Supporting Information

Novel sulfamide-type low-molecular-mass gelators: gelation of aqueous, organic, and aqueous/organic biphasic solutions by hydrogen bond-directed 2-D amphiphilic sheet assemblies

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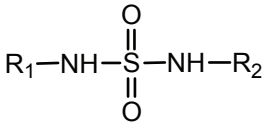
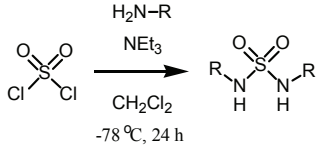
Synthesis of sulfamide derivatives 1 – 5



1: $R_1=R_2= C_8H_{17}$
2: $R_1=R_2= C_{14}H_{29}$
3: $R_1=R_2= (CH_2)_6O(CH_2CH_2O)_2CH_3$
4: $R_1= C_{14}H_{29}$, $R_2= (CH_2)_6O(CH_2CH_2O)_2CH_3$
5: $R_1= C_{14}H_{29}$, $R_2= (CH_2)_3OCH_2CH(OH)CH_2OH$

The symmetrically subsitutted derivatives **1-3** were synthesized accoding to the following scheme.

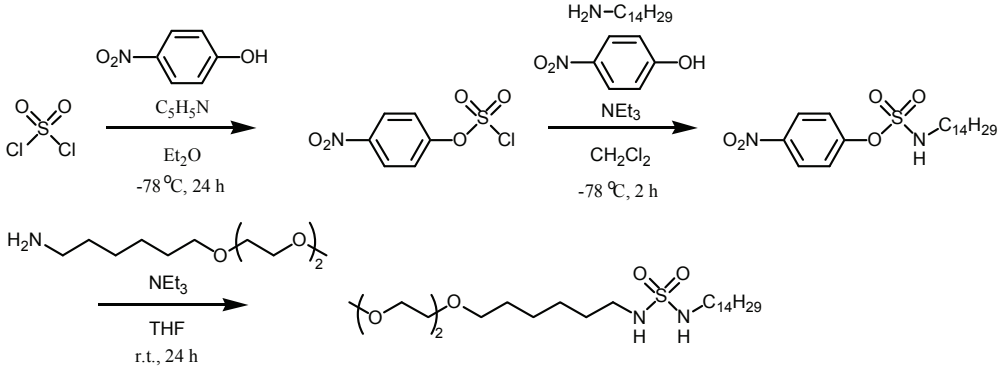


1 : Microcrystalline powder. Mp 124-125 °C. ^{1}H-NMR (400MHz, $CDCl_3$) 0.88 (6H, t, C*H*$_3$), 1.22-1.39 (20H, m, -C*H*$_2$-), 1.53 (4H, m, NHCH$_2$-C*H*$_2$-), 3.03 (4H, q, NH-C*H*$_2$-), 4.03 (2H, t, N*H*). FABMS : m/z=321.4 (calcd for $(M+H)^+$: 321.3).

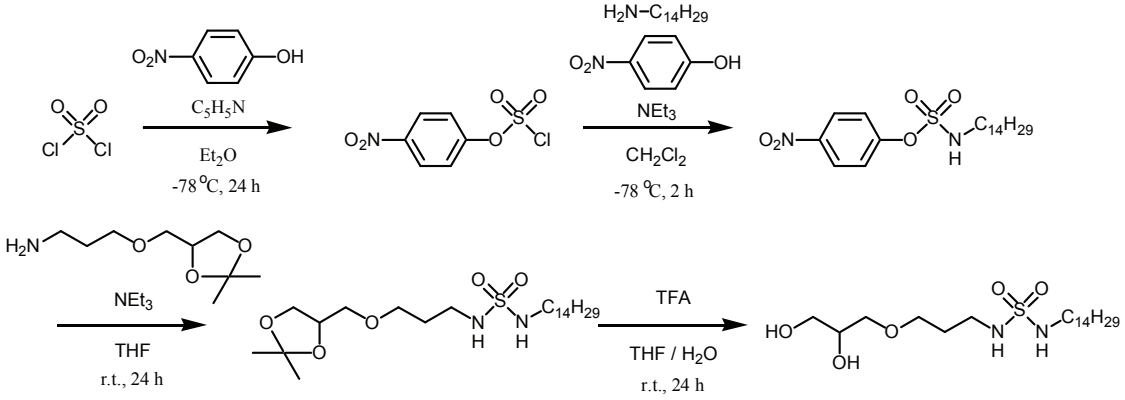
2 : White solid. Mp 126-127 °C. ^{1}H-NMR (400MHz, $CDCl_3$) 0.86-0.90 (6H, t, C*H*$_3$), 1.26 (48H, s, -C*H*$_2$-), 3.01-3.06 (4H, q, NH-*CH*$_2$-) 4.00-4.02 (2H, t, *NH*). Calcd. for $C_{28}H_{60}N_2O_2S$: C 68.79, H 12.37, N 5.73 %; found: C 69.03, H 12.36, N 5.42 %. HR-MS: m/z=489.4457 (calcd. for $(M+H)^+$: 489.4453).

3 : White solid. Mp 43-44 °C. ^{1}H-NMR (400MHz, $CDCl_3$) 1.35-1.60(16H, m, -*CH*$_2$-), 3.01-3.06 (4H, q, -NH-*CH*$_2$-), 3.39(6H, s, -O*CH*$_3$) 3.44-3.47 (4H, m, -*CH*$_2$-O-), 3.55-3.67 (16H, m, O-*CH*$_2$*CH*$_2$-O-), 4.12-4.15 (2H, t, *NH*). HR-MS: m/z=501.3202 (calcd. for $(M+H)^+$: 501.3209).

The asymmetrically substituted derivatives **4** and **5** were synthesized according to the method of Fettes et al. [1]



4 : White solid. Mp 87-88 °C. ^{1}H-NMR (400MHz, C_6D_6) 0.91-0.94 (3H, t, -*CH*$_3$), 1.07-1.51 (32H, m, -*CH*$_2$-),2.75-2.82 (4H, m, NH-*CH*$_2$-), 3.14 (6H, s, -O*CH*$_3$) 3.28-3.31 (2H, t, -*CH*$_2$-O-), 3.34-3.52 (8H, m, O-*CH*$_2$*CH*$_2$-O-),3.73-3.77(2H, tt, *NH*). HR-MS: m/z=495.3812 (calcd. for $(M+H)^+$: 495.3831).



5 : White solid. Mp 121-122 °C. ^{1}H-NMR (400MHz, DMSO) 0.84-0.87 (3H, t, -*CH*$_3$) 1.24 (22H, s, -*CH*$_2$-) 1.41-1.43 (2H, t, -*CH*$_2$-), 1.65-1.68 (2H, m NH-CH$_2$-*CH*$_2$-CH$_2$-O-), 2.73-2.76 (4H, q, -NH-*CH*$_2$-), 2.81-2.85 (4H, q, -NH-*CH*$_2$-), 3.23-3.42 (4H, m, -CH$_2$-O-CH$_2$-), 3.54-3.55(1H, m, *CH*) 4.47-4.49 (1H, t, -*CH*$_2$-OH), 4.61 (1H, d, *CH*$_2$-OH), 6.72-6.75(2H, tt, *NH*).
HR-MS: m/z=425.3047 (calcd. for $(M+H)^+$: 425.3049).

Measurements

^{1}H-NMR and IR spectra were recorded on a JEOL AL400 and a Shimadzu FTIR-8700 or a JEOL WINSPEC100 spectrometer, respectively. FABMS measurements were performed on a JEOL JMS-600H using glycerol as a matrix. XRD measurements were operated on a Rigaku RINT-2100 diffractometer (CuKα) in the range $0.7 < 2\theta < 30°$. For AFM measurements, silicon wafers were pressed onto gel surfaces, and the transferred gel samples were subjected to tapping mode AFM observation using a JEOL JSPM-4200 equipped with an Olympus silicon microcantilever (OMCL-AC160TS-C2, radius = 6 nm, resonance frequency=300kHz, spring constant = 42N/m). SEM image was obtained by a Hitachi High-Tech TM-1000.

Gelation abilities of the compound at 5 wt% were tested by the inversion method. [2] After solution of the compounds in each solvents by heating, the sample was cooled down to the ambient temperature.

Mode of molecular packing

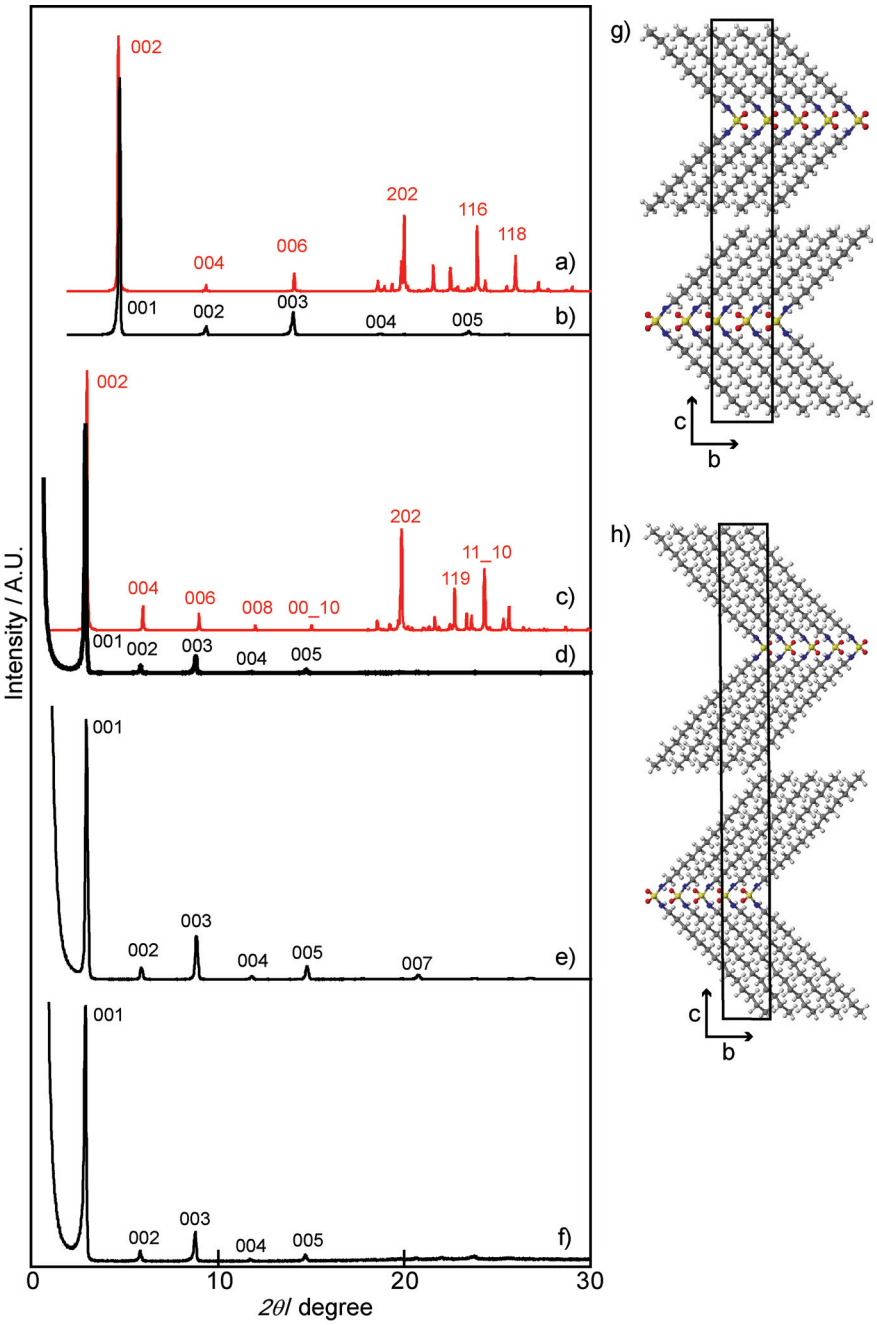


Figure S1 a) Simulated† (red) and b) observed (black) XRD patterns of **1**, c) simulated† (red) and d) observed (black) XRD patterns of **2**, e) XRD pattern of the **2**/benzene xerogel, f) XRD pattern of the **2**/ethanol xerogel, and estimated molecular packing of g) **1** and h) **2**.

†: Simulated from the reported crystal structure (CCDC: 159730, QIFGOB)[3] or by assuming that mode of the molecular packing was the same as that of **1** ; Because the unit cell of the crystal contains two layers, indices corresponding to the observed (00n) reflections are shown as (002n) in the simulated pattern.

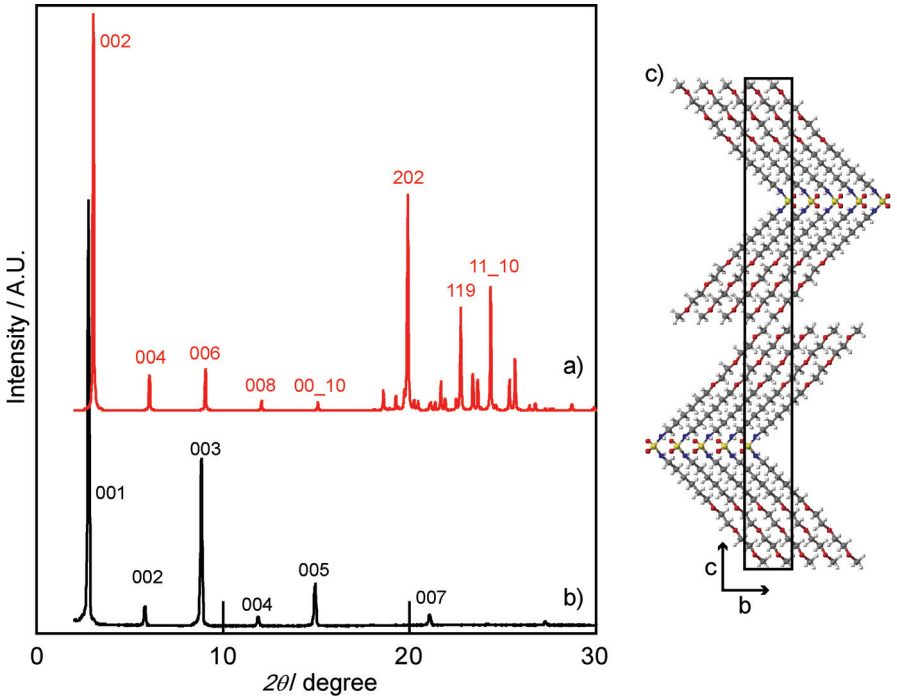


Figure S2 a) Simulated† (red) and b) observed (black) XRD pattern of a cast film of **3**, and c) estimated molecular packing.

†: See Figure S1.

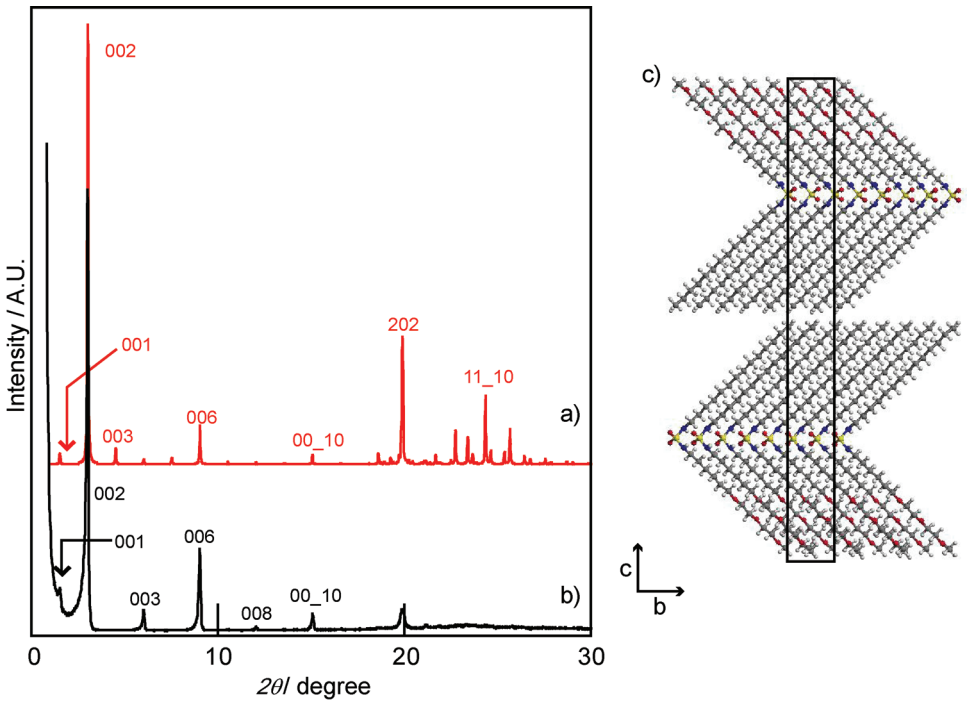


Figure S3 a) Simulated‡ and b) observed XRD pattern of a cast film of **4**, and c) estimated molecular packing.

‡ : Simulated by assuming that mode of the molecular packing was the same as that of **1**.

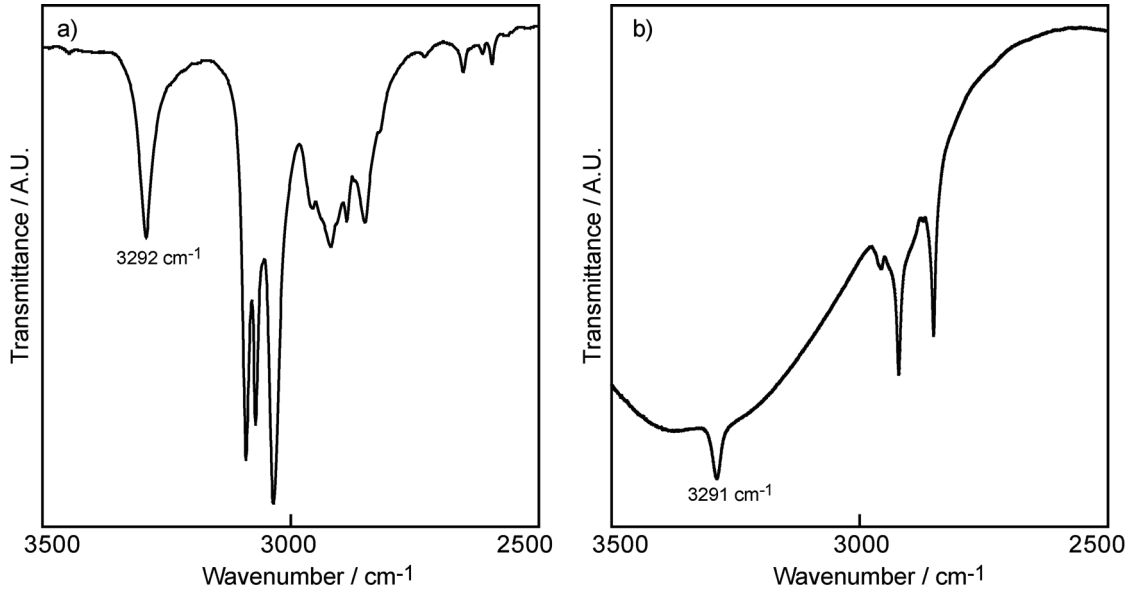


Figure S4 IR spectra of a) benzene organogel of **2** (5 wt%) and c) ethanol (33%)-containing hydrogel of **5** (5 wt%) placed between calcium fluoride plates..

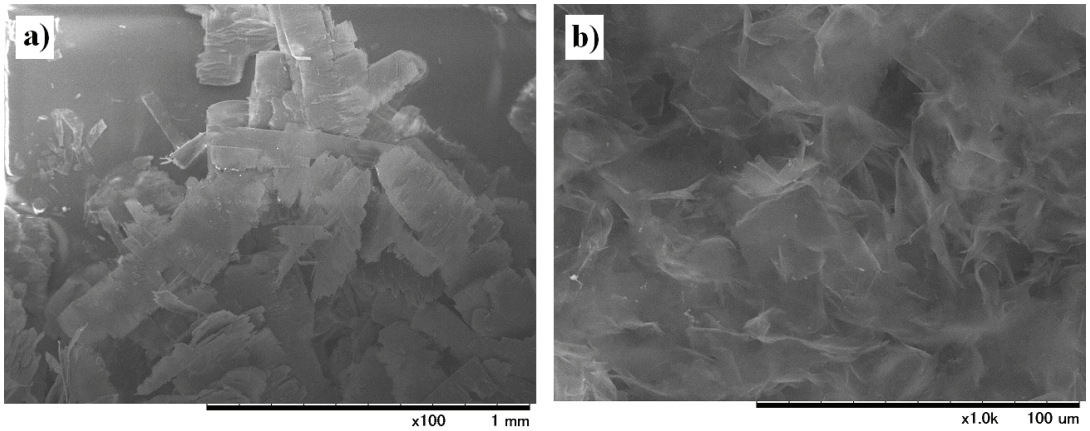


Figure S5 SEM images of the benzene xerogels of a) **2** and b) **5**.

1. K. J. Fettes, N. Howard, D. T. Hickman, S. Adah, M. R. Player, P. F. Torrence, J. Micklefield, *J. Chem. Soc., Perkin Trans. 1,* **2002**, 485.
2. K. Hanabusa, T. Miki, Y. Taguchi, T. Koyama and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1993**, 1382.
3. F. H. Allen, *Acta Cryst.*, 2002, **B58**, 380.