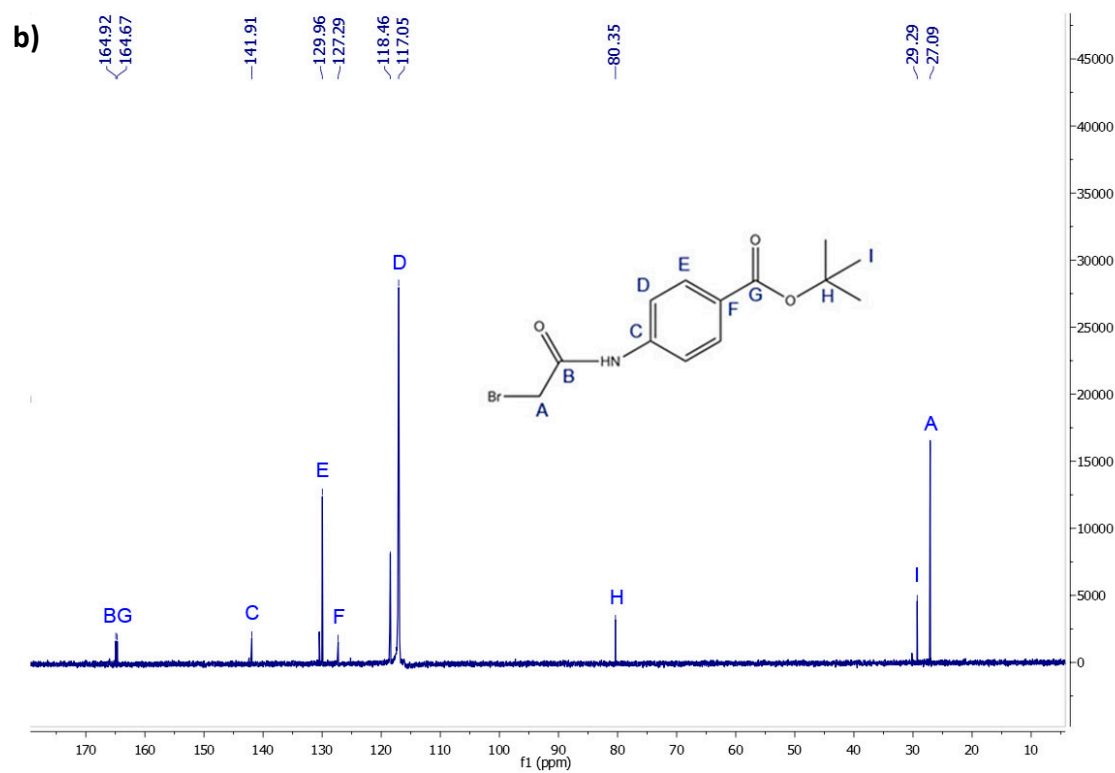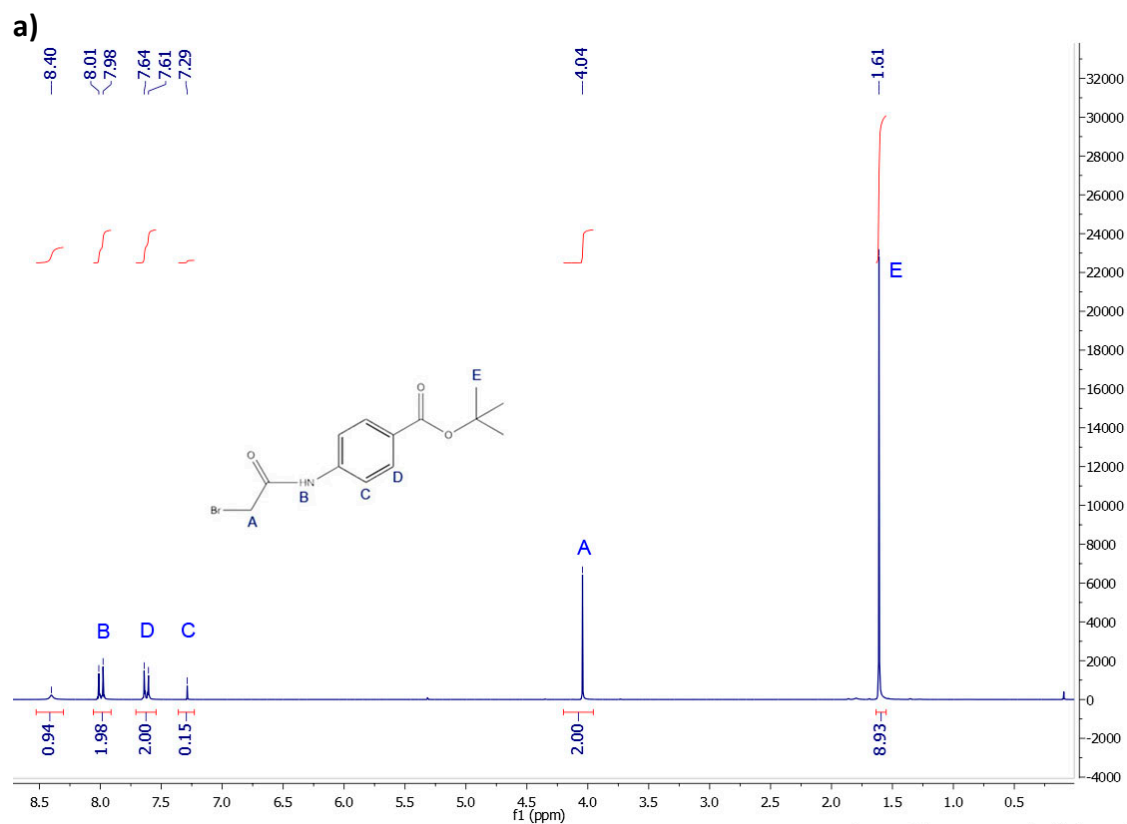# Supplementary Information

Two-step synthesis of heterometallic coordination polymers using a polyazamacrocyclic linker
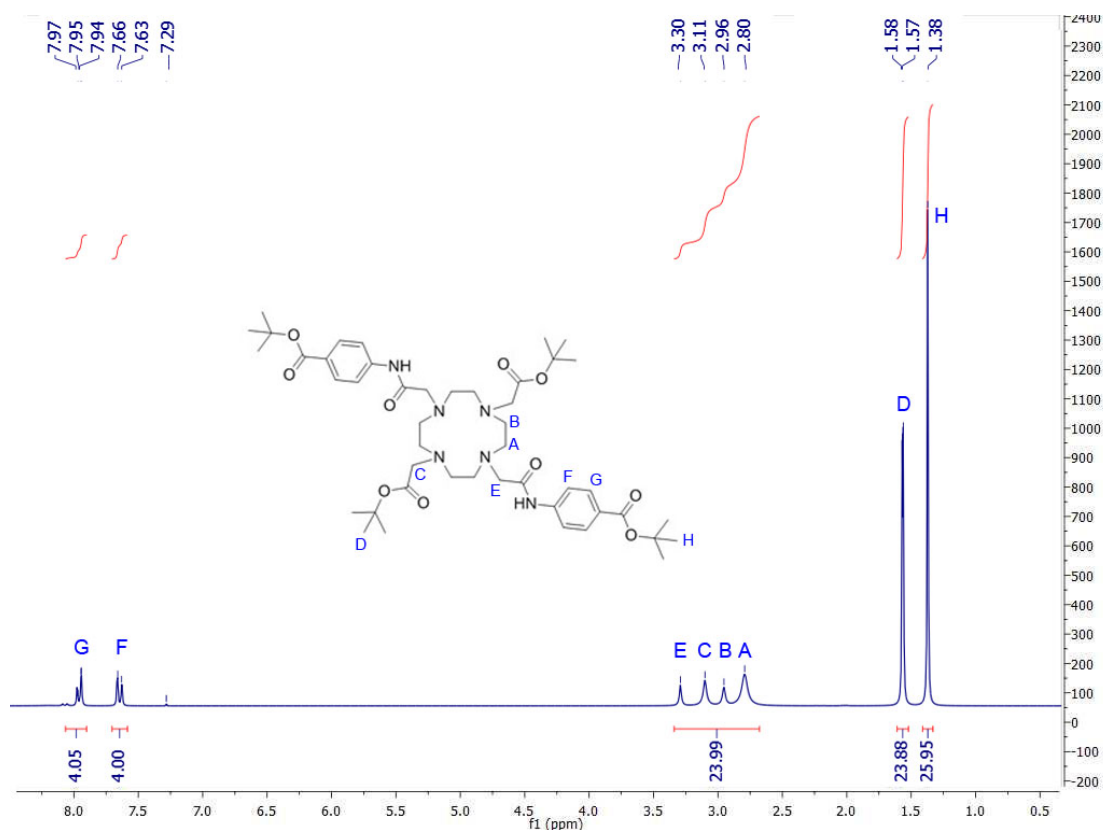
J. Aríñez-Soriano, J. Albalad, J. Pérez-Carvajal, I. Imaz, F. Busqué, J. Juanhuix and D. Maspoch

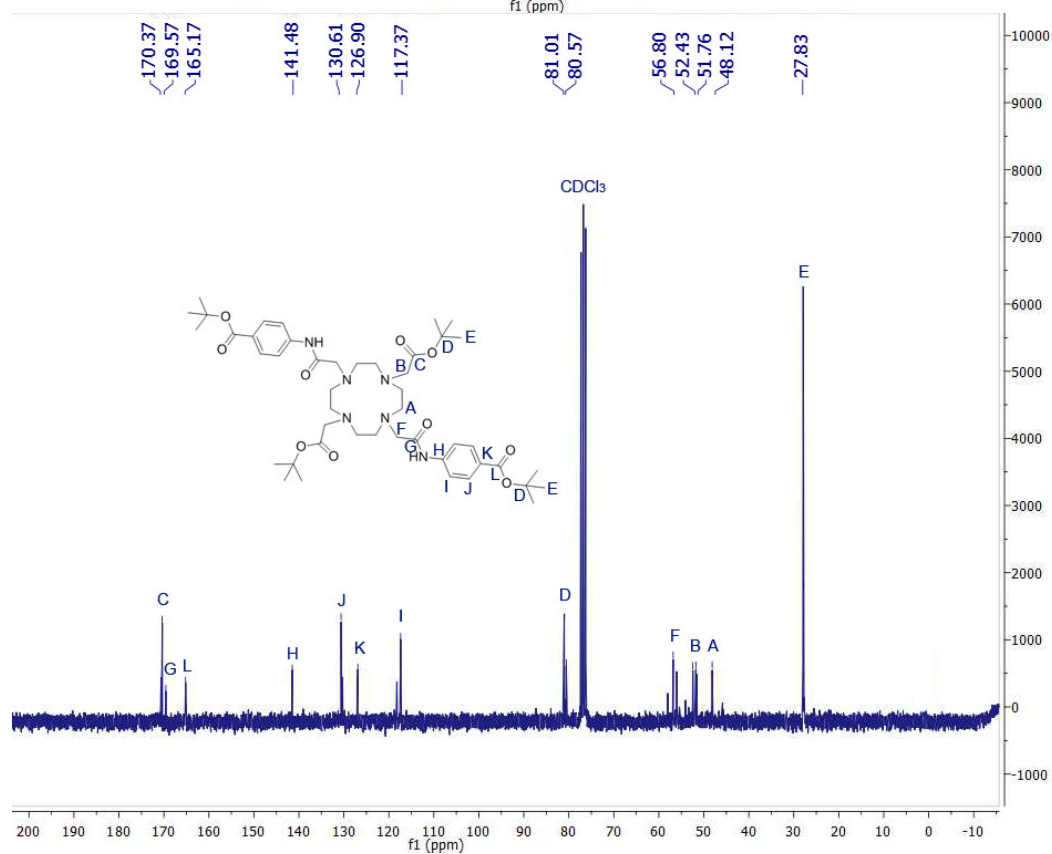**Figure S1.** Characterization of **1**: (a) ^{1}H-NMR (CDCl$_3$, 298 K, 360 MHz), and (b) ^{13}C-NMR (CDCl$_3$, 298 K, 90 MHz).

a)

b)

Figure S2. Characterization of **2**: (a) ^{1}H-NMR (CDCl$_3$, 298 K, 360 MHz), (b) ^{13}C-NMR (CDCl$_3$, 298 K, 90 MHz), and (c) ESI-TOF/MS spectrum.

a)

b)

c)

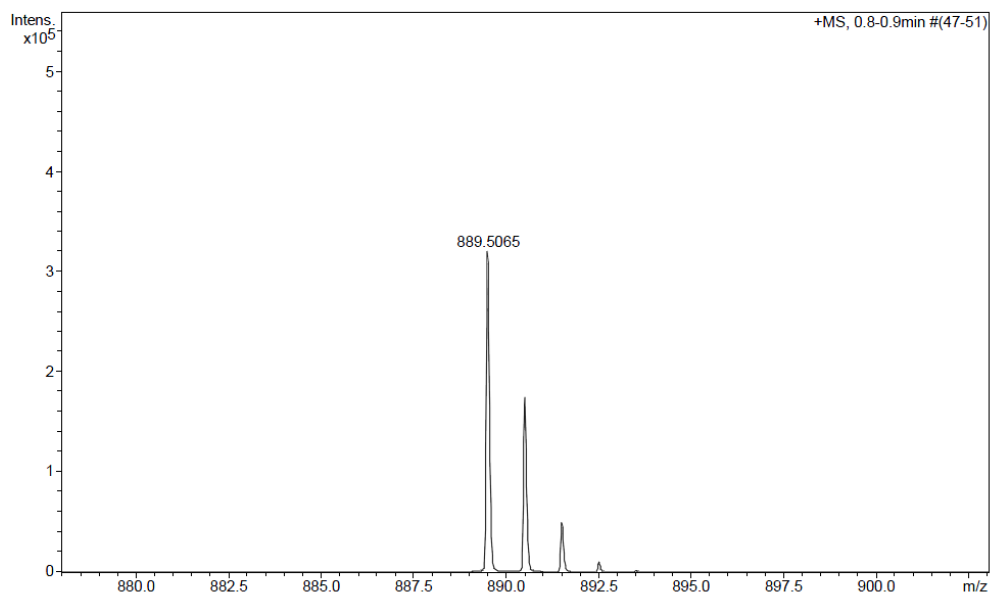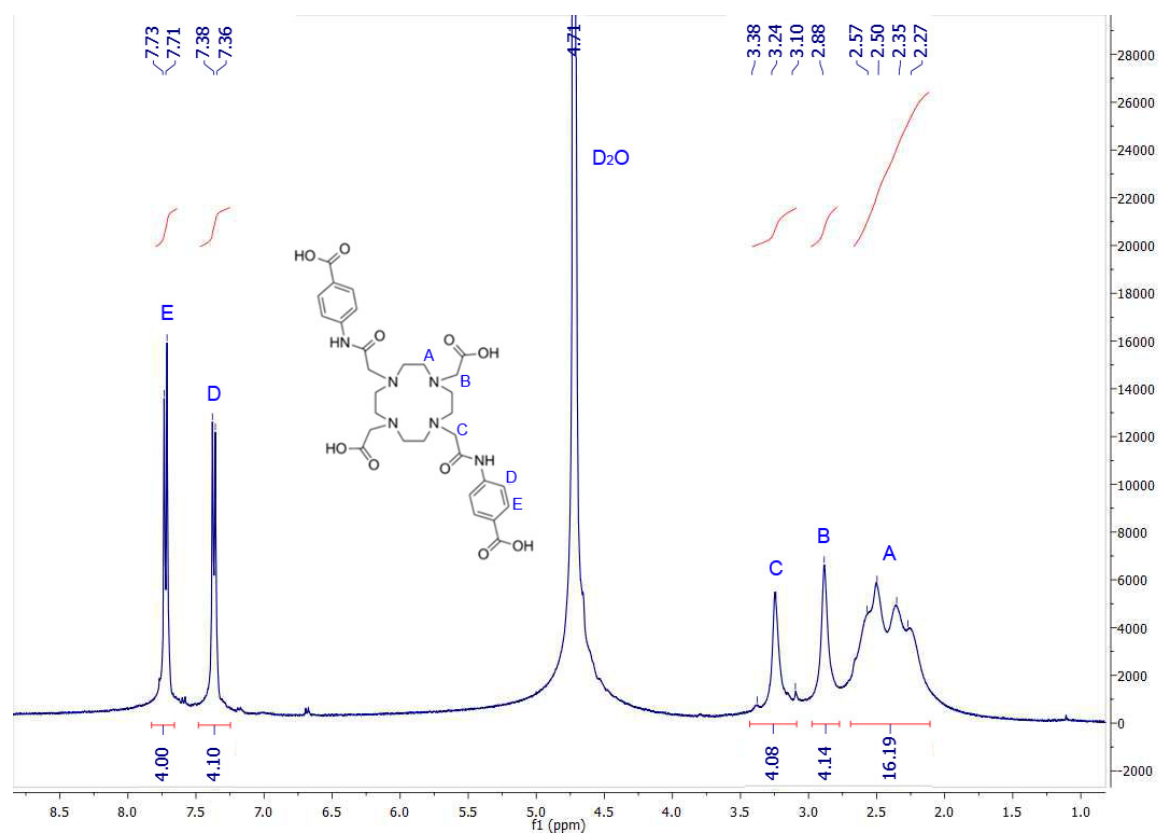| #	m/z	I	I %
1	889.5065	320137	100.0
2	890.5093	174966	54.7
3	891.5109	49802	15.6
4	892.5131	10089	3.2

Figure S3. Characterization of H$_4$**L1**: (a) ^{1}H-NMR (D$_2$O, 298 K, 400 MHz), (b) ^{13}C-NMR (D$_2$O, 298 K, 100 MHz), (c) ESI-TOF/MS spectrum, and (d) FT-IR spectrum.

a)

H Label	δ (ppm)	Integration	Mult (^{3}J$_{H-H}$ (Hz))	Assignation
H$_A$	2.43	16H	mult	NCH$_2$CH$_2$N
H$_B$	2.88	4H	s	NCH$_2$CONH
H$_C$	3.38	4H	s	NCH$_2$COO
H$_D$	7.37	4H	d (7.5 Hz)	Ar
H$_E$	7.72	4H	d (7.5 Hz)	Ar

b)
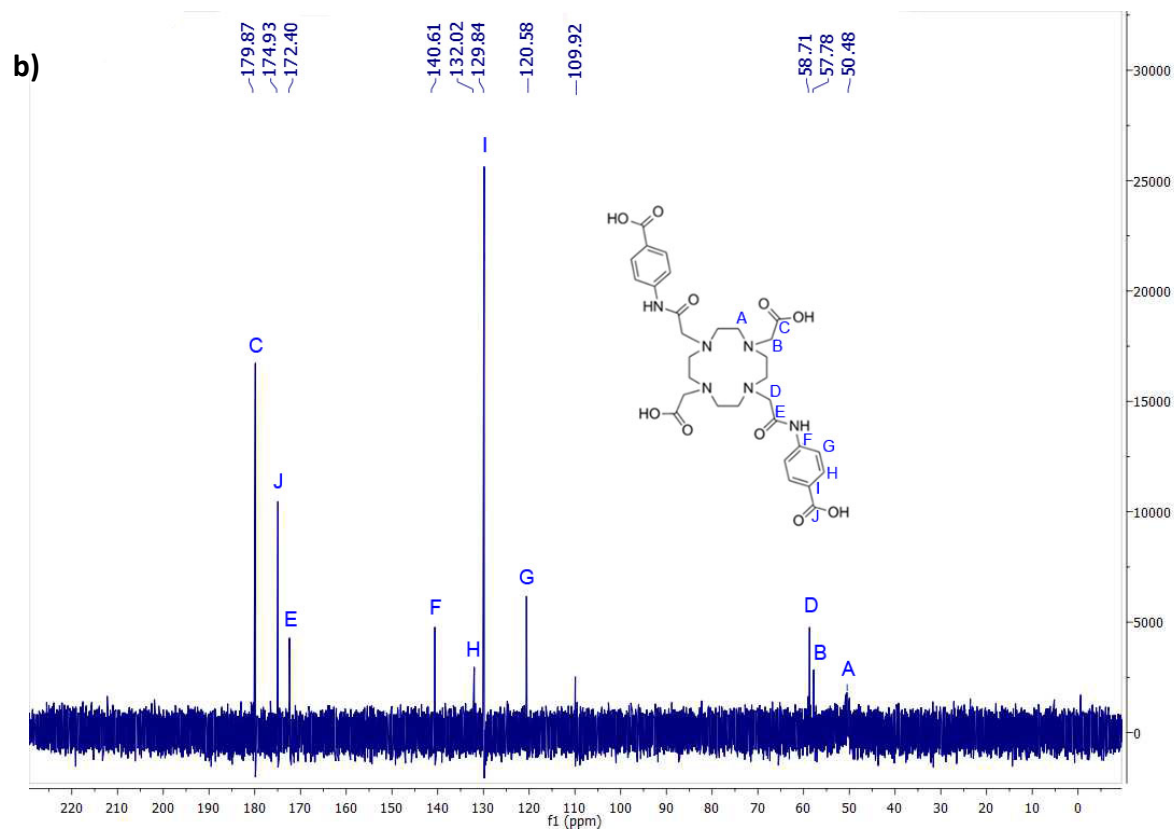
C Label	δ (ppm)	Assignation
C_A	50.5	NCH_2CH$_2$N
C_B	55.8	NCH_2COO
C_C	179.9	CH$_2$$COO$
C_D	58.7	NCH_2CONH
C_E	172.3	Ar-COO
C_F	140.6	NH-Ar
C_G	120.6	Ar
C_H	132.0	Ar
C_I	129.8	*Ar*-COO
C_J	174.9	CH$_2$$C$ONH

c)

#	m/z	I	I %
1	665.2534	136128	100.0
2	666.2559	46190	33.9
3	667.2580	10070	7.4
4	668.2586	1706	1.3
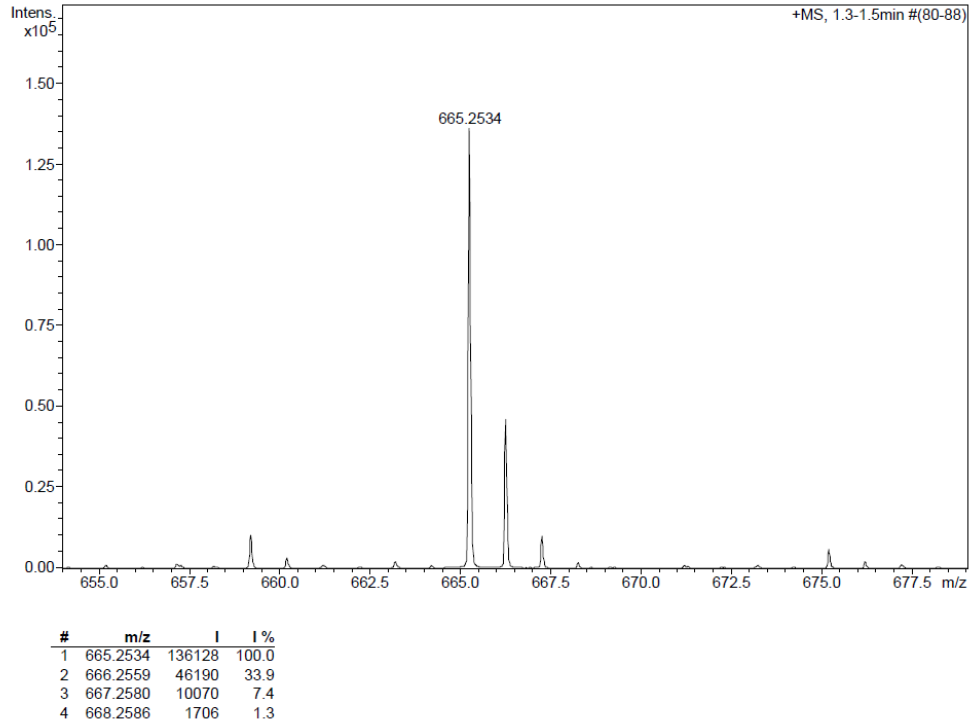
d)
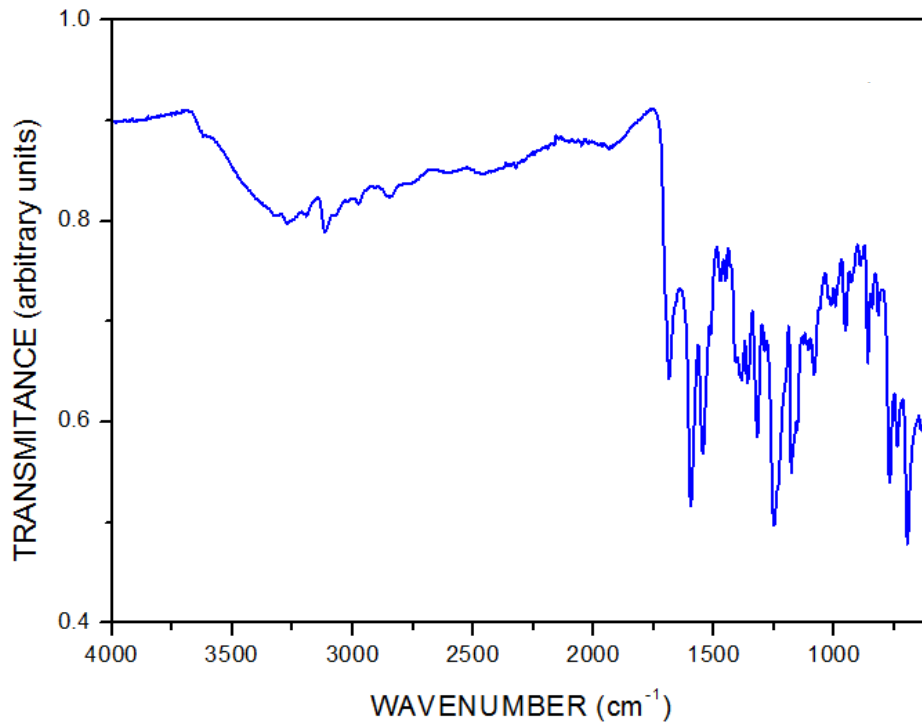
Figure S4. Characterization of **3**: (a) ESI-TOF/MS spectrum, and (b) FT-IR spectrum.

a)

#	m/z	I	I %
1	694.1802	6204	100.0
2	695.1795	2510	40.5
3	696.1862	1296	20.9

b)
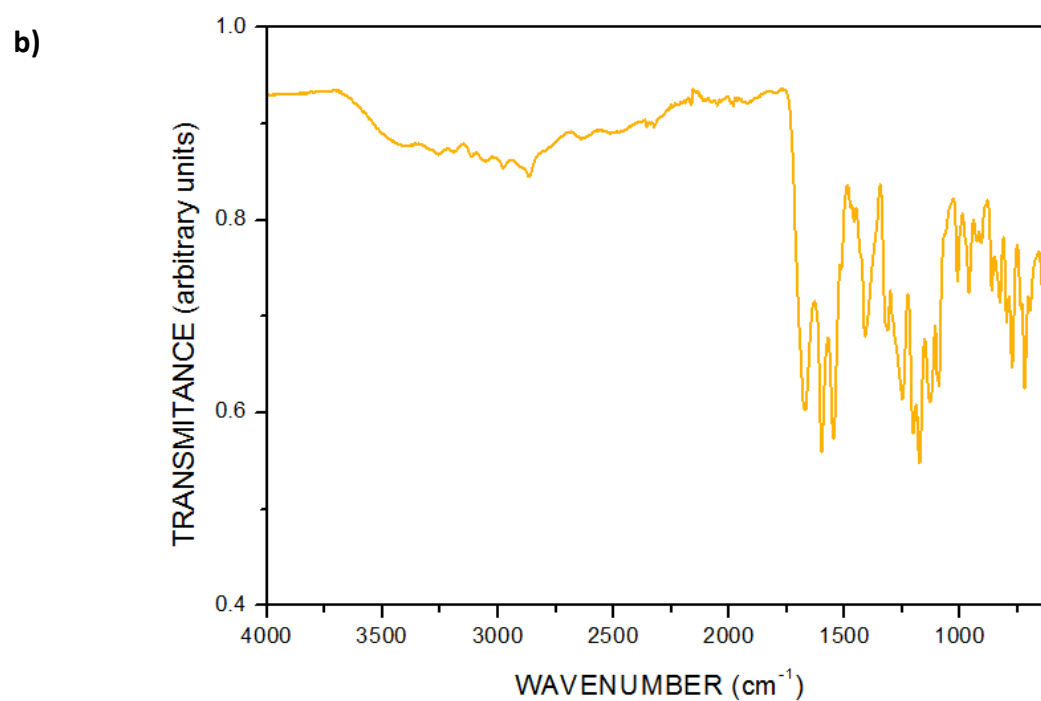
Figure S5. Characterization of **4**: (a) ESI-TOF/MS spectrum, and (b) FT-IR spectrum.

a)

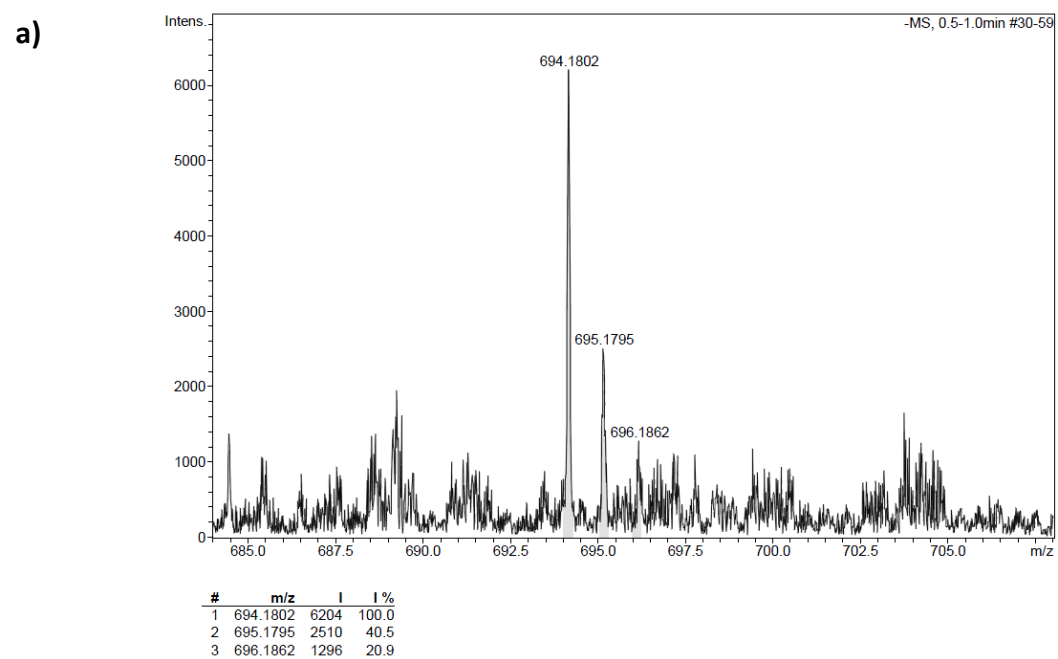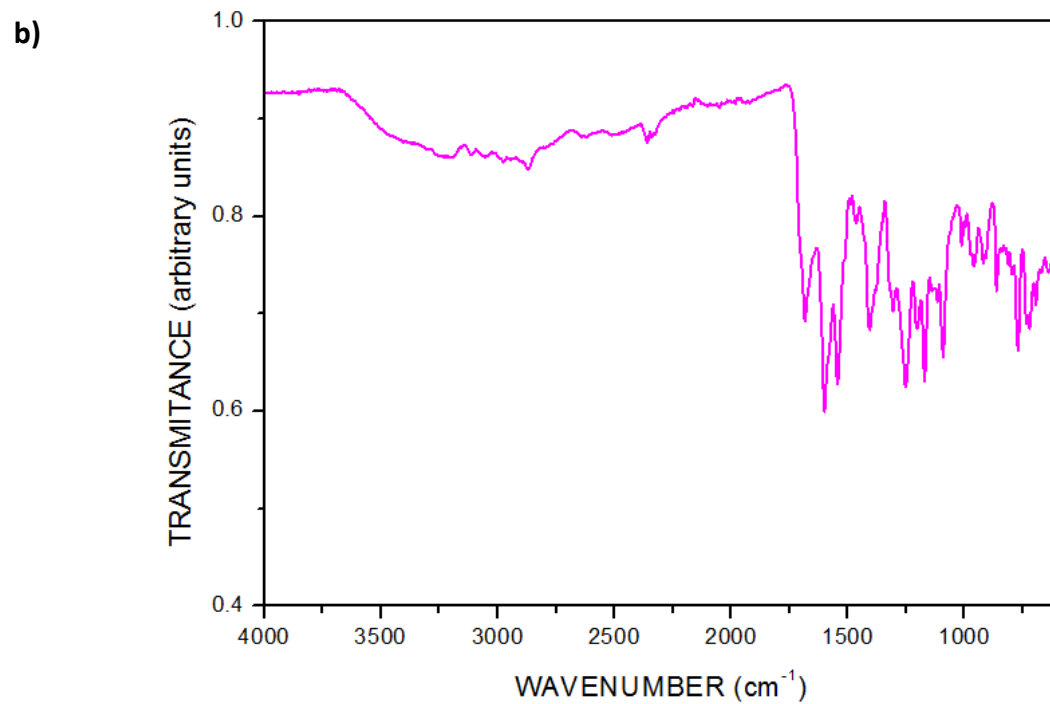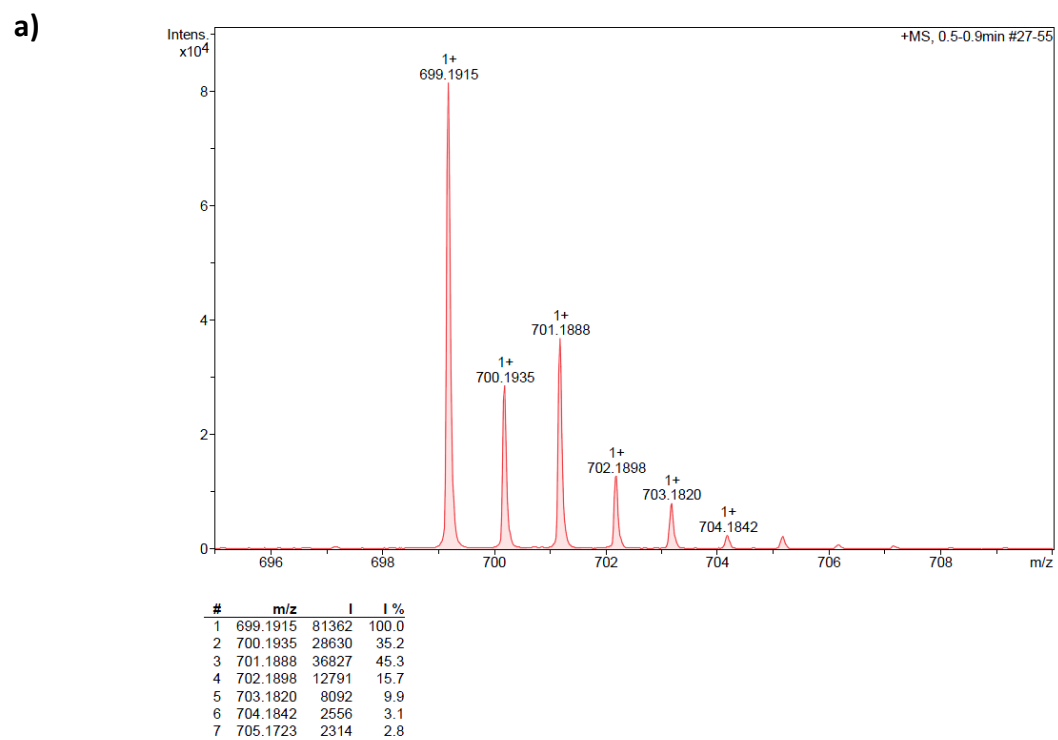| #	m/z	I	I %
1	699.1915	81362	100.0
2	700.1935	28630	35.2
3	701.1888	36827	45.3
4	702.1898	12791	15.7
5	703.1820	8092	9.9
6	704.1842	2556	3.1
7	705.1723	2314	2.8

b)

Figure S6. Characterization of **5**: (a) FT-IR spectrum, and (b) Powder X-Ray diffraction pattern of **5** (green), in comparison to the simulated pattern (black).

a)
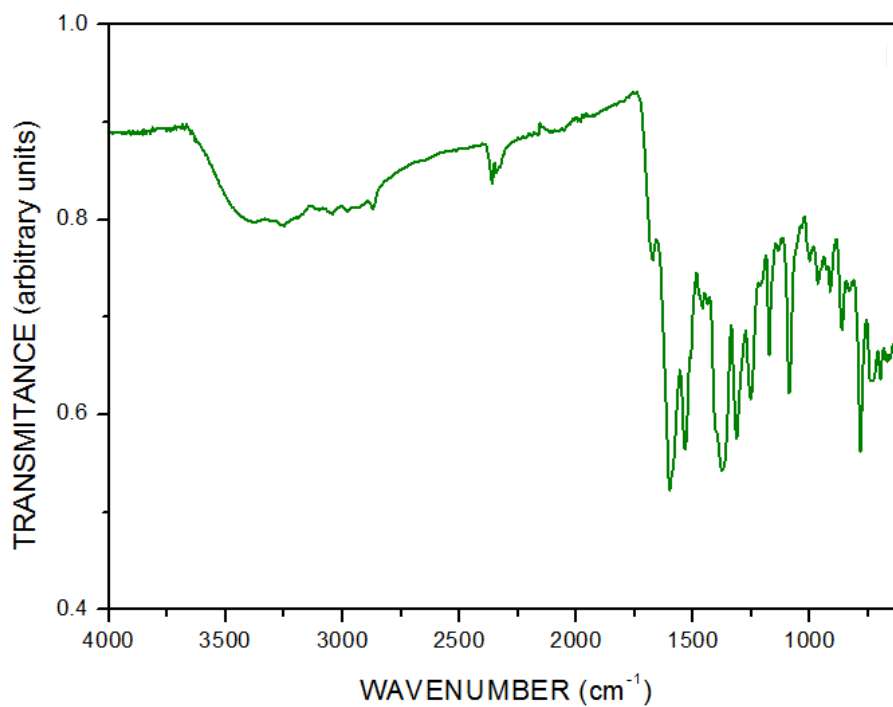
b)
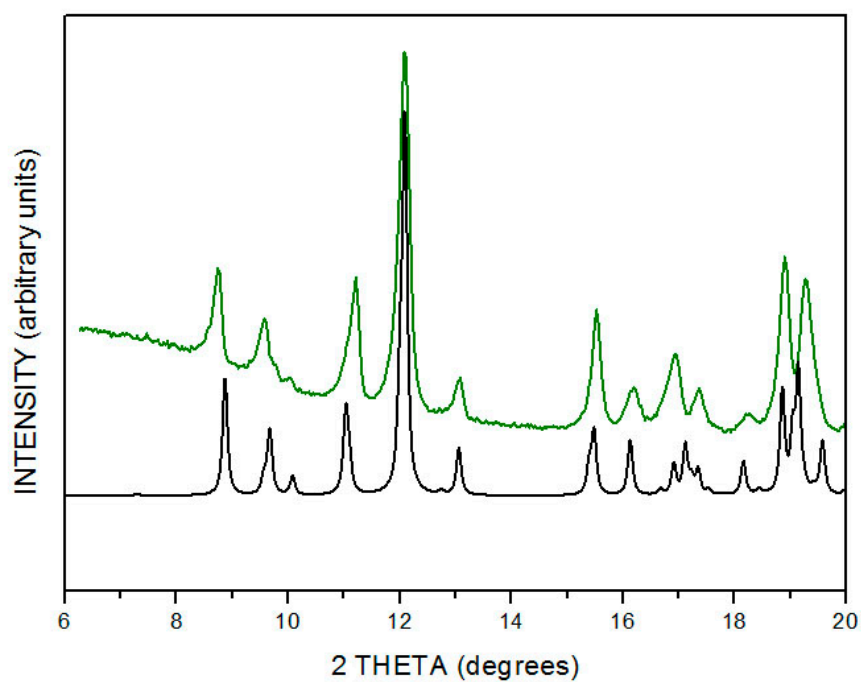
Figure S7. Characterization of **6**: (a) FT-IR spectrum, and (b) Powder X-Ray diffraction pattern of **6** (red), in comparison to the simulated pattern (black).

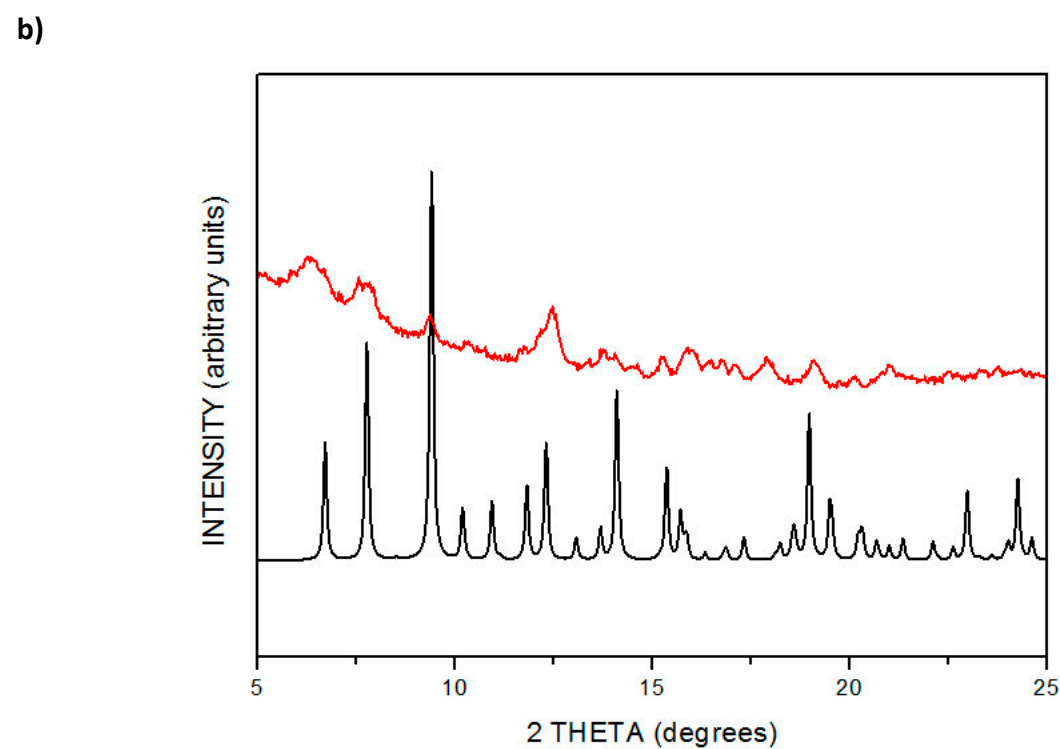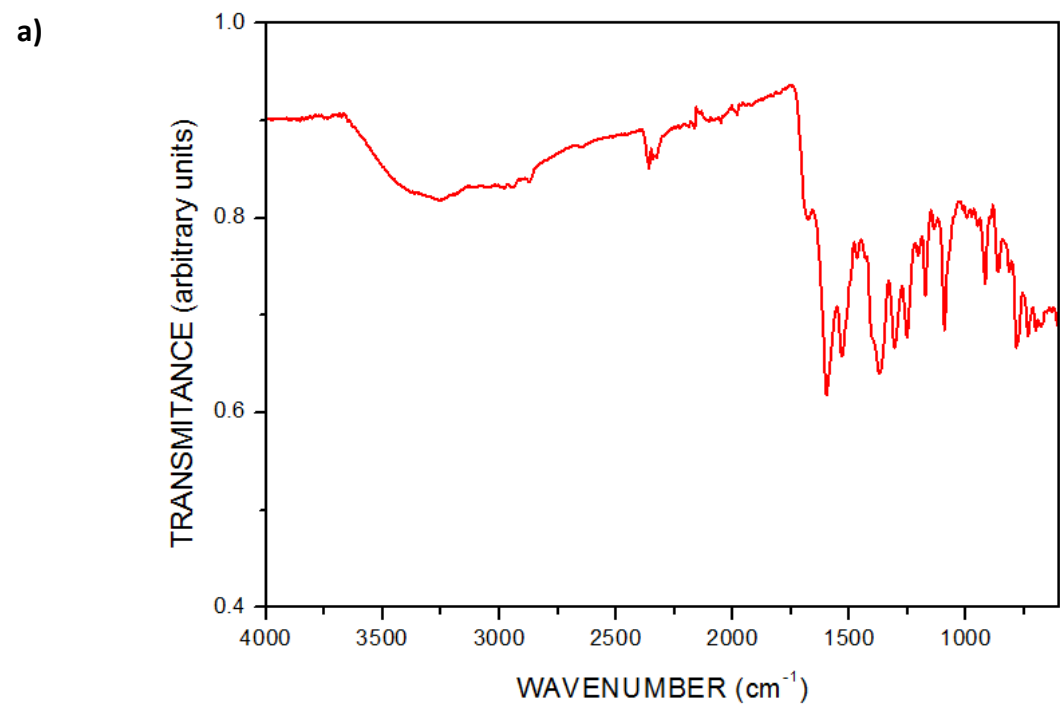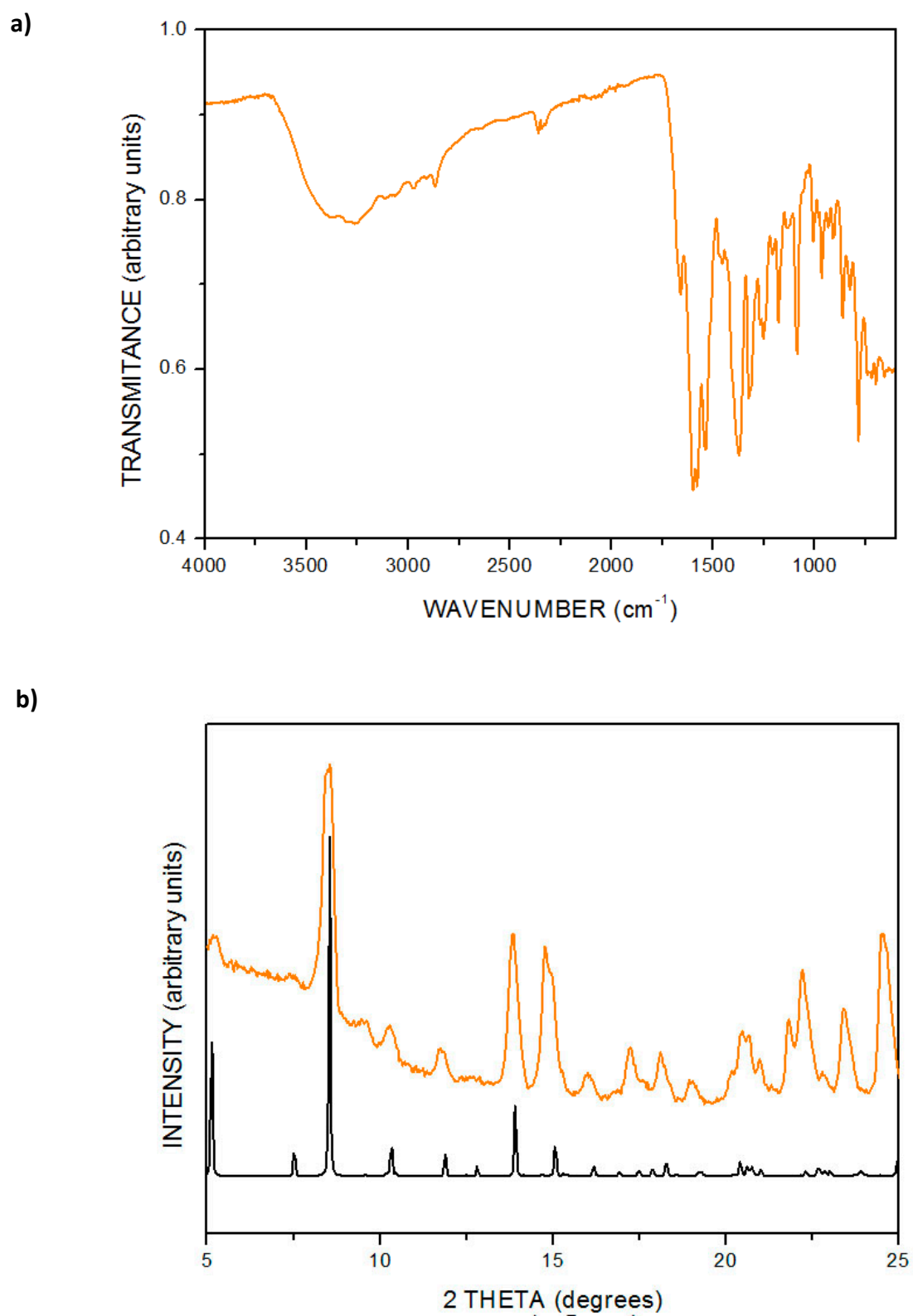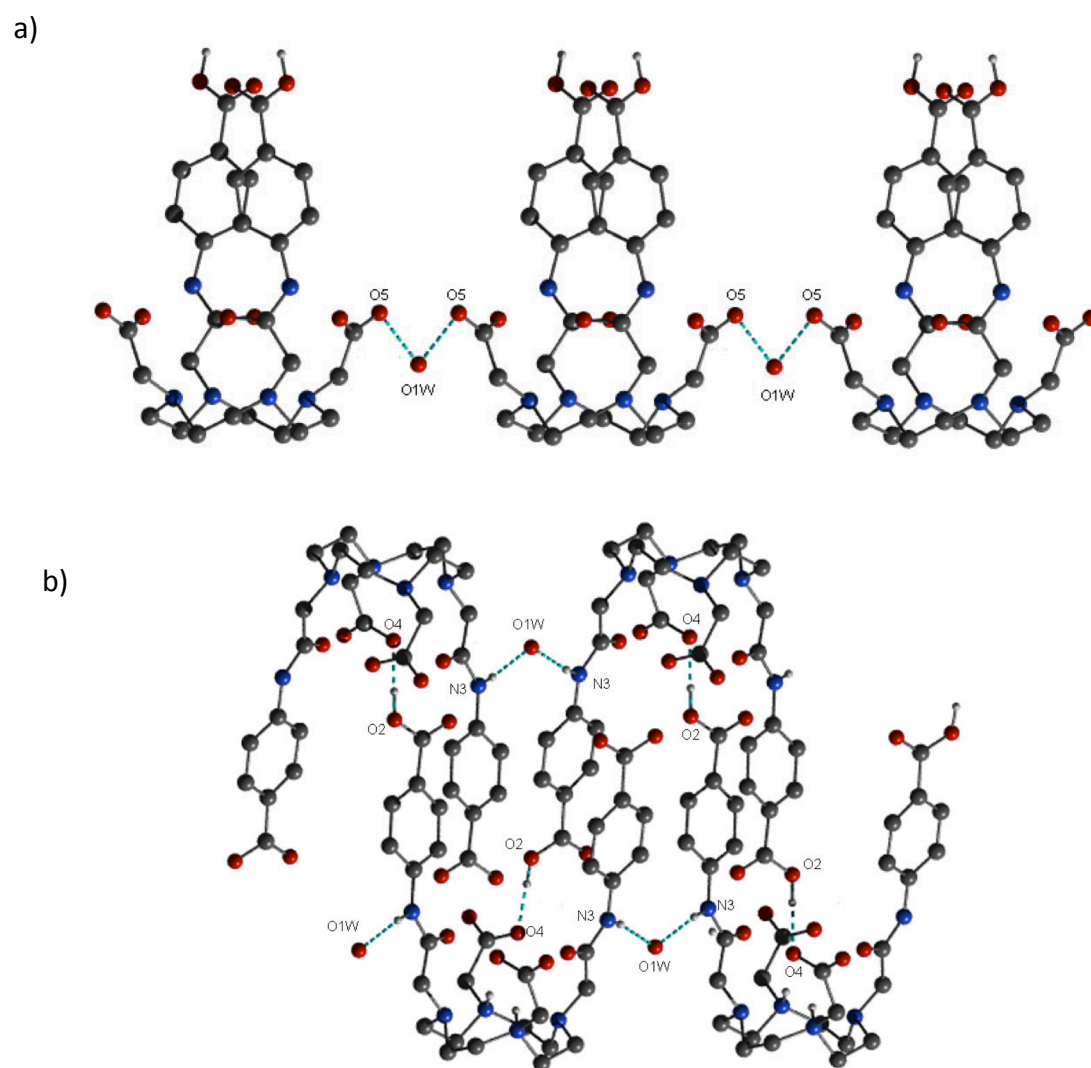**a)**

b)

Figure S8. Characterization of **7**: (a) FT-IR spectrum, and (b) Powder X-Ray diffraction pattern of 7 (orange), in comparison to the simulated pattern (black).

a)

b)

Figure S9. Views of the H-bonded packing of H_4L1. Hydrogen bonds are marked as sky blue dash lines. Hydrogen-bond geometry (Å, °) data is shown below.

a)

b)

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N3—H$\cdots$O1W^i	0.86	2.16	3.004(8)	169
O1W—H$\cdots$O5$^{ii,\ iii}$	--	--	2.813(0)	--
O2—H$\cdots$O4^{iv}	0.92	1.67	2.592(0)	174

Symmetry codes: (i) x, y, 1+z; (ii) 1/2-x, 1/2-y, 1-z; (iii) -1/2+x, 1/2-y, -1/2+z (iv) x, -y, 1/2+z

Figure S10. View of the H-bonded packing of **3**. Hydrogen bonds are marked as sky blue dash lines, and π-π stacking interactions are marked as green dash lines. Hydrogen-bond geometry (Å, °) data is shown below.

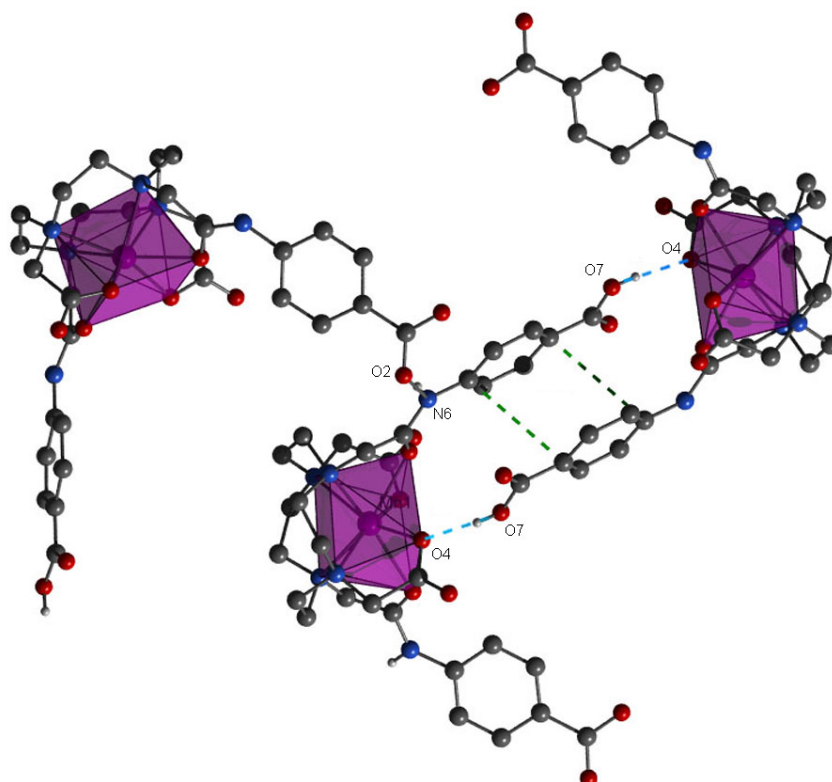| $D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O7—H⋯O4[i]	0.82	1.71	2.510(8)	163
N6—H⋯ O2[ii]	0.86	2.04	2.879(6)	164

Symmetry codes: (i) 2-x, 1-y, 3-z; (ii) 2-x, -1/2+y, 5/2-z

Figure S11. View of the H-bonded packing of **4**. Hydrogen bonds are marked as sky blue dash lines. Hydrogen-bond geometry (Å, °) data is shown below.
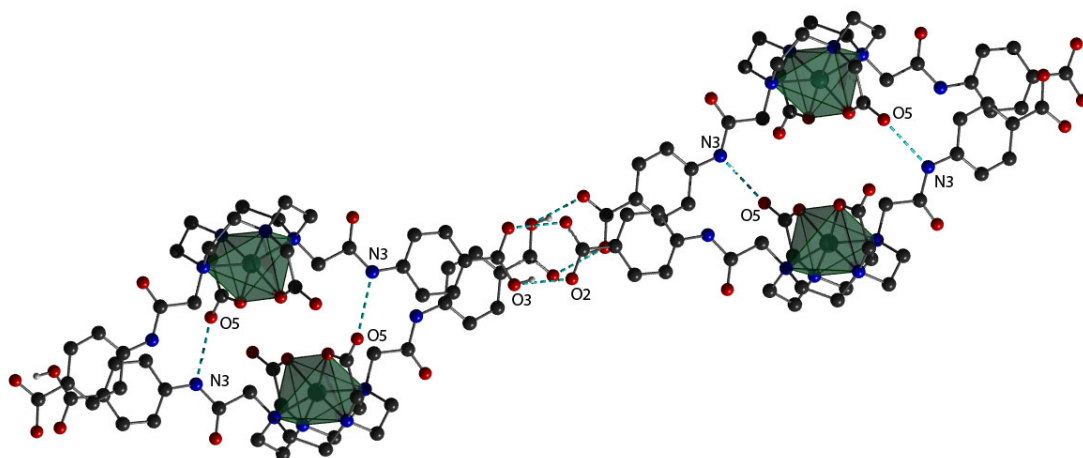
D—H···A	D—H	H···A	D···A	D—H···A
O3—H···O2^{i}	0.82	1.82	2.628(7)	168
N3—H··· O5^{ii}	0.86	1.93	2.791(5)	176
O1W—H···O4 $^{iii, iv}$	--	--	3.022(4)	--

Symmetry codes: (i) -x, -y, -2-z; (ii) 1-x, -y, -z; (iii) x, -y, -1/2+z; (iv) 1-x, -y, -z

Figure S12. View of the H-bonded packing of the double-strand chains in **5**. Hydrogen bonds are marked as green dash lines. Hydrogen-bond geometry (Å, °) data is shown below.
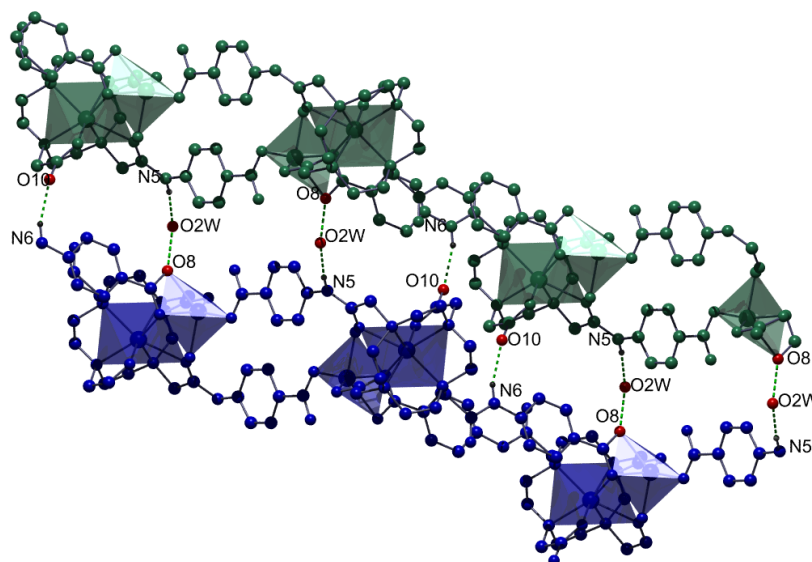
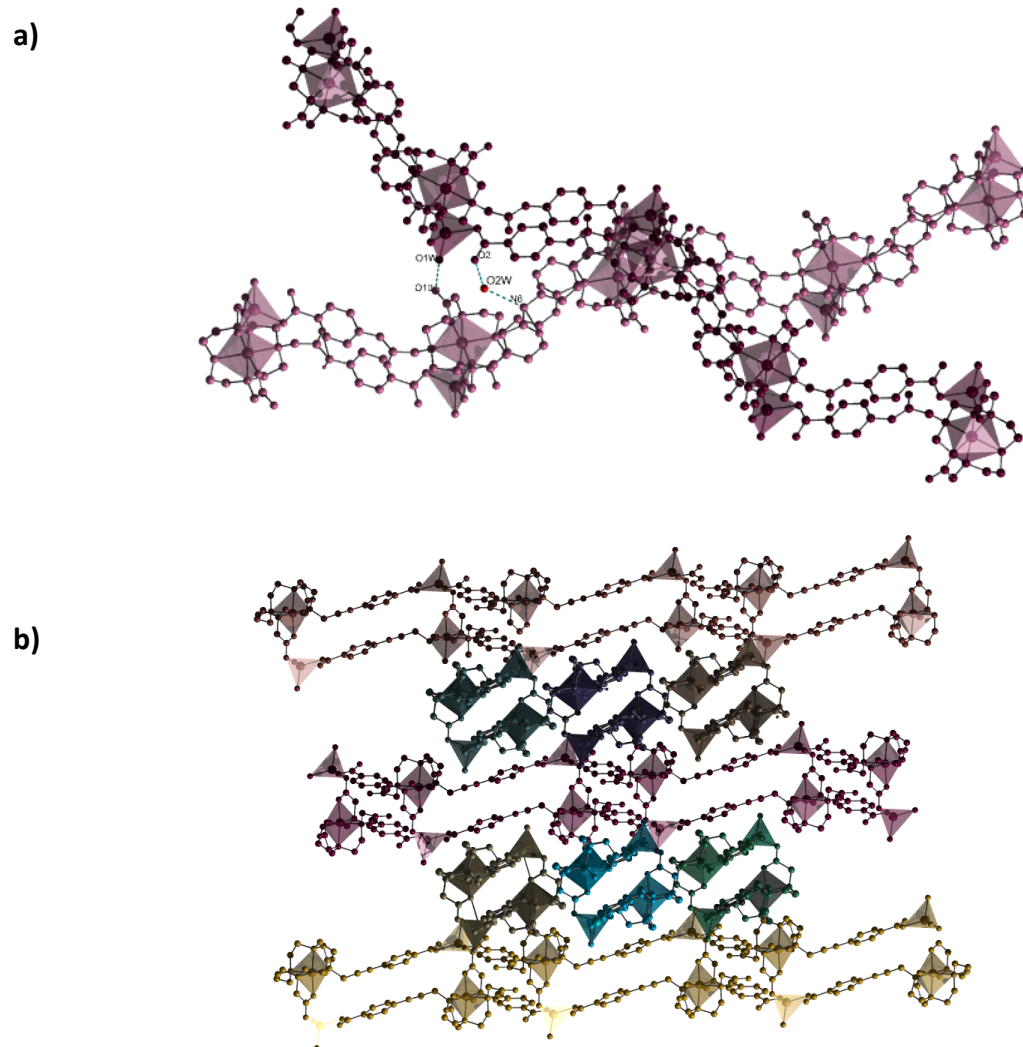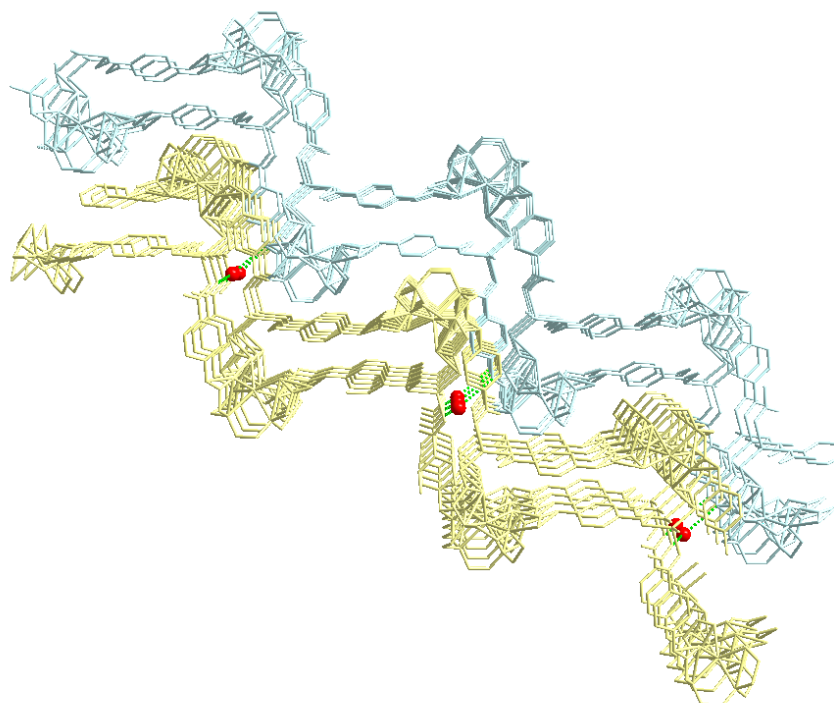| *D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H···O10[i]	0.86	2.03	2.852(6)	160
N5—H··· O2W	0.86	1.92	2.765(2)	169
O2W—H···O8[i]	--	--	2.850(3)	--

Symmetry codes: (i) 1-x, 1-y, -z

Figure S13. Views of a) the hydrogen bonds between double-strand chains in **6** and b) the packing of these double-strand chains along the [110] direction. Hydrogen bonds are marked as sky blue dash lines. Hydrogen-bond geometry (Å, °) data is shown below.

a)

b)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N6—H$\cdots$O2W	0.86	2.02	2.874(5)	170
O2W—H$\cdots$O2^{i}	--	--	2.818(1)	--
O1W—H$\cdots$O10^{ii}	--	--	2.591(0)	--

Symmetry codes: (i) 1/2-x, -1/2+y, 3/2-z; (ii) 1/2+x, 1/2-y, 1/2+z

Figure S14. View of the H-bonded packing of the layers of **7** via O4W water molecule along the *b* axis. Hydrogen bonds are marked as sky blue dash lines. Hydrogen-bond geometry (Å, °) data is shown below.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H···O4W[i]	0.86	2.13	2.941(7)	157
O4W—H··· O2	--	--	2.962(4)	--

Symmetry codes: (i) x, 2-y, -1/2+z

Figure S15. Powder X-Ray diffraction pattern resulting from the activated, amorphous 7'
once it has been exposed to a water sorption/desorption cycle (blue), in comparison to the
simulated pattern (black).