Supplementary Information

Thermal Induced 1D to 2D Polymer Conversion Accompanied by Major Packing Changes in a Single-Crystal-to-Single-Crystal Transformation

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Contents:

Experimental procedure:

[(4,4'-bpe•2H$^+$)(HSO$_4^-$)$_2$] (1): To the methanolic solution (3 mL) of *trans*-1,2-bis(4-pyridyl)ethylene (51 mg) dilute solution (33%) of sulfuric acid was added and the mixture was heated at 80 °C to get a clear and transparent solution. This was allowed to stand at room temperature for one week to get thick rod/block shaped crystals. Elemental analysis. Calcd (%) for $C_{12}H_{14}N_2O_8S_2$: C 38.09; H 3.73; N 7.40; found C 37.57, H 3.68, N 7.28.

1: Single rod shape crystal of [(4,4'-bpe•2H$^+$)(HSO$_4^-$)$_2$] was picked up for data collection.

1•p: obtained afterirradiation of UV-light (365 nm) to single crystal of **1** for 3 h.

1•ph: obtained after heating (60-70 ^{0}C) single crystal of **1•p** for 1h.Elemental analysis calcd (%) for$C_{30}H_{37}N_5O_{18}S_4$: C 40.77; H 4.22; N 7.92; found C 41.02, H 4.18, N 7.86.

1•php: obtained afterirradiation of UV-light (365 nm) to single crystal of **1•ph** for 3 h.

1A: Single block shaped crystal of [(4,4'-bpe•2H$^+$)(HSO$_4^-$)$_2$] was picked up for data collection.

1A•hobtained after heating (~70 ^{0}C) single crystal of **1A** for 1h.

Differential Scanning Calorimetry (DSC) measurements:

The DSC measurements on the crystalline materials of **1A** and **1A•h** for phase transition (temperature and enthalpy changes) experiment were conducted on Mettler Toledo DSC instrument. Heating and cooling were done at a rate of 10 K min^{-1} with the aid of liquid N_2 under constant Argon flow (20 mL min^{-1}). The samples (5-6 mg) were taken in an aluminum crucible and the experiment was carried out in the range of 25^{0}C to 300^{0}C.

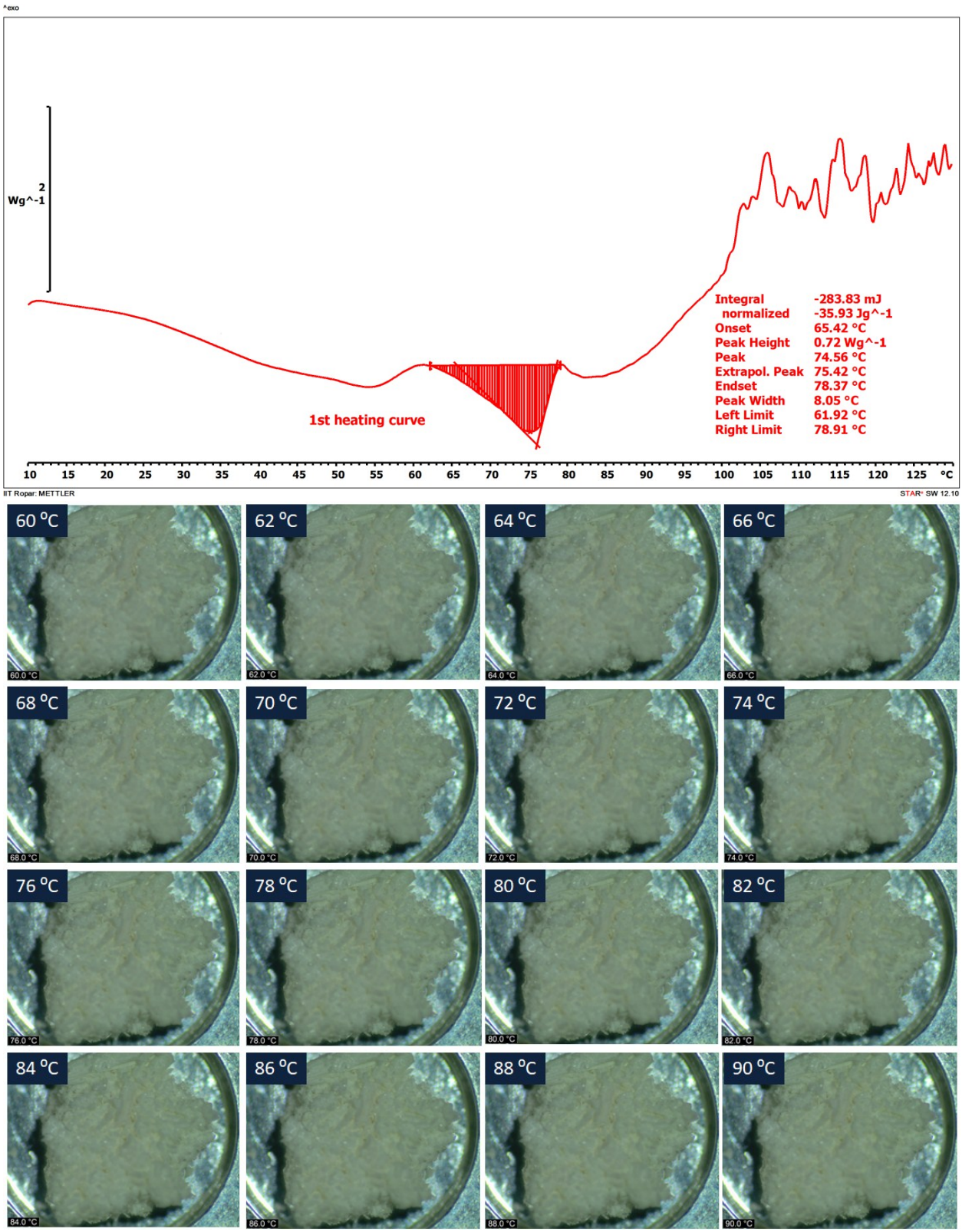


Fig. S1. DSC curve (top) and images (after every 2 ^{0}C of heating) of crystal **1A** from 60 ^{0}C to 90 ^{0}C.

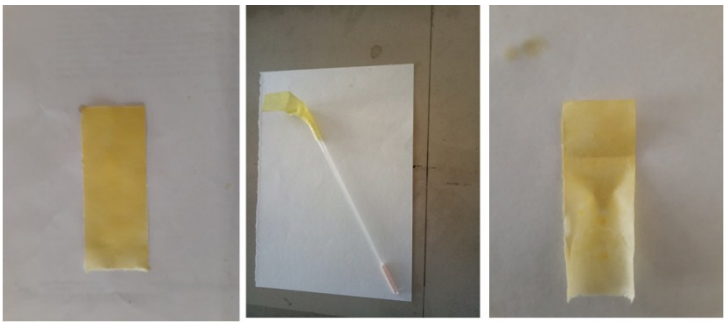


Fig. S2. Qualitative test for thermally induced transformation of **1A** to **1A•h** (color change of $K_2Cr_2O_2$ paper after heating crystals of **1A** at 80 ^{0}C on a preheated oil-bath, color of paper turns to light moss green color).

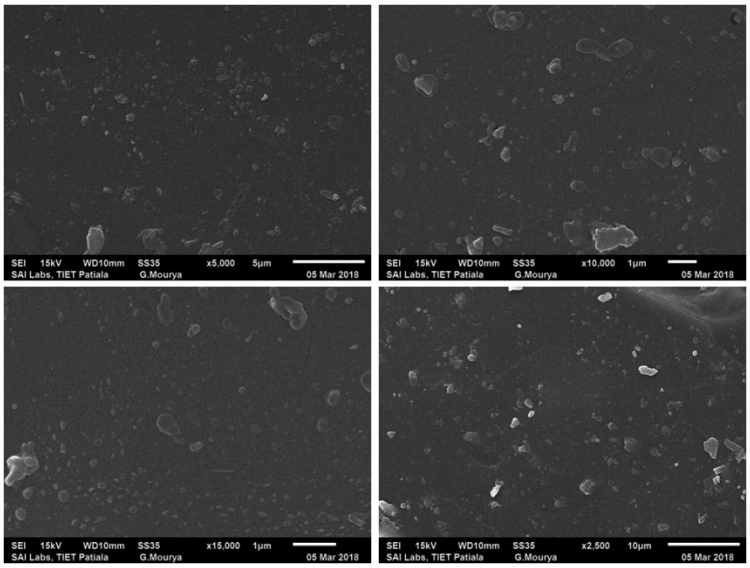


Fig. S3. SEM images of crystal **1A**.

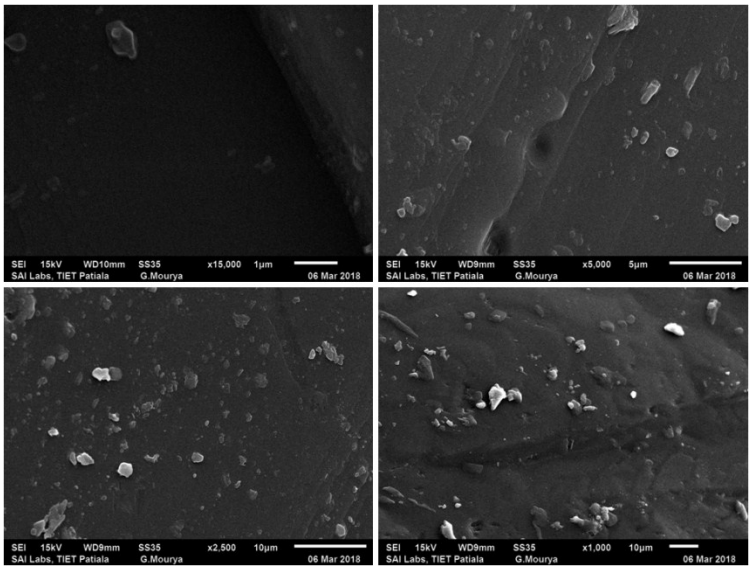


Fig. S4. SEM images of **1A•h**, after heating the same crystals of **1A** at 70 ^{0}C.

Table S1. Crystallographic data and structure refinements for **1**, **1•p, 1•ph** and **1•php** respectively.

	Crystal **1** (CCDC-939268)	Crystal **1•p** (CCDC-1504953)	Crystal **1•ph** (CCDC-1504954)	Crystal **1•php** (CCDC-1504955)
Empirical formula	$C_{12}H_{14}N_2O_8S_2$	$C_{12}H_{14}N_2O_8S_2$	$C_{30}H_{37}N_5O_{18}S_4$	$C_{60}H_{74}N_{10}O_{36}S_8$
Formula weight	378.37	378.37	883.89	1767.77
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P -1	P -1	P -1	P -1
***a* (Å)**	8.6748(4)	8.6740(4)	9.8602(5)	9.8660(3)
***b* (Å)**	9.2418(4)	9.2402(4)	11.0507(6)	11.0557(3)
***c* (Å)**	9.7123(5)	9.7072(4)	16.8724(9)	16.8860(5)
***α* (°)**	95.073(2)	94.987(2)	80.390(2)	80.416(2)
***β* (°)**	110.088(2)	109.996(2)	88.453(2)	88.478(2)
***γ* (°)**	90.128(2)	90.045(2)	86.193(2)	86.132(2)
***V* (Å³)**[c]	727.97(6)	727.97(5)	1808.42(17)	1811.79(9)
Z	2	2	2	1
Temperature (K)	100(1)	100(1)	100(1)	100(10)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm³)	0.19 x 0.16 x 0.12	0.19 x 0.16 x 0.12	0.19 x 0.16 x 0.12	0.19 x 0.16 x 0.12
ρ_{cal} Mg/m³	1.726	1.726	1.623	1.62
μ, mm⁻¹	0.415	0.415	0.352	0.351
F (000)	392	392	920	920
Independent reflection	2871	2875	7224	7381
Reflection used	10313	10417	25393	61739
R_{int} value	0.0182	0.0205	0.0409	0.0724
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
GOOF	1.030	1.042	1.031	1.037
Rindices[I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0799	R1 = 0.0353, wR2 = 0.0925	R1 = 0.0475, wR2 = 0.1166	R1 = 0.0395, wR2 = 0.0856
R indices(all data)	R1 = 0.0361, wR2 = 0.0843	R1 = 0.0430, wR2 = 0.0986	R1 = 0.0786, wR2 = 0.1316	R1 = 0.0633, wR2 = 0.0961

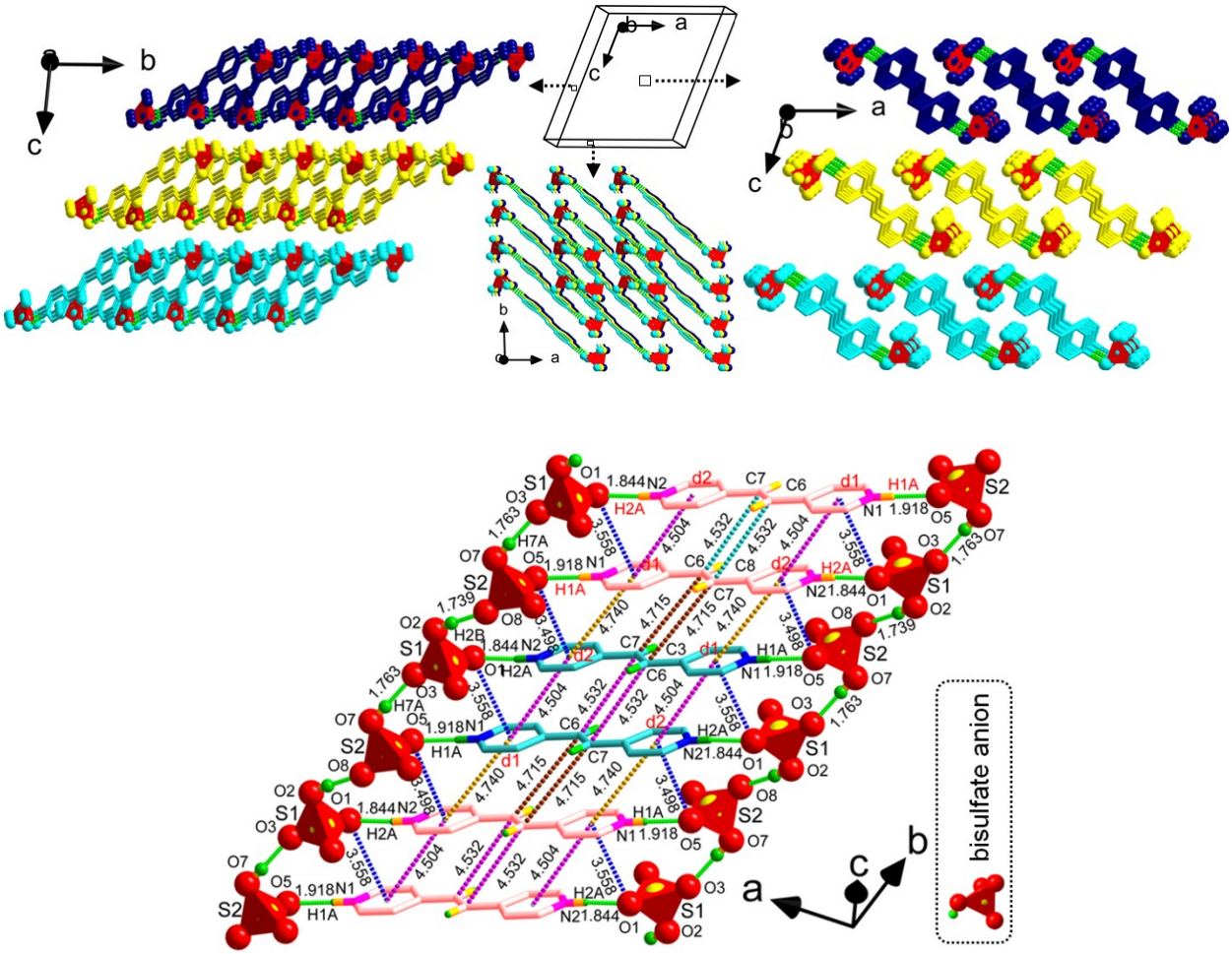


Fig. S5. Molecular packing in crystal **1** along three different axes (*top*) and hydrogen-bonded molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1** forming 1D polymeric chain (*bottom*).

Table S2. Selected bond distances and angles in **1**.

	Bond distances (Å)		Bond angles (^{0})	
both layer A & B	N1-H1A•••O5	1.918	N1-H1A•••O5	176.99 (11)
	N2-H2A•••O1	1.844	N2-H2A•••O1	173.98 (11)
between neighboring molecule of Layer A	C6•••C7	4.532	C6•••C7-C8	48.32 (92)
	d1•••d2	4.504		
	O1•••d1	3.558	O1•••d1-N1	73.19 (70)
	O7-H7A•••O3	1.763	O7-H7A•••O3	178.24 (28)
between neighboring molecule of Layer B	C6•••C7	4.715	C7•••C6-C3	45.46 (91)
	d1•••d2	4.740		
	O5•••d2	3.498	O5•••d2-N2	78.00 (69)
	O2-H2B•••O8	1.739	O2-H2B•••O8	175.46 (28)

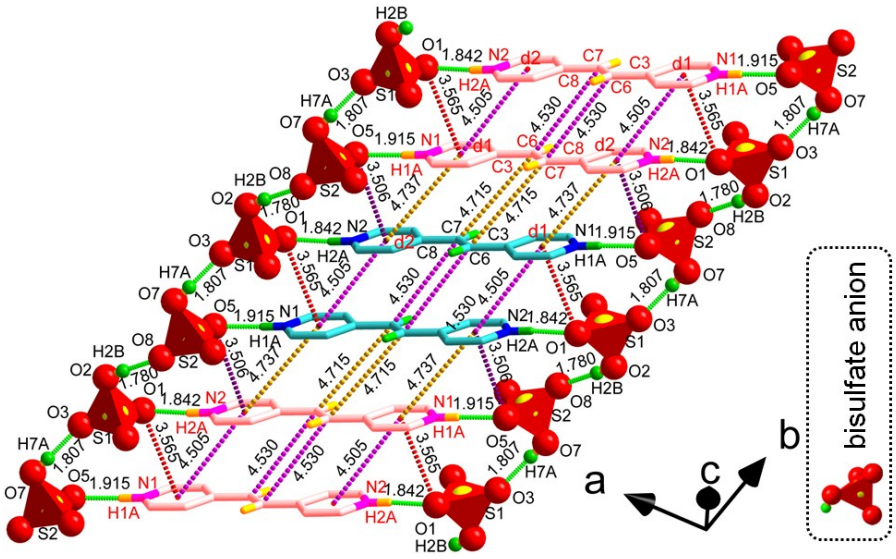


Fig. S6. Molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1•p**.

Table S3. Selected bond distances and angles in **1•p**.

	Bond distances (Å)		**Bond angles (^{0})**	
both layer A & B	N1-H1A•••O5	1.915	N1-H1A•••O5	176.54 (12)
	N2-H2A•••O1	1.842	N2-H2A•••O1	173.71 (12)
between neighboring molecule of layer A	C6•••C7	4.530	C6•••C7-C8	48.40 (97)
	d1•••d2	4.505		
	O1•••d1	3.565	O1•••d1-N1	73.34 (78)
	O7-H7A•••O3	1.807	O7-H7A•••O3	177.80 (29)
between neighboring molecule of layer B	C6•••C7	4.715	C7•••C6-C3	45.60 (96)
	d1•••d2	4.737		
	O5•••d2	3.506	O5•••d2-N2	77.96 (80)
	O2-H2B•••O8	1.780	O2-H2B•••O8	177.40 (36)

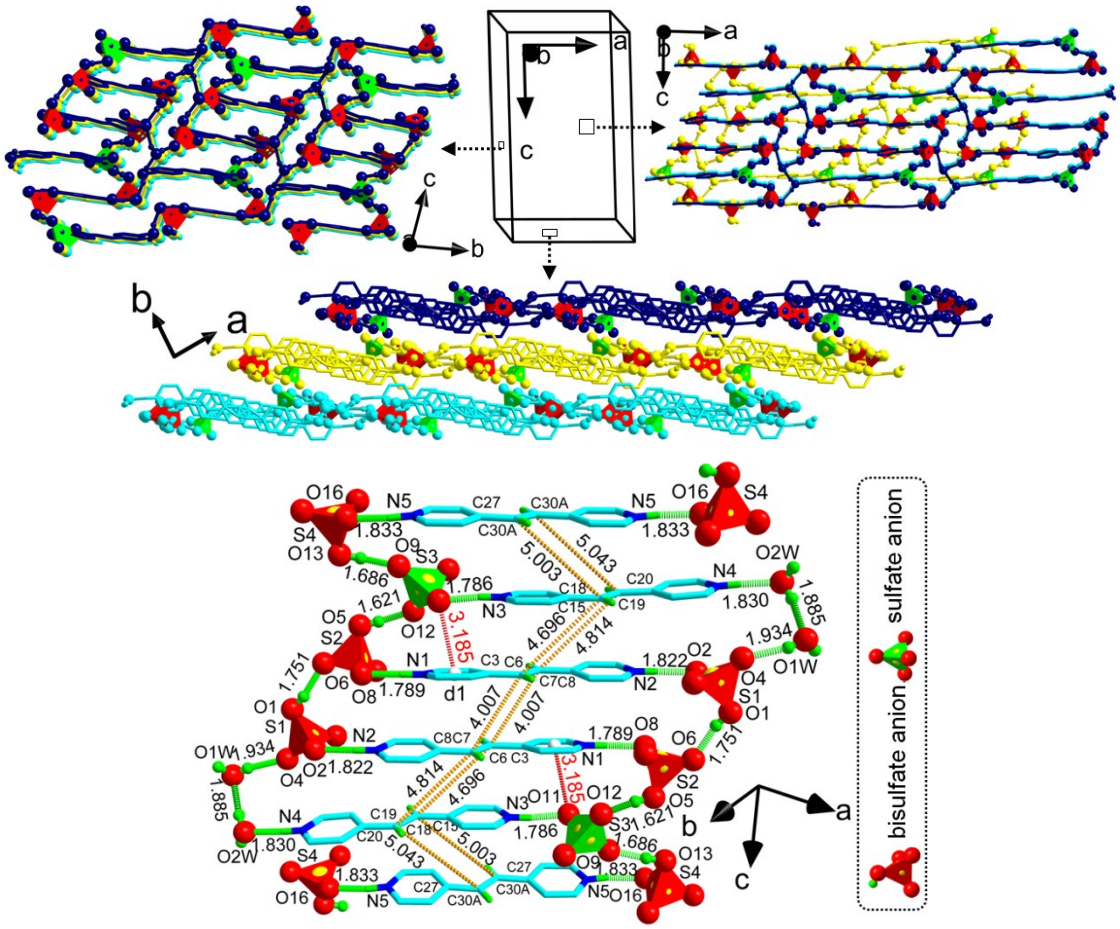


Fig. S7. Molecular packing in crystal **1•ph** along three different axes (*top*) and hydrogen-bonded molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1•ph** forming 2D polymeric sheet (*bottom*).

Table S4. Selected bond distances and angles in **1•ph**.

	Bond distances (Å)		**Bond angles (^{0})**	
	N1-H1•••O8	1.789	N1-H1•••O8	166.45 (21)
	N2-H2•••O2	1.822	N2-H2•••O2	176.63 (15)
	N3-H3•••O11	1.786	N3-H3•••O11	173.45 (15)
	N4-H4•••O2W	1.830	N4-H4•••O2W	177.07 (37)
	N5-H5•••O16	1.833	N5-H5•••O16	168.95 (39)
between neighboring molecule of layer A	C30A•••C18	5.003	C30A•••C18-C15	44.40 (16)
	C30A•••C19	5.043	C19•••C30A-C27	41.95 (17)
	O13-H13A•••O9	1.686	O13-H13A•••O9	168.60 (40)
between neighboring molecule of layer B	C18•••C6	4.696	C6•••C18-C15	44.63 (15)
	C19•••C7	4.814	C19•••C7-C8	46.02 (15)
	O11•••d1	**3.185**	**O11•••d1•••N1**	**78.77 (10)**
	O5-H5A•••O12	1.621	O5-H5A•••O12	172.13 (16)
	O2W-H2W2•••O1W	1.885	O2W-H2W2•••O1W	168.53 (36)
	O1W-H1W1•••O4	1.934	O1W-H1W1•••O4	168.38 (41)
between neighboring molecule of layer C	C6•••C7	4.007	C7•••C6-C3	59.45 (15)
	O1-H1A•••O6	1.751	O1-H1A•••O6	165.07 (15)

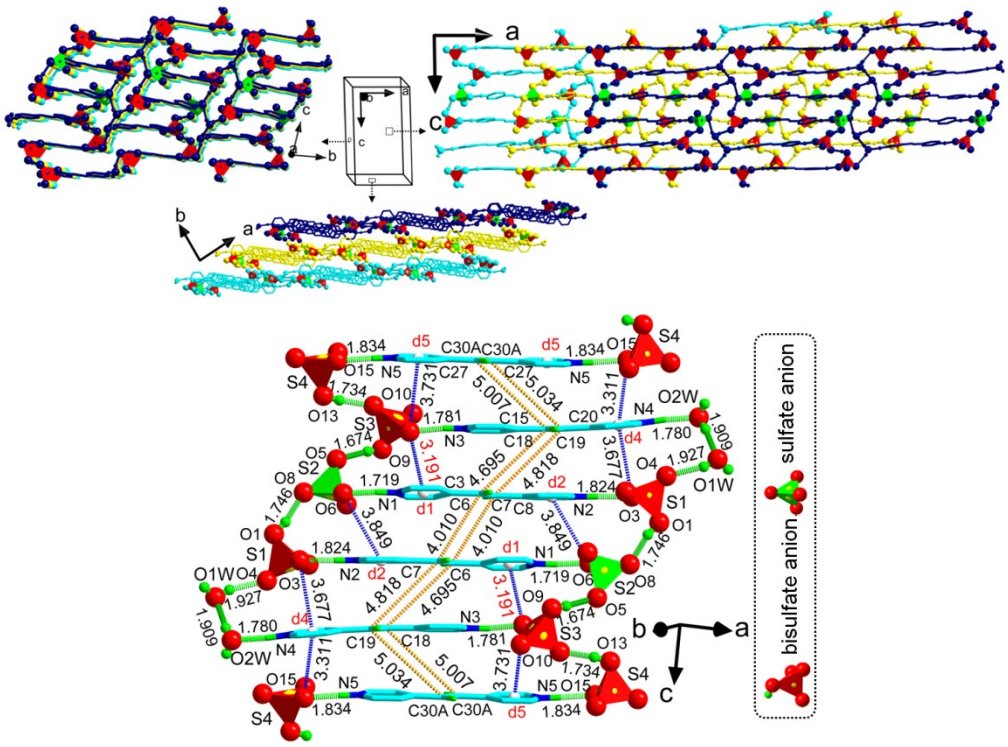


Fig. S8. Molecular packing in crystal **1•php** along three different axes (*top*) and hydrogen-bonded molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1•php** forming 2D polymeric sheet (*bottom*).

Table S5. Selected bond distances and angles in **1•php**.

	Bond distances (Å)		**Bond angles (°)**	
between neighboring molecule of Layer A	N1-H1A•••O6	1.719	N1-H1A•••O6	169.69 (28)
	N2-H2A•••O3	1.824	N2-H2A•••O3	176.58 (14)
	N3-H3•••O12	1.781	N3-H3•••O12	173.87 (14)
	N4-H4A•••O2W	1.780	N4-H4A•••O2W	173.52 (29)
	N5-H5A•••O15	1.834	N5-H5A•••O15	172.49 (36)
	C30A•••C18	5.007	C30A•••C18-C15	44.60 (11)
	C30A•••C19	5.034	C19•••C30A-C27	42.00 (14)
	O12•••d5	3.731	O12•••d5•••N5	84.25 (89)
	O15•••d4	3.311	O15•••d4•••N4	77.29 (89)
	O13-H13•••O10	1.734	O13-H13•••O10	173.28 (41)
between neighboring molecule of Layer B	C6•••C18	4.694	C6•••C18-C15	44.67 (11)
	C7•••C19	4.816	C19•••C7-C8	46.14 (11)
	O12•••d1	3.191	O12•••d1•••N1	78.70 (90)
	O3•••d4	3.677	O3•••d4•••N4	85.22 (89)
	O9-H9•••O5	1.674	O9-H9•••O5	173.47 (50)
	O2W-H2W2•••O1W	1.909	O2W-H2W2•••O1W	173.17 (28)
	O1W-H1W1•••O4	1.927	O1W-H1W1•••O4	165.72 (32)
between neighboring molecule of Layer C	C6•••C7	4.010	C7•••C6-C3	59.24 (11)
	O6•••d2	3.849	O6•••d2•••N2	60.78 (86)
	O1-H1•••O8	1.746	O1-H1•••O8	168.45 (13)

Shortest Anion•••π($O_{HSO4/SO4}$•••π) interaction(s) in **1**, **1•p**, **1•ph**, **1•php**:

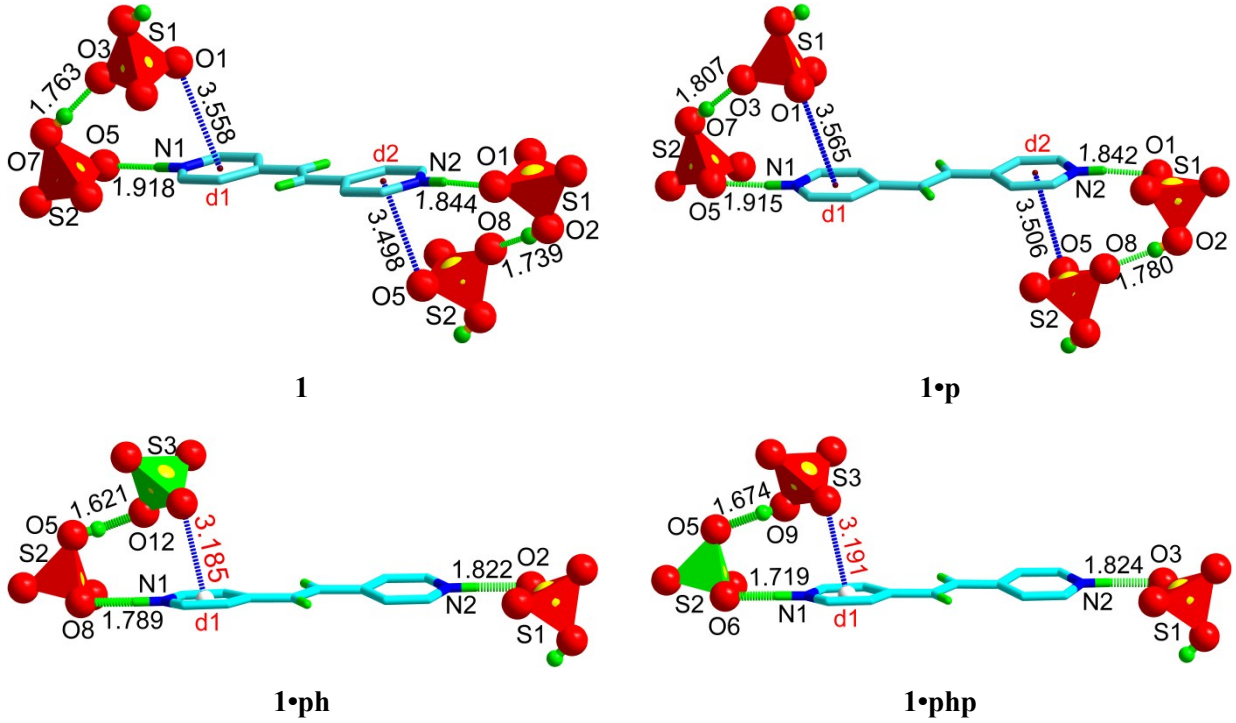


Fig. S9. Non-covalent interaction of O_{HSO4}-atom to pyridyl centroid of **4,4'-bpe•2H**$^+$ moiety of **1**.

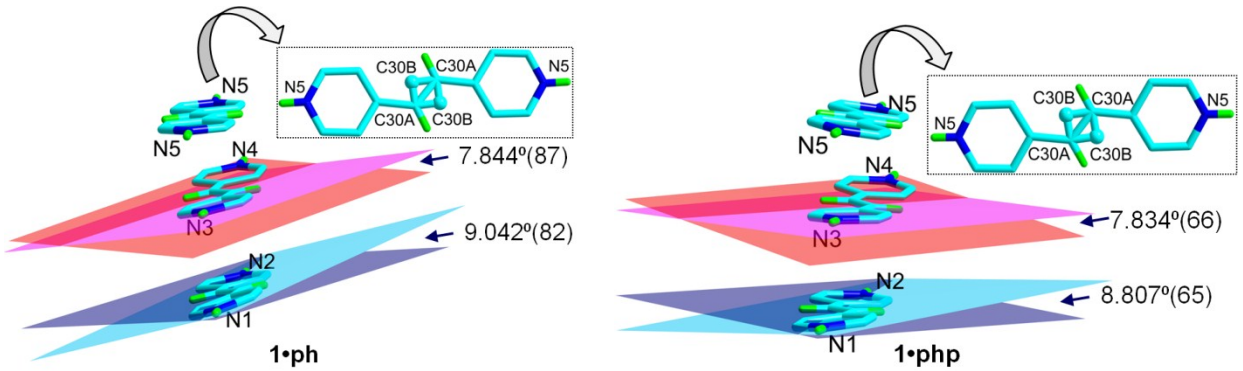


Fig. S10. The disorder of the olefinic C-atom in **1•ph** (*left*, inside inset) and **1•php** (*right*, inside inset) of one **4,4'-bpe•2H**$^+$ moiety in each. The protonated pyridyl ring of the remaining two **4,4'-bpe•2H**$^+$ moiety is out of plane (twisted along olefinic bond) and the corresponding dihedral angle between planes passing through pyridyl ring is shown by blue arrow.

Table S6. Crystallographic data and structure refinement parameters for **1A** and **1A•h** respectively.

	Crystal **1A** (CCDC-1504956)	Crystal **1A•h** (CCDC-1504958)
Empirical formula	$C_{12}H_{14}N_2O_8S_2$	$C_{60}H_{74}N_{10}O_{36}S_8$
Formula weight	378.37	1767.77
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
***a* (Å)**	8.6670(2)	9.8533(5)
***b* (Å)**	9.2424(3)	11.0612(6)
***c* (Å)**	9.7010(3)	16.9145(9)
***α* (°)**	95.062(2)	80.528(2)
***β* (°)**	110.090(2)	88.607(2)
***γ* (°)**	90.142(2)	86.101(2)
***V* (Å^3)**	726.51(4)	1814.00(17)
Z	2	1
Temperature (K)	100.0(1)	100.0(1)
Wavelength (Å)	0.71073	0.71073
Crystal size (mm^3)	0.30 x 0.12 x 0.10	0.30 x 0.12 x 0.10
ρ_{cal} Mg/m^3	1.730	1.618
μ, mm^{-1}	0.416	0.351
F (000)	392	920
Independent reflection	2958	7260
Reflection used	20962	24941
R_{int} value	0.0276	0.0291
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
GOOF	1.021	1.031
R indices[I>2sigma(I)]	R1 = 0.0252, wR2 = 0.0668	R1 = 0.0413, wR2 = 0.1012
R indices(all data)	R1 = 0.0284, wR2 = 0.0698	R1 = 0.0598, wR2 = 0.1107

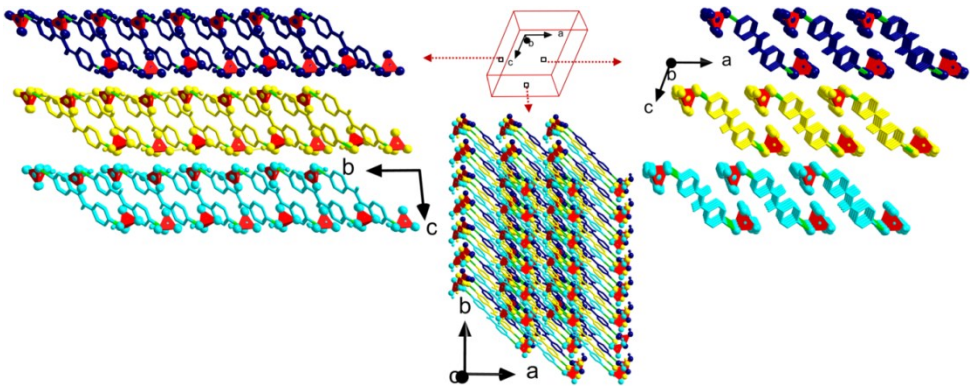


Fig. S11. Molecular packing of **4,4'-bpe•2H$^+$** moieties in **1A** along three different axes. Each chain is shown by different color.

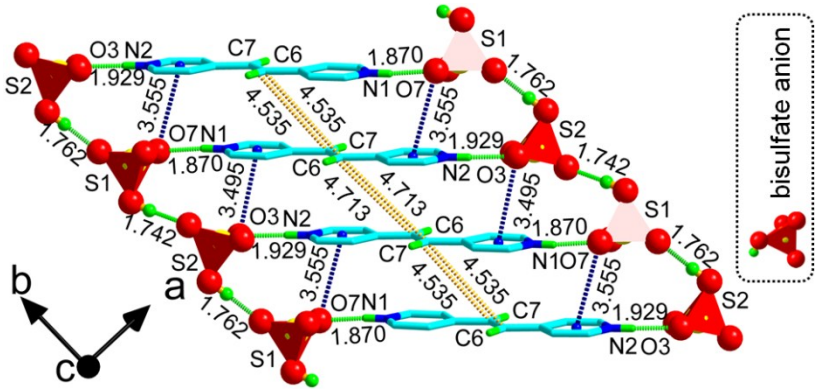


Fig. S12. Molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1A**.

Table S7. Selected bond distances and angles in **1A**.

	Bond distances (Å)		Bond angles (°)	
between neighboring molecule of Layer A	N1-H1B•••O7	1.870	N1-H1A•••O7	174.42 (20)
	N2-H2B•••O3	1.929	N2-H2A•••O3	178.54 (20)
	C6•••C7	4.535	C7•••C6-C3	48.38 (70)
	O7•••d2	3.555	O7•••d2•••N2	73.31 (59)
between neighboring molecule of Layer B	O1-H1A•••O8	1.762	O1-H1A•••O8	177.87 (78)
	C6•••C7	4.713	C6•••C7-C8	45.62 (70)
	O3•••d1	3.495	O3•••d1•••N1	78.11 (58)
	O5-H2A•••O4	1.742	O5-H2A•••O4	175.42 (79)

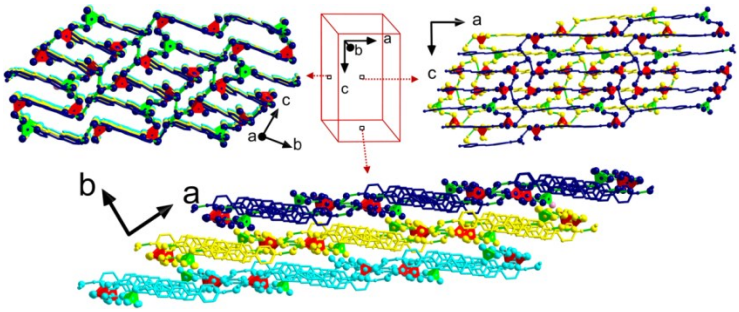


Fig. S13. Molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1A•h** along three different axes. Each 2D layer is shown by different color.

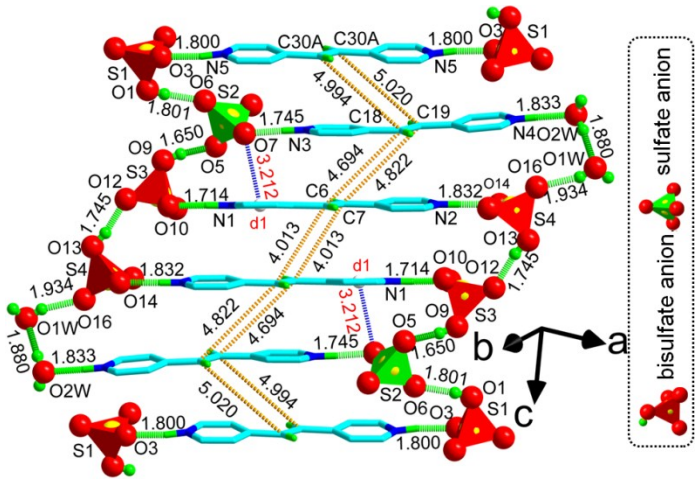
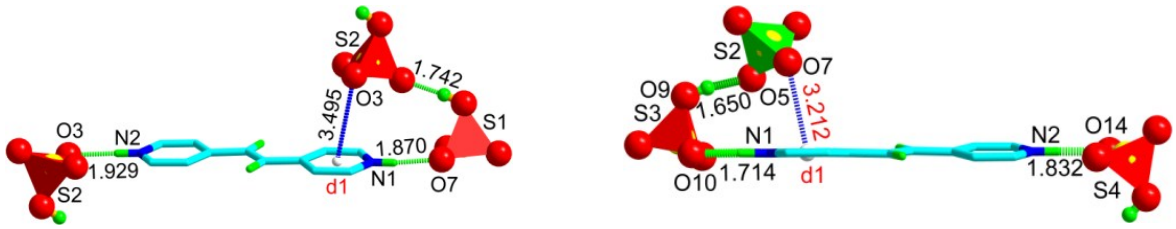


Fig. S14. Molecular packing of **4,4'-bpe•2H**$^{+}$ moieties in **1A•h**.

Table S8. Selected bond distances and angles in **1A•h**.

	Bond distances (Å)		**Bond angles (^{0})**	
between neighboring molecule of layer A	N1-H1•••O10	1.714	N1-H1•••O10	165.24 (34)
	N2-H2•••O14	1.832	N2-H2•••O14	177.09 (14)
	N3-H3•••O7	1.745	N3-H3•••O7	176.55 (36)
	N4-H4•••O2W	1.833	N4-H4•••O2W	174.90 (30)
	N5-H5•••O3	1.800	N5-H5•••O3	169.90 (35)
	C30A•••C18	5.003	C30A•••C18-C15	44.81 (11)
	C30A•••C19	5.043	C19•••C30A-C27	42.17 (12)
	O1-H1A•••O6	1.686	O1-H1A•••O6	171.30 (39)
between neighboring molecule of layer B	C18•••C6	4.694	C6•••C18-C15	44.84 (11)
	C19•••C7	4.822	C19•••C7-C8	46.47 (11)
	O7•••d1	**3.212**	**O7•••d1•••N1**	**78.45 (90)**
	O9-H9A•••O5	1.650	O9-H9A•••O5	165.57 (55)
	O2W-H2W2•••O1W	1.880	O2W-H2W2•••O1W	171.29 (28)
	O1W-H1W1•••O16	1.934	O1W-H1W1•••O16	160.74 (31)
between neighboring molecule of layer C	C6•••C7	4.013	C7•••C6-C3	58.91 (12)
	O13-H13A•••O12	1.745	O13-H13A•••O12	168.15 (13)

Shortest anion O_{SO4}•••π interaction(s) in **1A** and **1A•h**:



1A **1A•h**

Fig. S15. Non-covalent interaction of O_{SO4}•••$\pi_{pyridyl}$ in **1A** and **1A•h** respectively.

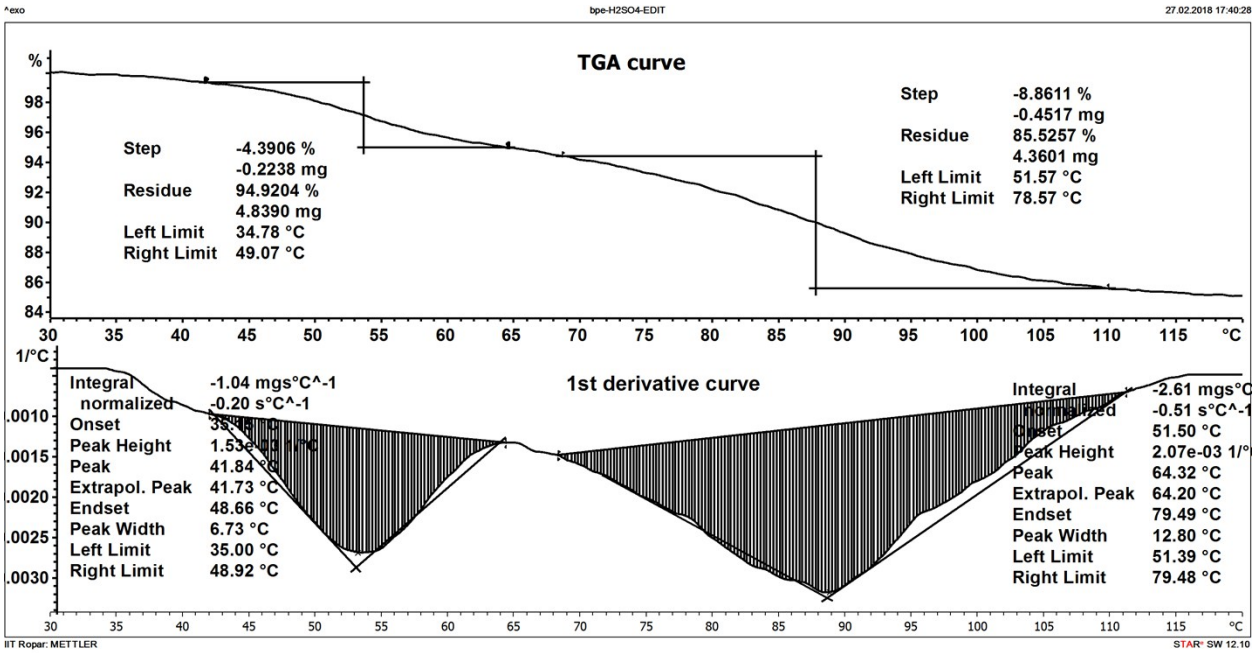


Fig. S16. Thermogravimetric analysis curve of **1A**. Since, crystal was temperature sensitive so fresh sample was used for TGA without drying in vacuum. At ~50^0C, amount loss is because of methanol (used for sample preparation and at ~70^0C, amount loss is because of one molecule each of SO_2 and H_2O.

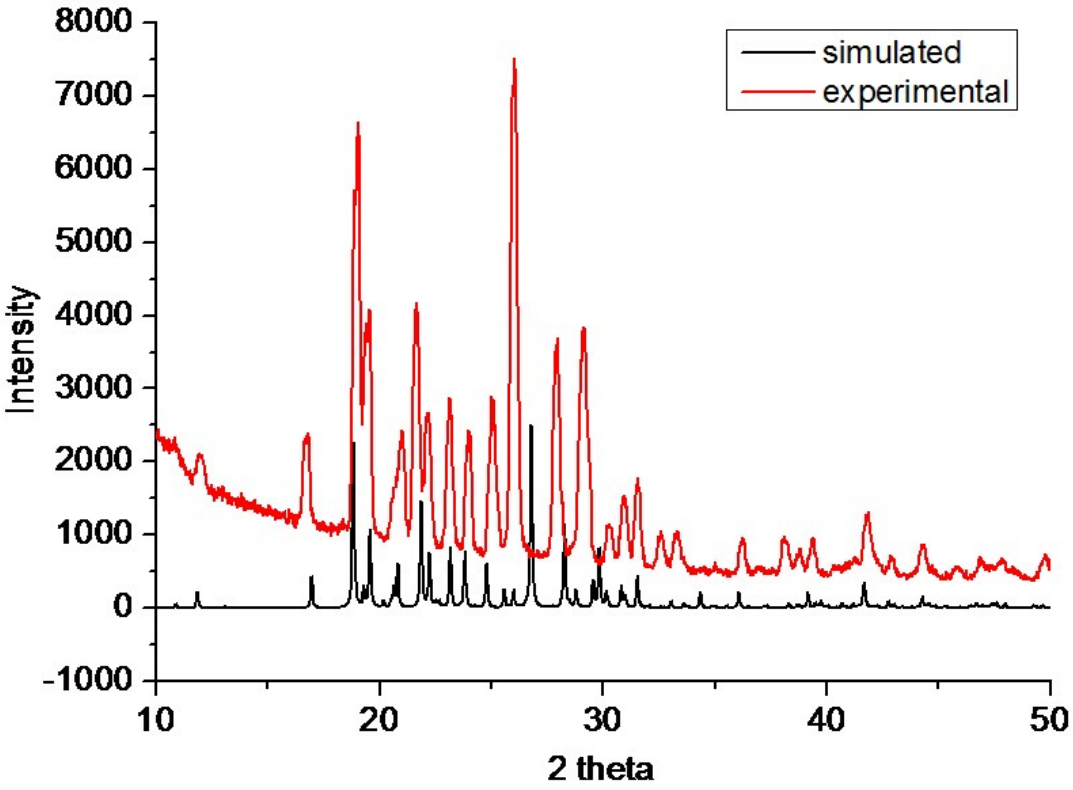


Fig. S17. X-ray powder pattern for **1A**.

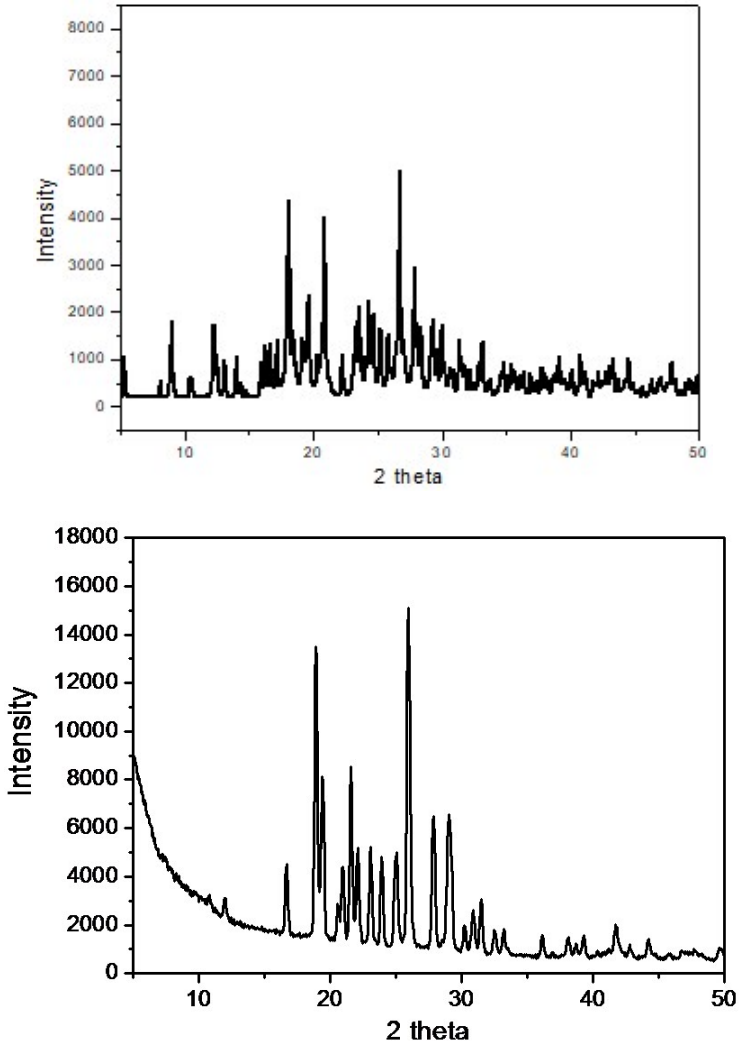


Fig. S18. X-ray powder pattern for **1A•h**, the calculated powder pattern for the hkl reflections based on the single-crystal model (*top*) and that of experimentally observed powder pattern (*bottom*).

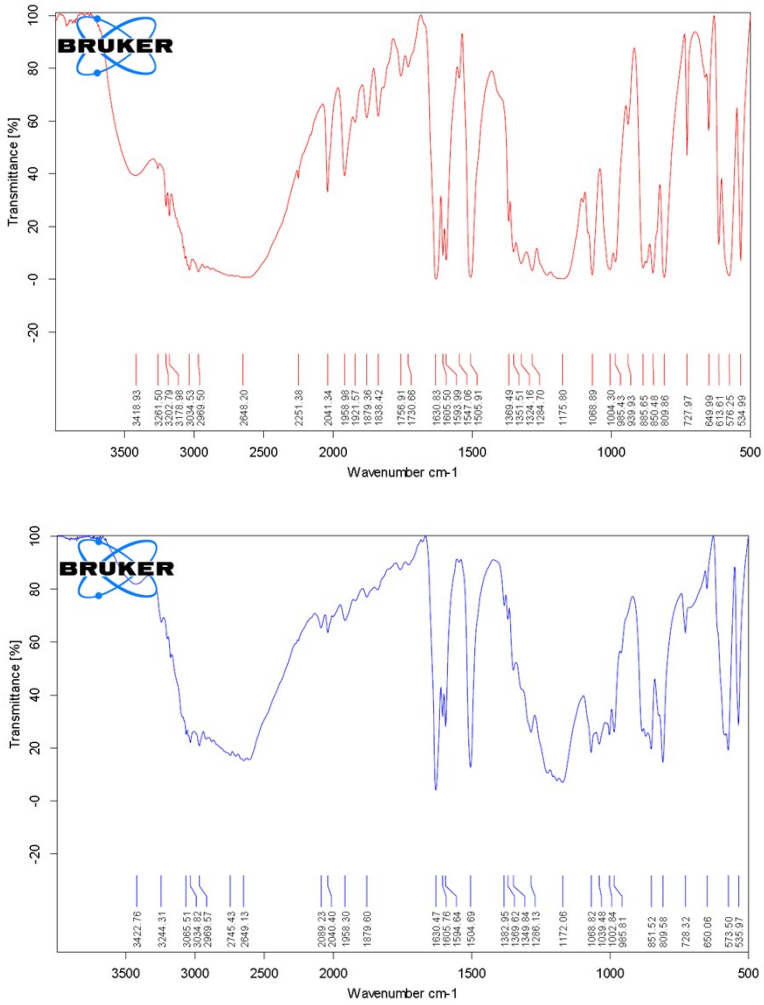


Fig. S19. IR-spectra of **1A** (*top*) and **1A•h** (*bottom*).