Electronic Supporting Information for:

Validation of the supramolecular synthon preference through DFT and physicochemical property investigations of pyridyl salts of organo-sulfonates

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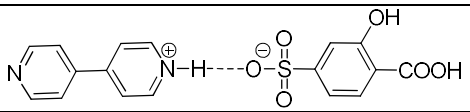
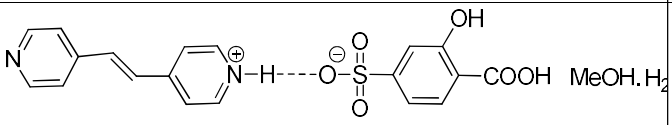
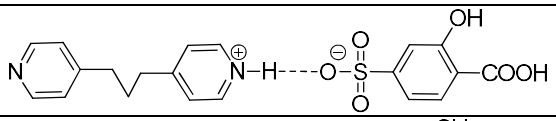
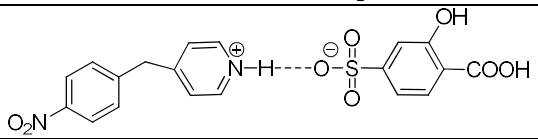
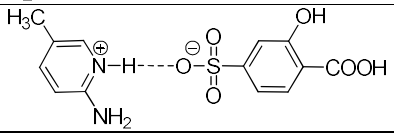
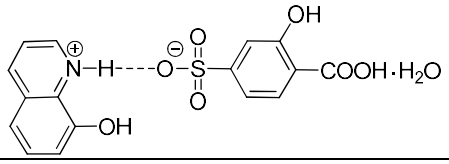
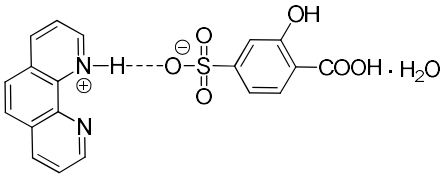
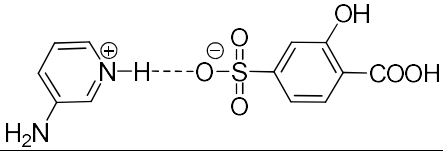
Chart ESI-1. Bond angles and distances of molecular salts formed from 5-sulfosalicylic acid with different base conformers having direct Sulfonate-Pyridinium interaction.

S.No.	Molecular Formula	Bond Distance N-H…O	Bond Angle N-H…O	Cif Code	Reference
1)		2.660 Å	178.39°	1038154	1
2)		2.713 Å	161.°46	1882488	2
3)		2.747 Å	160.25°	1882490	2
4)		2.732 Å	172.27°	925161	3
5)		2.855 Å	161.41°	788504	4
6)		2.733 Å	139.88°	248163	5
7)		2.789 Å	141.09°	989838	6
8)		2.797 Å	153.87°	669197	7

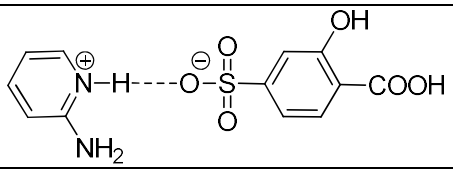
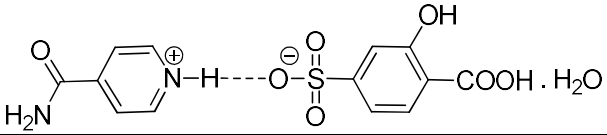
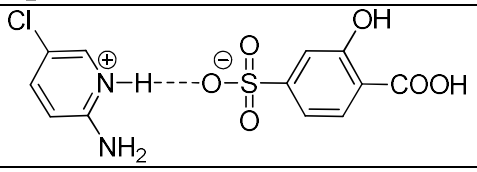
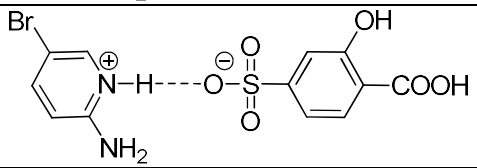
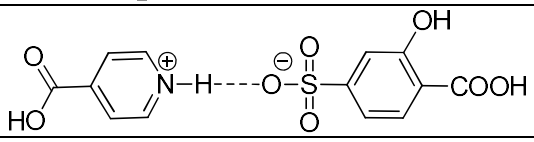
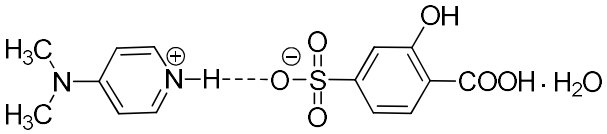
9)		2.805 Å	177.52°	286383	8
10)		2.834 Å	125.08°	968379	9
11)		2.999 Å	146.28°	792417	10
12)		2.811 Å	159.94°	792480	10
13)		2.902 Å	148.12°	696479	11
14)		2.725 Å	160.10°	894924	12

Table ESI-1. Comparative melting point of compounds and their reactants.

Reactant 1	**M.P.**	**Reactant 2**	**M.P.**	**Product**	**M.P.**
5-SSA	110°C	4-Ph-Py	77°C	1	236°C
8-HQSA	>250°C	4-Ph-Py	77°C	2	>250°C
4-SA-Sy	>250°C	4,4'-BPP	60°C	3	113°C

Table ESI-2. Solubility of compounds in different solvents.

Solubility	**H_2O**	**CH_3OH**	**C_2H_5OH**	**C_2H_6O**	**CH3COOH**	**$CHCl_3$**	**DCM**	**THF**	**DMF**	**DMSO**
Compound 1	Soluble	Partially Soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble	Soluble
Compound 2	Partially Soluble	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble	Soluble
Compound 3	Partially Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble	Soluble

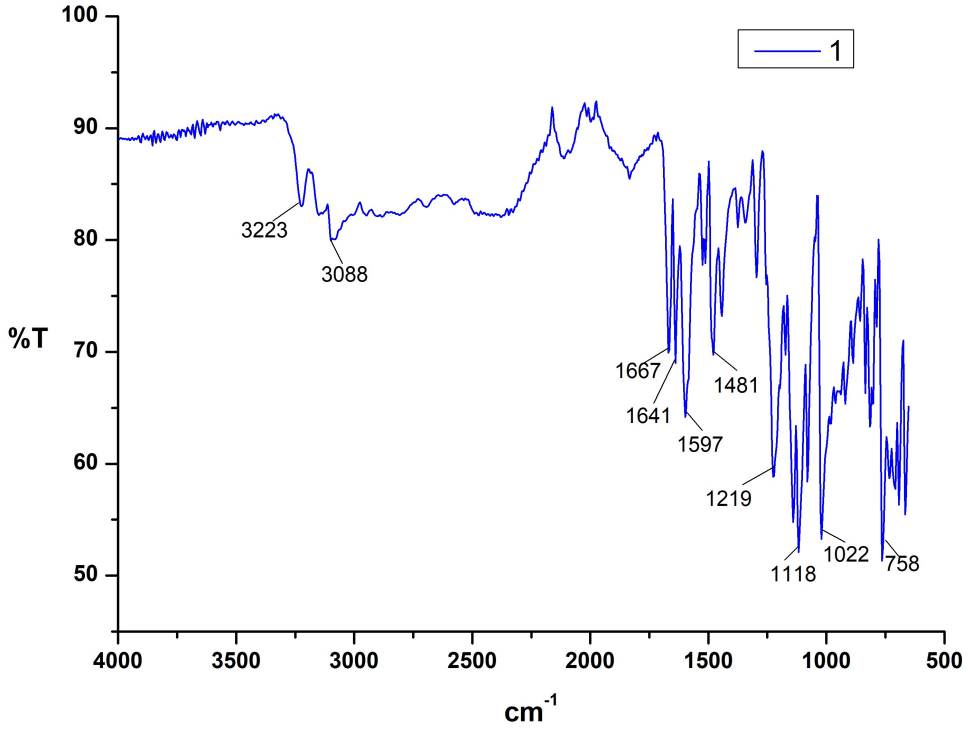


Figure ESI-1. FT-IR spectrum of **1**.

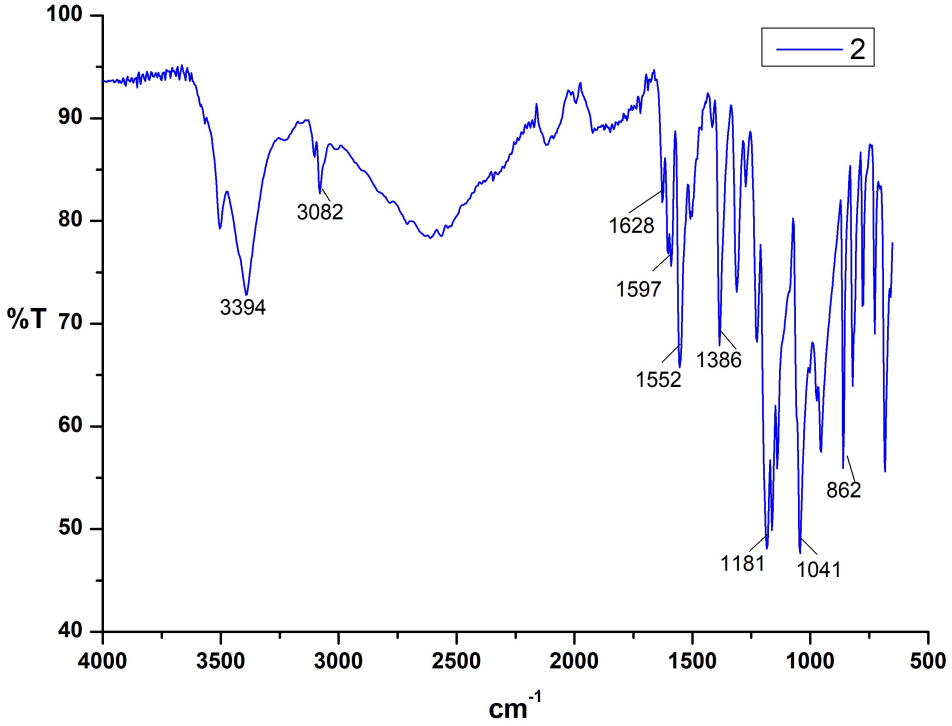
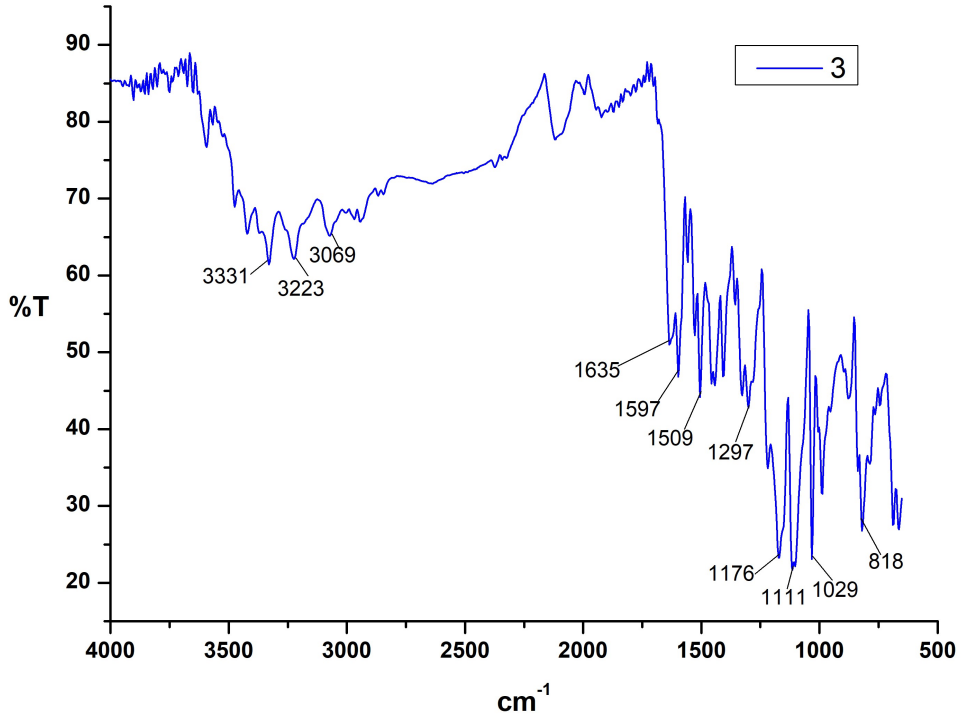


Figure ESI-2. FT-IR spectrum of **2**.



FigureESI-3. FT-IR spectrum of **3**.

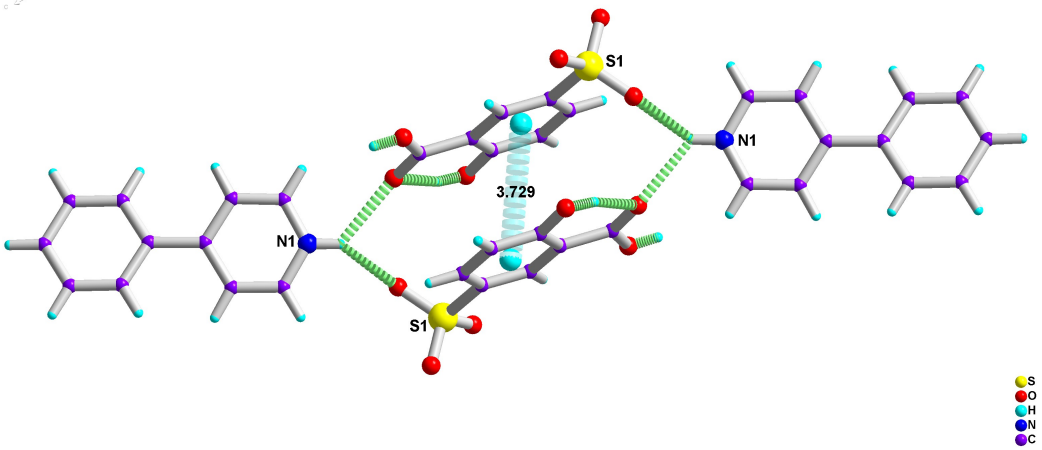


Figure ESI-4. Centro-symmetric dimer in 1.

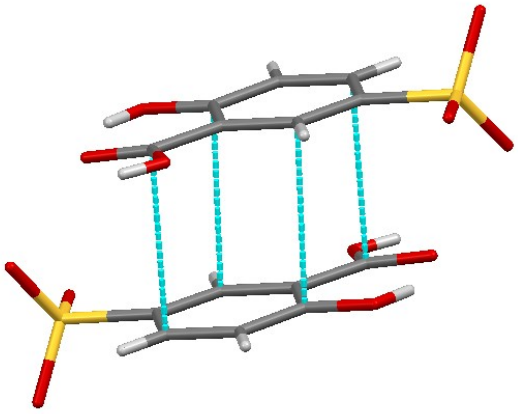


Figure ESI-5. Π-π interaction in **1**.

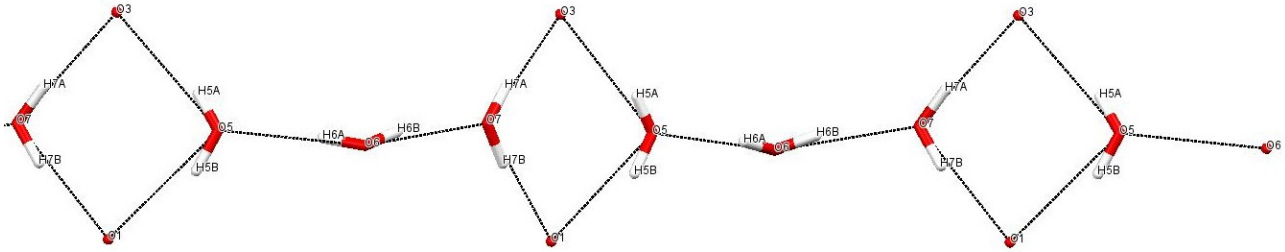


Figure ESI-6. T4(0)A1 type of infinite water chains formed in **2.**

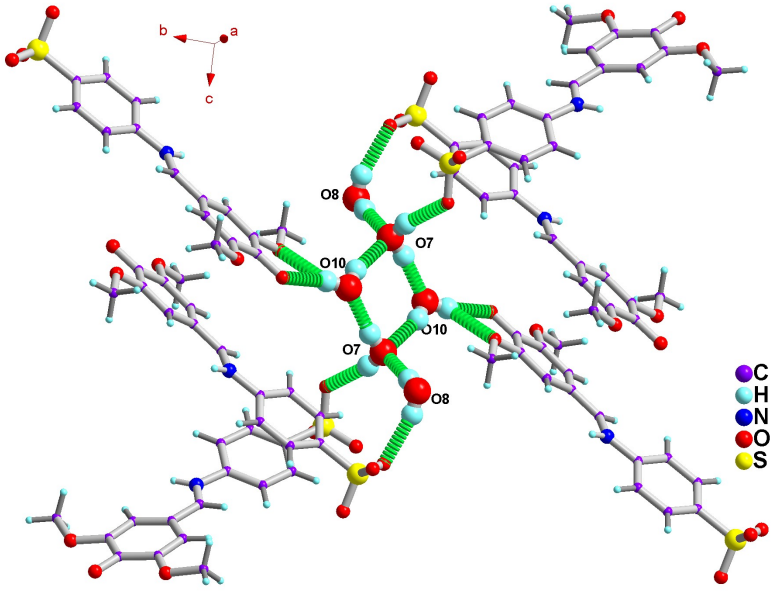


Figure ESI-7. Hexameric water cluster (W6) with cyclic R4 core, highlighted by green bonds, in **2**.

Table ESI-3. Bond angles and distances of different Interactions of lattice water molecules in **2**.

S.No.	Interaction O-H…O	Bond Distance D-H…A	Bond Angle D-H…A
1)	O5-H5B---O1	**2.040 Å**	**154.50°**
2)	07-H7B---O1	**1.991 Å**	**166.40°**
3)	O5-H5A---O3	**2.100 Å**	**161.79°**
4)	O7-H7A---O3	**1.975 Å**	**171.44°**
5)	O6-H6A---05	**1.964 Å**	**160.95°**
6)	O4-H4A---O6	**1.761 Å**	**171.48°**
7)	O6-H6B---O7	**1.892 Å**	**161.75°**

Table ESI-4. Bond angles and distances of different Interactions of lattice water molecules in **3**.			
S.No.	**Interaction** **O-H… O**	**Bond Distance** **D-H…A**	**Bond Angle** **D-H…A**
1)	O7-H7B---O1	**1.987 Å**	**167.01°**
2)	09-H9A---O1	**1.971 Å**	**167.26°**
3)	O8-H8B---O3	**2.074 Å**	**155.12°**
4)	O10-H10A---O4	**1.946 Å**	**157.56°**
5)	O9-H9B---06	**2.232 Å**	**150.54°**
6)	O8-H8A---O7	**2.002 Å**	**171.98°**
7)	O10-H10B---O7	**2.061 Å**	**160.30°**
8)	O7-H7A---O10	**1.863 Å**	**163.63°**

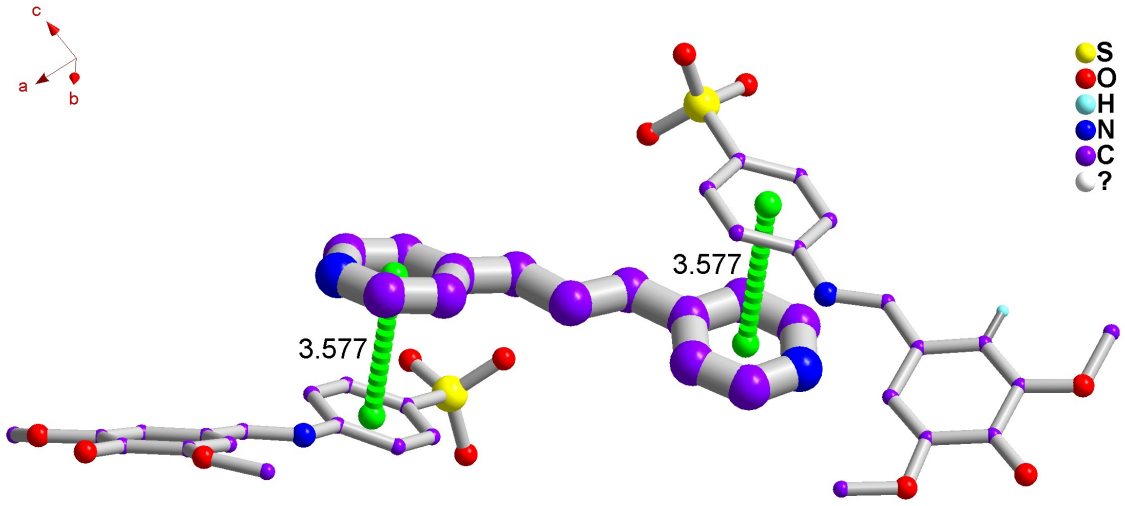


Figure ESI-8. Pie interactions between crystal formersin **3**.

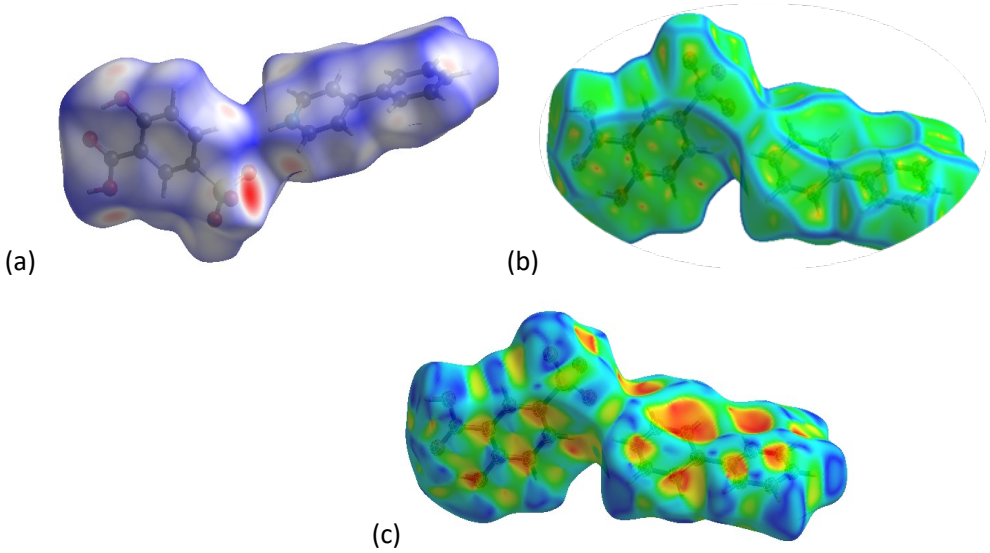


Figure ESI-9.(a)Hireshfeld surface, (b)Curvedness and (c) Shape index surfaces of **1**.

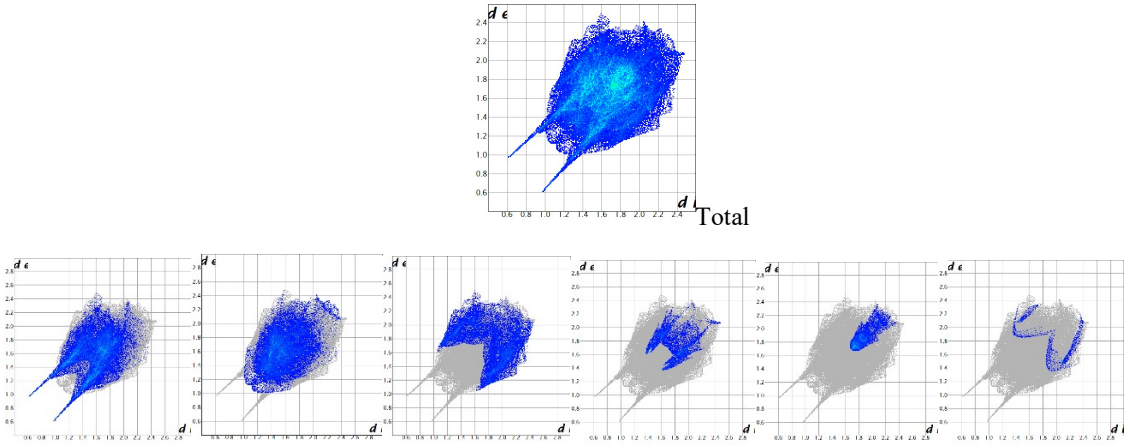


Figure ESI-10. Total and individual figerprint plots of **1**.

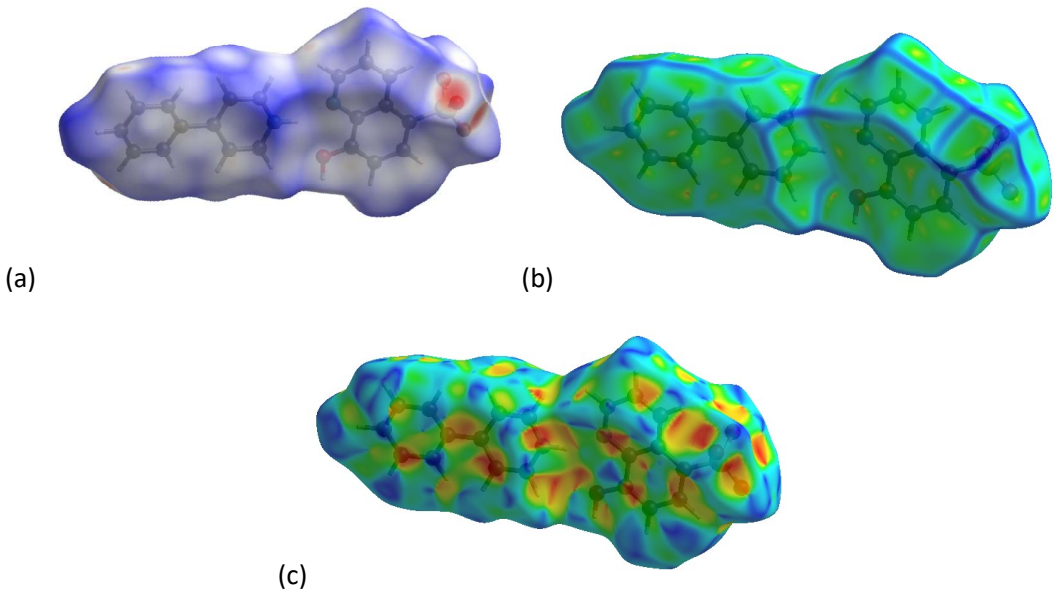


Figure ESI-11.(a) Hireshfeld surface, (b)Curvedness and (c) Shape index surfaces of **2**.

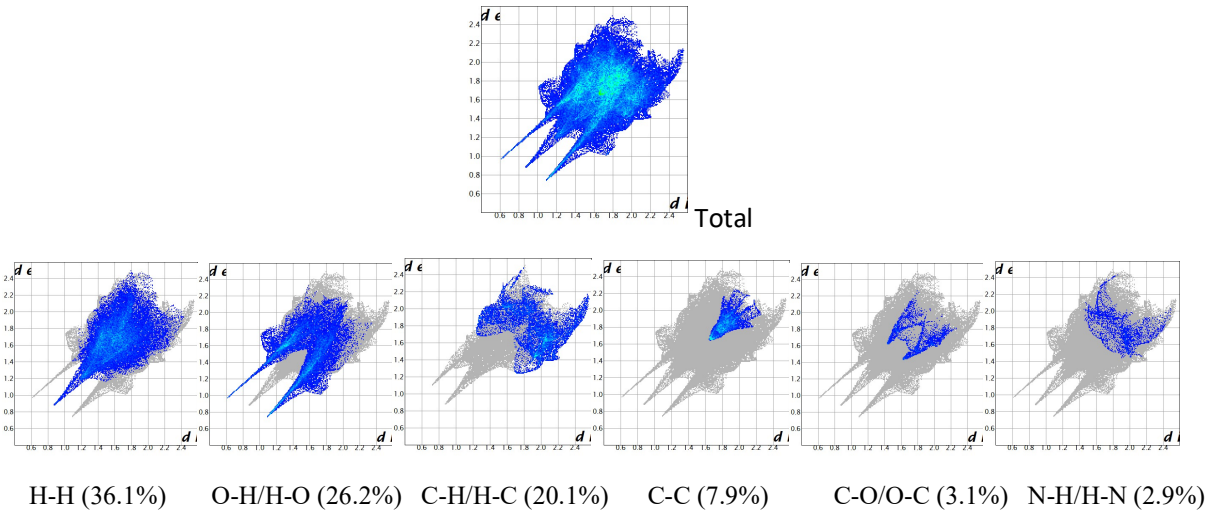


Figure ESI-12. Total and individual figerprint plots of **2**.

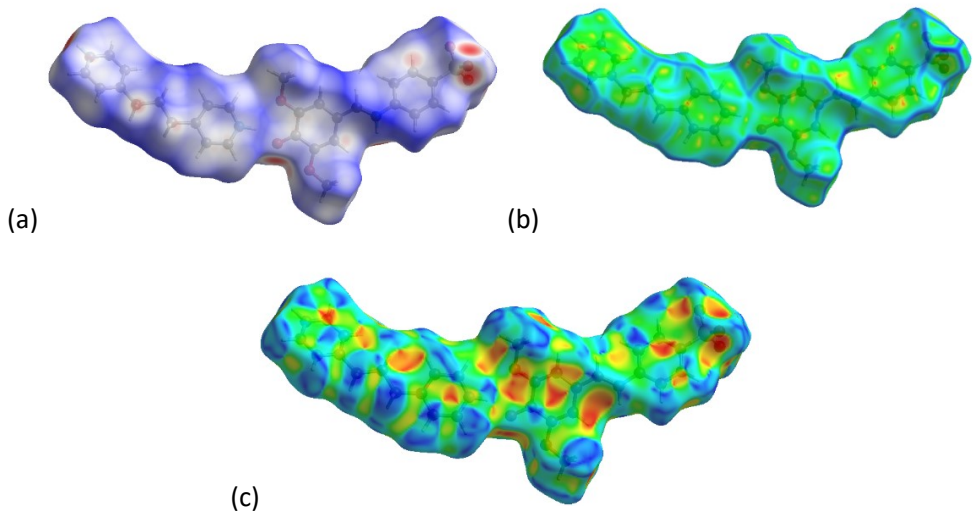
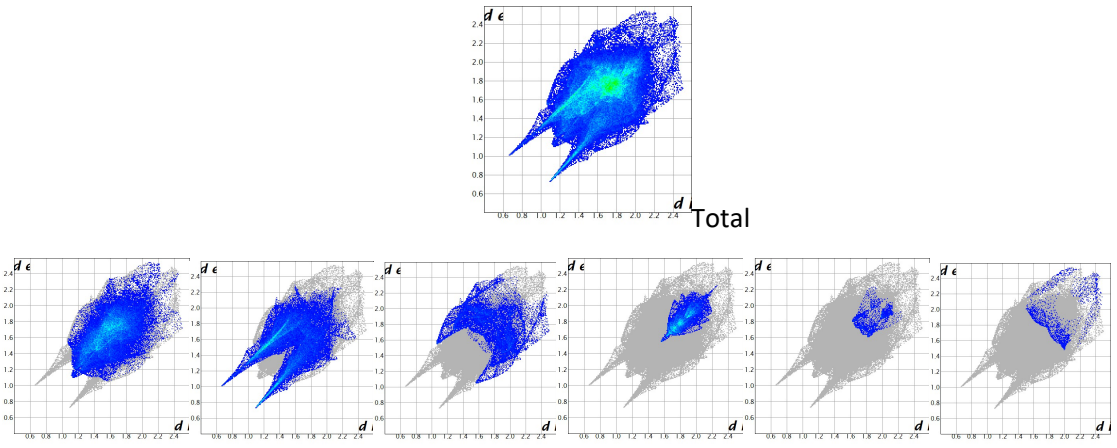


Figure ESI-13. (a)Hireshfeld surface, (b)Curvedness and (c) Shape index surfaces of **3**.



H-H (40.5%) O-H/H-O (32.2%) C-H/H-C (11.6%) C-C (10.4%) C-O/O-C (1.7%) N-H/H-N (1.4%)

Figure ESI-14. Total and individual figerprint plots of **3**.

Table ESI-5. Hirshfeld surface property information of **1**.

Name	**Minimum**	**Mean**	**Maximum**	**Units**
d_i	0.623	1.673	2.501	Å
d_e	0.623	1.678	2.534	Å
d_{norm}	-0.779	0.371	1.187	
Shape index	-0.997	0.234	0.997	
Curvedness	-3.517	-0.987	0.444	

Table ESI-6. Percentage of total surface area for close contacts between atoms inside and outside the surface in **1**.

Inside atoms	**Outside atoms**					
	S	O	H	N	C	Total
C	.	4.0	12.0	.	6.0	22.0
H	0.0	16.5	28.6	0.6	8.5	54.2
N	.	0.1	1.0	.	.	1.1
O	.	0.4	18.7	0.1	3.5	22.7
S	.	0.0	0.1	.	.	0.1
Total		21.0	60.3	0.7	18.0	

Table ESI-7. Hireshfeld surface property information of **2**.

Name	**Minimum**	**Mean**	**Maximum**	**Units**
d_i	0.622	1.700	2.547	Å
d_e	0.753	1.691	2.531	Å
d_{norm}	-0.782	0.428	1.381	
Shape index	-0.997	0.225	0.998	
Curvedness	-4.162	-1.054	0.381	

Table ESI-8. Percentage of total surface area for close contacts between atoms inside and outside in **2**.

Inside atoms	**Outside atoms**					
	S	O	H	N	C	Total
C	.	1.8	13.1	0.8	7.9	23.6
H	0.1	12.5	36.1	1.1	7.6	57.3
N	.	0.0	1.8	.	0.8	2.6
O	.	1.4	13.7	.	1.3	16.4
S	.	.	0.1	.	.	0.1
Total	0.1	15.6	64.9	1.9	17.6	

Table ESI-9. Hireshfeld surface property information of **3**.

Name	Minimum	Mean	Maximum	Units
d_i	0.665	1.624	2.504	Å
d_e	0.746	1.666	2.576	Å
d_{norm}	-0.718	0.401	1.275	
Shape index	-0.996	0.229	0.999	
Curvedness	-3.560	-1.024	0.350	

Table ESI-10. Percentage of total surface area for close contacts between atoms inside and outside the in **3**.

Inside atoms	Outside atoms					
	S	O	N	H	C	Total
C	.	1.0	0.4	5.5	10.4	17.4
H	0.1	18.1	0.7	40.5	6.0	65.4
N	.	0.5	0.3	0.7	0.6	2.1
O	.	0.2	0.2	14.1	0.7	15.1
S	.	.	.	0.0	.	0.0
Total	0.1	19.8	1.5	60.9	17.7	

Table ESI-11: Contribution of different interactions in 1, **2** and **3**.

COMPOUND	1	2	3
O-H...O-N	35.2	26.1	32.2
H...H	28.6	36.1	40.5
C-H...H-C	20.4	20.1	11.6
C...C	6.0	7.9	10.4
N-H...H-N	1.5	2.9	1.4
C-O...O-C	7.5	3.1	1.7

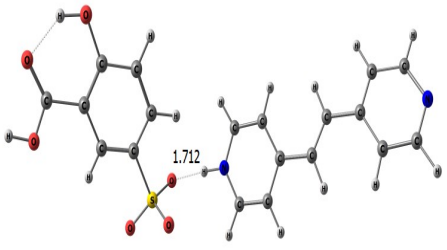
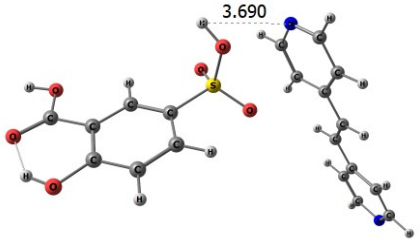
Table ESI-12. Calculated interaction energy (IE) for salt and co-crystal and the difference in interaction energy values (ΔIE). All values are kJ/mol.

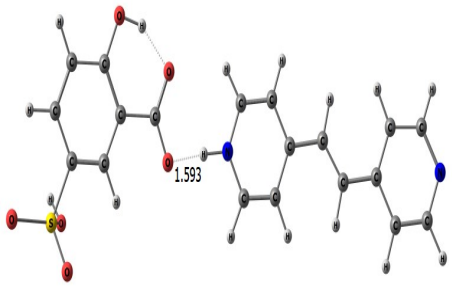
	Interaction	IE (kJ/mol)	ΔIE (salt-Cocrystal)
I	**Salt** **Co-crystal**	-99.1 -14.0	85.1
II	**Salt** **Co-crystal**	-48.5 -39.7	8.8
III	**Salt** **Co-crystal**	-14.8 -10.4	4.4
IV	**Salt** **Co-crystal**	**-108.8** **-97.3**	**11.5**
V	**Salt** **Co-crystal**	**-108.1** **-90.8**	**17.3**

Table ESI-13. Interaction energy (IE) of various sulfonate-pyridinium salt with methyl pyridine as a monomer.

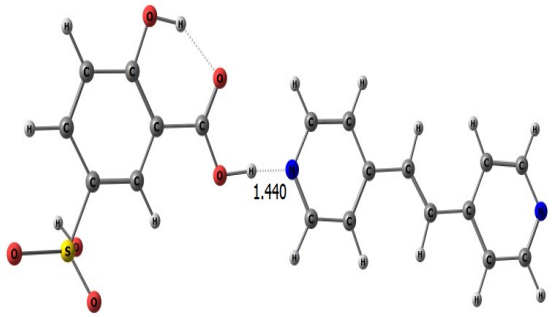
Crystal	**IE(kJ/mol)**
I	-104.2
II	-52.9
III	-19.1
IV	-108.8
IVa	-111.7
V	-108.0
VI	-37.9

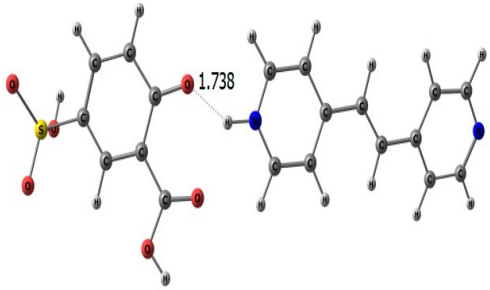
Table ESI-14. Optimized geometries of various charge assisted sulfonate-pyridinium salt/co-crystals. Selected bond distances in Å.

Salt	**Co-crystal**
 **I**	

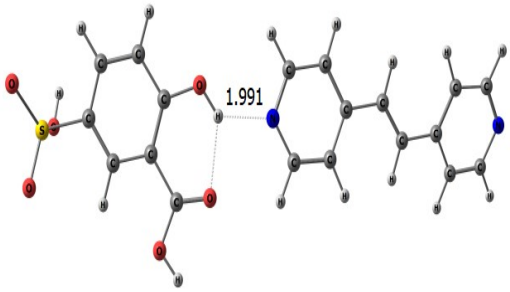


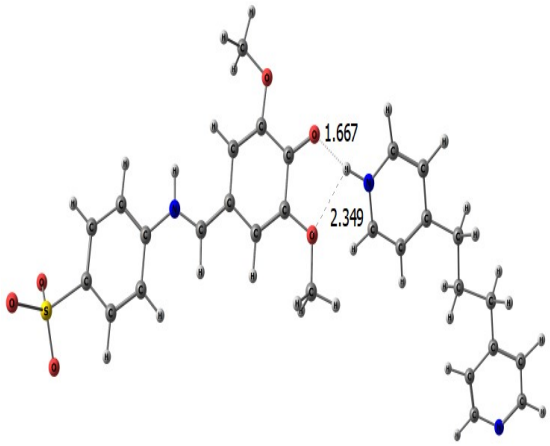
II



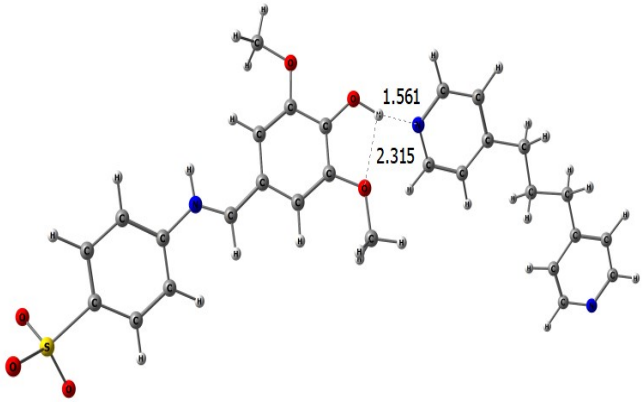


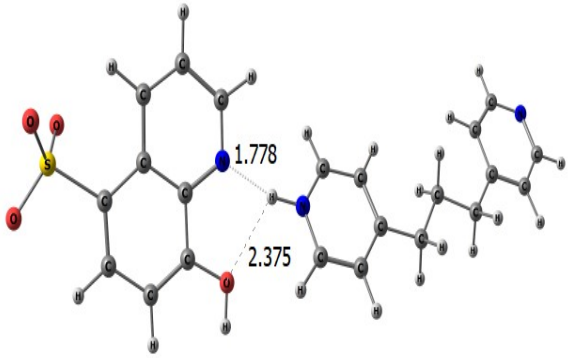
III



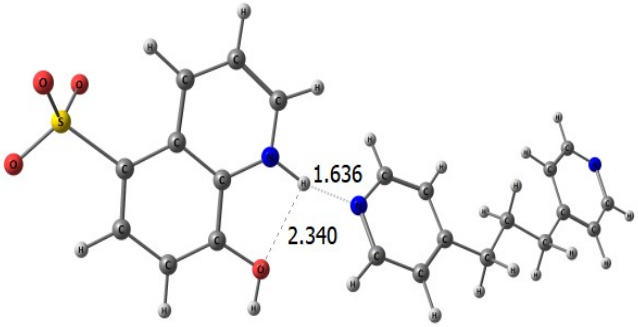


IV





V



V

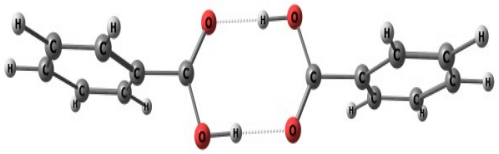
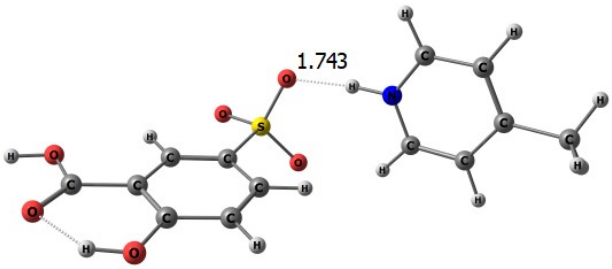
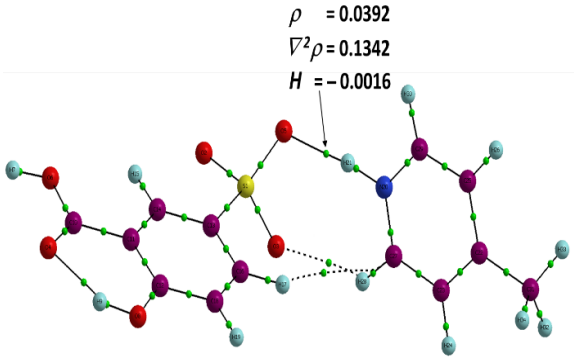
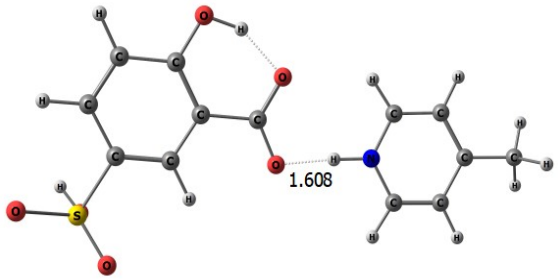
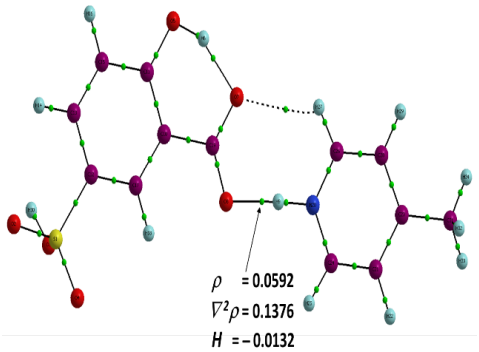
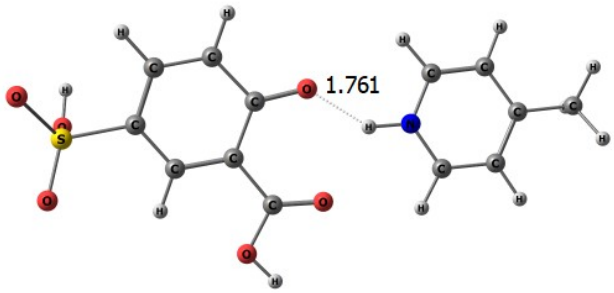
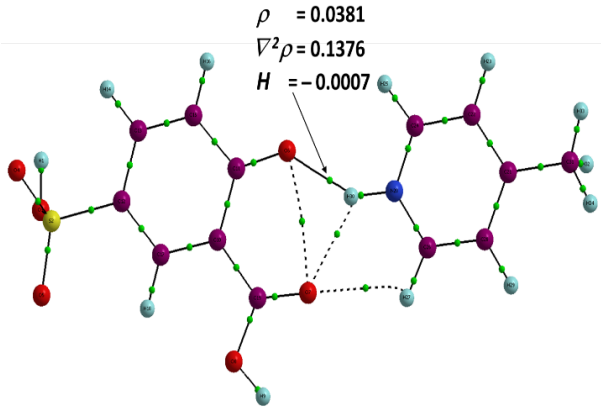
	 VI

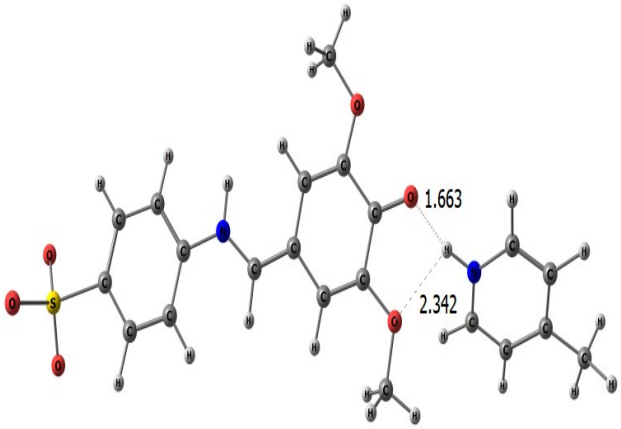
Table ESI-15. Optimized geometries as well as the corresponding QTAIM topological plots of various charge assisted sulfonate-pyridinium salt keeping methyl pyridine as a monomer. Selected bond distance in Å. The bond critical points are designated as smallgreen spheres. AIM parameters (in au) electron density (ρ), Laplacian of electron density ($\nabla^2\rho$) and total energy density (H) at the bcps of selected bonds are also shown.

 I	
 II	

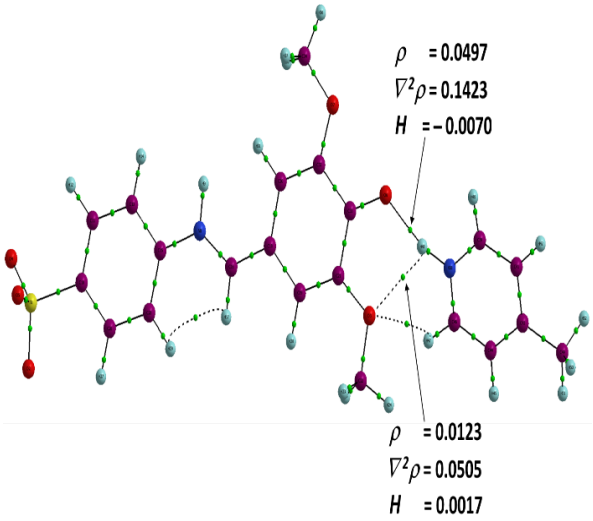

1.761

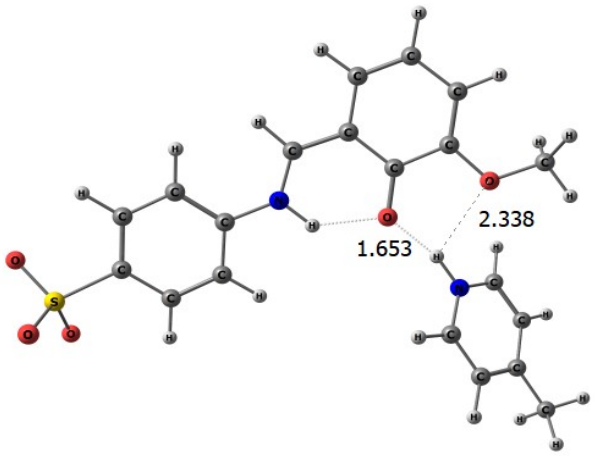
III


ρ = 0.0381
∇²ρ = 0.1376
H = – 0.0007

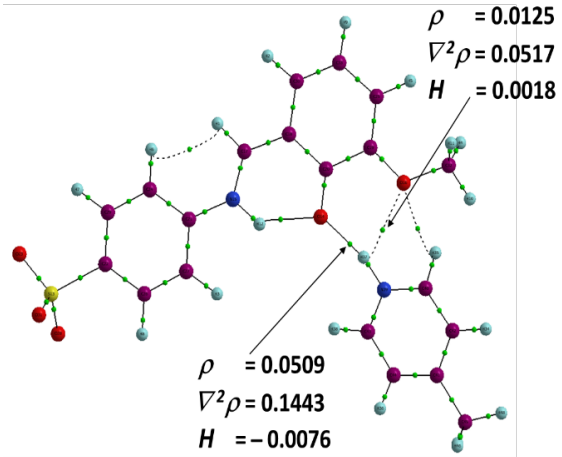

1.663
2.342

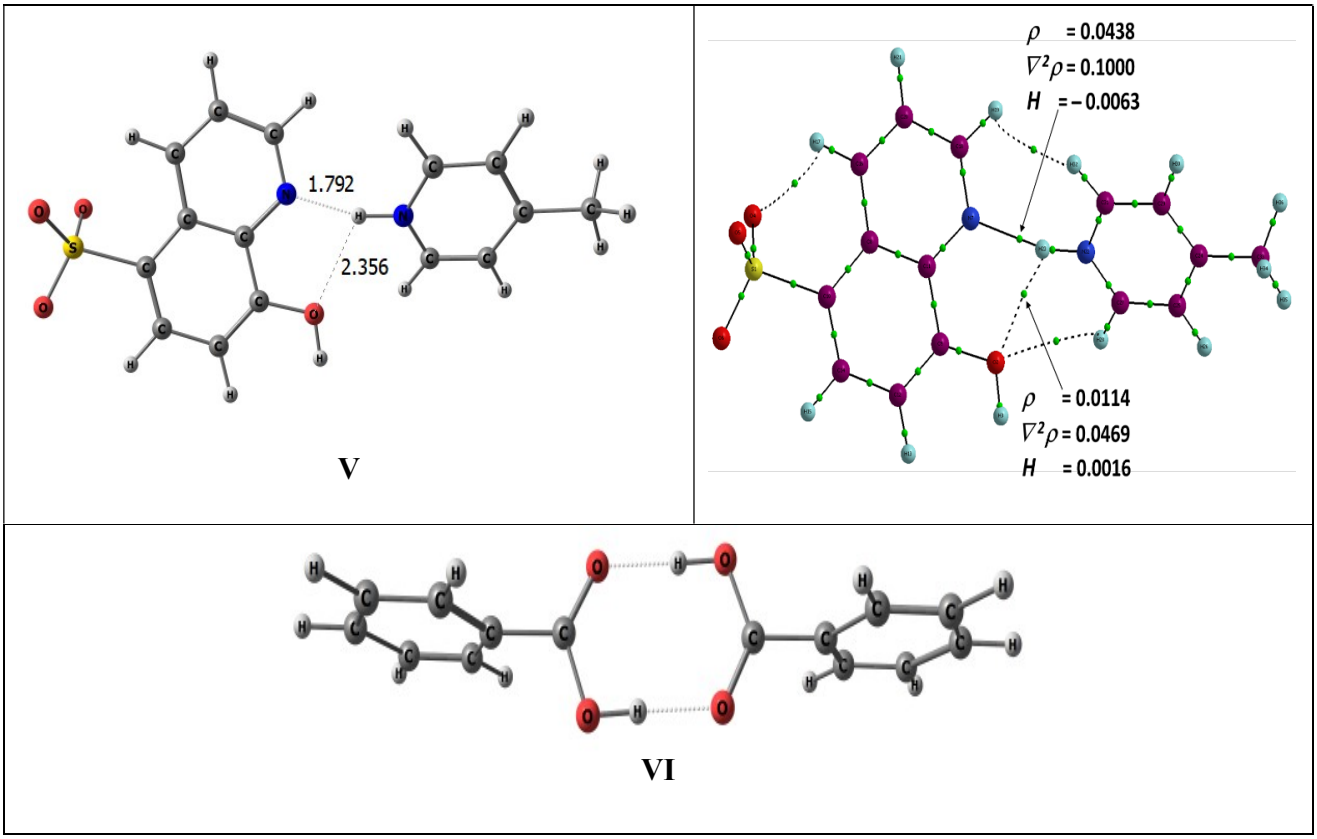
IV

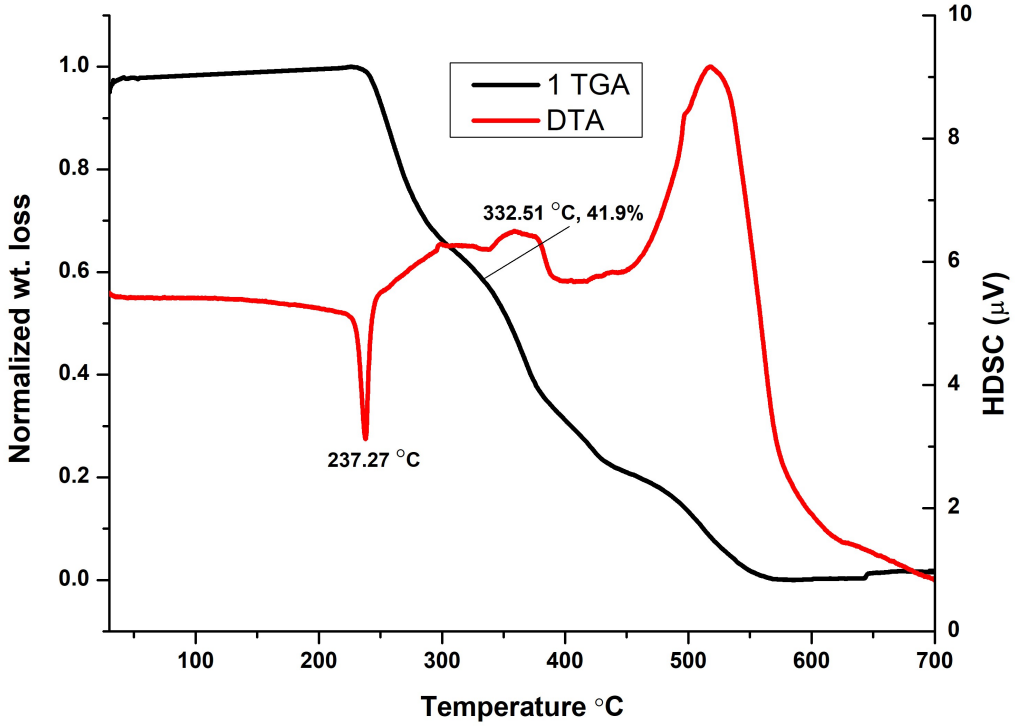

ρ = 0.0497
∇²ρ = 0.1423
H = – 0.0070
ρ = 0.0123
∇²ρ = 0.0505
H = 0.0017


2.338
1.653

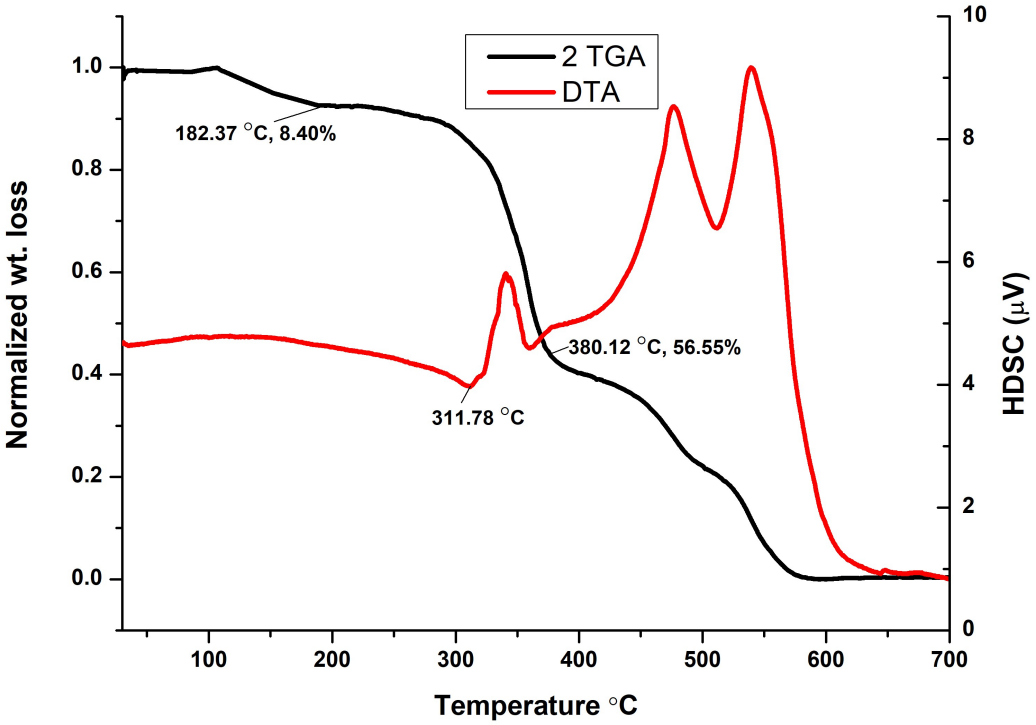
IVa


ρ = 0.0125
∇²ρ = 0.0517
H = 0.0018
ρ = 0.0509
∇²ρ = 0.1443
H = – 0.0076

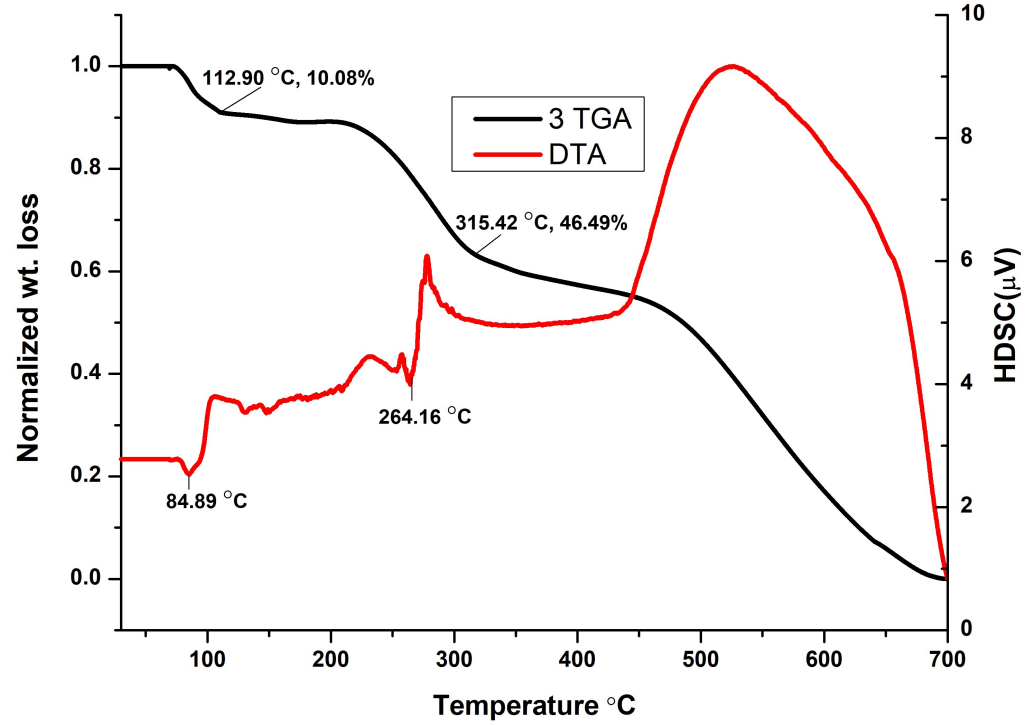

1.792
2.356
V
ρ = 0.0438
∇²ρ = 0.1000
H = – 0.0063
ρ = 0.0114
∇²ρ = 0.0469
H = 0.0016
VI


1 TGA
DTA
332.51 °C, 41.9%
237.27 °C
Normalized wt. loss
HDSC (μV)
Temperature °C
1.0
0.8
0.6
0.4
0.2
0.0
10
8
6
4
2
0
100
200
300
400
500
600
700

FigureESI-15. TGA-DTA Thermograms of 1.



FigureESI-16. TGA-DTA Thermograms of **2**.



FigureESI-17. TGA-DTA Thermograms of **3**.

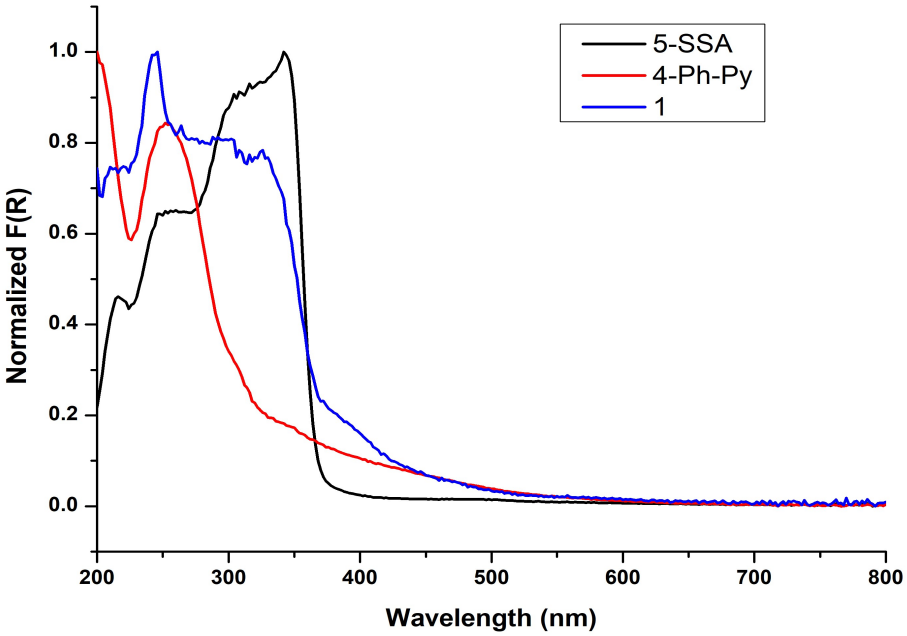


Figure ESI-18.K-M plots of 5-SSA, 4-Ph-Py and **1**.

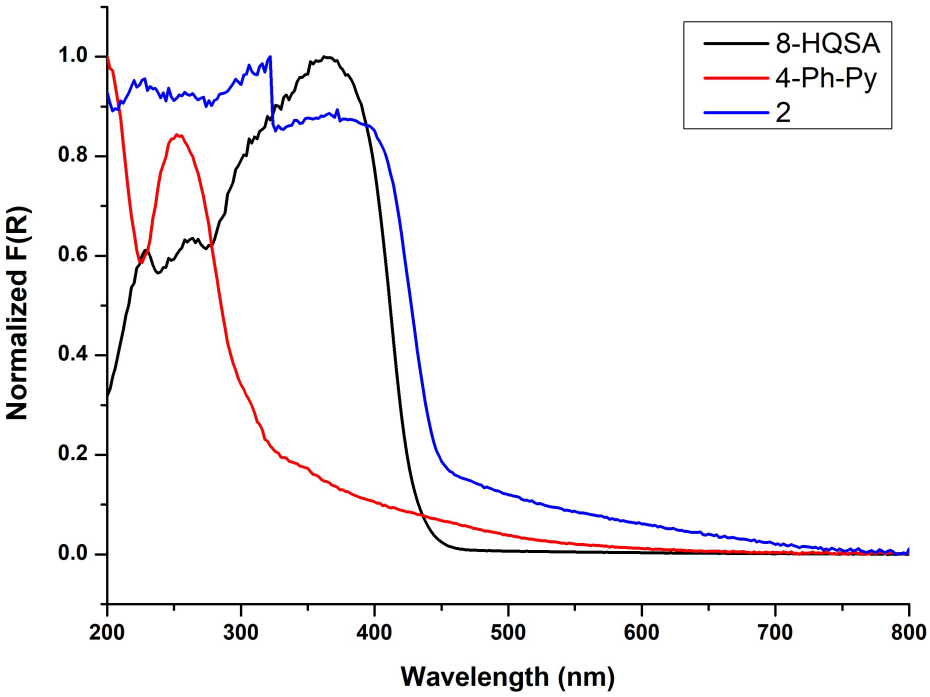


Figure ESI-19.K-M plots of 8-HQSA, 4-Ph-Py and **2**.

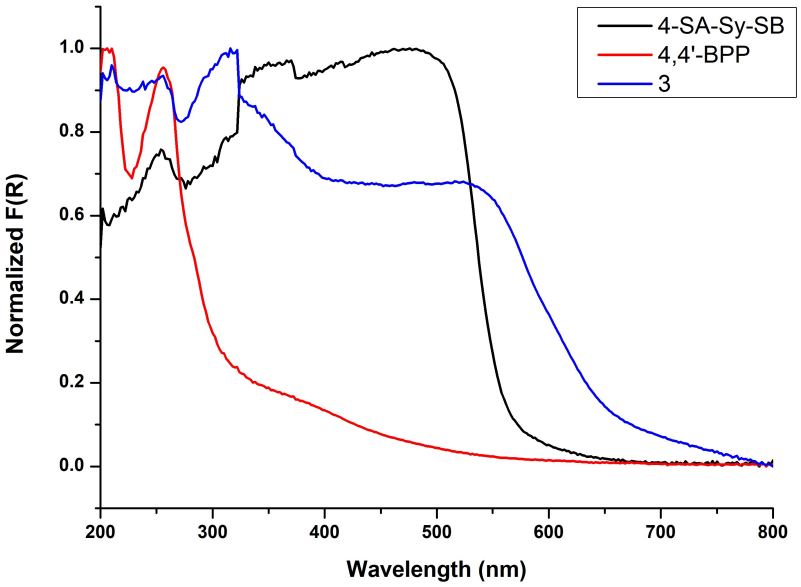


Figure ESI-20.K-M plots of 4-SA-Sy, 4,4'-BPP and **3**.

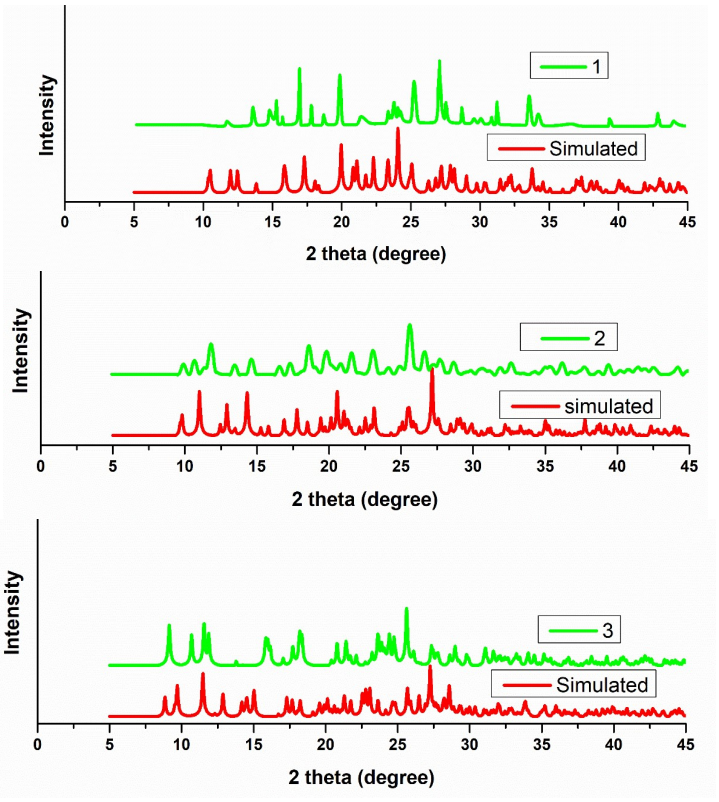
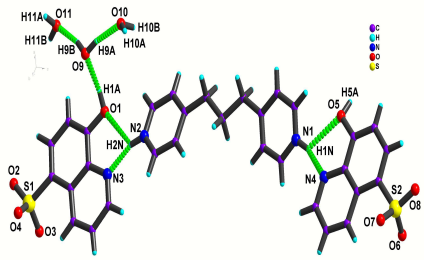
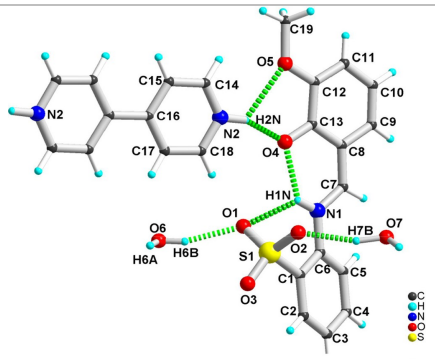
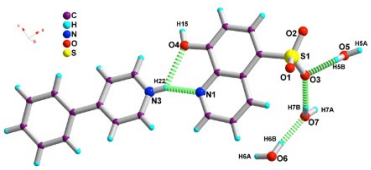


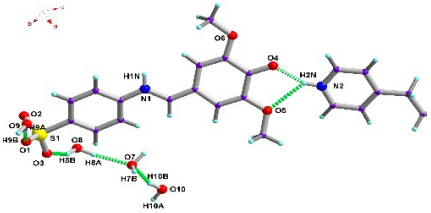
Figure ESI-21. Experimental P-XRD curves (green) of **1**, **2**, and **3** compared with simulated P-XRD curves (red) of **1**, **2** and **3**.

Table ESI-16. Comparative aqueous solubility of reactants and products.

Compound	5-SAA	4-Ph-Py	1
Solubility	**26.83mg/ml**	**0.12mg/ml**	**0.62mg/ml**
Compound	8-HQSA	4-Ph-Py	2
Solubility	**0.21mg/ml**	**0.12mg/ml**	**0.33mg/ml**
Compound	4-SA-Sy	4,4′-BPP	3
Solubility	**0.04mg/ml**	**0.35mg/ml**	**0.51mg/ml**

Chart ESI-2. Bifurcated hydrogen bonding interactions reported by us.

S.No.	Compound	Bifurcated Interaction	Bond Distance D-H…A	Bond Angle D-H…A	Molecular Structure Diagram
1)	**$[(4,4'\text{-BPP-}2H)^{2+}(4HQSAH)^{2-}.(H_2O)_3]$**	N2-NH2---O1	**2.473 Å**	**125.05°**	 **CCDC Submission. 1988032**
		N2-NH2---N3	**1.919 Å**	**162.38°**	
		N1-NH1---O5	**2.450 Å**	**122.67°**	
		N1-NH1---N4	**1.889 Å**	**161.52°**	
2)	**$[(4,4\text{-BPY-}2H)^{2+}(2\text{-SA-oVH})^{2-}2H_2O]$**	N2-NH2---04	**1.701 Å**	**159.23°**	 **CCDC Submission 1981823**
		N2-NH2---O5	**2.464 Å**	**123.32°**	
3)	**$[(8\text{-HQSA-H})^{-}(4\text{-Ph-Py-H})^{+}.3H_2O]$ (2)**	N3-NH3---O4	**2.406 Å**	**127.79°**	 **CCDC Submission 2032728**
		N2-NH2---N1	**1.198 Å**	**158.02°**	

4)	**[(4,4'-BPP-H)$^{2+}$(4-SA-Sy-H)$^{2-}$. 4H_2O] (3)**	N2-NH2---O4	**1.805 Å**	**157.24°**	 **CCDC Submission 2032729**
		N2-NH2---O5	**2.471 Å**	**127.51°**	