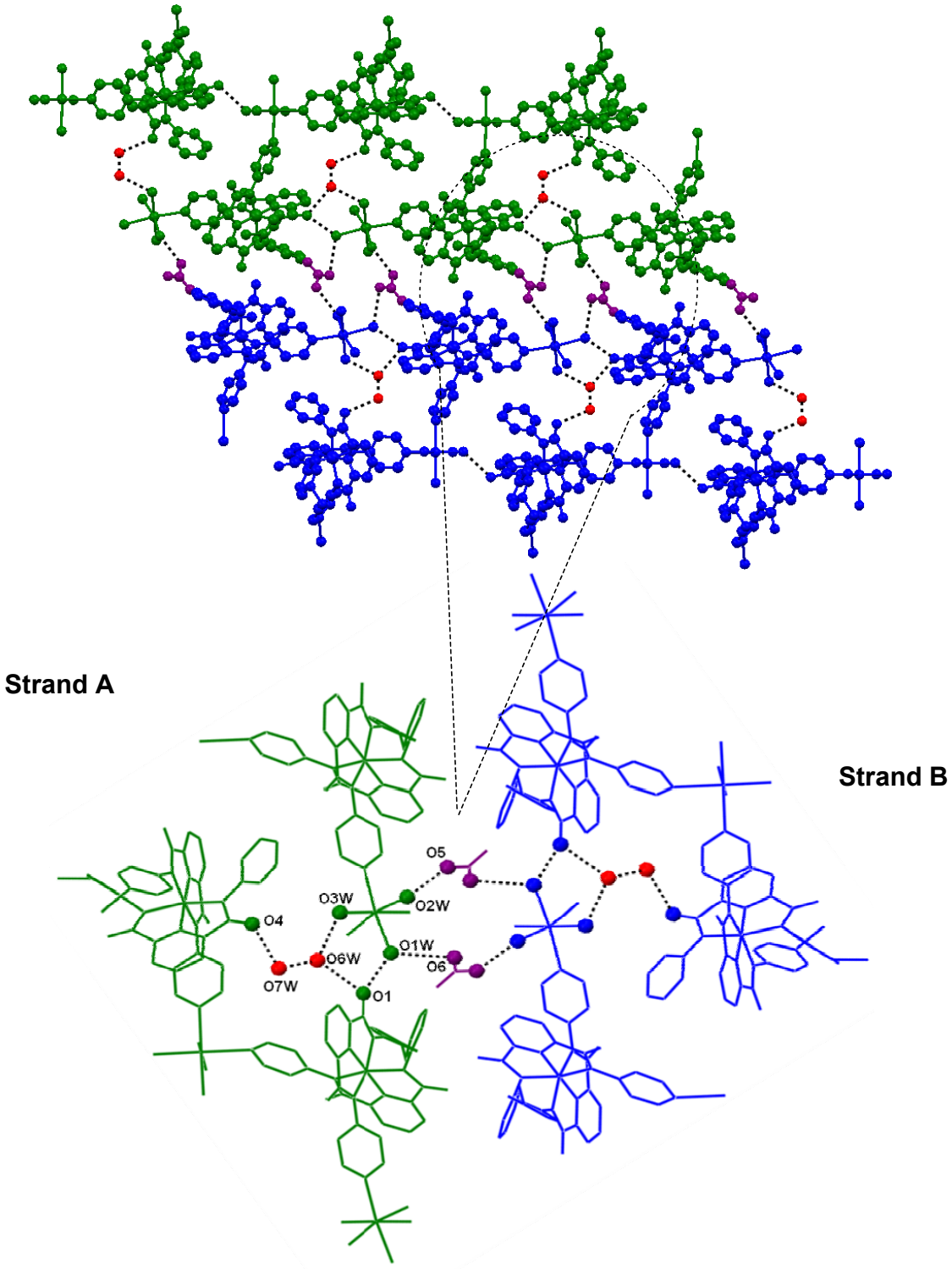

Figure S6. Views of network **3b** with partial numbering scheme showing that strands **A** and **B** are connected to each other via hydrogen – bonding between coordinated (shown in green) and uncoordinated water molecules (shown in red) and uncoordinated nitrate ions (shown in purple). Hydrogen atoms have been omitted for clarity.

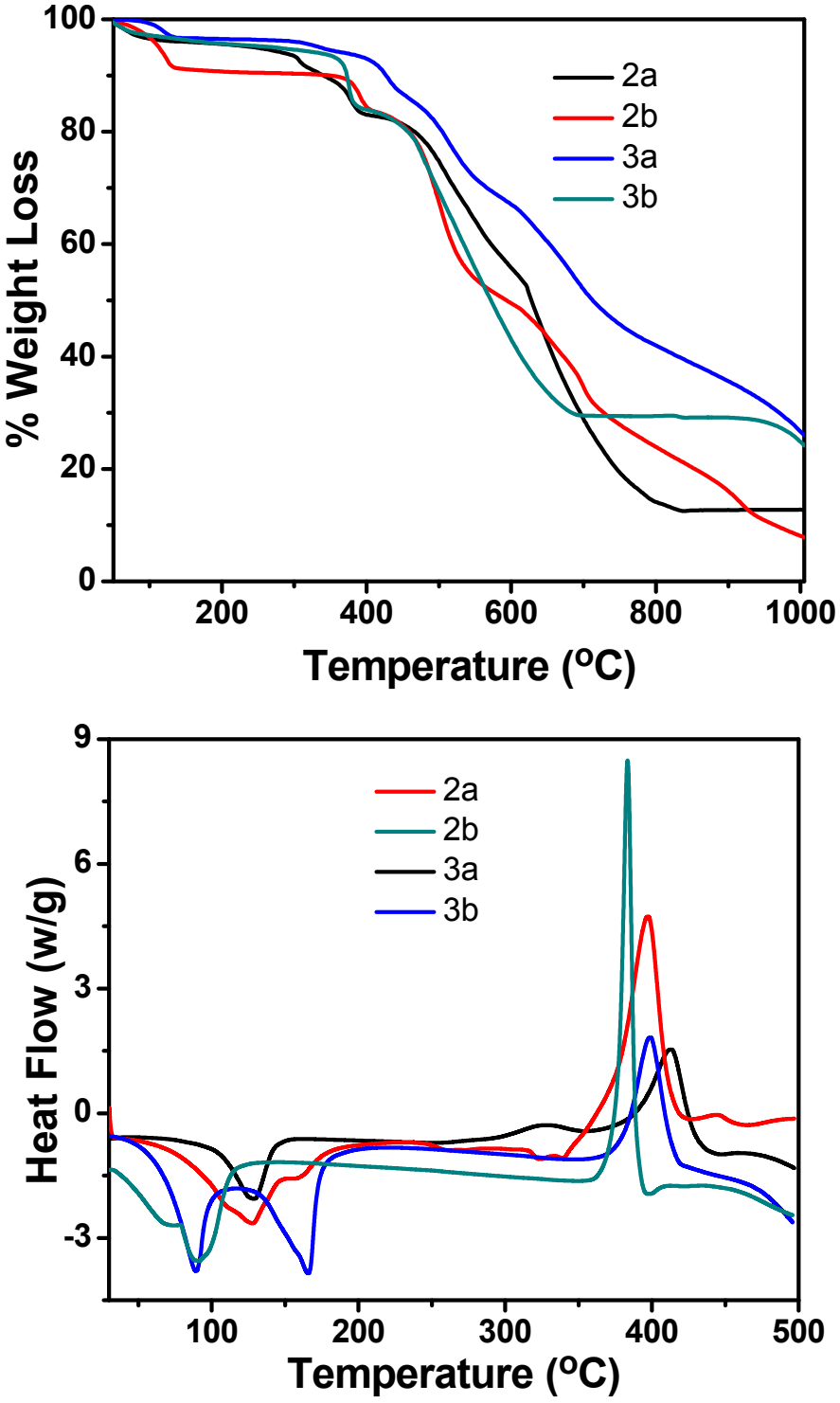

Figure S7. TGA (upper) and DSC (lower) plots for networks **2a**, **2b**, **3a**, and **3b**.

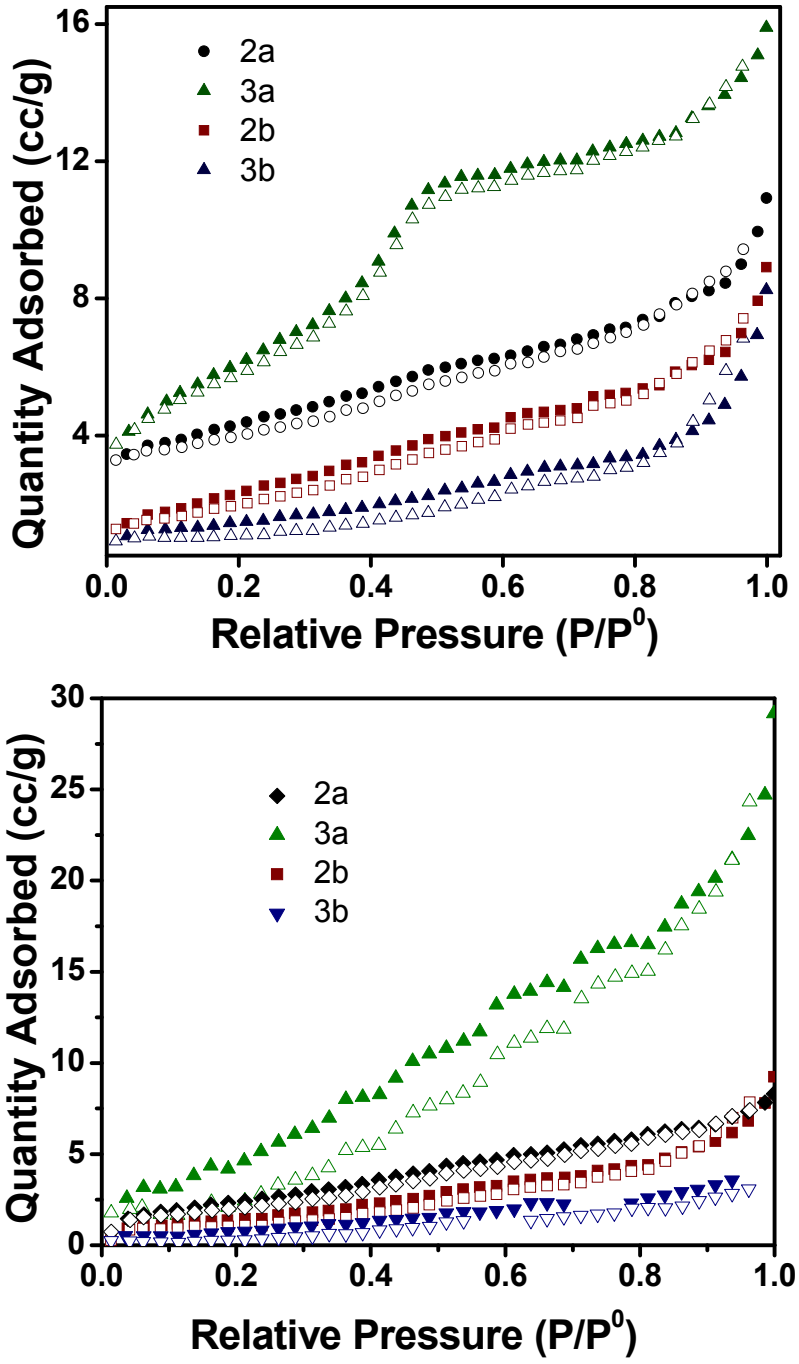

Figure S8. Gas adsorption isotherms measured at 77 K (upper) and 298 K (lower) for networks **2a**, **2b**, **3a**, and **3b**. Filled and open symbols denote the sorption and desorption, respectively.

Table S1. Geometrical parameters of the O–H···O, C-H···O and C-H···N hydrogen bonds involved in the network **3b**. D = donor; A = acceptor.

D-H···A	**d(D-H, Å)**	**d(H···A, Å)**	**d(D···A, Å)**	**<(D-H···A, °)**
O1W-H2W1···O6	1.11	2.10	3.031(15)	139
O1W-H2W1···O7	1.11	2.15	3.194(10)	155
O1W-H1W1···O1[a]	1.11	1.70	2.787(7)	165
O2W-H2W2···O2[b]	1.04	1.82	2.788(7)	154
O2W-H1W2···O5[c]	0.73	2.19	2.833(10)	146
O2W-H1W···O6[c]	0.73	2.39	3.091(15)	161
O3W-H1W3···O6W	0.67	2.08	2.729(7)	165
O3W-H2W3···O4W[b]	0.89	1.83	2.648(11)	152
O4W-H2W4···O2	1.06	1.67	2.724(10)	170
O5W-H1W5···O6W[d]	1.06	1.94	2.795(8)	136
O5W-H2W5···O3[e]	0.92	1.99	2.817(8)	149
O6W-H1W6···O1[a]	0.97	1.82	2.794(7)	176
O6W-H2W6···O7W	1.02	1.73	2.660(9)	149
O7W-H2W7···O4[f]	0.77	2.04	2.799(8)	177
C1-H1···O7[g]	0.93	2.54	3.110(11)	120
C10-H10···N9	0.93	2.60	3.272(8)	129
C26-H26···O6	0.93	2.39	3.196(15)	145
C34-H34···O7[d]	0.93	2.50	3.312(13)	146

Symmetry transformations used to generate equivalent atoms:
a = 1+x, y, z
b = 1/2-x, 1/2+y, 1/2-z
c = 1-x, 1-y, -z
d = -1/2+x, 1/2-y, -1/2+z
e = 1-x, -y, -z
f = x, y, 1+z
g = 1/2-x, -1/2+y, 1/2-z

Table S2.[a] Gas adsorption and desorption studies performed at 77 K and 298 K for networks **2a**, **2b**, **3a**, and **3b**.

Result	**2a**		**2b**		**3a**		**3b**	
	77 K	298K	77 K	298K	77 K	298K	77 K	298K
BET surface area (m^2/g)	5.862	5.337	4.923	2.273	22.14	17.76	7.917	8.493
Langmuir surface area (m^2/g)	6.179	5.400	4.059	2.600	29.63	16.88	8.813	10.06
Total pore volume (cm^3/g)	0.013	0.014	0.008	0.005	0.024	0.45	0.013	0.012
BJH cumulative desorption surface area (m^2/g)	4.968	16.08	7.082	4.731	24.72	33.16	9.354	19.41
BJH cumulative desorption pore volume (m^3/g)	0.013	0.018	0.011	0.007	0.025	0.055	0.014	0.016
BJH desorption pore diameter (Å)	40.46	11.06	28.89	32.52	34.18	28.88	28.89	11.16
Average pore diameter (Å)	87.09	10.71	69.95	97.23	44.44	10.16	69.66	60.55
Quantity of N_2 adsorbed (cm^3/g)	8.3	9.13	8.98	3.66	15.9	29.16	11.06	7.90

[a]The error bar on the surface area values are in the order of ca. 5%.