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Supporting Information

Supramolecular Hydrogel Derived from a Simple Organic Salt Capable of Proton Conduction

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Experimental Section

Materials, Methods and Synthesis

Materials

All chemicals were commercially available and were used without any further purification. All solvents were of laboratory reagent (LR) grade and were used without any distillation.

Methods

FTIR spectra were recorded by a Perkin Elmer FTIR spectrometer (spectrometer two) instrument. Both ¹H and ¹³C NMR spectra were recorded with 400 and 500 MHz spectrometers (Bruker Ultrashield Plus-500). TEM images were captured with a JEOL JEM 2100F (for FEG-TEM) and JEOL JEM 2010/11 (for High Resolution Transmission Electron Microscopy (HR-TEM)) instrument using 300 mesh carbon coated copper TEM grids. Rheology studies were carried out with the Anton Paar Modular Compact Rheometer MCR 102.

Synthesis of Salts

The salts were synthesized by reacting the acids (i.e. benzene sulfonic acid and naphthalene-2-sulfonic acid) to a set of primary amines (benzylamine, phenethylamine, 1-naphthylmethylamineand 1-(1-naphthyl) ethylamine) in 1:1 molar ratio in MeOH in presence of dichloromethane (DCM). In a typical experiment, calculated amount of the reactants were taken in a beaker (25 ml). MeOH (~8 ml) containing DCM (~2 ml) was added to the reaction mixture followed by sonication (10-15 minutes) to make a homogeneous solution. The beaker was then kept overnight in open air at room temperature to obtain the dried salt. The salt so obtained was thoroughly washed with pet ether.

Physicochemical Data

BSBA: Creamy White Solid; ¹H NMR (400 MHz, DMSO-D₆) δ 8.15 (s, 3H), 7.62 – 7.32 (m, 10H), 4.06-4.01 ppm (q, *J* = 5.8 Hz, 2H). ¹³C NMR (100 MHz, DMSO-D₆) δ 148.2,148.1, 137.2, 128.8, 128.6, 128.6, 128.4, 128.4, 127.6, 127.6,126.7, 125.4, 33.0 ppm(Figure S2).

BSPh: Brownish White Solid; ¹H NMR (400 MHz, DMSO-D₆) δ 7.79 – 7.24 (m, 13H), 3.06 – 3.02 (m, 2H), 2.87 – 2.83 ppm (m, 2H). ¹³C NMR (100 MHz, DMSO-D₆) δ 135.4, 133.3, 129.6,128.8, 128.7, 128.3, 127.6, 126.8, 126.1, 125.4, 125.3, 122.7, 45.5, 21.0 ppm. (Figure S3).

BSNm: Light Brown Solid; ¹H NMR (400 MHz, DMSO-D₆) δ 8.16-8.14 (d, J = 7.9 Hz, 2H), 8.02-7.98 (t, J = 9.2 Hz, 2H), 7.67 – 7.54 (m, 6H), 7.32-7.31 (m, 2H), 4.54 ppm (s, 2H). ¹³C NMR (100 MHz, DMSO-D₆) δ 148.3, 133.2, 130.6, 130.0, 130.0, 129.1, 128.6,128.4, 128.3, 127.6, 127.2, 126.7, 126.2, 125.4, 125.3, 123.4ppm.(Figure S4).

BSNe: Light Brown Solid; ¹H NMR (400 MHz, DMSO-D₆) δ 8.35 (s, 1H), 8.19-8.17 (d, J = 8.2 Hz, 1H), 8.02-7.96 (m, 2H), 7.71 – 7.58 (m, 6H), 7.32-7.30 (m, 2H), 5.32-5.27 (q, J = 6.6 Hz, 1H), 1.61-1.60 (d, J = 6.7 Hz, 3H) ppm.¹³C NMR (100 MHz, DMSO-D₆) δ 148.2, 135.3, 133.3, 129.7, 128.8, 128.7, 128.4, 128.3, 127.6, 127.5, 126.8,126.2, 125.4, 125.4, 122.8, 122.7, 45.6, 20.9ppm. (Figure S5).

N2SBA: Creamy White Solid; ¹H NMR (500 MHz, DMSO-D₆) δ 8.14 (s, 1H), 7.98 – 7.88 (m, 3H), 7.87-7.85 (d, *J* = 8.5 Hz, 1H), 7.72-7.70 (m, 1H), 7.54 – 6.98 (m, 9H), 4.06-4.02 (q, *J* = 5.8 Hz, 2H) ppm.¹³C NMR (100 MHz, DMSO-D₆) δ 145.5, 133.8, 132.8, 132.1, 128.8, 128.6, 128.4, 127.4, 127.2, 126.5, 126.3, 124.1, 124.0, 123.9, 123.8, 42.4 ppm.(Figure S6).

N2SPh: Creamy White Solid; ¹H NMR (500 MHz, DMSO-D₆) δ 8.16 (s, 1H), 7.98 – 7.72 (m, 7H), 7.54 – 7.51 (m, 2H), 7.34-7.24 (m, 5H), 3.06 – 3.03 (m, 2H), 2.87 – 2.84 ppm (m, 2H).¹³C NMR (100 MHz, DMSO-D₆) δ 145.5, 145.2, 137.2, 132.8, 132.1, 128.6, 128.4, 127.4, 127.3, 126.7, 126.5, 126.3, 124.1, 124.0, 123.9, 123.8, 33.0, 33.0 ppm. (Figure S7).

N2SNm: Light Brown Solid;¹H NMR (500 MHz, DMSO-D₆) δ 8.15-8.13 (d, J = 10.0 Hz, 2H), 8.01 – 7.85 (m, 6H), 7.73-7.71 (m, 1H), 7.65 – 7.51 (m, 8H), 4.51 ppm (s, 2H).¹³C NMR (100 MHz, DMSO-D₆) δ 145.5, 133.2, 132.7, 132.1, 130.6, 129.8, 129.1, 128.6, 128.4, 127.4, 127.2, 126.7, 126.4, 126.3, 126.2, 125.3, 124.0, 124.0, 123.9, 123.3 ppm. (Figure S8).

N2SNe: Brown Solid; ¹H NMR (500 MHz, DMSO-D₆) δ 8.19 – 8.14 (m, 2H), 8.01 – 7.70 (m, 7H), 7.69 – 7.51 (m, 8H), 5.26-5.22 (q, *J* = 6.6 Hz, 1H), 1.59-1.57 ppm (d, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, DMSO-D₆) δ 145.7, 136.6, 133.3, 132.7, 132.1, 129.7, 128.8, 128.4, 127.4, 127.2, 126.6, 126.3, 126.2, 126.0, 125.4, 124.0, 122.7, 122.6, 45.6, 21.6 ppm. (Figure S9).

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Figure S1: IR data comparison between the parent amines (Benzylamine, Phenethylamine, Naphthylmethylamine and 1-(1-naphthyl) ethylamine and the salts (**BSBA, BSPh, BSNm, BSNe, N2SBA, N2SPh, N2SNm and N2SNe**) proving the formation of salts.



Figure S2: ¹H NMR and ¹³C NMR spectra of BSBA in DMSO-d₆.



Figure S3: ¹H NMR and ¹³C NMR spectra of BSPh in DMSO-d₆.



Figure S4: ¹H NMR and ¹³C NMR spectra of **BSNm** in DMSO-d₆.



Figure S5: ¹H NMR and ¹³C NMR spectra of BSNe in DMSO-d₆.



Figure S6: ¹H NMR and ¹³C NMR spectra of N2SBA in DMSO-d₆.



Figure S7: ¹H NMR and ¹³C NMR spectra of N2SPh in DMSO-d₆.



Figure S8: ¹H NMR and ¹³C NMR spectra of N2SNm in DMSO-d₆.





Figure S9: ¹H NMR and ¹³C NMR spectra of N2SNe in DMSO-d₆.

X-ray Diffraction

X-ray quality single crystals of the salts (BSBA, BSNm, BSNe, N2SBA, N2SPh, N2SNm) were grown at room temperature by slow evaporation technique from various solvent systems (Table S2). Single crystal X-ray diffraction data were collected using various diffractometer (Bruker APEX II, CCD area detector, Mo K_{α}, $\lambda = 0.7107$ Å, Bruker APEX III D8 Venture, PHOTON II detector, Cu K_{α}, $\lambda = 1.54184$ Å). Data collection, data reduction, structure solution and refinement were carried out using the software packages of the corresponding diffractometer. All the structures were solved by direct methods and refined in a routine manner. Hydrogen atoms were geometrically fixed. In the crystal structure of the salt BSBA, there wasdisorderin both the anionic and cationic moieties; the site occupancy factors (SOFs) of the disordered moieties were refined to 0.48 and 0.52 using second variable (FVAR) in Shelxl. All the non-hydrogen atoms were treated anisotropically. CCDC-numbers 1872174, 1872170, 1872169, 1872173, 1872172, 1872171 contain the crystallographic data for BSBA, BSNm, BSNe, N2SBA, N2SPh, N2SNm respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Powder X-ray diffraction data collection

The RigakuSmartlab (Source 40 KV, 110 mA) equipped with 1D detector (Hypix-3000) (Cu K_{α 1} radiation, $\lambda = 1.5406$ Å, scan speed= 5⁰/min, step size = 0.01⁰) was used to collect powder XRD data.

Referenc e Code	Space Group	Types of Synthon	Structure
		0D	
1. UYAZIF	P2/c	0D_(12)	¹ HN-CPF3 50j

Table S1: Sulfonate salt synthon table

2. DICGIG	C2/c	0D (12)	Ph3CNH3
			0
			soj
3. DICGOM	I-4c2	0D_(12)	Ph ₃ CNH ₃ ⁺
			PhSO3
4. DICGUS	P21/a	0D (12)	
	1		
			H ₃ CSO ₃

5. JAKLEP	P4/nnc	0D_(12)	'H ₁ NCPh3
			50)
	1	1D	
6. QEPXEP	P2 ₁	1D CYLINDRICAL	*uuu
			Ph
7. YONHUF	C2	1D CYLINDRICAL	
			s rhn
			NHŠ
			~
			0 pTos
8. YUZWUM	C2	1D CYLINDRICAL	
			SO3
			H3C NH3
9. RITBUT	P2 ₁ /n	ID CYLINDRICAL	*H ₃ N.OMe
			pĭosO'
			OMe

10. DUTKAF	C2/c	1D CYLINDRICAL	NH [*]
			_+
			Et
			0 pTos
11. LUQFEJ	P2 ₁ 2 ₁ 2 ₁	1D (8)	
			Et
			*H3N N
			\rangle
			EL
			FaC
12. PIDLUM	P2 ₁	1D_(10,4)	PhCHs
			HJC HJC
13. VEQDOK	P2 ₁	1D_(10,4)	CH3 055
			iPr COOIBu
			сооме
			NH ¹ 3 .0 ³ 8 0

14. XIYZEL	P2 ₁ 2 ₁ 2 ₁	1D_(10,4)	\square
			Hisc CH3 pTol
			NH [‡] SO [‡]
15. YUJJEU	P2 ₁ /c	1D (10)	
	1	_(')	
			$F \langle \rangle$
			"O ₃ SCF ₃
16. GAXTOQ	P2 ₁	1D_(12)	SO3
			NH3
			H ₃ C Ph
			Dh
17. KALJIT	P-1	1D_(12)	CH₂Ph
			pTol-SO3
			NH ₃
18. RUCGAY	P1	1D_(12)	
			·038
			NH3
			H ₃ C Ph

19. ULAZUD	P-1	1D_(12,8,4);(12)	NH3
			0 pTos
20. UPALAZ	P2 ₁ /m	1D_(12)	so;
			NH3
21. XARVIX	P-1	1D_(12)	*H,N
			Hac
22 XARVIII	P-1	1D (12)	CH3 O pTcs
22. MIK V 05	1-1	10_(12)	
			*H ₂ N
			НаС ОСТАНИИ СТАТИ
			CHs
22 VOITID	D 1	1D (12)	0:pTos
23. AUJ 11D	1-1	112_(12)	
			Hac
			HBU CH3

24 XOZTOW	D1	1D (12)	
24. A0210W	F1	I D_ (12)	
			.032
			NH [*] 3
			H ₃ C Ph
25. XOZTUC	P-1	1D_(12)	
			NH3
			H ₉ C Ph
26. YAGNEB	P2 ₁ /n	1D_(12)	F
			Oi
27. UKEVUD	P-1	1D_(12)	'HyN
28. YAGNIF	P2 ₁ /c	1D_(12)	
			0 <u> </u>
			NHS

29. PAVKOO	P-1	1D_(12)	*H ₃ NEt		
			0 . 		
30. HOLGIZ	P2 ₁ /n	1D_(12)			
			El ^r CH ₃ O ⁱ ——pTos		
31. YECDIW	P2 ₁ /c	1D_12	Pr CH ₃		
			50j		
			H _N N		
32. MIZVOI	P-1	1D_(12,8)			
33. ABACOX	P2 ₁ /n	1D_(12,8)	CH ₃		
			CH ₃		
			NH ₃ *		
			OpTos		
	2D				

34. YUOCIX	P2 ₁	2D (16)	0	—pTos
	-			
			+	
25 VOIOOE	D 0	$\Delta \mathbf{D} (14 4)$	H ₃ N	pTol
35. XUJQUE	$P_{na}Z_1$	2D_(14,4)]
	D2 /	3D (1()	NH ₃	0
36. CEHBAU	$P2_1/n$	2D_(16)	O pTos	
				NO ₂
			/	
				Ý
				NH [‡]
				INF13

37. PEXLUZ	P2 ₁ 2 ₁ 2 ₁	2D_(18)	×H43
			HJC CH3
			Ph
			ious o
38. QOGRIN	P2 ₁ /n	2D (18)	
			pTolSO'3
			NC CN
39. OBUYER	P-1	2D (12,4)	NH3
			 CI
			O ⁻ pTos
40. VUCBAY	P-1	2D (12,4)	
			Br NH3
			pios
41. XUHDAG	P2 ₁ /c	2D_(24,12)	
			soj
			*H ₃ NCH ₂ Ph

42. YEDRIM	Phea	2D (24.12)	CH3
	<i>b</i> cu		0
			$\left[\bigcirc \right]$
			*HJNCH3
			.018
			NO2
43. AZUSET	P-1	2D_(36,16,12)	NHS
			MeQ
			\downarrow
			° o'
			Br
		AD (12.9)	
44. HAVYEL	$P_{2_1} Z_1 Z_1$	2D (12,8)	H₃C
			NH ₃
			Fic
			⁻ O ₃ SCF ₃
45. HIBFII	$P2_1/n$	2D (6.6.6)	PhNH3
	1	x-y-y-y	
			F ₈ C ₈
46. SIQBEB	P2 ₁ /c	2D (10,6,6)	SO3
			NO ₂



Figure S10: Supramolecular synthons obtained in the CSD search with REFCODE.

Crystal structure of the salt BSBA

The single crystal of BSBA subjected to SXRD belonged to the monoclinic crystal system (centrosymmetric monoclinic space group C2/c). The asymmetric unit comprised one ion pair and one solvate water molecule. The phenyl ring of the benzyl ammonium cation was disordered. On the other hand, the whole anionic species was also disordered, both over two positions (refined site occupancy factors (SOF) = 0.48 and 0.52). The primary supramolecular synthon present in the crystal structure was 1D cylindrical sustained by N-H^{...}O interactions [N^{...}O = 2.864(2)-2.974(2) Å; \angle N-H^{...}O = 141.6-169.5°], which were further bridged by O-H...O

hydrogen bonding [O...O = 2.806 Å] involving the solvate water molecules and sulfonate O atoms resulting in an overall 2D hydrogen bonded networks (HBNs) that propagated along the b-axis and packed in parallel fashion along the *a*-axis stabilized by dispersion forces (Figure S11).



Fig S11: Crystal structure illustration of the salt BSBA.

Crystal structure of the salt BSNe

SXRD data revealed that the salt BSNe expectedly crystallized in the centrosymmetric space group (triclinic, $p\bar{i}$) as the amine used in the reaction was racemic. Unlike BSBA, the crystal structure of BSNe was devoid of any disorder or lattice occluded solvent. The asymmetric unit contained the ion pairs. The supramolecular synthon present in the crystal structure was 1D cylindrical synthon generated due to N-H^{...}O hydrogen bonding [N^{...}O = 2.805(4)-2.873(4) Å; \angle N-H^{...}O = 144.1-163.7°], propagated along the *a*-axis; such 1D HBNs were packed in parallel fashion sustained by dispersion forces (Figure S12).



Fig S12: Crystal structure illustration of the salt BSNe.

Crystal structure of the salt BSNm

The single crystal of BSNm displayed the centrosymmetric triclinic space group $P_{\overline{1}}$. The asymmetric unit contained one ion pair. 1D supramolecular synthon having alternating 12 and 8 membered hydrogen bonded rings [1D(12,8)] sustained by N-H^{...}O interactions [N^{...}O = 2.832(5)-2.8886(6) Å; \angle N-H^{...}O = 154.7-168.3°] involving the ion pairs was present in the crystal structure. The 1D HBNs were further packed in parallel fashion propagating along the *a*-axis stabilized by dispersion forces (Figure S13).



Fig S13: Crystal structure illustration of the salt BSNm.

Crystal structure of the salt N2SBA

The asymmetric unit of the single crystal of N2SBA belonging to the centrosymmetric monoclinic space group $P2_1/c$ contained one ion pair. Careful analysis revealed that the supramolecular synthon present in the crystal structure was 2D HBN containing 20, 8 and 4 member hydrogen bonded rings or 2D(20,8,4) sustained by N-H^{...}O interactions [N^{...}O = 2.858(4)-3.021(4) Å; \angle N-H^{...}O = 144.9-162.7°]. The 2D HBNs were propagated parallel to the b-c plane and packed along the a-axis stabilized by dispersion forces (Figure S14).



Fig S14: Crystal structure illustration of the salt N2SBA.

Crystal structure of the salt N2SNm

The single crystal of N2SNmanalyzed by SXRD belonged to the centrosymmetric monoclinic system (space group $P2_1/c$). The asymmetric unit comprised one ion pair. The supramolecular synthon present in the crystal structure was 2D HBN characterized by various hydrogen bonded rings (12, 8, 6 and 4 member rings) or 2D(12,8,6,4) sustained by N-H^{...}O interactions [N^{...}O = 2.838(4)-3.169(4) Å; \angle N-H^{...}O = 120.3--159.7°]. The 2D HBN was parallel to the b-c plane and packed in parallel fashion along the a-axis stabilized by dispersion forces (Figure S15).



Fig S15: Crystal structure illustration of the salt N2SNm.

Crystal structure of the salt N2SPh

The single crystal of N2SPh mounted for SXRD studies belonged to the centrosymmetric triclinic space group *P*ī. The asymmetric unit contained one ion pair. The supramolecular synthon observed in the crystal structure was 1D(12) HBN sustained by N-H^{...}O interactions $[N^{...}O = 2.786(3)-2.962(2) \text{ Å}; \angle N-H...O = 153.1-166.1^{\circ}]$ propagating along the b-axis. The 1D hydrogen bonded chains were packed in parallel fashion along the b-c plane stabilized by dispersion forces (Figure S16).



Fig S16: Crystal structure illustration of the salt N2SPh.

Table S2: Crystal data

Identification Code	BSBA	BSNm	BSNe	N2SBA	N2SPh	N2SNm
Crystallizing solvent	MeOH+DCM	MeOH+DCM	MeOH+DCM	Water	MeOH	MeOH+DCM
CCDC No.	1872174	1872170	1872169	1872173	1872172	1872171
Empirical Formula	C ₁₃ H ₁₆ NO _{3.5} S	C ₁₇ H ₁₇ NO ₃ S	$C_{18}H_{19}NO_{3}S$	$C_{17}H_{17}NO_3S$	$C_{18}H_{19}NO_3S$	$C_{21}H_{19}NO_3S$
Formula Weight	274.33	315.37	329.40	315.37	329.40	365.43
Temperature/K	296.15	296.15	116.63	296.15	296.15	296.15
Crystal System	monoclinic	triclinic	Triclinic	monoclinic	triclinic	monoclinic
Crystal Size/mm ³	$0.36 \times 0.32 \times 0.28$	0.24 imes 0.18 imes 0.15	0.24 imes 0.2 imes 0.18	$0.29 \times 0.23 \times 0.18$	0.28 imes 0.23 imes 0.18	$0.34 \times 0.3 \times 0.26$
Space Group	C2/c	P-1	P-1	P21/c	P-1	P21/c
a/Å	31.768(8)	5.432(8)	5.4468(3)	16.352(19)	5.8765(17)	18.261(15)
b/Å	5.5762(12)	9.545(14)	9.8135(6)	10.823(12)	7.649(2)	7.799(6)
c/Å	15.750(3)	15.32(2)	15.2598(10)	9.736(11)	18.388(5)	12.919(11)
$\alpha/^0$	90	96.31(2)	103.033(2)	90	92.938(4)	90
β/ ⁰	108.619(3)	93.878(19)	93.291(2)	105.376(13)	94.963(4)	107.200(11)
γ^{0}	90	97.640(19)	97.938(3)	90	93.182(4)	90
Volume/ Å ³	2644.0(10)	779.6(19)	783.72(8)	1661(3)	820.8(4)	1758(3)
Density ($\rho_{colc}g/cm^3$)	1.378	1.343	1.396	1.261	1.333	1.381
u/mm ⁻¹	0.250	0.219	0.221	0.206	0.211	0.205
Ż	8	2	2	4	2	4
F(000)	1160.0	332.0	348.0	664.0	348.0	768.0
Radiation	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	2.706 to 52.97	2.684 to 46.142	5.504 to 56.434	2.582 to 57.724	2.226 to 55.96	2.334 to 49.722
Index ranges	$\begin{array}{c} -39 \leq h \leq 39, \ -6 \leq k \leq 6, \\ -19 \leq l \leq 19 \end{array}$	$-5 \le h \le 5, -10 \le k \le 10, -16 \le l \le 16$	$-6 \le h \le 7, -13 \le k \le 11, -20 \le 1 \le 20$	$\begin{array}{c} -21 \leq h \leq 22, -14 \leq k \leq \\ 14, -13 \leq l \leq 12 \end{array}$	$-7 \le h \le 7, -9 \le k \le 10,$ $-23 \le 1 \le 23$	$\begin{array}{c} -21 \leq h \leq 21, \ -9 \leq k \leq \\ 9, \ -15 \leq l \leq 15 \end{array}$
Reflections collected	33600	13527	9206	21873	22704	17863
Independent reflections	2713 [$R_{int} = 0.1014$, $R_{sigma} = 0.0452$]	2155 [$R_{int} = 0.0562$, $R_{sigma} = 0.0384$]	$3762 [R_{int} = 0.0554, R_{sigma} = 0.0839]$	$4088 [R_{int} = 0.0312, R_{sigma} = 0.0227]$	$3704 [R_{int} = 0.0298, R_{sigma} = 0.0226]$	$3015 [R_{int} = 0.0514, R_{sigma} = 0.0380]$
Data/restraints/paramet ers	2713/1/289	2155/0/200	3762/0/210	4088/0/200	3704/0/209	3015/0/236
Goodness of fit on F^2	1.089	1.056	1.060	1.053	1.110	1.096
Final R indexes[I>=2σ(I)]	$R_1 = 0.0487, wR_2 = 0.1249$	$R_1 = 0.0413, wR_2 = 0.0932$	$R_1 = 0.0682, wR_2 = 0.1594$	$R_1 = 0.0399, wR_2 = 0.1194$	$R_1 = 0.0446, wR_2 = 0.1197$	$R_1 = 0.0443, wR_2 = 0.1106$
Final R indexes [all data]	$\begin{array}{c} R_1 = 0.1169, \ wR_2 = \\ 0.1761 \end{array}$	$\begin{array}{c} R_1 = 0.0688, \ wR_2 = \\ 0.1085 \end{array}$	$\begin{array}{c} R_1 = 0.1062, \ wR_2 = \\ 0.1800 \end{array}$	$\begin{array}{c} R_1 = 0.0658, \ wR_2 = \\ 0.1423 \end{array}$	$\begin{array}{c} R_1 = 0.0643, \ wR_2 = \\ 0.1406 \end{array}$	$\begin{array}{c} R_1 = 0.0731, \ wR_2 = \\ 0.1357 \end{array}$
Largest diff. peak/hole/e Å ⁻³	0.26/-0.32	0.19/-0.28	0.72/-0.78	0.26/-0.24	0.33/-0.35	0.47/-0.40



Figure S17: ORTEP Plot of BSBA (50% probability).

Table S3: Hydrogen Bonds for BSBA								
D H A	d(D-H)/Å	d(HA)/Å	d(DA)/Å	<d-h-a th="" °<=""></d-h-a>				
N1 H1AO3A ¹	0.890	2.165	2.834 (2)	131.41				
N1-H1A $O3B^2$	0.890	2.232	2.974 (2)	140.69				
N1-H1BO1B ³	0.890	2.073	2.872 (2)	148.96				
N1 H1BO1A ⁴	0.890	2.076	2.904 (2)	154.32				
N1-H1CO2B	0.890	1.985	2.863 (2)	168.59				
N1-H1C O2A	0.890	2.105	2.976 (2)	165.71				
O4-H4C O1A	0.850	2.160	2.980 (2)	162.00				
O4-H4D O1A	0.850	2.180	2.980 (2)	156.00				
O4-H4D O2A	0.850	2.540	3.200 (2)	135.00				

Table S3: Hydrogen Bonding Parameter table of BSBA

¹[x, y+1, z], ²[x, y+1, z], ³[-x+1, -y+2, -z+1], ⁴[-x+1, -y+2, -z+1].



Figure S18: ORTEP Plot of BSNm (50% probability).

Table S4: Hydrogen Bonds for BSNm									
D H A $d(D-H)/Å$ $d(H.A)/Å$ $d(D.A)/Å$ $$									
N1-H1AO3 ¹	0.890	0.890 1.999 2.862 (163.14					
N1-H1B O2	0.890	1.960	2.832 (5)	166.24					
N1-H1CO3 ² 0.890 2.056 2.886 (6) 154.68									
1 2									

 Table S4: Hydrogen Bonding Parameter table of BSNm

¹[x+1, y, z], ²[-x+1, -y, -z+1].



Figure S19: ORTEP Plot of BSNe (50% probability).

Table S5: Hydrogen Bonds for BSNe									
D H A $d(D-H)/Å$ $d(H.A)/Å$ $d(D.A)/Å$ $< D-H-A/°$									
N1-H1A	O2	0.910	1.920	2.805 (4)	163.62				
N1-H1B	$O1^1$	0.910	2.086	2.873 (4)	144.14				
N1-H1CO1 ² 0.910 2.002 2.858 (4) 156.20									

¹[-x+1, -y+1, -z+1], ²[x+1, y, z].



Figure S20: ORTEP Plot of N2SBA (50% probability).

Table S6: Hydrogen Bonds for N2SBA									
D H A $d(D-H)/Å$ $d(HA)/Å$ $d(DA)/Å$ $< D-H-A/^{\circ}$									
N1-H1A	O3 ¹	0.890	2.076	2.886 (4)	150.91				
N1-H1B	$O2^2$	0.890	2.382	3.152 (4)	144.90				
N1-H1B	O3 ³	0.890	2.206	3.021 (4)	152.06				
N1-H1C	CO2	0.890	1.996	2.858 (4)	162.76				

Table S6: Hydrogen Bonding Parameter table of N2SBA

¹[-x+1, y+1/2, -z+1/2],²[x, -y+3/2, z+1/2],³[x, -y+3/2, z+1/2].



Figure S21: ORTEP Plot of N2SPh (50% probability).

Table S7: Hydrogen Bonds for N2SPh									
D	D H A d(D-H)/Å d(HA)/Å d(DA)/Å								
N1	H1AO1 ¹	0.890	2.545	3.040 (2)	115.82				
N1	H1AO1 ²	0.890	2.102	2.962 (2)	162.10				
N1	H1B O3	0.890	1.914	2.786 (3)	166.09				
N1	H1C $O2^3$	0.890	2.501	3.036 (3)	119.21				
N	1 $H1CO2^4$	0.890	2.067	2.892 (2)	153.87				
11 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1									

 Table S7: Hydrogen Bonding Parameter table of N2SPh

¹[x-1, y, z], ²[-x+1, -y+1, -z+1], ³[x-1, y, z], ⁴[-x+1, -y, -z+1].



Figure S22: ORTEP Plot of N2SNm (50% probability).

Table S8: Hydrogen Bonds for N2SNm								
D	Η	<d-h-a th="" °<=""></d-h-a>						
N1	H1A	$O2^1$	0.890	2.626	3.169 (4)	120.3		
N1	H1A	$O3^2$	0.890	2.286	3.123 (4)	156.52		
N1	H1B	04	0.890	2.006	2.838 (4)	155.03		
N1	H1B	$O4^3$	0.890	2.506	3.088 (4)	123.46		
N1	H1C	$O2^4$	0.890	2.551	2.998 (4)	111.86		
N1	H1C	O3 ⁵	0.890	2.098	2.949 (4)	159.71		

Table S8: Hydrogen Bonding Parameter table of N2SNm

¹[-x+1, -y+2, -z+1], ²[x, -y+3/2, z+1/2], ³[-x+1, -y+2, -z+1], ⁴[x, -y+3/2, z+1/2], ⁵[-x+1, -y+1, -z+1].

Gelation and T_{gel} experiments

The gels were prepared by dissolving the gelator salts in pure water (hydrogel) or in the corresponding organic solvent (organogel) by heating the solution to make it completely soluble and then keeping it at room temperature. The gel formation was confirmed by tube-inversion method wherein the gel was found to withstand its own weight against gravity. Minimum gelator concentration (MGC) was determined by gradually diluting a 4 wt % w/v gel till gel formation was ceased. Dropping ball method was employed to determine T_{gel} (gel to sol dissociation temperature). In a typical experiment, a glass ball (weighing 216.4 mg) was carefully placed on a gel bed (1 ml, at MGC) prepared in a test tube (internal diameter -11mm) and immersed in an oil

bath fitted with a thermometer. The oil bath was gradually heated and the temperature at which the ball touched the bottom of the test tube was recorded as the T_{gel} .

Solvent	BSBA	BSPh	BSNm	BSNe	N2SBA	N2SPh	N2SNm	N2SNe
H ₂ O	S	S	S	S	S (C)	GP	^{1.33} CG ₅₂	GP
MS	Р	Р	GP	GP	GP	GP	Weak gel	GP
PhNO ₂	Р	Р	GP	GP	GP	GP	GP	Р
PhCl	GP	Р	GP	GP	Р	Р	Р	GP
PhBr	Р	Р	GP	GP	GP	GP	GP	GP
DMSO	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S
DMA	S	S	S	S	S	S	S	S
Toluene	Р	Р	Р	Р	INS	Р	Р	Р
o-Xylene	Р	Р	Р	Р	INS	Р	Р	Р
m-Xylene	Р	Р	Р	Р	INS	Р	Р	Р
p-Xylene	Р	Р	Р	Р	INS	Р	Р	Р
Mesitylene	Р	Р	Р	Р	INS	Р	Р	Р
Dioxane	S	S	S	S	S	S	S	S
EG	S	S	S	S	S	S	S	S
MGC GTgel - Minimum Gelling Concentration Gel _{Gel dissociation temperature} , S-Soluble, INS-Insoluble, GP-Gelatinous precipitate, P-Precipitate, C - Crystal								

Table S9: Gelation Table

Electron Microscopy

A small amount of freshly prepared gel (at MGC) was scooped and carefully smeared on a carbon-coated Cu grids (300 mesh) for TEM and the images were recorded at an accelerating voltage of 200 kV without staining.



Figure S23a: FEG-TEM Image of the MS gel of N2SNm.



Figure S23b: FEG-TEM Image of the hydrogel (1.33 wt%) along with the SAED pattern and EDX analysis.

Atomic force Microscopy (AFM)

The hydrogel (1.33 wt%) was carefully smeared on a clean surface of a mica foil (1.0 x 1.0cm) attached to a AFM stub and dried overnight at room temperature. The AFM images were recorded in tapping-mode in an OXFORD instrument model no MFP-3D. The image and height profile analysis were carried out using WSxM 5.0 Develop software.

Confocal Microscopy

The hydrogel (N2SNm salt_1.33 wt %) prepared afresh was instantly smeared over the slide surface of the 35 mm confocal dish and the images were recorded by using a 40X objective under a CARL-ZEISS inverted laser scanning confocal microscope (LSM 880).

Rheology studies

A small amount of freshly prepared gel was scooped and placed on the stationary plate of the rheometer and parallel plate geometry (diameter - 25 mm, 1 mm gap) was employed to carry out the rheological experiments.



Figure S24: Amplitude Sweep Experiments of the Hydrogels of N2SNm salt.

Conducting Behaviour as measured in Direct Current :

I-V measurements were carried out using Keithley 2450 source meter instrument. Siglent SDM 3055 digital multimeter was used to carry out temperature dependent resistance data.



Figure S25: Gel capable of lit a light with Cartoon diagram of the conducting experiment setup.

I-V measurement:

1.33 wt% gel was prepared in a 15 ml screw cap vial containing 40 mg of salt in 3 ml of mili-Q water by dissolving with heating followed by cooling to room temperature. A pair of Cu-plate electrode with same width and height (width 1cm, dipped height 1cm) was dipped into the gel in such a way so that they were 1.5 cm apart. Then biasing was applied between those two Cu-electrodes. I-V measurements were carried within the voltage range -1.2V to +1.2V.



Figure S26: I-V characteristic graph of the bulk solid and xerogel of N2SNm salt.

Temperature vs. resistance measurement:

In a 15 ml screw cap vial 40 mg of synthesized salt was dispersed in 3 ml of milli-Q water. A pair of Cu-plate electrode (width 1cm, dipped height 1cm and they are 1.5 cm apart) and a temperature sensor (PT100) were dipped into this dispersed solution. Then biasing was applied between two Cu-electrodes. The whole system was then placed on a heating mantel and the system was allowed to heat with simultaneous recording of the resistance. On getting a clear hot solution from the suspension, the heating mantel slowly and carefully removed from the experimental setup and allowed to cool down to form gel. During the whole experiment resistance was measured with temperature.

Proton conductivity measurement:

The impedance spectroscopy of Gel-1.33 wt% (both hydrogel and D₂O gel) were measured using a LCR meter (HIOKI, model IM 3536) in the frequency range of 4 Hz-8 MHz. Here, electrical measurement was carried out by dipping two copper plates into the Gel-1.33 wt%. Proton conductivity was calculated using the relation $\sigma_p = d/(R_b \times A)$, where σ_p = proton conductivity, d = distance between the two Cu-electrodes within the gel (1.5 cm), R_b = bulk resistance of the gel measured from the impedance spectroscopy Nyquist plot and A = area of the Cu-electrode covered by the gel (1 cm²).Z-fit(EC-Lab) software was used to fit Nyquist plot by using equivalent circuit.



Figure S27: Frequency dependence of real conductivity spectroscopy of the bulk solid at 27 °C.



Figure S28: Nyquist and the Frequency dependence of real conductivity spectroscopy (compared with the hydrogel) of the D_2O gel at 27 °C.

UV measurement:

The absorption spectra were collected for the acid, amine and the final gelator salt using Hewlett–Packard 8453 diode array spectrophotometer equipped with a Peltier temperature controller.



Figure S29: Characteristic UV plots of the salt and its parent acid and amine.