Supporting Information

Probing the role of weaker interactions in immobilization of solvents in a new class of supramolecular gelator

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Experimental section:

Instrumentation

FTIR spectroscopy: FTIR Spectra were recorded on a Perkin Elmer –RX FTIR instrument. Solid samples were recorded as an intimate mixture with powdered KBr.

NMR Experiments: The 1H- NMR spectra were measured by using a Bruker AVANCE, 400MHZ for 1H-NMR with TMS as internal standard.

Scanning Electron Microscopic Study. Morphologies of all reported gel materials were investigated using scanning electron microscopy (SEM). For SEM study, the gel materials were dried to give xerogel, then the micrographs were taken in a SEM apparatus (JEOL JSM5610 LV microscope)

X-ray Diffraction Study. The X-Ray diffraction patterns were recorded for compounds **1b** and **1d** in solid state and xerogels obtained by evaporating methanol using Rigaku powder X-ray diffractometer model Multiflex 2kW. The typical width is 0.250° and minimum height is 200 cps.

Single Crystal X-ray studies: The X-ray intensity data of a well-defined crystals of **1b** and **3b** were collected at room temperature (293K) by using a CCD area-detector diffractometer (X'calibur system – Oxford diffraction, 2010) which is equipped with graphite monochromated MoKα radiation (λ=0.71073 Å). Data were corrected for Lorentz, polarization and absorption factors. The structure was solved by direct methods using SHELXS97 (Sheldrick, 2008). All non-hydrogen atoms of the molecule were located from the E-map. Full-matrix least-squares refinement was carried out by using SHELXL97 software (Sheldrick, 2008). The geometry of the molecule is determined by PLATON (Spek, 2009). All the hydrogen atoms were positioned geometrically and were treated as riding on their parent C atoms.

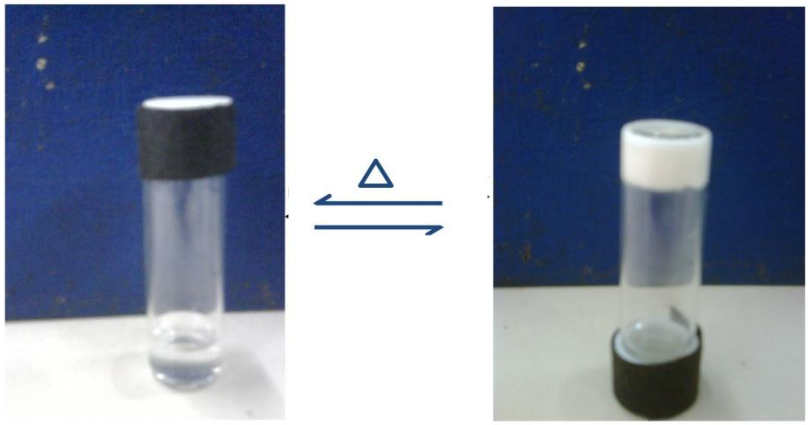
Crystals of **3d** was obtained from methanol in a slow evaporative condition at room temperature. Diffraction data for **3d** was collected using MoKα (λ=0.7107Å) radiation on a SMART APEX diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement are carried out using the software package of SMART APEX. Graphics are generated using MERCURY 3.0

All structures are solved by direct methods and refined in a routine manner. In all cases, nonhydrogen atoms are treated anisotropically. Whenever possible, the hydrogen atoms are located on a difference Fourier map and refined. In other cases, the hydrogen atoms are geometrically fixed.

Materials. 2-Amino thiazole(97%),2-Amino-4-Methylethiazole(98%),2-Amino-5-Methylethiazole(98%),Decanoic acid(96%) ,Dodecanoic acid(98%), Tridecanoic acid(97%), Tetradecanoic acid(99%) (All from Aldrich) were used as received.

The other chemicals were of the highest commercial grade available and were used without further purification. The liquids used for the preparation of gels were reagent grade. All solvents used in the synthesis were purified, dried and distilled as required.

Gelation Test. A weighted amount of potential gelator(1wt%) and a measured volume of selected pure organic solvent were placed into a test tube and the system was heated in an oil or water bath until all solid materials were dissolved. The solution was cooled to room temperature and finally, the test tube was turned upside down to observe if the solution inside could still flow. A positive test is obtained if the flow test is negative. Systems in which only solution remained until the end of the tests are referred as solutions (S). Systems that are clear solutions when they are hot but precipitation or crystallization occurs when they are cooled down to room temperature are denoted by P (precipitation) and R (recrystallization), respectively.



Photographic image of sol-gel transition of 3d in methanol

***T*gel Measurement.** Temperatures of gel-to-sol transition (*T*gel) were determined by using a conventional "falling ball" method. In this test, a small glass ball (63mg) was carefully placed on the top of the gel to be tested, which was produced in a test tube . The tube was slowly heated in a thermostated oil bath until the ball fell to the bottom of the test tube. The temperature at which the ball reaches at the bottom of test tube is taken as T_{gel} of that system.

General Synthesis methodology: Oxalyl chloride (2ml, 20 mmol) was added slowly to a stirred solution of aliphatic carboxylic acid (2 mmol) in dry dichloromethane(10mL) under a nitrogen atmosphere, and stirring was continued under a nitrogen atmosphere for 12 h. Excess oxalyl chloride and solvent were then removed by distillation under reduced pressure. The acid chloride so obtained was dissolved in dry dichloromethane (10 mL) and added to the amine (2 mmol) in triethylamine (0.3ml,2.15mmol). The mixture was stirred under a nitrogen atmosphere for overnight. The reaction mixture then added to dilute hydrochloric acid (5%), and extracted with chloroform. The product residue after removing chloroform was purified by repeated recrystalization from ethyl acetate/pet ether mixture.

N-(thiazol-2-yl)decanamide (**1a**): Yield 78%, m.p. 105 °C,^{1}H NMR (400MHZ, $CDCl_3$, TMS); δ7.490 (d, 1H; CH), 7.065 (d,1H;CH), 2.596-2.558(t,2 H;CH_2), 1.810-754 (m,2H,CH_2),1.407-1.270 (m,12H,CH_2), 0.905-0.871 (t,3H;CH_3). MS (HRMS): m/z 254.40 (M)+. IR(KBr): 3456, 3172, 2848,

1690, 1576, 1495, 1467, 1424, 1378, 1325, 1274, 1213, 1175, 1068, 960, 873, 810, 777, 625, 519, 474 cm^{-1}.

N-(thiazol-2-yl)dodecanamide **(1b)**: Yield 82%, m.p. 116°C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS); δ 7.458 (d,1H;CH), 7.029 (d,1H;CH), 2.595-2.557 (t,2H;CH_2),1.830-1.754 (m,2H, CH_2), 1.425-1.266 (m,16H,CH_2), 0.908-0.874 (t,3H;CH_3). MS (HRMS): m/z 281.85(M) +. IR(KBr): 3450, 3271, 3180, 2916, 2849, 1687, 1580, 1467, 1422, 1381, 1327, 1278, 1204, 1115, 1065, 960, 810, 776, 625, 519, 417 cm^{-1}.

N-(thiazol-2-yl)tridecanamide **(1c)**: Yield 76%, m.p.110 °C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS); δ 7.458 (d, 1H; CH), 7.282 (d, 1H;CH), 2.587-2.549 (t,2H;CH_2),1.827-1.752 (m,2H, CH_2), 1.424-1.265 (m, 18H, CH_2), 0.909-0.875 (t, 3H; CH_3). MS (HRMS): m/z 295.81(M) +. IR(KBr): 3484, 3176, 2944, 1691, 1560, 1492, 1468, 1319, 1274, 1175, 1063, 960, 874, 777, 714, 626, 520 cm^{-1}.

N-(thiazol-2-yl)tetradecanamide **(1d)**: Yield 72%, m.p. 140 °C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS); δ 7.458 (d,1H; CH), 7.026 (d, 1H; CH), 2.586-2.547 (t, 2H; CH_2), 1.808-1.771 (m, 2H, CH_2), 1.406 - 1.368 (m, 20H, CH_2), 0.911-0.877 (t, 3H; CH_3). MS (HRMS): m/z 310.46 (M)+. IR(KBr): 3271,3175, 2917, 1685, 1581, 1467, 1380, 1382, 1284, 1169, 1066, 958, 873, 777, 718, 626, 520, 457 cm^{-1}.

N-(4-methylthiazol-2-yl)decanamide **(2a):** Yield 69%, m.p. 64°C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS) : δ 6.564 (s,1H;CH), 2.611-2.573 (t,2H,CH_2), 2.407 (s,3H;CH_3),1.767-1.730 (m,2H; CH_2), 1.328-1.261 (m,12H;CH_2) 0.891-0.879 (t,3H;CH_3). MS (HRMS): m/z 268.43 (M)+. IR(KBr): 3481, 2857, 1882, 1697, 1567, 1567, 1465, 1377, 1319, 1280, 1213, 1115, 1080, 1017, 956, 846, 723, 644, 602, 525, 473 cm^{-1}.

N-(4-methylthiazol-2-yl)dodecanamide **(2b):** Yield 70%, m.p. 90 °C. $^{1}HNMR$ (400MHZ, $CDCl_3$,TMS): δ 6.653 (s,1H;CH), 2.700-2.662 (t,2H,CH_2), 2.513 (s,3H;CH_3), 1.799-1.743 (m,2H;CH_2), 1.376-1.265 (m,16H;CH_2), 0.900-0.879 (t,3H;CH_3). MS (HRMS): m/z 296.67(M)+. IR(KBr): 3540, 3170, 2850, 1904, 1695, 1562, 1465, 1278, 1167, 1072, 956, 848, 645, 572, 538, 475, 425 cm^{-1}.

N-(4-methylthiazol-2-yl)tridecanamide **(2c):** Yield 76%, m.p71 °C,^{1}H NMR (400MHZ, $CDCl_3$,TMS): δ 6.529 (s,1H;CH), 2.561-2.523 (t,2H,CH_2), 2.393 (s,3H;CH_3), 1.769-1.666 (m,2H;CH_2), 1.268-1.262 (m,18H;CH_2), 0.898-0.879 (t,3H;CH_3). MS (HRMS): m/z 310.51(M)+. IR(KBr): 3536, 3175, 2915, 1905, 1694, 1567, 1552, 1467, 1276, 1167, 1130, 1075, 1001, 949, 846, 774, 721, 641, 573, 533, 409 cm^{-1}.

N-(4-methylthiazol-2-yl)tetradecanamide **(2d):** Yield 69%, m.p.60 °C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS): δ 6.553 (s,1H;CH), 2.540-2.419 (t,2H,CH_2), 2.388 (s,3H;CH_3), 1.789-1.693 (m,2H;CH_2), 1.373-1.266 (m,20H;CH_2), 0.922-0.912 (t,3H;CH_3). MS (HRMS): m/z 324.34 (M)+. IR(KBr): 3541, 3281, 2916, 1988, 1683, 1550, 1467, 1408, 1376, 1310, 1263, 1176, 1012, 946, 846, 721, 640, 576, 541 cm^{-1}.

N-(5-methylthiazol-2-yl)decanamide **(3a):** Yield 81%, m.p. 102 °C, ^{1}H NMR (400MHZ, m/z $CDCl_3$, TMS): δ 7.063 (s,1H; CH), 2.539-2.502 (t,2H;CH_2), 2.432 (s,3H;CH_3),1.808-1.733 (m,2H;CH_2), 1.415-1.292 (m,12H;CH_2), 0.905-0.871 (t,3H;CH_3). MS (HRMS): m/z 268.25 (M) +. IR(KBr): 3448, 3181, 3059, 2918, 1697, 1583, 1461, 1410, 1378, 1311, 1279, 1112, 1071, 922, 874, 672, 527, 496 cm^{-1}.

N-(5-methylthiazol-2-yl)dodecanamide **(3b):** Yield 79%, m.p. 114 °C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS); δ 7.135 (s,1H; CH), 2.610 – 2.573 (t,2H;CH_2), 2.457 (s,3H;CH_3), 1.813-1.739 (m,2H;CH_2), 1.388-1.268 (m,16H; CH_2) , 0.910-0.893(t,3H;CH_3). MS (HRMS): m/z 295.93 (M) +. IR(KBr): 3482, 3180, 3059, 2918, 1698, 1586, 1463, 1410, 1379, 1312, 1280, 1211, 1165, 1112, 1068, 940, 835, 786, 722, 673, 527, 428 cm^{-1}.

N-(5-methylthiazol-2-yl)tridecanamide **(3c):** Yield 83%, m.p. 106°C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS): δ 7.063 (s,1H; CH), 2.542-2.504 (t,2H;CH_2), 2.434 (s,3H;CH_3), 1.802-1.732 (m,2H;CH_2), 1.398-1.265 (m,18H;CH_2), 0.912-0.875 (t,3H;CH_3). MS (HRMS): m/z 309.93(M) +. IR (KBr): 3444, 3267, 3185, 2917, 1681, 1587, 1463, 1418, 1379, 1303, 1164, 1081, 958, 827, 796, 718, 625, 525 cm^{-1}.

N-(5-methylthiazol-2-yl)tetradecanamide **(3d):** Yield 80%, m.p. 125 °C, ^{1}H NMR (400MHZ, $CDCl_3$, TMS): δ 7.065 (s,1H;CH), 2.537 –2.499 (t,2H; CH_2), 2.433 (s,3H;CH_3),1.809-1.735 (m,2H;CH_2), 1.400-1.26 (m,20H;CH_2), 0.912- 0.877 (t,3H;CH_3). MS (HRMS): m/z 324.18(M)+ . IR(KBr): 3283, 3180, 2918, 2849, 1698, 1587, 1462, 410, 1379, 1312, 1280, 1188, 1165, 1110, 1032, 993, 953, 835, 786, 672, 527, 458 cm^{-1}.

Table S1: Gelation studies of compounds in various solvents

	1a	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**	**3c**	**3d**
Methanol	S	C	C	G (1.869)	S	S	S	S	S	G (2.570)	G (2.118)	G (0.657)
Ethanol	S	S	C	G (2.160)	S	S	S	S	S	G (2.828)	G (2.173)	G (0.805)
n-pentanol	S	S	S	G (2.808)	S	S	S	S	S	G (4.444)	G (4.201)	G (2.127)
n-heptanol	S	S	S	S	S	S	S	S	S	G (4.762)	G (4.926)	G (3.831)
Water	P	P	P	P	P	P	P	P	P	P	P	P
THF	S	S	S	S	S	S	S	S	S	S	S	S
Iso octane	S	P	P	G (2.422)	S	S	S	S	P	P	P	G (0.909)
Xylene	S	S	C	C	S		S	S		S	S	P
Cyclohexane	P	P	P	G (2.406)	S	P	S	P	P	P	P	G (3.174)
n-octadecane	P	W.G	G (1.000)	G (0.703)	S	P	S	P	P	G (2.216)	G (2.371)	G (1.166)

G=gel, P=precipitate, S=solution, W.G=weak gel,()= minimum gel concentration in wt% (w/v)

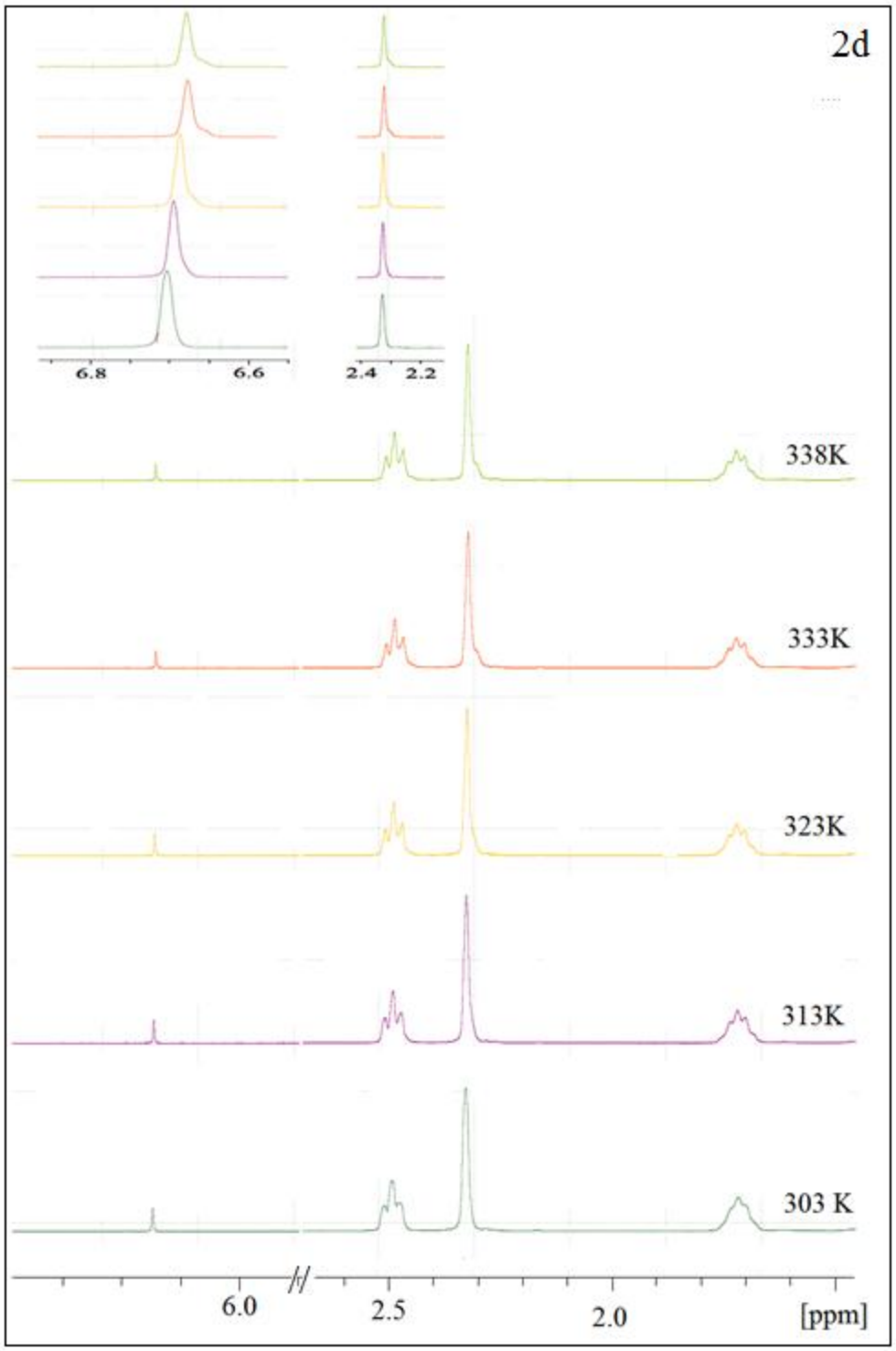


Fig. S1: Variable temperature ^{1}H NMR of **2d** in CD_3OD. Inset shows the expanded view of aromatic and $-CH_3$ proton of thiazole moiety

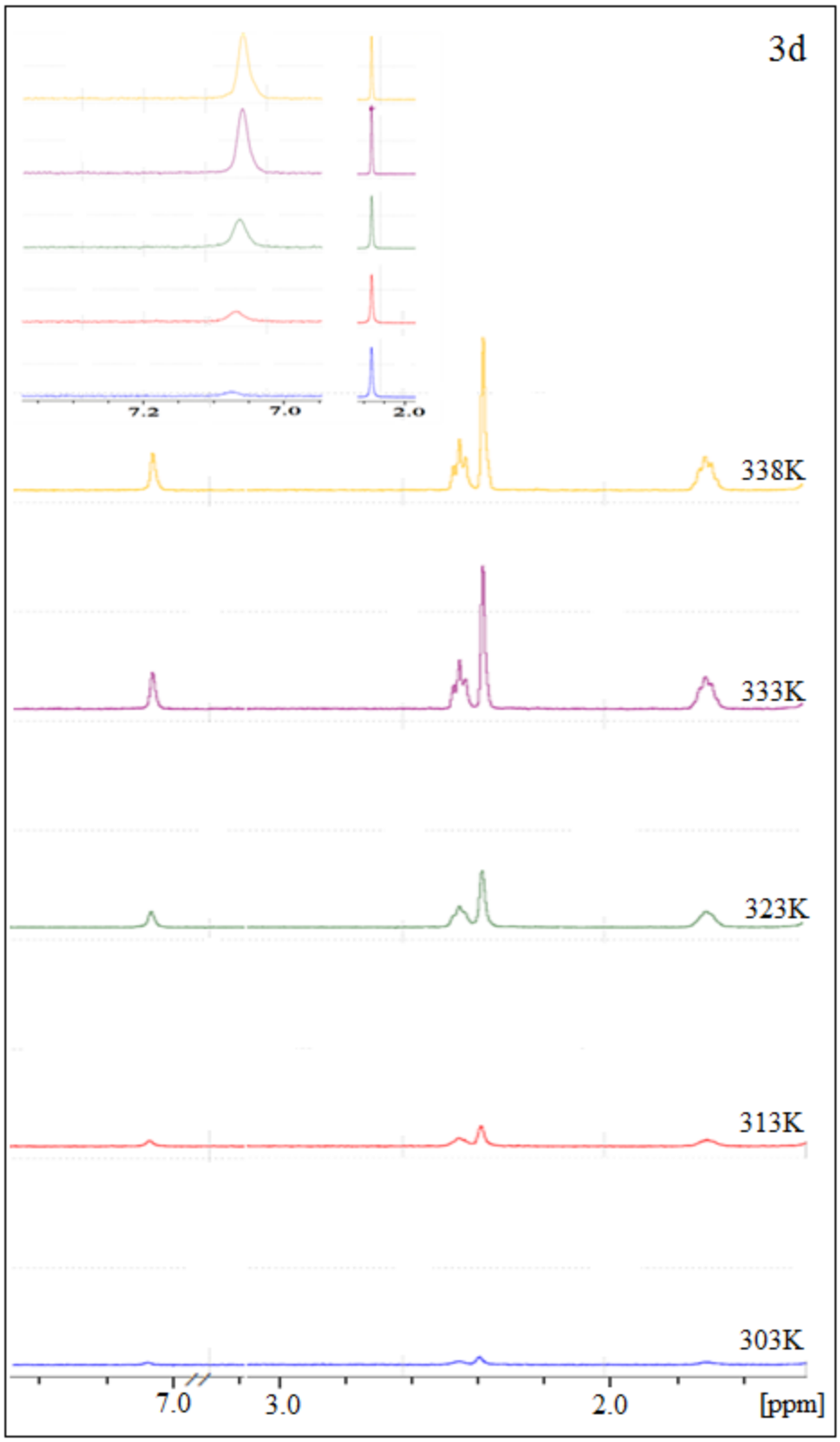


Figure S2: Variable temperature ^{1}H NMR of compound **3d**

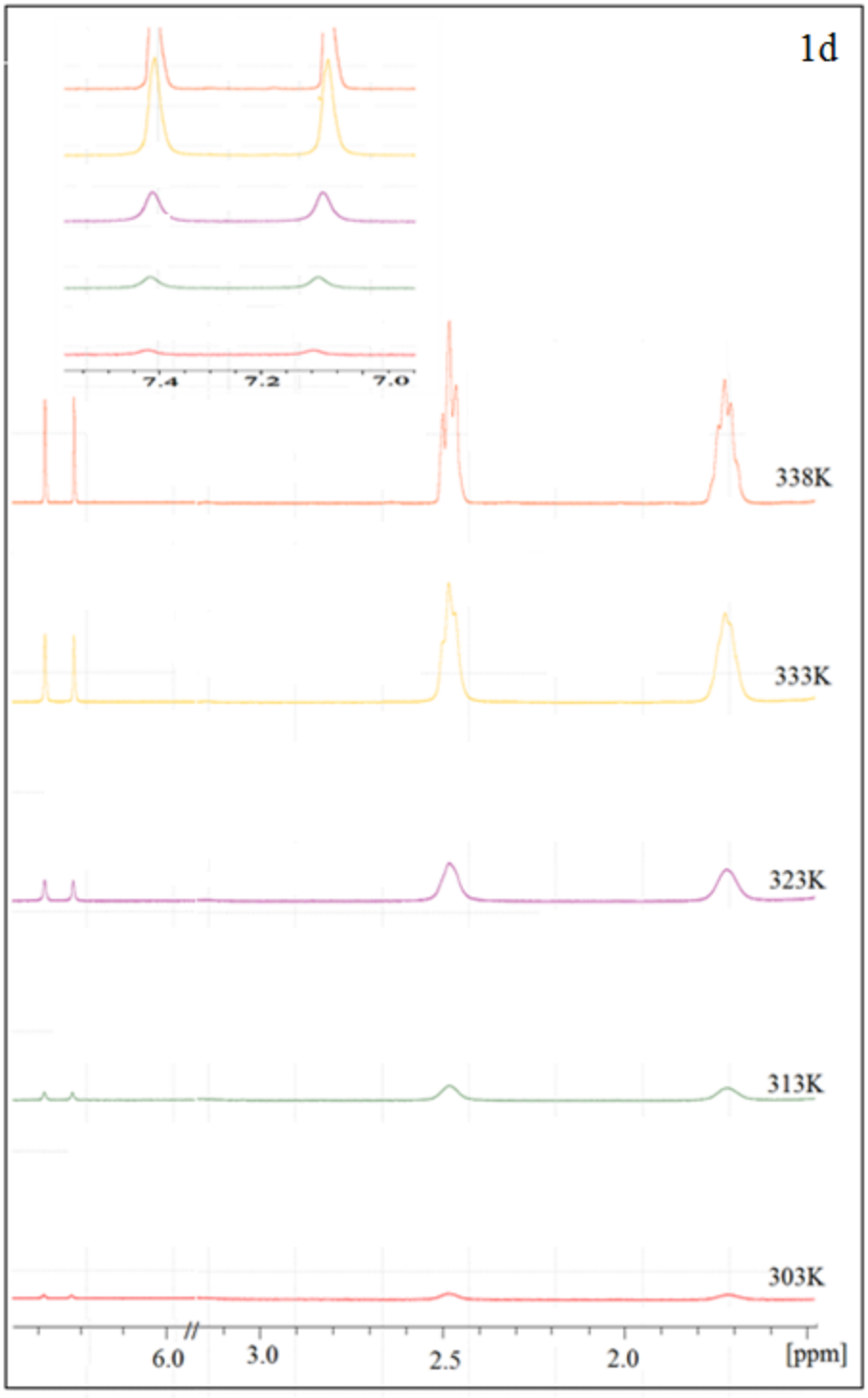


Figure S3: Variable temperature ^{1}H NMR of compound **1d**

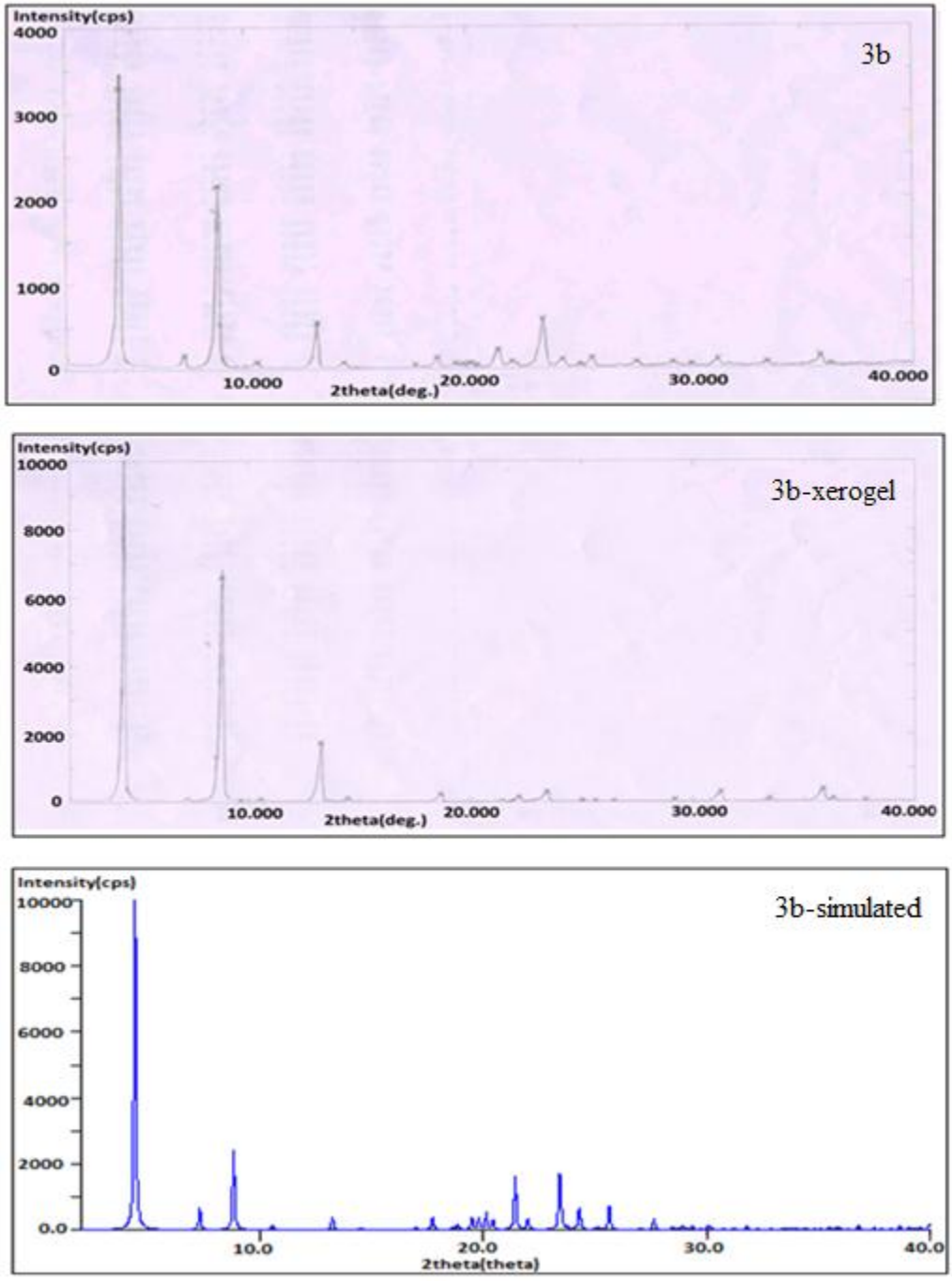


Figure S4: Comparative powder X-ray diffraction pattern of compounds **3b** in solid, xerogel and simulated (Single crystal structure)

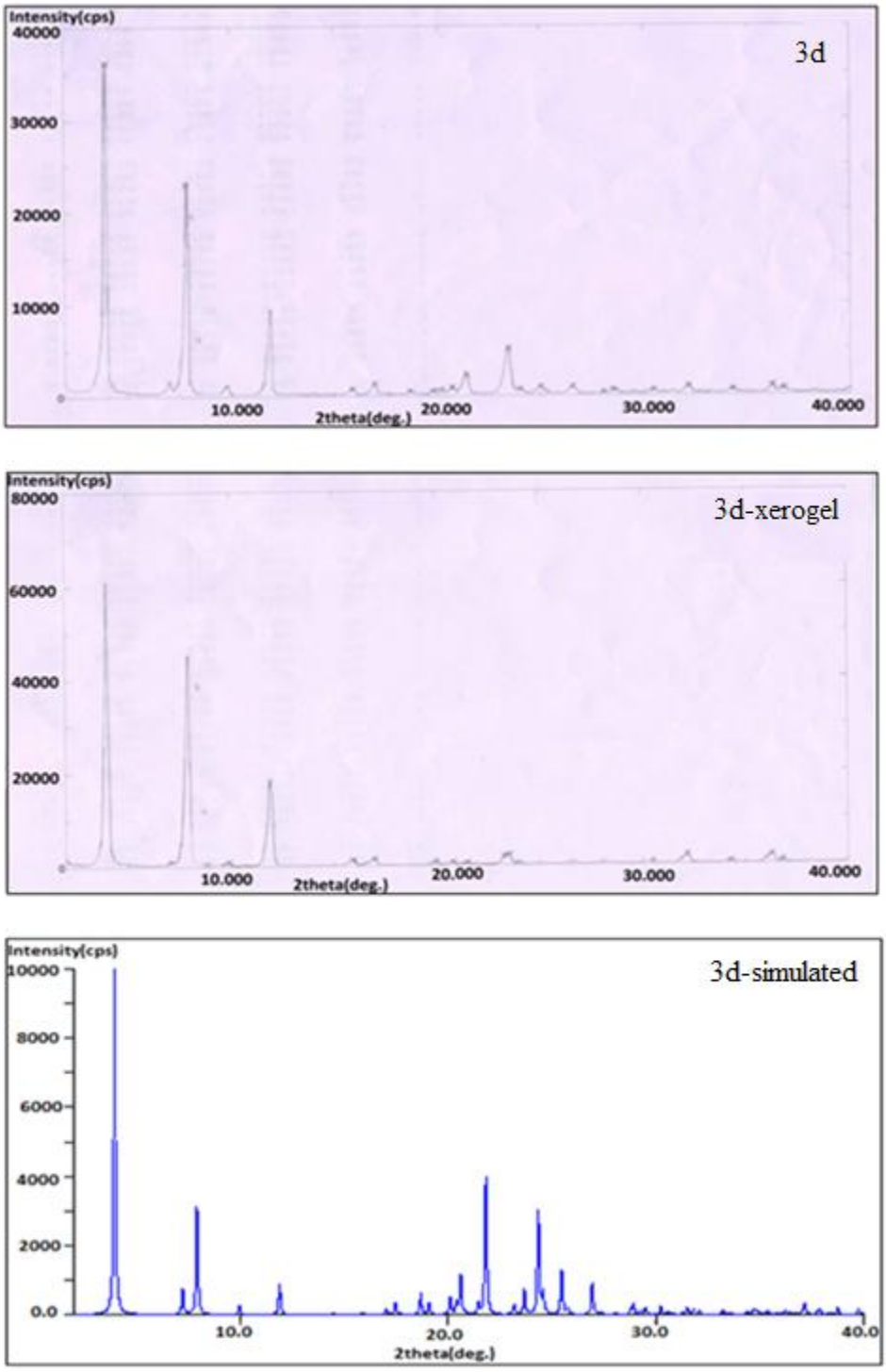


Figure S5: Comparative powder X-ray diffraction pattern of compounds **3d** in solid, xerogel and simulated (single crystal structure)

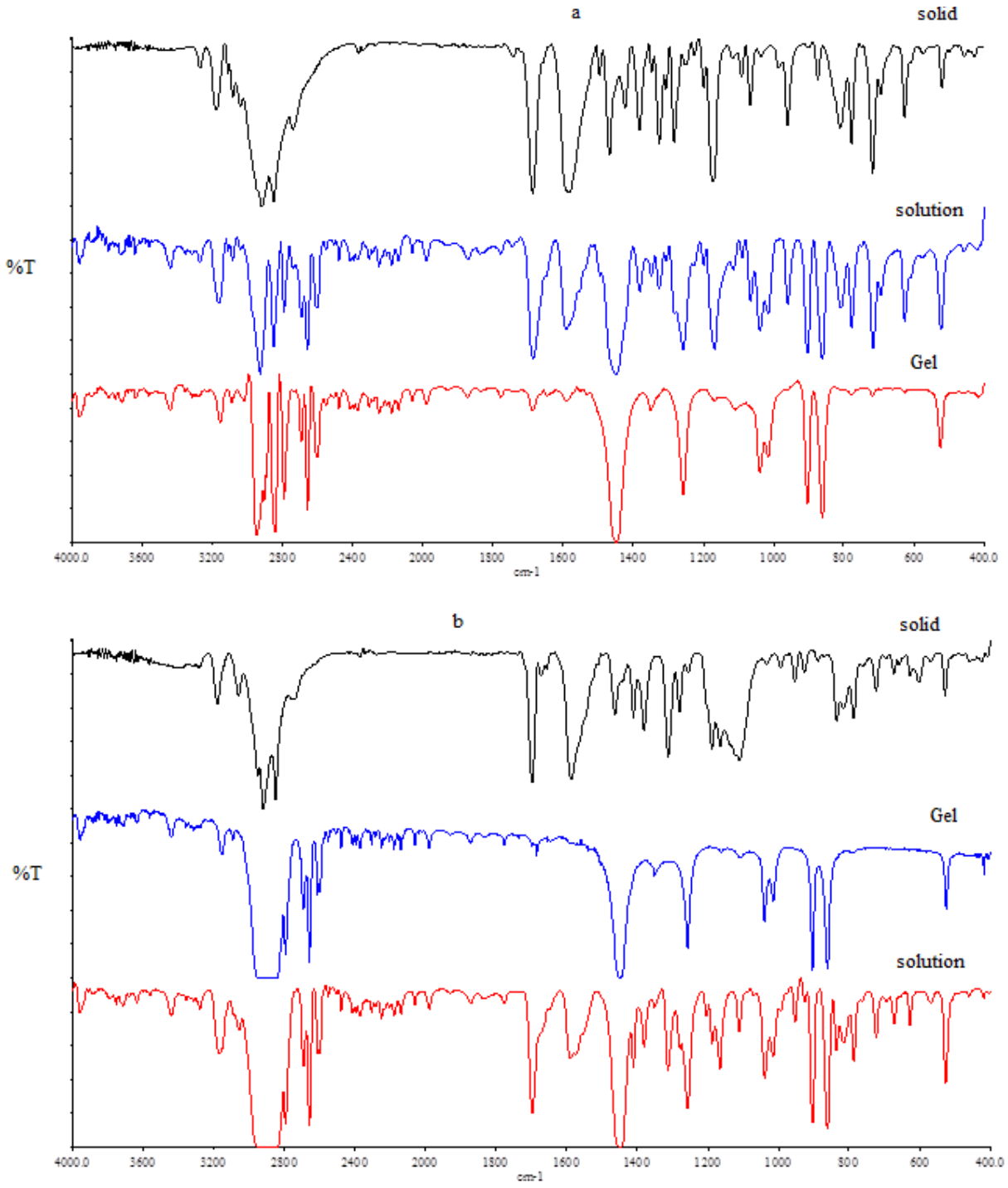


Figure S6: IR spetra of compounds (a)**1d** and (b)**3d** in cyclohexane