SUPPORTING INFORMATION

Reverse thermal gelation of aromatic solvents by a series of easily accessible organic salt based gelators

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Materials and Methods: All the chemicals (Aldrich) and solvents are (A.R. grade, S.D. Fine Chemicals, India) commercially available and used without any further purification except azobenzene-4,4'-dicarboxyllic acid. It was prepared following a European patent[21] by locally available chemicals (Loba Chemie Pvt. Ltd.). Petrol used in the gelation experiments have been purchased from the local market. Microanalyses are performed on a Perkin Elmer elemental analyzer 2400, Series II. FT-IR spectra are recorded using Perkin-Elmer Spectrum GX. Powder X-ray patterns are recorded on XPERT Philips (CuKα radiation, λ = 1.5418Å) Diffractometer. Scanning Electron Microscopy (FT-SEM) is performed on a JEOL; JSM-6700F. Single Crystal X-ray diffraction data are recorded on a BRUKER AXS, SMART APEX II, Structure Was solved through APEX2 software.

Preparation of Salts: Salts were prepared by mixing azobenzene-4,4'-dicarboxyllic acid with the corresponding longchain amines according to Scheme 2 in both 1:2 and 1:1 molar ratio acid:amine in MeOH in a R.B.. The resultant mixture was subjected to sonication for a few minutes and followed by strong heating to ensure the homogeneous mixing of the two components. Finally by evaporation of solvent in a rotavapour, the

orange compounds were obtained and subjected to various physicochemical analyses and a gelation test.

Physico-chemical data for the salts

1. **2.16 Hexadecylammoniumazobenzene-4,4′-dicarboxylate:** m.p. 166°C. Anal. Calc. for $C_{46}H_{80}N_4O_4$: C, 73.36; H, 10.71; N, 7.44. Found: C, 72.84; H, 10.11; N, 7.59. FT-IR (KBr): 2953, 2914, 2848, 1589, 1520, 1469, 1381, 1305, 1217, 1159, 1099, 1006, 974, 875, 796, 704, 495cm^{-1}. ^{1}H NMR(CD_3OD) (300MHz) δ = 8.09 (4H, d, J = 8.05Hz), 7.89 (4H, d, J = 8.5Hz), 2.88 (4H, t, J = 7.5 Hz, $^+NH_3CH_2CH_2(CH_2)_{13}CH_3$), 1.62-1.60 (4H, m, $^+NH_3CH_2CH_2(CH_2)_{13}CH_3$), 1.36-1.25 (52H, m, $^+NH_3CH_2CH_2(CH_2)_{13}CH_3$), 1.87 (6H, t, J = 6.75Hz, $^+NH_3CH_2CH_2(CH_2)_{13}CH_3$).
2. **2.15 Pentadecylammoniumazobenzene-4,4′-dicarboxylate:** m.p. 162°C. Anal. Calc. for $C_{44}H_{76}N_4O_4$: C, 72.88; H, 10.56; N, 7.73. Found: C, 73.03; H, 10.54; N, 7.73. FT-IR (KBr): 2920, 2850, 2189, 1587, 1525, 1467, 1373, 1303, 1217, 1095, 1006, 875, 796, 719, 705, 623, 495cm^{-1}. ^{1}H NMR(CD_3OD) (500MHz) δ = 8.13-8.11 (4H, m), 7.93-7.91(4H, m), 2.91 (4H, t, J = 7.75 Hz, $^+NH_3CH_2CH_2(CH_2)_{12}CH_3$), 1.65-1.63 (4H, m, $^+NH_3CH_2CH_2(CH_2)_{12}CH_3$), 1.36-1.28 (48H, m, $^+NH_3CH_2CH_2(CH_2)_{12}CH_3$), 0.92-0.89 (6H, m, $^+NH_3CH_2CH_2(CH_2)_{12}CH_3$).
3. **2.14 Tetradecylammoniumazobenzene-4,4′-dicarboxylate:** m.p. 159-162°C. Anal. Calc. for $C_{42}H_{72}N_4O_4$: C, 72.37; H, 10.41; N, 8.04. Found: C, 72.49; H, 10.49; N, 8.28. FT-IR (KBr): 2918, 2850, 2187, 1631, 1587, 1519, 1467, 1371, 1304, 1217, 1096, 1007, 876, 798, 721, 499 cm^{-1}. ^{1}H NMR(CD_3OD) (500MHz) δ = 8.11-8.08 (4H, m), 7.91-7.88 (4H, m), 2.89 (4H, t, J = 7.75 Hz, $^+NH_3CH_2CH_2(CH_2)_{11}CH_3$), 1.90-1.1.88(4H, m, $^+NH_3CH_2CH_2(CH_2)_{11}CH_3$), 1.34 (44H, m, $^+NH_3CH_2CH_2(CH_2)_{11}CH_3$), 0.88 (6H, t, J = 6.75Hz, $^+NH_3CH_2CH_2(CH_2)_{11}CH_3$).
4. **2.12 Dodecylammoniumazobenzene-4,4′-dicarboxylate:** m.p. 159-162°C. Anal. Calc. for $C_{38}H_{64}N_4O_4$: C, 71.21; H, 10.06; N, 8.74. Found: C, 71.19; H, 10.01; N, 8.47. FT-IR (KBr): 3416, 2956, 2916, 2850, 2771, 2665, 2540, 2187, 1952, 1664, 1627, 1610, 1583, 1539, 1467, 1359, 1305, 1213, 1101, 1004, 877, 854, 798, 721, 705, 621, 493, 451 cm^{-1}. ^{1}H NMR(CD_3OD) (500MHz) δ = 8.10 (4H, d, J = 8.50), 7.99 (4H, d, J = 8.50), 2.89 (4H, t, J = 7.75 Hz, $^+NH_3CH_2CH_2(CH_2)_9CH_3$), 1.65-1.61 (4H, m, $^+NH_3CH_2CH_2(CH_2)_9CH_3$), 1.35-1.32 (36H, m, $^+NH_3CH_2CH_2(CH_2)_9CH_3$), 0.88 (6H, t, J = 7.00Hz, $^+NH_3CH_2CH_2(CH_2)_9CH_3$).
5. **2.11 Undecylammoniumazobenzene-4,4′-dicarboxylate:** m.p. 161-163°C. Anal. Calc. for $C_{36}H_{60}N_4O_4$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.32; H, 9.86; N, 9.16. FT-IR (KBr): 2956, 2918, 2851, 2185, 1661, 1626, 1589, 1541, 1466, 1362, 1306, 1213, 1101, 1005, 877, 798, 706, 494 cm^{-1}. ^{1}H NMR(CD_3OD) (500MHz) δ = 8.10 (4H, d, J = 8.50Hz), 7.91 (4H, d, J = 8.50Hz), 2.90(4H, t, J = 7.75 Hz, $^+NH_3CH_2CH_2(CH_2)_8CH_3$), 1.65-1.60 (4H, m, $^+NH_3CH_2CH_2(CH_2)_8CH_3$), 1.36-1.26 (32H, m, $^+NH_3CH_2CH_2(CH_2)_8CH_3$), 0.88 (6H, t, J = 7.00Hz, $^+NH_3CH_2CH_2(CH_2)_8CH_3$).
6. **2.10 Decylammoniumazobenzene-4,4′-dicarboxylate:** m.p. 162-164°C. Anal. Calc. for $C_{34}H_{56}N_4O_4$: C, 69.83; H, 9.65; N, 9.58. Found: C, 69.84; H, 9.72; N, 9.59. FT-IR (KBr): 2956, 2916, 2850, 2661, 2185, 1953, 1664, 1627, 1583, 1541, 1359, 1305, 1215, 1180, 1101, 1058, 1004, 877, 854, 798, 705, 493, 434 cm^{-1}. ^{1}H NMR(CD_3OD) (500MHz) δ = 8.11 (4H, d, J = 8.00Hz), 7.91 (4H, d, J = 8.50Hz), 2.89 (4H, t, J = 7.75Hz,

$^{+}NH_3CH_2CH_2(CH_2)_7CH_3$), 1.65-1.62 (4H, m, $^{+}NH_3CH_2CH_2(CH_2)_7CH_3$), 1.37-1.28 (28H, m, $^{+}NH_3CH_2CH_2(CH_2)_7CH_3$), 0.88 (6H, t, J = 6.75Hz, $^{+}NH_3CH_2CH_2(CH_2)_7CH_3$).

7. **1.16 Hexadecylammoniumhydrogen azobenzene-4,4′-dicarboxylate:** mp 195°C Anal. Calc. for $C_{30}H_{45}N_3O_4$: C, 70.42; H, 8.86; N, 8.21. Found: C, 70.68; H, 9.10; N, 8.07. FT-IR (KBr): 2914, 2849, 2669, 2550, 1687, 1680, 1602, 1589, 1547, 1529, 1470, 1381, 1292, 1217, 872, 796, 781, 702 cm^{-1}.
8. **1.15 Pentadecylammoniumhydrogen azobenzene-4,4′-dicarboxylate:** mp 187-189°C Anal. Calc. for $C_{29}H_{43}N_3O_4$: C, 69.99; H, 8.71; N, 8.44. Found: C, 69.60; H, 8.69; N, 8.52. FT-IR (KBr): 2918, 2851, 2669, 2552, 1687, 1601, 1526, 1468, 1375, 1298, 1215, 1126, 1097, 1005, 867, 769, 700, 619, 538, 490 cm^{-1}.
9. **1.14 Tetradecylammoniumhydrogen azobenzene-4,4′-dicarboxylate:** m.p. 179-180°C. Anal. Calc. for $C_{28}H_{41}N_3O_4$: C, 69.53; H, 8.54; N, 8.69. Found: C, 69.71; H, 8.74; N, 8.64. FT-IR (KBr): 2953, 2918, 2851, 2667, 2552, 1687, 1602, 1529, 1468, 1377, 1294, 1215, 1126, 1097, 1005, 867, 769, 700, 538, 491 cm^{-1}.
10. **1.12 Dodecylammoniumhydrogen azobenzene-4,4′-dicarboxylate:** m.p. 161-165°C Anal. Calc. for $C_{26}H_{37}N_3O_4$: C, 68.54; H, 8.19; N, 9.22. Found: C, 68.43; H, 8.57; N, 9.14. FT-IR (KBr): 2957, 2918, 2851, 2666, 2550, 2185, 1948, 1686, 1626, 1603, 1585, 1539, 1468, 1427, 1362, 1302, 1213, 1126, 1101, 1007, 933, 872, 798, 779, 700, 619, 538, 494 cm^{-1}.
11. **1.11 Undecylammoniumhydrogen azobenzene-4,4′-dicarboxylate:** mp 194-198°C Anal. Calc. for $C_{25}H_{35}N_3O_4$: C, 68.00; H, 7.99; N, 9.52. Found: C, 67.46; H, 8.17; N, 9.24. FT-IR (KBr): 2957, 2918, 2851, 2664, 2550, 2183, 1688, 1630, 1603, 1583, 1537, 1468, 1427, 1360, 1296, 1215, 1126, 1101, 1005, 872, 781, 698, 640, 621, 557, 538, 494 cm^{-1}.
12. **1.10 Decylammoniumhydrogen azobenzene-4,4′-dicarboxylate:** mp 202°C Anal. Calc. for $C_{24}H_{33}N_3O_4$: C, 67.42; H, 7.78; N, 9.83. Found: C, 67.13; H, 7.81; N, 9.85. FT-IR (KBr): 2955, 2918, 2850, 2664, 2550, 2183, 1948, 1687, 1628, 1603, 1583, 1537, 1468, 1427, 1360, 1296, 1215, 1126, 1101, 1005, 872, 798, 781, 696, 538, 492 cm^{-1}.

Table S1: Gelation data

Salts	DMSO	DMF	Methyl Salicylate	Ph-NO2	Ph-Cl	1,2-dichloro benzene	Ph-me	o-Xylene	m-xylene	p-xylene	Petrol	MeOH	H_2O	Ethylene glycol
2.16	**2.77(101)**	**S**	**C**	**C**	**2.22**	**4.0**	**4.0**	**2.85**	**2.85**	**2.85**	**INS**	**INS**	**INS**	**1.33(94)**
2.15	**WG**	**FP**	**C**	**C**	**2.5**	**WG**	**2.85**	**2.85**	**2.85**	**2.85**	**INS**	**INS**	**INS**	**1.48(78)**
2.14	**6(111)**	**6(52)**	**C**	**WG**	**2.0**	**4.0**	**WG**	**WG**	**6.0**	**WG**	**INS**	**P**	**INS**	**3(114)**
2.12	**2.7(NM)**	**C**	**P**	**P**	**WG**	**C**	**WG**	**P**	**WG**	**WG**	**WG**	**P**	**P**	**P**
2.11	**WG**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**S**
2.10	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**S**
1.16	**2.8(NM)**	**S**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**2.8(NM)**
1.15	**S**	**S**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**4**
1.14	**S**	**S**	**INS**	**INS**	**INS**	**4**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**
1.12	**S**	**S**	**INS**	**INS**	**INS**	**4**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**
1.11	**S**	**S**	**INS**	**INS**	**4(NM)**	**4**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**
1.10	**S**	**S**	**INS**	**INS**	**INS**	**4**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**	**INS**

[a]Numerical values indicate minimum gelator concentration in wt% (w/v); numerical values within parenthesis are the gel-to-sol dissociation temperature (T_{gel}) in °C (note that T_{gel} for aromatic gels could not be determined as they were reverse-thermal gels; S = solution; C = colloid; WG = weak gel; FP = fibrious precipitate, P = precipitate, INS = insoluble, NM = not measured.
T_{gel} was measured by dropping ball method; the details are given below:
In a typical experiment, a glass ball (0.242 g) was placed carefully on the surface of a gel (500µl) taken in a test tube (11.0 mm diameter). The test tube was then immersed in an oil bath which was heated gradually. The temperature noted when the glass touched the bottom of the test tube was the T_{gel}.

Single crystal X-ray data.

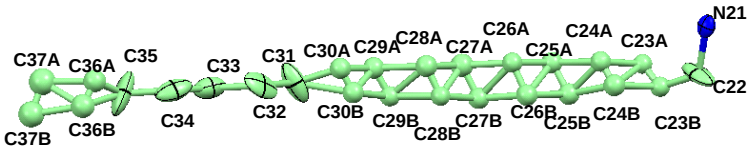
Data were collected using MoKα (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX. All structures were solved by direct method and refined in a routine manner. In most of the cases, nonhydrogen atoms were treated anisotropically. All the hydrogen atoms were geometrically fixed. CCDC (CCDC No. 819160-819161) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S2: Crystal data

Crystal parameters	1.16	1.15
CCDC No	819161	819160
Empirical formula	C_{30} H_{45} N_3 O_4	C_{29} H_{43} N_3 O_4
Formula weight	508.67	497.66
Crystal size/mm	0.41 X 0.18 X 0.10	0.42X 0.30 X 0.14
Crystal system	Triclinicc	Triclinicc
Space group	P-1	P-1
a /Å	6.323(3)	6.4221(11)
b/Å	14.956(7)	14.631(3)
c /Å	16.823(8)	15.001(3)
$\alpha/^0$	113.730(6)	95.239(6)
$\beta/^0$	95.041(7)	94.880(7)
$\gamma/^0$	94.696(7)	99.656(7)
Volume/$Å^3$	1438.8(12)	1376.5(5)
Z	2	2
F(000)	550	540
μ MoKα /mm^{-1}	0.078	0.080
Temperature/K	296(2)	296(2)
R_{int}	0.0586	0.1166
Range of h, k, l	-5/ 5, -13/13, -15/15	-6/6, -13/14, -14/14
θmin/max/°	1.33/19.37	1.37/20.76
Reflections collected/unique/ observed [I>2σ(I)]	7895 /2443/1528	10569 / 2854/ 1429
Data/restraints/ parameters	2443/ 0/ 316	2854 /0/347
Goodness of fit on F^2	1.220	0.961
Final R indices [I>2σ(I)]	R_1 = 0.1015 wR_2 = 0.2955	R_1 = 0.0636 wR_2 = 0.1390
R indices (all data)	R_1 = 0.1396 wR_2 = 0.3346	R_1 = 0.1430 wR_2 = 0.1773

Molecular Plots and Hydrogen Bonding Parameters for the compounds

Compound: 1.16



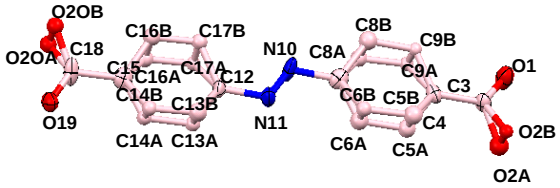


Table S3: Hydrogen bonding parameters of 1.16

1.16				
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21*A*···O20B^{i}	0.89	1.92	2.786 (10)	164
N21—H21*A*···O20A^{i}	0.89	1.92	2.790 (11)	164
N21—H21B···O19^{ii}	0.89	2.26	2.982 (7)	138
N21—H21C···O19^{iii}	0.89	1.94	2.817 (7)	170
Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) *x*+1, *y*, *z*−1; (iii) −*x*+1, −*y*+1, −*z*+1.				

Compound: 1.15

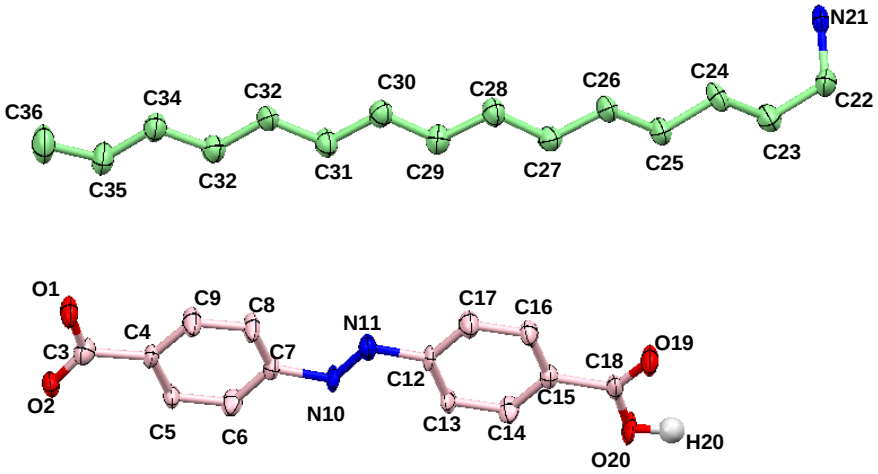


Table S4: Hydrogen bonding parameters of 1.15

1.15				
D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21—H21···O1^{i}	0.96 (7)	1.65 (7)	2.602 (5)	1.77 (6)
N22—H22*A*···O2^{ii}	0.91	1.91	2.801 (5)	165
N22—H22*C*···O1^{iii}	0.91	1.92	2.799 (6)	162
N22—H22*B*···O2^{iv}	0.91	2.22	2.959 (5)	138
Symmetry codes: (i) *x*+1, *y*, *z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) *x*+1, *y*−1, *z*+1.				