

# Design and Syntheses of Hybrid Supramolecular Architectures: Based on $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ Metallotectons and Diverse Organic Cations

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**Figure S1.** The close-packed 3D H-bonded framework of **8** ( $\text{Cl}^-$  and  $\text{H}_2\text{O}$  molecules have been deleted).

**Figure S2.** ORTEP view of the asymmetric unit of  $[\{(\text{H}_2\text{-L}_6)_2\text{Fe}_2(\text{OH})_2(\text{C}_2\text{O}_4)_4\} \cdot 2\text{H}_2\text{O}]$  (**7**) with ellipsoids cut at the 30% probability level.

**Figure S3.** Detail of the connection between ten  $[\text{H-L}_7]^+$  cation and one  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  anion.

**Figure S4.** The close-packed 3D H-bonded framework of **8** ( $\text{Cl}^-$  and  $\text{H}_2\text{O}$  molecules have been deleted).

**Figure S5.** Thermogravimetric analyses (TGA) curves of **2** and **5-8**.

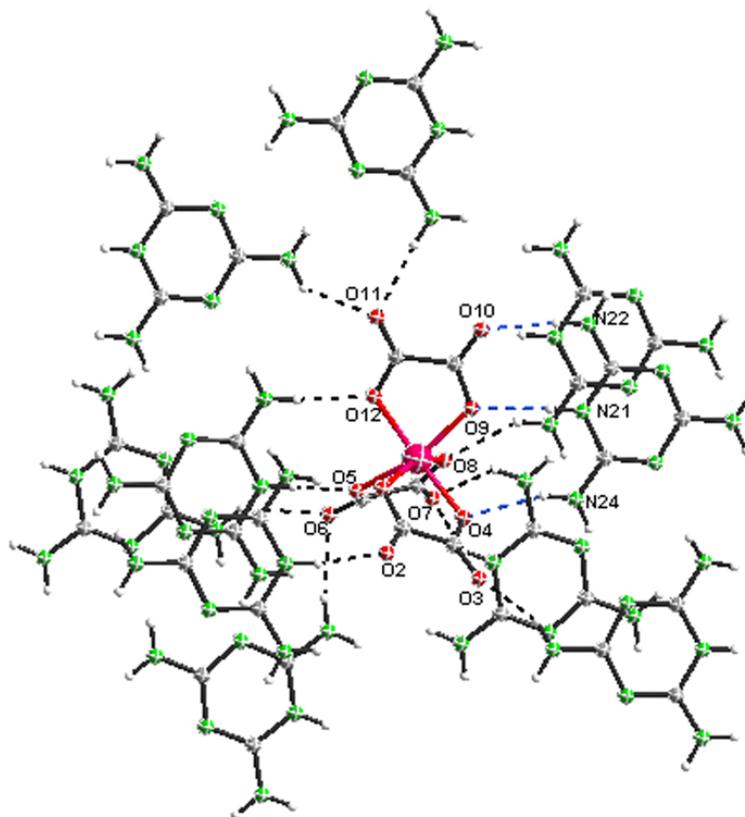
**Figure S6.** IR curves of **1-8**

**Table S1** Hydrogen-Bond Geometries in the Crystal Structures of **1-8**

**Figure S1.** The close-packed 3D H-bonded architecture of **3**. Each independent 2D network is depicted with a different color.

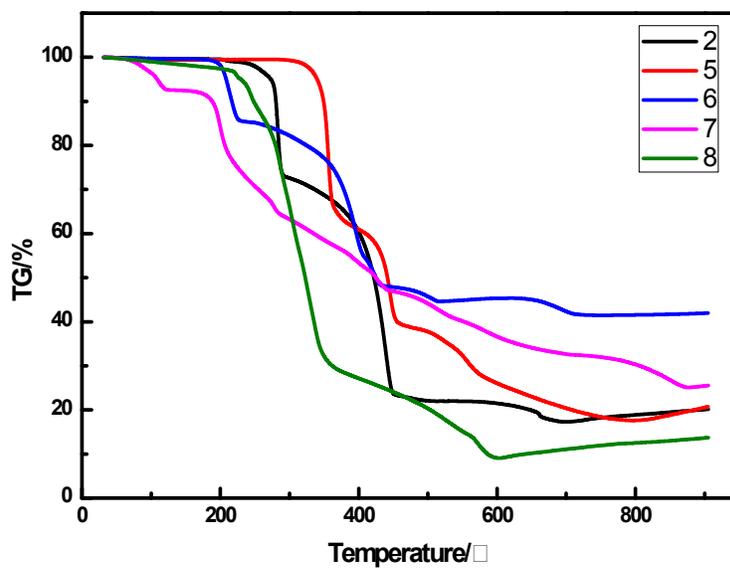
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**Figure S4.** The close-packed 3D H-bonded framework of **8** (Cl<sup>-</sup> and H<sub>2</sub>O molecules have been deleted).

**Figure S5.** Thermogravimetric analyses (TGA) curves of **2** and **5-8**.

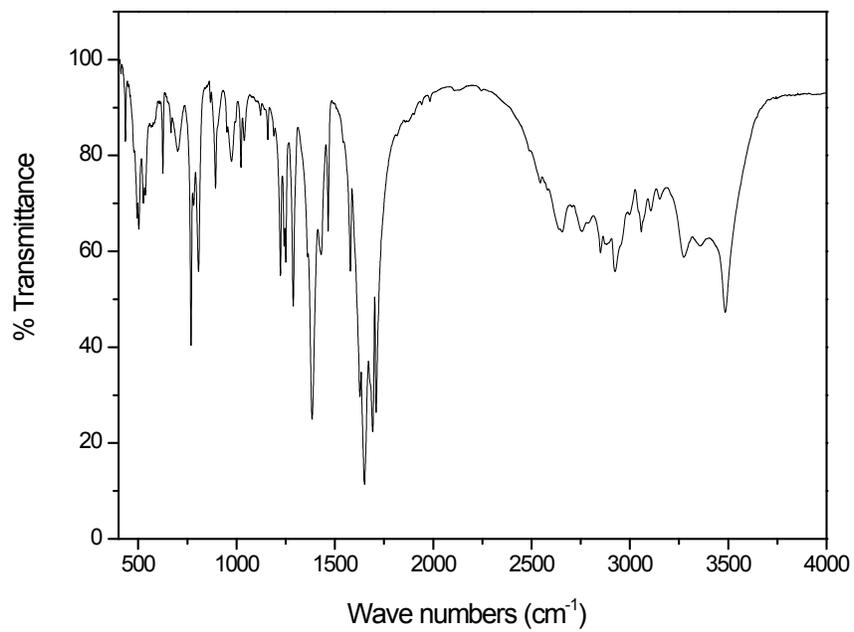


**Table S1** Hydrogen-Bond Geometries in the Crystal Structures of 1-8

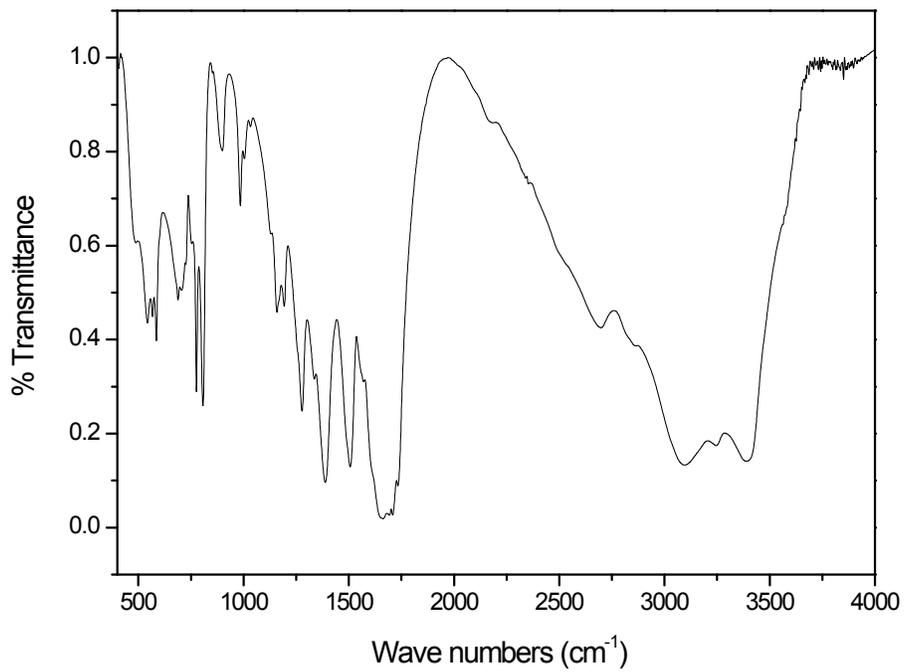
Compound	D-H...A (Å)	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (deg)	symmetry
1	N1-H1...O1	0.86	1.89	2.725	162	-x, y, 1/2-z
	N2-H2...O7	0.86	1.85	2.710	177	-1/2+x, y, 1-z
	O7-H7B...O6	0.85	1.95	2.769	163	1/2-x, -y, z
2	N3-H3...O11	0.86	1.94	2.735	154	x, -1+y, z
	O9-H9A...O7	0.85	1.98	2.819	169	
	O9-H9B...O10	0.85	1.89	2.742	176	
	O10-H10A...O3	0.85	2.18	2.916	145	x, 1+y, z
	O10-H10B...O2	0.85	1.99	2.765	152	-x, 1+y, z
	O11-H11A...O6	0.85	2.24	2.982	146	1+x, y, z
	O11-H11A...O7	0.85	2.43	2.920	117	1+x, y, z
	O11-H11B...O9	0.85	1.95	2.794	170	
	C7-H7...O5	0.93	2.39	3.188	143	1-x, -y, 1-z
	C17-H17...O2	0.93	2.34	3.132	143	
3	N1-H1...O4	0.86	1.81	2.660	171	
	N3-H3...O4	0.88	2.13	2.788	131	2-x, 1-y, 2-z
	N3-H3...O5	0.88	2.43	3.236	154	2-x, 1-y, 2-z
	C4-H4B...O5	0.97	2.51	3.362	147	x, y, -1+z
	C11-H11A...O6	0.97	2.40	3.36	170	1-x, 1-y, 2-z
4	N1-H1...O2	0.86	2.41	3.046	131	-x, y, -1/2-z
	N1-H1...O3	0.86	2.03	2.786	147	-x, y, -1/2-z
	C4-H4B...O3	0.96	2.49	3.184	129	-x, y, -1/2-z
	C6-H6...O6	0.93	2.53	3.101	120	-1/2+x, 1/2+y, -1+z
5	N1-H1...O2	0.86	2.09	2.783	137	-x, -y, 1-z
	N1-H1...O3	0.86	2.17	2.901	143	-x, -y, 1-z
	O13-H13C...O4	0.88	2.21	3.004	151	-x, y, 1/2-z
	O13-H13D...O11	0.87	2.22	3.006	150	1+x, y, z
	C7-H7...O12	0.93	2.36	3.251	161	1+x, y, z
	C16-H16...O7	0.93	2.37	3.017	127	1/2-x, 1/2-y, 1-z
6	N4-H4...O1	0.86	2.01	2.868	174	-1/2+x, 1/2-y, -1/2+z
	C5-H5...O2	0.93	2.45	3.218	140	1/2+x, -1/2+y, z
7	N1-H1A...O5	0.89	2.07	2.875	150	-x, 1-y, 1-z
	N1-H1B...O2	0.89	2.11	2.906	148	-1+x, y, z
	N1-H1B...O3	0.89	2.23	2.872	128	-1+x, y, z
	N1-H1C...O7	0.89	2.08	2.958	168	-x, 2-y, 1-z
	N2-H2A...O1	0.89	2.34	2.903	121	-1+x, y, z
	N2-H2A...O2	0.89	2.25	3.053	150	1-x, 2-y, 1-z
	N2-H2B...O3	0.89	2.00	2.813	152	1-x, 1-y, 1-z
	N2-H2C...O10	0.89	1.92	2.806	175	1-x, 2-y, 1-z
	O9-H9...O6	0.78	2.23	2.963	155	-x, 1-y, -z
	O10-H10A...O9	0.71	2.44	3.107	157	x, 1+y, z
O10-H10B...O8	0.69	2.35	2.920	141		
8	N2-H2...O13	0.86	1.84	2.700	173	1+x,y,z

N4-H4A···N19	0.86	2.09	2.947	173	1-x,-y,1-z
N4-H4B···O11	0.86	2.05	2.754	138	
N5-H5A···O6	0.86	2.20	3.055	170	2-x,-1/2+y,1/2-z
N5-H5B···C11	0.86	2.67	3.4033	144	1-x,-y,1-z
N6-H6A···N7	0.86	2.16	3.019	173	
N6-H6B···N8	0.86	2.19	2.949	148	
N9-H9···O5	0.86	1.94	2.782	165	-1+x,y,z
N10-H10A···N3	0.86	2.10	2.960	176	
N10-H10B···O12	0.86	2.02	2.867	168	-1+x,y,z
N11-H11A···C11	0.86	2.41	3.240	162	x,1/2-y,1/2+z
N12-H12A···N13	0.86	2.15	3.006	179	1-x,1/2+y,1/2-z
N12-H12B···O14	0.86	2.31	2.950	132	-1+x,1/2-y,-1/2+z
O13-H13A···C11	0.85	2.27	3.096	163	1-x,-y,1-z
O13-H13B···O2	0.85	1.98	2.756	152	x,1/2-y,1/2+z
N14-H14···O2	0.86	1.87	2.716	169	x,1/2-y,1/2+z
O14-H14A···N12	0.85	2.39	2.950	124	1+x,1/2-y,1/2+z
O14-H14B···C11	0.85	2.73	3.348	130	1-x,-y,1-z
N16-H16A···O14	0.86	2.27	3.101	164	2-x,-y,1-z
N16-H16B···O3	0.86	2.07	2.856	151	1+x,1/2-y,1/2+z
N17-H17A···N8	0.86	2.16	3.019	179	1-x,-1/2+y,1/2-z
N17-H17B···C11	0.86	2.53	3.212	137	1-x,-y,1-z
N18-H18A···N20	0.86	2.16	2.944	152	1+x,y,z
N22-H22A···O11	0.86	2.12	2.980	176	1-x,-1/2+y,1/2-z
N22-H22B···O10	0.86	1.96	2.804	168	x,1/2-y,1/2+z
N23-H23A···N1	0.86	2.14	2.997	173	-x,1/2+y,1/2-z
N23-H23B···O6	0.86	2.30	2.987	136	-1+x,y,z
N24-H24A···N15	0.86	2.20	3.057	177	-1+x,y,z
N24-H24B···O7	0.86	2.44	3.040	128	

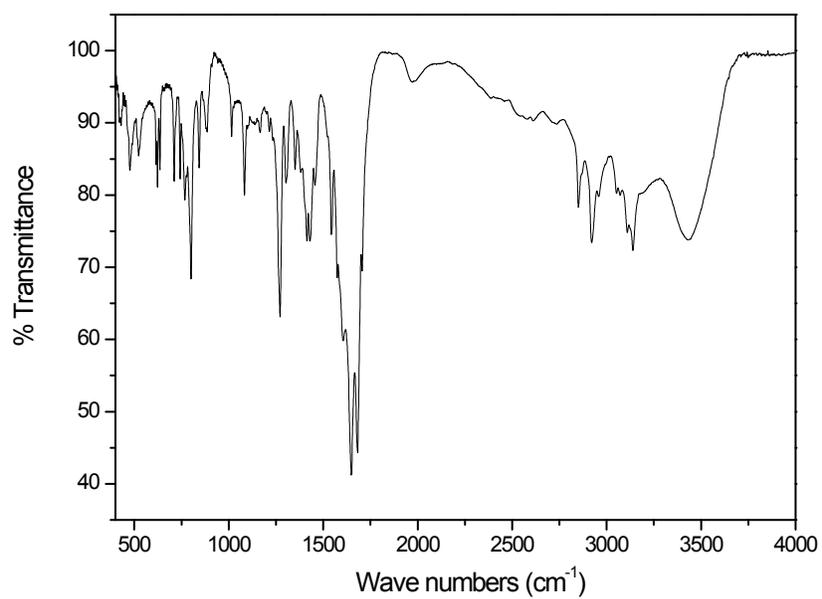
**Figure S6.** IR curves of **1-8**



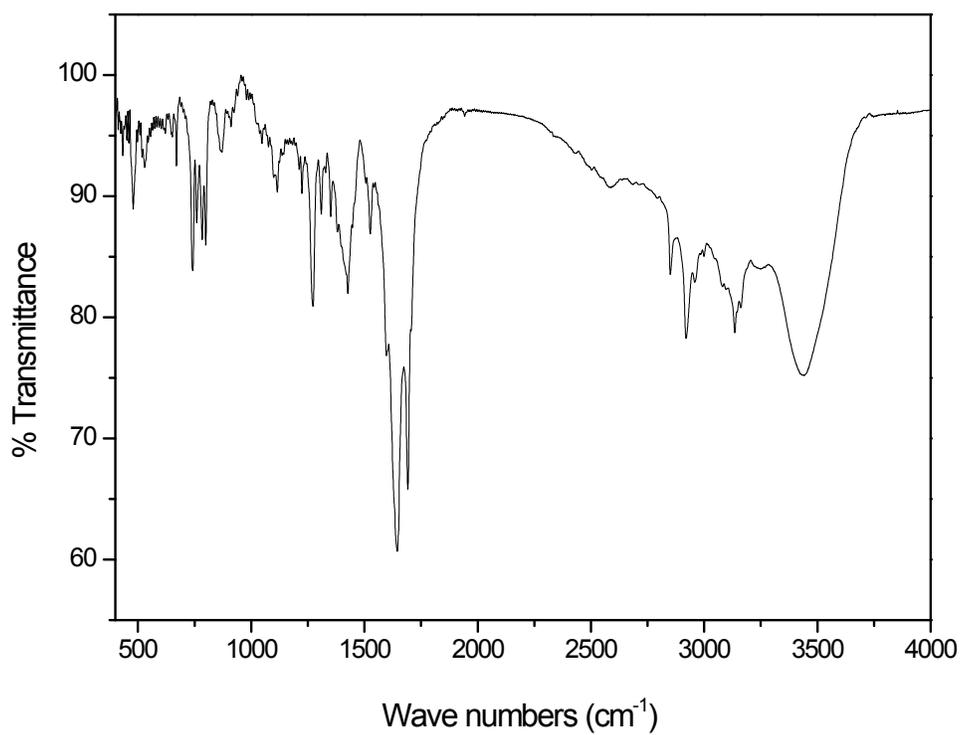
The IR curve of **1**



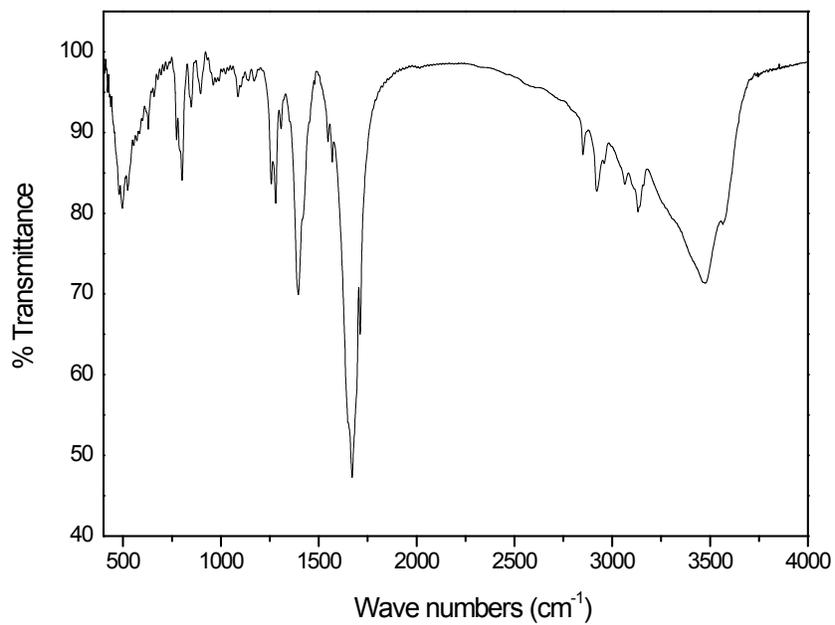
The IR curve of **2**



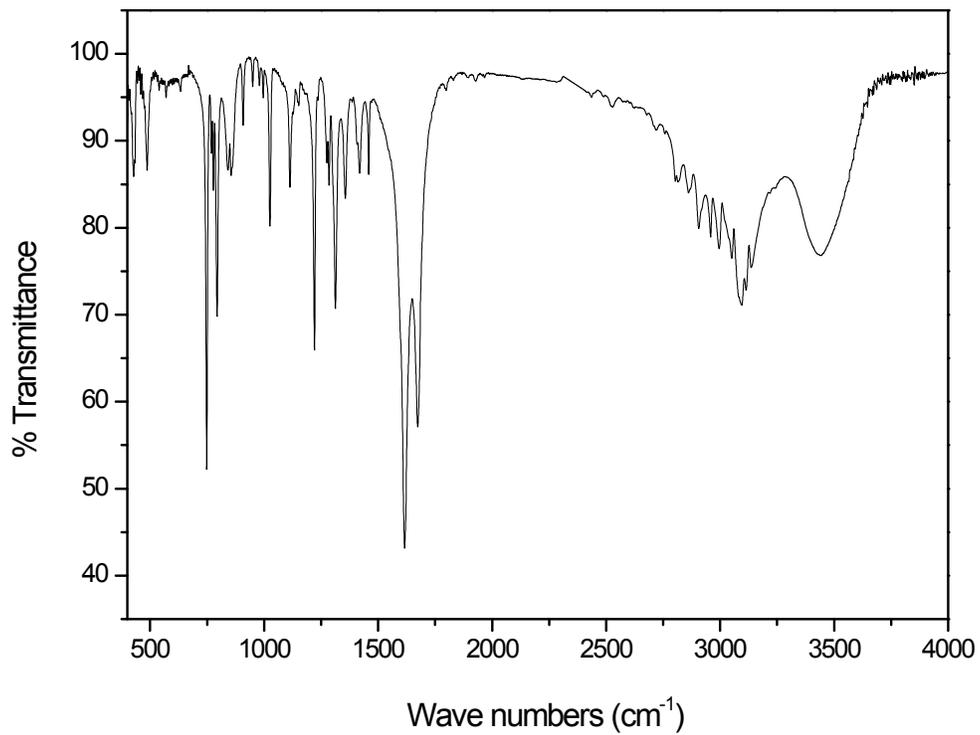
The IR curve of **3**



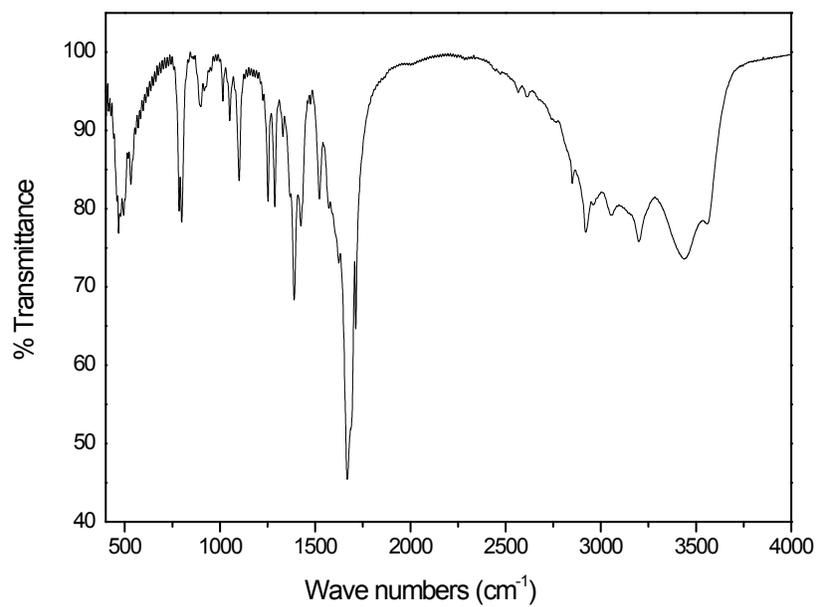
The IR curve of **4**



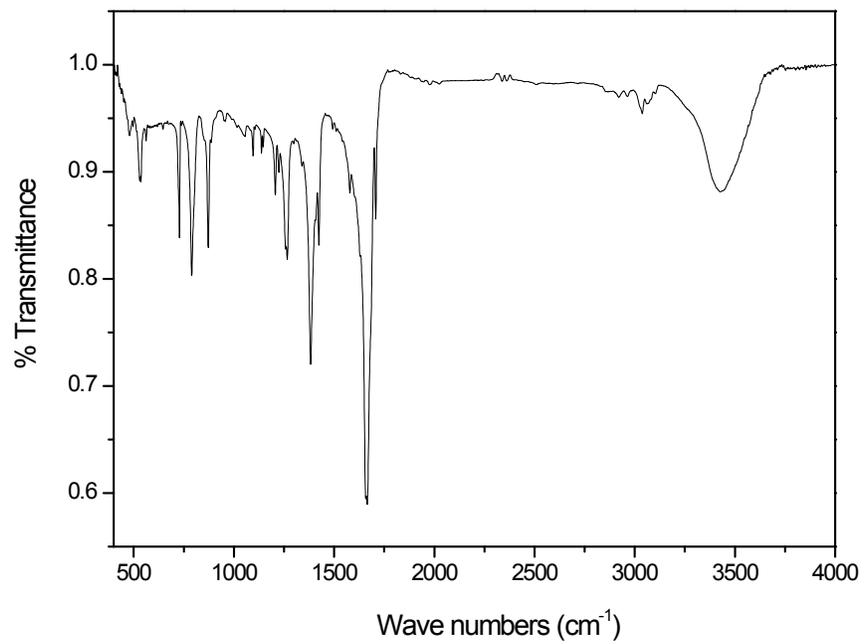
The IR curve of **5**



The IR curve of **6**



The IR curve of **7**



The IR curve of **8**