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Irreversible Thermochromism in Organic Salts of Sulfonated Anils

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KEYWORDS: Supramolecular synthon, structure-property relationship, cocrystal

ABSTRACT:Condensation of p-amino benzene sulfonic acids with salicylaldehyde and o-vanillin and that of oaminobenzene sulfonic acid with o-vanillin via mechanochemical grinding followed by heating under reflux yielded 4-[(2-Hydroxy-benzylidene)-amino]-benzenesulfonic acid [4-SA-BA-2H (1a)], 4-[(2-Hydroxy-3-methoxybenzylidene)-amino]-benzenesulfonic acid [4-SA-oV-2H (2a)] and 2-[(2-Hydroxy-3-methoxy-benzylidene)amino]-benzenesulfonic acid [2-SA-oV-2H (3a)], respectively. Anticipating the formation of sulfonate…pyridinium supramolecular synthon, organic salts [(4,4'-BPY-2H)²⁺(4-SA-BA-H)₂] (1), [(4,4'-BPY-2H)²⁺ (4-SA-oV-H)₂.4H₂O] (2) and [(4,4'-BPY-2H)²⁺(2-SA-oV-



H) $_{2}^{2}$ 2H₂O] (3) have been obtained by in-situ as well as post-synthetic reaction of **1a-3a** with 4,4'-bipyridine. Crystallographic investigations of the molecular salts reveal intriguing structural features and indicate the ubiquitous formation of hydroxylate...pyridinium interaction over otherwise robust sulfonate...pyridinium synthon when hydroxyl group has adjacent methoxy group. **1** crystallizes as anhydrous salt with direct charge assisted sulfonate...pyridinium interaction between crystal formers forming 2-dimensional layers which π -interlock to form rare 3-dimensional yellow solid. Crystal formers in hydrated salts**2** and **3** associate through ionic hydroxylate...pyridinium interaction instead of anticipated sulfonate...pyridinium synthon. The organo-sulfonate ionsin **2** and **3**associate with help of octameric and tetrameric water clusters into 2-dimensional and 1-dimensional assemblies, respectively, which are further bridged by bis-pyridinium ions into 3-dimensional colored ionic solids. The enhanced optical behavior of **1-3** on formation from **1a-3a** is investigated through diffuse reflectance studies. Schiff base **1a** and it's salt **1** exhibit redshift on heating, both **2a** and **2**, as well as, **3a** do not respond notably to heat while as **3** undergoes a remarkable blue shift on heating. Optical studies vis-à-vis crystallographic investigations rule out the conventional and general mechanism *i.e.* enol⇔cis-keto isomerization, and instead strongly indicate packing changes to be the cause of irreversible thermochromism observed in **1** and **3**. Furthermore, the resultant molecular salts exhibit significant thermal and chemical stability and their formation is also substantiated by spectroscopic and analytical methods.

INTRODUCTION

In material chemistry, it is well perceived that properties follow from structure i.e. "function follows form".¹ However, the relationship between molecular packing and consequent properties is not well understood and to design bespoke materials it is imperative to further explore the structure-property relationship.²⁴ Thermochromism isan uncommon property which involves reversible or irreversible color change with temperaturevariation and the phenomenon finds utility as thermometers, thermo-sensitive recording paper, temperature-indicating labels, sun-protecting glazing, battery testers, temperature sensors, and temperature-controlled light filters.⁵⁻⁹Inorganic complexes provide more examples of thermochromic materials than organic molecules.^{6,10}Thermochromism of inorganic complexes isgenerally triggered by local crystal field alteration or polarization induced charge transfer phenomenon.^{10,11,12}N-Salicylidene aniline and its derivatives (anils) represent an important but less explored class of organic compounds with a tendency to exhibit solid-state thermo- and

photochromism due to prototropic and isomeric forms.¹³⁻¹⁷ Determination of the relationship between structure and optical properties to understand the switching mechanism in solid-state has been of special focus since their discovery. The photochromism of these molecules is well explored and primarily attributed to cis↔trans-keto isomerism while thermochromism, attributed to enol↔cis-keto prototrophism, is less explored, Chart 1. Empirical rules indicate that planner or nearly planner anils ($\phi < 20^{\circ}$) in close-packed environments exhibit thermochromic behavior and otherwise photochromism is exhibited.¹⁸ Rational attempts have been made to modulate the structural and packing behavior of these molecules through structural modifications, introduction of bulky groups and crystal engineering.¹⁹⁻²²

Crystal engineering or supramolecular approach is rapidly growing research domain in designing the optical materials.²¹⁻²⁵Crystal engineering has been pursued to modulate environment or create free volumes around anil molecules to induce photo- and thermochromism.^{18, 21-22}Cocrystallization

provides a convenient opportunity to modulate the environment around anil molecules and hence their behavior towards heat and light.²⁶⁻²⁹ Moreover astute selection of the crystal coformer may lead to analogous solid forms, but with different properties. Various studies involving modulation of the crystal structure through packing effect and/or size of the coformer on the chromic properties of anils have been reported.^{28,29}

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The supramolecular synthon approach³⁰ has been utilized with notable success to develop bespoke multicomponent crystals with utility in pharmacy³¹, agriculture³² and industry³³⁻³⁵. A robust supramolecular synthon should exhibit facile manifestation in addition to significant strength and directionality. Robust supramolecular interactionspreferentially lead to the isolation of high-energykinetic productsover stable but elusive thermodynamic products, which however, are stabilized by numerous favorable secondary interactions. Together with tecton theory, supramolecular synthon approach has been utilized to design crystals and has been finitely successful in structural prediction.³⁶Nevertheless, the design and cogent structure prediction still remain a conundrum for crystal engineers and the area is being perceived emphatically. The discovery of newer robust supramolecular synthons can be a salient approach to develop the-state-of-art materials and understand the structure-property relationship.

Chart 1.Conventional mechanism of thermo-and photochromism in anils with their absorption regions in typical diffuse reflectance spectra.



Of recent, we have described the rational utility of lesser reported sulfonate...pyridinium synthon and advocated its case for consideration as a robust supramolecular synthon.^{37,38}Extending the scope of utility of thisstable secondary interaction we are reporting cogent derivatization of the arylsulfonic acids into sulfonated anils which are furtherdeployed for the development of molecular crystals. As mentioned appropriate crystal coformers can attune molecular packing and help in achieving larger free volumes in the crystal structures of anils. 4,4'-bipyridyl has been utilized as a coformer with the aim to form sulfonate ... pyridinium synthon based molecular complexes with modulated packing. Interestingly, the molecular complexes obtained from the precursors, depicted in Chart 2, do respond to heat but not to light, and they do not obey the conventional mechanism of thermochromism depicted in Chart 1. Crystallographic and optical studies of the reported complexes provide comprehensibleunderstanding to rule out the conventional mechanism of thermochromism and instead validate attribution of the phenomenontochange in the crystal packing.

EXPERIMENTAL

Methods and Materials

4-Aminobenzene sulfonic acid (4-ABSA-H) (99%, Sigma-Aldrich), 2-aminobenzene sulfonic acid (2-ABSA-H)(99%, Sigma-Aldrich), Salicyldehyde (99%, Sigma-Aldrich), ovanilin (99%, Sigma-Aldrich), p-vanilin (99%, Sigma-Aldrich) and 4,4'-bipyridyl (>99.9%, Sigma-Aldrich) were used as procured. Single distilled H₂O and methanol were used as solvents. Melting points were determined on the MP70 Melting Point System capillary apparatus (Mettler Toledo). pH was determined on Labtronics Micro Processor pH meter (LT-49) at 44.1 °C. Infrared spectroscopic data of the sulfonate anils 1a-3a and their molecular salts 1-3 were obtained using Agilent Technologies Cary 630 FT-IR (4000-650cm⁻¹) in ATR mode. Ground crystals of 1a-3a and 1-3 were placed on the crystal plate of the infrared instrument and the spectrum was recorded. ¹H NMR spectra were recorded on Bruker 400 MHz spectrometer in DMSO-d₆ as solvent. Thermal gravimetric analyses and differential thermal analyses of these samples were performed on a Simultaneous Thermal Analyser-STA (LINSEIS, USA 6807/8835/16) using alumina crucible at heating rate 10°C. Diffuse reflectance measurements of the products were recorded on Schimadzu-2600 spectrometer as BaSO₄ discs and converted to Kubelka-Munk and Tauc plots in origin using appropriate conversion formula. The free volume V_{free} was evaluated by considering the unit cell volume ($V_{unit cell}$), the anion (V_{anion}), the cation (V_{ca-} tion) and the solvent (V_{solvent}) volumes as well as Z, the number of molecules in the unit cell, as discussed previously,²⁸using formula:

 $V_{free} = [V_{unit \ cell} - Z * (V_{anion} + V_{cation} + V_{solvent})]/Z.$ The anion, cation and solvent volumes were calculated online using Molinspiration Galaxy 3D Structure Generator v2018.01 beta. Molecular structure and packing diagrams have been plotted in Diamond software with aid of Mercury software.

Chart 2. Starting materials used for synthesis of 1-3.



SC-XRD Studies

Single-crystal X-ray data were collected on a Rigaku Saturn CCD diffractometer using a graphite monochromator (Mo K α , $\lambda = 0.71073$ Å). The selected crystals were mounted on the tip of a glass pin using mineral oil and placed in the cold flow produced with anCryo-cooling device. Complete hemispheres of data were collected using ω and φ scans (0.3°, 16 s perframe). Integrated intensities were obtained with Rigaku Crystal Clear-SM Expert 2.1 software, and they were corrected for absorption correction. Structure solution and refinement were performed with the SHELX package. The structures were solved by direct methods and completed by iterative cycles of Δ F syntheses and full-matrix least-squares refinement against F. Crystal refinement parameters of **1-3** are given in Table 1.

Synthesis

4-((2-hydroxybenzylidene)amino)benzenesulfonic acid [4-SA-BA-2H (1a)]. 4-ABSA-H (86 mg, 0.5 mmol) was dissolved in 10 mL of hot distilled water and salicylaldehyde (1173 μL, 0.5 mmol) was taken in 10 mL of methanol, two solutions were mixed together to give yellow solution. The resultant solution was refluxed for about an hour, filtered and kept for slow evaporation to yield light yellow crystalline solid. Yield: 225 mg, 76%; M.P: >250 °C; pH (of resultant solution at 141.1 °C): 2.68; IR, ν, (neat): 3429 (br), 2981 (w), 2113 (br), 1647 (s), 1576 (s), 1464 (s), 1159 (vs), 1121 (vs), 1032 (s). ¹H NMRδ, 400 MHz, DMSO-*d*₆, ppm: 9.01 (s, 1H), 8.95 (s, 1H), 8.87 (d, 4H, ³J_{H-H} = 1.2 Hz), 8.11 (d, 4H, ³J_{H-H} = 1.2 Hz), 7.54 (d, 2H, ³J_{H-H} = 1.6 Hz), 7.36 (t, 1H, ³J_{H-H} = 1.6 Hz), 7.01 (d, 2H, ³J_{H-H} = 1.2 Hz), 6.97 (t, 1H, ³J_{H-H} = 0.8 Hz).

[(4,4'-BPY-2H)²⁺(4-SA-BA-H) $\frac{1}{2}$] (1): 4-ABSA-H (86 mg, 0.5 mmol) and salicylaldehyde (1173 μL, 0.5 mmol) were dissolved separately in 10 mL of hot distilled water and methanol, respectively, and the solutions were mixed with stirring. To the resultant solution 4,4'-BPY (78 mg, 0.5mmol), dissolved in 10 mL of methanol, was added with stirring. The final solution was refluxed for an hour, filtered and crystallized by slow evaporation at ambient temperature. Orange blocks were obtained in 3-4 days.Yield: 301 mg; 66%; MP.: 225 °C; pH: 3.24; IR, v, (neat): 3421 (br), 2981 (w), 2109 (br), 1651 (s), 1505 (s), 1395 (s), 1170 (vs), 1118 (vs), 1028 (s). ¹H NMR, δ, 400 MHz, DMSO-*d*₆, ppm: 9.07 (s, 1H), 8.96 (s,1H), 8.92 (d, 4H, ³J_{H-H}= 1.2 Hz), 7.54 (d, 2H, ³J_{H-H}= 1.6 Hz), 7.36 (d, 1H, ³J_{H-H}= 1.2 Hz), 7.21 (d, 2H, ³J_{H-H}= 1.6 Hz), 7.02 (t, 1H, ³J_{H-H}= 1.6 Hz), 6.97 (t, 1H, ³J_{H-H}= 0.8 Hz).

4-((2-hydroxy-3-methoxybenzylidene)amino)benzenesulfonic

acid [4-SA-oV-2H(2a)].4-ABSA-H(86 mg, 0.5 mmol) and ovanillin (78 mg, 0.5 mmol) were dissolved separately in 10 mL of hot distilled water and methanol, respectively and the solutions were mixed together with stirring. The resultant solution was refluxed and stirred for an hour, filtered hot and kept for slow

evaporation to yield orange crystalline solid in 4 days. Yield: 225 mg; 69 %; MP.: 240°C; pH: 2.89; IR, v, (neat): 3421 (br), 2981 (w), 2109 (br), 1657 (s), 1595 (s), 1505 (s), 1291 (s), 1173 (vs), 1118 (vs), 1008 (s). ¹H NMR, δ , 400 MHz, DMSO-*d*₆, ppm: 10.28 (s, 1H), 9.08 (s, 1H), 7.74(d, 2H, ³J_{H-H} = 1.6 Hz), 7.49 (d, 2H, ³J_{H-H} = 1.6 Hz), 7.49 (d, 2H, ³J_{H-H} = 1.6 Hz), 7.26 (d, 1H, ³J_{H-H} = 1.6 Hz), 6.97 (t, 1H, ³J_{H-H} = 2.0 Hz), 3.85 (t, 3H).

 $[(4,4'-BPY-2H)^{2+}(4-SA-oV-H)_{2}\cdot 4H_2O]$ (2). 4-ABSA-H (86 mg, 0.5 mmol) and o-vanillin (76 mg, 0.5 mmol) were dissolved separately in 10 mL of hot distilled water and methanol, respectively and mixed with stirring. To the resultant solution 4,4'-BPY (78 mg, 0.5 mmol) in methanol was added and the final solution was refluxed with stirring for an hour. The solution obtained was filtered and crystallized by slow evaporation to yield red blocks in 3-5 days. Yield: 356 mg; 64%; MP.: 114 °C; pH: 3.55; IR, v, (neat): 3425 (br), 3011 (w), 2094 (br), 1638 (s), 1601 (s), 1374 (s), 1173 (vs), 1118 (vs), 1028 (s). ¹H NMR, δ , 400 MHz, DMSO- d_6 , ppm: 10.21 (s, 1H), 8.94 (d, 4H, ${}^{3}J_{H-H} = 1.6$ Hz), 8.24 (d, 4H, ${}^{3}J_{H-H} = 1.6$ Hz), 7.66 (d, 2H, ${}^{3}J_{H-H} = 1.6$

Hz), 7.36 (d, 1H, ${}^{3}J_{H-H}$ = 1.6 Hz), 7.24 (d, 1H, ${}^{3}J_{H-H}$ = 1.6 Hz), 7.12 (d, 1H, ${}^{3}J_{H-H}$ = 1.2 Hz), 6.90 (t, 1H, ${}^{3}J_{H-H}$ = 2.0 Hz), 3.80 (s, 3H).

$\label{eq:2-(2-hydroxy-3-methoxybenzylidene)} a mino) benzene sulfonic$

acid [2-SA-oV-2H (3a)]. 2-ABSA-H (86 mg, 0.5 mmol) and ovanillin (76 mg, 0.5 mmol) were dissolved separately in 10 mL of hot distilled water and methanol, respectively. The solutions were mixed together and the resultant solution was refluxed and stirred for two hours, filtered and kept for slow evaporation. Yellow crystals were obtained in 3-5 days. Yield: 221 mg; 68%; MP.:>250 °C; pH: 2.71; IR, v, (neat): 3391 (br), 2100 (br), 1636 (s), 1609 (s), 1512 (s), 1201 (vs), 1167 (vs), 1014 (s). ¹H NMR, δ , 400 MHz, DMSO- d_6 , ppm: 10.27 (s, 1H), 8.23 (s, 1H), 7.82 (d, 1H, ³J_{H-H} = 1.2 Hz), 7.65 (d, 1H, ³J_{H-H} = 1.2 Hz), 7.46 (t, 1H, ³J_{H-H} = 1.6 Hz), 7.37 (d, 1H, ³J_{H-H} = 1.2 Hz), 7.32 (t, 1H, ³J_{H-H} = 1.2 Hz), 7.26 (t, 1H, ³J_{H-H} = 1.2 Hz), 7.16 (d, 1H, ³J_{H-H} = 1.2 Hz), 3.81 (s, 3H).

[(4,4'-BPY-2H)²⁺(2-SA-oV-H) 2.2H2O] (3). 2-ABSA-H (86 mg, 0.5mmol) and o-vanillin (76 mg, 0.5 mmol) were dissolved separately in 10 mL of hot distilled water and methanol, respectively. The solutions were mixed with stirring and solution of 4,4'-BPY (78 mg, 0.5 mmol) in methanol was added to the resultant solution. Final solution was stirred under reflux for two hours, filtered and kept for slow evaporation. Intense brown (or apparently black) crystals were obtained in 2-5 days. Yield: 349 mg; 67%; MP.: 220 °C; pH: 3.39; IR, v, (neat): 3488 (br), 3087 (w), 2120 (br), 1622 (s), 1588 (s), 1505 (s), 1194 (vs), 1132 (vs), 1001 (s). ¹H NMR,δ, 400 MHz, DMSO-*d*₆, ppm: 10.24 (s, 1H), 8.3 (s, 1H), 8.89 (d, 4H, ${}^{3}J_{H-H} = 1.2$ Hz), 8.17 (d, 4H, ${}^{3}J_{H-H} = 1.2$ Hz), 7.82 (d, 1H, ${}^{3}J_{H-H} = 0.8$ Hz), 7.70 (d, 1H, ${}^{3}J_{H-H} = 0.8$ Hz), 7.47 (d, 1H, ${}^{3}J_{H-H}$ = 1.6 Hz), 7.37 (t, 1H, ${}^{3}J_{H-H}$ = 1.2 Hz), 7.25 (t, 1H, ${}^{3}J_{H-H}$ = 1.2 Hz),7.17 (d, 1H, ${}^{3}J_{H-H} = 1.2$ Hz), 6.90 (t, 1H, ${}^{3}J_{H-H} = 1.2$ Hz), 3.31 (s, 3H).

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Table 1.Crystal data details of molecular salts1-3.

Compound	1	2	3
CCDC No.	1981821	1981822	1981823
Empirical formula	C18H15N2O4S	C19H25N2O9S	C19H21N2O7S
Fw	355.38	457.47	421.44
Temp [K]	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a, [Å]	5.773(7)	9.513(7)	8.8556(5)
b, [Å]	7.613(8)	10.309(6)	11.3511(6)
<i>c</i> , [Å]	18.38(2)	12.079(8)	11.5730(7)
<i>α</i> , [°]	86.89(3)	71.52(2)	117.113(6)
β, [°]	87.270(19)	85.22(2)	102.490(5)
γ, [°]	83.52(2)	76.044(18)	98.873(4)
$V, [Å^3]$	800.8(16)	1090.3(13)	967.26(9)
Ζ	2	2	2
D(calcd)	1.474	1.393	1.447
$\mu [{\rm mm}^{-1}]$	0.229	0.201	0.213
Θ range [°]	25.500	25.000	25.000
Reflns collected	2935	3844	3419
Indep. Reflns	2454	3174	2948
GOF	1.065	1.030	1.136
$R1(I_0 > 2\sigma(I_0))$	0.0468	0.0519	0.0407
wR2(all data)	0.1468	0.1592	0.1472

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Solvent assisted mechanical grinding of amino-arylsulfonic acids: 4-aminobenzene sulfonic acid (4-ABSA-2H) and 2aminobenzene sulfonic acid (2-ABSA-2H), with corresponding benzaldehydes, followed by heating under reflux in methanol yielded sulfonated Schiff bases 4-[(2-Hydroxy-[4-SA-BAbenzylidene)-amino]-benzenesulfonic acid 4-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-2H](1a), benzenesulfonic acid [4-SA-oV-2H](2a) and 2-[(2-Hydroxy-3methoxy-benzylidene)-amino]-benzenesulfonic acid [2-SAoV-2H] (3a)as colored amorphous solids. The molecular complexes $[(4,4'-BPY-2H)^{2+}(4-SA-BA-H)_{2}]$ (1), $[(4,4'-BPY-4)^{2+}(4-SA-BA-H)_{2}]$ $(2H)^{2+}(4-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2-SA-oV-H)_2(2H)^{2+}(2H)^$ $oV-H_{2}^{-}.2H_{2}O$ (3) have been obtained by reflux of **1a-3a** with 4,4'-BPY as well as by in-situ mechano-reflux reaction of the organo-sulfonic acids with the benzaldehydes in presence of 4,4'-BPY. Products 1a-3a and 1-3 have been obtained in good yields and their formation is substantiated by various spectroscopic, analytical and thermal methods of analyses.

Fourier transform infrared (FT-IR) spectroscopic studies of 1a-3a and 1-3 support their formation. The absorption bands at around 1205-1115 and 1350-1300 cm⁻¹ correspond to S=O stretching of sulfonic group while as absorption bands at 1660-1620 cm⁻¹ and 1600-1505 cm⁻¹ corresponding to C=N and C=C stretching, respectively. Figure ESI-1-6. Compounds 1-3 exhibit stability towards non-polar and less polar solvents and are soluble in solvents of high polarity only, Table ESI-1. The ¹H NMR spectra of **1a-3a** and **1-3**, reported in DMSO- d_6 , are consistent with their formation in terms of both the observed chemical shift and peak intensity ratio. ¹H NMR spectra with peak assignments are provided in supported information, Figure ESI-7-12. All the products have been further characterized by thermo-gravimetry and their definitive solid-state structures and crystal packing has been established by single crystal-X-ray diffraction (SC-XRD) method. Furthermore, the intriguing optical properties of the thermochromic products are reported.

Structural Studies

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59 60 Structure description of 1.Molecular salt 1, obtained by *in-situ* reaction of 4-ABSA-2H and salicylaldehyde with 4,4'-BPY, crystallizes in triclinic centro-symmetric space group *P*-1. 1 is non-solvated with onemolecule of anionic sulfonatedSchiff base 1a and half molecule of bis-pyridinium in the asymmetric unit. The anionic Schiff base is nearly planar with torsion angle of $3.93(1)^{\circ}$ between aryl rings and is stabilized by cis-enol intramolecular hydrogen bondinginteraction O4-H4O…N1 [D…A: 2.625(1) Å; D-H…A: 153.88(2)°]. Existence of 1 in enol form is also indi-

cated by shorterimine C4-N1and longer hydroxyl C9-O4 bond length value of 1.277(2) and 1.346(1) Å, respectively. The sulfonate sulphur is in distorted tetrahedral geometry with average O-S-O and C-S-O bond angle of 112.12° and 106.18°, respectively. Two crystal structural analogues of anil sulfonate anion in 1 have been reported previously in the cationic matrix of [Cu(phen)₃]²⁺ and diallyl hexyl ammonium cations.^{21,29} In both reported forms the sulfonated anil anion exists in nearly planer enol form as confirmed from torsion angle and bond length values of imine (C=N) and C-O (hydroxyl). The 4,4'-BPYcoformer is protonated on both ends with N···N linear distance of 6.993(1)Å and dihedral angle value of 1.06(2)° between pyridinium rings.Protonation at nitrogen centersofbis-pyridinium [4,4'-BPY-2H]²⁺is substantiated by relaxed C14-N2-C16 bond angle value of 121.44(1)°. Bis-pyridinium centers bridge twoSchiff base anions through anticipated sulfonate...pyridiniumsupramolecular interactions to form non-stoichiometric salt [(4,4'-BPY-2H)²⁺(4-SA-BA-H) $\frac{1}{2}$]. Furthermore, the supramolecular synthon in 1 manifests itself in cyclic $R_2^2(7)$ form, consisting of N2-H2N···O2 [2.701(1)Å; 170.92(2)°] and weak C16-H16…O3 [3.193Å; 131.21°] interactions. Molecular structure diagram of 1 is depicted in Figure 1.



Figure 1. Molecular structure diagram of $[(4,4'-BPY-2H)^{2+}(4-SA-BA-H)^{-}](1)$.

Each bis-pyridinium crystal former in 1 exhibits intriguing hydrogen bonding behaviour by coordinating six different molecules of acid co-formers forming centro-symmetric [(4,4'-BPY-2H)²⁺(4-SA-BA-H) $_{6}^{-1}$ ⁴ cluster, stabilized by two R $_{2}^{-1}$ (7) synthons: consisting of C15-H15...O1 [3.343(1) Å; 172.30(7)°] and C17-H17...O1 [3.376(2) Å; 174.09(2)°], and two C14-H14····O3 [2.985(3) Å; 108.76(6)°] $R_2^2(7)$ interactions. and two sulfonate ... pyridiniumsynthons, Figure ESI-13. Furthermore, the sulfonate end of each Schiff base anion interacts with three different molecules of bis-pyridinium ions to form2-D layered tapes, Figure ESI-14, which are also stabilized by slipped π - π interactions between the aryl rings of Schiff base anions and bispyridinium cations, FigureESI-15. The 2-D layeredtapes further



Figure 2. Packing diagram of $[(4,4'-BPY-2H)^{2+}(4-SA-BA-H)_2]$ (1), depicting assembly of tri-layers (depicted in different colors for clarity) into rare 3-D π -interlocked supramolecular framework.

aggregate to form rare π -interlocked 3-D aggregate, stabilized by π -stackingof the Schiffbase aryl centers and weak C3-H3···O4 [3.621(5)Å; 153.17(1)°] interactions. The packing diagram of **1a** is depicted in Figure 2, in which different colors represent different 2-D layered tapes.

Structure description of 2.Red crystals of the molecular salt 2 were obtained by in-situreaction of 4-ABSA-2H, o-vanillin and 4,4'-BPY in water-methanol solvent system. 2crystallizes in centro-symmetric triclinic lattice: P-1. One anion of sulfonated Schiff base and half of bis-pyridinum cation, in addition to four lattice water molecules constitute itsasymmetric unit. The sulfonated Schiff base exists in plannar-cis-keto form with dihedral angle of 4.77(1)° between aryl rings. Stabilized by intramolecular interaction N1-H1N····O4 [2.599(1) Å; 139.24(2)°], cis-keto form of Schiff base in 2 is corroborated by longer imine C7-N1[1.306(3) Å], shorter C9-O4 [1.301(2) Å] bond distance and relaxed C4-N1-C7 [127.21(2)°] bond angleas compared to similar structural parameters of value 1.277(2) Å, 1.346(2) Å, and 122.43(1)°, respectively in the en-ol form of the sulfonated Schiff base anion in 1. The sulfonate sulfur center has distorted tetrahedral geometry with nearly identical S-O bond length ranging from 1.445(1) to 1.453(2) Å and average O-S-O bond angle value of 112.25°. As compared to gentle yellow 1, the intense red colouration of 2 may be attributed to existence of acid former in ketoform. Molecular structure diagram of 2 is depicted in Figure 3.



Figure 3. Molecular structure diagram of $[(4,4'-BPY-2H)^{2+}(2-SA-oV-H)_2^{-}.4H_2O]$ (2).

4,4'-BPY is protonated on both ends with linear N···N distance of 6.988Å.The relaxed C17-N2-C19 bond angle value of 120.86(3)° substantiates protonation of pyridyl nitrogen centers. Although it is difficult to ascertain whether sulfonic or hydroxyl hydrogen has protonated the imine nitrogen, however apparently the hydroxyl hydrogen is involved in the charge assisted hydroxylate...pyridinium interaction. Interestingly, instead of the anticipated direct charge assisted sulfonate ··· pyridinium interaction the bis-pyridnium cations bridge two molecules of anil anions by hydrogen bonding interaction with keto oxygen:N2-H2N...O4 [2.601(2)Å, 153.62(1)°], with assistance from the adjacent methoxy-pyridinium bifurcated interaction N2-H2N···O5 [3.138(2) Å; 128.49(1)°]. Furthermore, as in 1, all the bis-pyridinium hydrogens areinvolved in weak C-H···O interactions with two sulfonated Schiff bases through C19-H19...O3 [3.367(2) Å; 133.09(1)°], C18-H18····O1 [3.414(1) Å; 170.80(2)°] and C16-H16····O1 [3.479(3) Å; 174.71(2)°], and two molecules of water via C17-H17...O8 [3.377(2) Å; 134.04(2)°] interaction forming [(4,4'-BPY-2H)²⁺(4-SA-oV-H)₄⁻.2H₂O]²⁻ cluster, Figure ESI-16.

Molecular salt 2 is significantly hydrated and the four lattice water molecules residue within the triclinic unitcell while as the crystal formers occupy cell periphery, Figure ESI-17. The water molecules undergo aggregation to formrare octameric cluster with cyclic tetrameric core.Water clustersin crystal lattices areof great interest for understanding the role of solvent molecules in crystal packing and their presence in biological systems makes them more significant. Based on the computational data various tetrameric water clusters have been predicted. Tetrameric core of water octamer in 2, formed by donating and accepting one hydrogen bond by each water molecule is in good agreement with the one predicted by Vaitheeswaran et. al.,³⁹ except for the orientation of dangling hydrogen atoms, which are further engaged in the present case. The water cluster existing in the lattice of 2 and its interaction with the crystal formers is depicted in Figure 4.Cyclic tetrameric cores in the octameric water cluster W8in 2and methanol-water solvent hexamer W_4M_2 (W = water and M = methanol), reported by us earlier,37 are similar. The comparative structures and bond parameters of W8 and W_4M_2 are given in Figure ESI-18. Each of the diagonal water molecules (O7) in the cyclic core of 2 further associates with two water molecules, by donating a hydrogen bond,O7-H7A...O9 [2.758(3) Å; 173.91(1)°] and accepting a hydrogen bond O7…H6B-O6 [2.959(1) Å; 171.11(8)°]. The peripheral water molecules (O6 and O9) and a water molecule (O8) in the tetrameric cyclic core aggregate eight sulfonated anil anions via O-H…O interactions.Reoccurrence of the W_4 cyclic cluster indicates tendency of its facile manifestation and may be a robust supramolecular solvent-cluster-binder.



Figure 4. Rare water cluster W_8 in the lattice of $[(4,4'-BPY-2H)^{2+}]$



Figure 5. Packing diagram of $[(4,4'-BPY-2H)^{2+} (2-SA-oV-H)^{-2}.4H_2O]$ (2). The hydrogen bonded water channels are depicted as pink spheres and bis-pyridinium linkers are highlighted in blue.

 $(4-SA-oV-H) - 2.4H_2O]$ (2).

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58 59 60 The water molecules associate the sulfinilate anils into 2-D networks withalternate $R_4^4(8)$ and $R_4^4(10)$ hydrogen bonded rings, Figure ESI-19. The 2-D layers are bridged by bispyridnium linkers into 3-D supramolecule depicted in Figure 5.

Molecular structure

description of 3.Dark brown crystals of 3 are obtained by slow evaporation of reaction mixture obtained by three component in-situ reaction. The molecu-



Figure 7. Packing diagram of $[(4,4'-BPY-2H)^{2+}(2-SA-oV-H)_2^2-2H_2O]$ (3), bis-pyridinium cations are highlighted in blue.

lar salt crystallizes in centro-symmetric triclinic crystal system: P-1, with an anion of Schiff base 3a, half of pyridinium ion and two molecules of lattice water in the asymmetric unit. Sulfonated base exists in non-planer keto form with C1-C6-C8-C13 torsion angle value of 21.2° between the aryl rings. As has been previously reported for the free ligand3a(see discussion), the sulfonic hydrogen is shifted to imine nitrogenN1 and forms the bifurcated hydrogen bond with sulfonate and keto oxygen centers: O1...H1N-N1 [2.883(1) Å; 132.50(1)°] and O4…H1N-N1 [2.717(1)Å; 130.86(2)°], respectively. Hydroxyl hydrogen of o-vanilin shifts to the pyridyl nitrogen leading to ionichydroxylate...pyridinium interaction N2-H2N...O4 [2.640(2) Å; 159.23(1)°] instead of anticipated sulfonate ... pyridinium synthon formation. The hydroxylate...pyridinium interaction in 3 is assisted by bifurcated interaction of pyridinium hydrogen with adjacent methoxy oxygen: N2-H2N···O5 [3.111(2) Å; 123.32(1)°]thereby forming $R_1^{(2)}(2)$ synthon, similar to that in 2. Protonation of pyridyl nitrogen N2 in 4,4'-BPY and existence ofSchiff base in keto form is substantiated by relaxed C14-N2-C18 bond angle value of 120.48(2) °and shorter C13-O4 and longer C7-N1bond distance of 1.280(2) and 1.310(1)Å, respectively. The molecular structure diagram of 3 is depicted in Figure 6.



Figure 6. Molecular structure diagram of $[(4,4'-BPY-2H)^{2+}(2-SA-oV-H)_2^{-},2H_2O]$ (**3**).

Sulfonated Schiff base anions assemble with help of the lattice water molecules into 1-Dtapes through O6-H6A···O7 [2.874(2) Å; 162.21(1)°], O6-H6B···O1 [2.819(1) Å; 161.97(2)°], O7-H7A···O3 [2.813(2) Å; 166.73(1)°] and O7-H7B...O2 [2.339(1) Å; 164.23(1)°] interactions. Similar to Hbonded tapes reported for organo phosphates and phosphonates,⁴⁰ the 1-D anionic tapes of 3 consist of alternate orthogonally displaced hexagonal $[R_4^4(4)]$ and octagonal $[R_6^{6}(6)]$ H-bonded rings in chair conformations, Figure ESI-20. The resultant 1-D tapes are bridged by bis-pyridinium ions into ionic 2-D reticular sheets (Figure ESI-21), which are further assembled by weak dispersive H···H [2.224(1) Å; C-H···H 130.09°] interactions into 3-D solid, Figure 7.H···H London dispersive forces have been identified recently and utilization of theses interaction to design or modulate crystal structures remains an incredible challenge.⁴¹As in3, the weak dispersive H...H interactions have also been reported by us to be the only supramolecular interaction associating 2-D sheets in an organic complex into 3-D solid.38

Thermal studies

Sulfonated Schiff bases 1a-3a exhibit high melting points, while their salts melt at relatively lower temperatures, Table ESI-2.The melting points of the products 1a-3a and 1-3are also substantiated by endothermic peaks in DTA curves, Figure ESI-22-27. TGA curves of 1a-3a indicate presence of solvent molecules and their high thermal stability upto 250 °C. It is pertinent to highlight that sodium salt of **1a**, reported earlier, exhibits higher thermal stability than 1a.²¹Molecular salt 1doesnot undergo early weight loss and remains stable till 230 °C, 2 and 3 undergoes early weight loss of nearly 8 and 5%, corresponding to loss of four and two water molecules in their crystal lattice, respectively. Organic salts 1 and 2 exhibit slightly lower thermal stability than corresponding sulfonatedSchiff bases while as 3 exhibits augmented stability than itsSchiff base former 3a. Comparative normalized TGA curves of 1a-3a and 1-3 are depicted in Figure 8, while the separate TGA/DTA curves of the products are depicted in Figure ESI-22-27.

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Figure 8.Comparative normalized TGA curves of sulfonated Schiff bases **1a-3a** and their organic salts **1-3**.

Optical studies

To understand the optical behavior and its response towards heat in the sulfonated anils 1a-3a and their organic slats 1-3, diffuse reflectance (DR-UV-Vis) studies have been carried out. 1a shows notable color change from light to intense yellow when heated at 85 °C while 2a and 3a do not undergo noteworthychange in colorwhen heated upto 150 °C. Comparative Kubelka-Munk (K-M) function of 1a-3a and their heated forms 1a'-3a' are depicted in Figure 9a and Figure ESI-28-30. Thermochromism in anil type molecules is a famous phenomenon and generally attributed to proton dynamics between enol and cis-keto forms. Sulfonated anils with lower packing coefficients have been reported to exhibit both opto- and thermochromism due to enol⇔cis-keto⇔trans-keto isomerism. However, as indicated by K-M plots the color transformation in 1a-3a cannot be accounted tosuch isomerization in these molecules. Tauc plots of 1a-3a indicate shift in the band gap on heating, Figure ESI-31-33. The sulfonated anils do not exhibit photochromism.

Organic salts **1-3**, obtained by reaction of the sulfonated anils with bipyridyl also respond to the heat as indicated by color changesin **1'-3'**. The K-M plots of **1-3** are depicted in Figure 9b and Figure ESI-34-36.Optical Images of 1a-3a and 1-3 are

provided in Chart ESI-1. 1and 2 behavealmost similar to that of 1a and 2a when heated at110°C, by undergoingcolor intensification which is also reflected in their diffuse refluctance spectrum. However, the molecular salt 3 responds strikingly to heat as indicated by color change from intense brown to brick red. The blue shift in the absorption of 3 on heating is also substantiated by K-Mfunctions. Interestingly, besides strong blue shift on heating, 3 does also undergo observable color change on grinding. The comperative K-M plots of 3, its grinded form 3G and heated form 3' are further discussed in next section. Band gapvalues in the molecular salts 1-3 are low compared to the sulfonated anils 1a-3a. Lowering of band gap on the salt formation may be attributed to strong π - π interactions, as observed in the crystal structures of 1-3. Moreover, band gap change in 1and 2 is mild and pronounced in 3, when the molecular salts are heated, indicating heat induced packing changes may be responsible for the the striking thermochromism in 3. Tauc plots of 1-3 are given as Figure ESI-37-39.

DISCUSSION

Our recent results about he development of molecular complexes based on sulfonate-pyridinium syntnon, ubiquitously in salt form, encouraged us to further utilize the supramolecular interaction for designing new materials. Anil derivatives of 4-and 2aminobenzenesulfonic acids 1a-3awere synthesised to explore their anticipated optical behaviour towards heat and light. However, **1a**only exhibits notable optical response to heat. Defining criteria to exhibit thermo- and photochromism in anils has been attributed to enol-cis-keto (prototropism) and cis-trans-keto (isomerism) transformations, respectively. Lack of thermochromism in 1a-3a may be attributed to protonation of the imine nitrogen by sulfonic hydrogen, as has been confirmed by previously reported crystal structure of **3a**,⁴² Figure 10, hence ruling out the enol-cis-keto prototropism.Diffuse reflectance studies of 1a-3a also rule out enol-keto transformation. And the absence of photochromism in these anils may be due to close packing or planer configuration or both.Failure to crystallize 1a and 2a and aim to modulate molecular packing in **1a-3a** prompted us to co-crystallize the sulfonated anils with bipyridyl.Interestingly, besides undergoingredshift on salt formation, the molecular salts 1 and 3 exhibit markable irreversible thermochromism as well.



Figure 9.(a) Comparative Kubelka-Munk plots of sulfonated Schiff bases 1a-3a and their heated forms 1a'-3a'.(b) Comparative Kubelka-Munk function of organic salts 1-3 and their heated forms 1'-3'.



Figure 10. Molecular structure of **3a** (CCDC No. VUQLIE), lattice water molecules are omitted for clarity.⁴²

Crystal formers in non-solvated molecular salt 1 associate via anticipated charge assisted sulfonate ... pyridinium interaction and aggregate into rare π -interlocked supramolecule. In 2 and 3 the water-arylsulfonate aggregates are bridged by bis-pyridinium ions throughmethoxy assisted hydroxylate ... pyridinium interactions into 3-D solids, leading to a significant observation: in presence of adjacent/ortho methoxy groups, phenolic hydroxalate ... pyridinium interaction dominates over otherwise robustsulfonate ... pyridinium synthon formation. As has been reported by usformation of sulfonate ... pyridinium synthon (or transfer of sulfonate hydrogen to pyridyl nitrogen)is ubiquitous interaction as observed in 5sulfosalicylic acid bearing carboxylic, hydroxyl as well as sulfonate groups, indicating preferential formation of sulfonate...pyridinium interaction over hydroxylate...pyridinium and carboxylate...pyridinium synthon.³⁶Structural analyses indicate the driving force for formation of hydroxalate ... pyridinium synthon in 2 and 3 possibly is the bifurcated hydrogen bonding of pyridinium hydrogen with phenoxy and ortho-methoxy group, Chart 3.

Chart 3. Depiction of possible interactions (I-IV) in functionalized arylsulfonates. **Yes** and **No** imply whether the interactions are formed or not.



Diffuse reflectance studies of the molecular salts 1-3 substantiate red shift in their absorption vis-a-vis1a-3a, observed in their optical images depicted in Chart ESI-1. The salts 1 and 2 nearly replicate the optical behaviour of the corresponding Schiff bases towards heat while as 3 exhibits striking blue shift in the absorption on heating. Based on he crystal structure studies and K-M functions thermochromism in these salts cannot be attributed to prototropism. The photochromism in 1-3 is not observed and may be attributed to close packing of the components in the lattice as indicated by V_{free} value of 100, 142 and 119 Å³ for 1-3, respectively, while as V_{free} requirement for execution of the phenomenon is >170 Å^{3,27} Infra red and thermo-gravametric investigations of 1a-3a and 1-3indicate loss of lattice water when heated till color change, however the phenomenon can't be attributed to solvent loss induced packing changes as it is observedeven in non-solvated salt 1. Moreover, to our interest intense brown 3 undergoes color change even on grinding (3G)and the resultant powder undergoes continuous color change on heating until it attains brick red complexion (3'). Optical pictures of the three forms:3, 3G and 3', are depicted in Figure 11c. Tauc plots of 1a-3a, Figure ESI-31-33, and 1-3, Figure ESI-37-39, confirm band gap increase in the products on heating. Particularly in case of 3, as the absorption is continuously blue-shifted with grinding and heating the band gap increases on grinding in **3G** and heating in **3'** to 1.76 and 1.88 eV, respectively, compared to 1.70 eV in **3**, strongly indicating change in the molecular packing in the solid. Hence ruling out the prototropism and lattice solvent loss as plausible explanation for thermochromism, the phenomenon plausibly originates due to change in crystal packing of the products. K.M. functions and Tauc plots of **3**, **3G** and **3'** are depicted in Figure 11a and 11b.



Figure 11. Kubelka-Munk and Tau plots of 3, 3G and 3' (a and b) and optical images of 3, 3G and 3' (c).

CONCLUSION

Sulfonated anils 1a-3a have been synthesized in good yield byrefluxing the mechanically grinded paste of reactants in aqueous methanol and were subsequently converted to organic slats 1a-3a by reaction with 4,4'-BPY. 1a-3a and 1-3 do not exhibit anticipated enol↔cis-keto↔trans-keto isomerism induced by heat and light as indicated by their Kubelka-Munk functions and supported by previously reported crystal structure of 3a. However, the products respond to heat but not to light. Organic salts 1-3 exhibit red shift on formation from 1a-3a indicated by their colors and substantiated by diffuse reflectance studies. Faint but notable thermochromism observed in 1a and 2a is replicated in 1 and 2, while unlike 3a, 3 exhibits remarkable thermochromism. Tauc plots of 1a-3a and 1-3 and their heated forms 1a'-3a' and 1'-3', respectively, together with 3G (grinded form of 3) indicate change in crystal packing causes the thermochromism. Currently we are generating more data to investigate the phenomenon in greater detail.

Crystallographic studies of the organic salts 1-3 reveal manifestation of anticipated direct sulfonate...pyridinium in 1, while as crystal formers in2and3assemble through hydroxylate...pyridinium synthon. Organic salt 1 aggregates as rare π interlocked solid while rare octameric water cluster W₈ in 2 and weak H…H London dispersive forces in 3 lead to formation of 3dimensional ionic solids. Unlike the ubiquitous formation of sulfonate...pyridinium synthon even in presence of carboxylate and hydroxyl groups, as reported earlier, preference for the formation of hydroxylate...pyridinium synthon in 2 and 3 may be attributed to the presence of adjacent methoxy group which strengths the $R_1^2(2)$ bifurcated interaction.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

FT-IR of **1a-3a** and **1-3**.¹Hspectra of **1a-3a** and **1-3**.Structure and packing diagrams of **1a-3a** and **1-3**.TGA-DTA thermograms of **1a-3a** and **1-3**. Diffuse reflectanceUV-Vis spectra, K-M plots and tauc plots of pristine components and **1a-3a**

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CCDC 1981821-1981823contain the supplementary crystal-5 lographic data for this paper. These data can be obtained free 6 of charge via www.ccdc.cam.ac.uk/data_request/cif, or by 7 emailing data_request@ccdc.cam.ac.uk, or by contacting The 8 Cambridge Crystallographic Data Centre, 12 Union Road, 9 Cambridge CB2 1EZ, UK; fax: +44 1223 336033. 10 AUTHOR INFORMATION 11 12 **Corresponding Author** 13

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and 1-3.Optical images of crystals1a-3a and 1-3 and their

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heated forms 1a'-3a' and 1'-3'.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

4-ABSA-H, 4-aminobenzene sulfonic acid; 2-ABSA-H, 2aminobenzene sulfonic acid; 4,4'-BPY, 4,4'-bipyridyl; K-M function, Kubelka-Munk function.

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Irreversible Thermochromism in Organic Salts of Sulfonated Anils

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TOC Graphic



Synopsis

Sulfonate...pyridinium synthon based molecular salts 1-3 obtained from sulfonated anils 1a-3a have been reported to exhibit trivial to striking irreversible thermochromism. Optical studies vis-à-vis crystal-lographic investigations rule out the conventional and general mechanism *i.e.* enol-cis-keto isomerization, and instead indicate packing changes to be the cause of irreversible thermochromism.