Electronic Supplementary Information for:

Supramolecular approach to the formation of magneto-active physical gels

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1. Materials and methods

All chemical reagents and solvents were obtained from commercial sources and used without further purification. As for tetrahydrofuran (THF), commercially available anhydrous solvents were used. All synthetic reactions were carried out under an argon atmosphere. IR measurements were conducted on a Jasco FT/IR-660 Plus spectrometer. UVVis absorption spectra were recorded on a Agilent 8453 spectrometer. Elemental analyses were carried out with a Yanaco MT-6 CHN autodcorder. Mass spectra (MALDI-TOF-MS) were recorded on a Perspective Biosystems Voyager-DE STR spectrometer using dithranol as the matrix. Phase transition behavior of the materials was examined by differential scanning calorimetry (DSC) using a NETSCH DSC 204 Phoenix. The heating and cooing rates were 5 K min⁻¹. The sol-gel transition temperature was taken at the maximum of the transition peak on cooling. Tapping mode atomic force microscope (AFM) observation was performed with a Digital Instruments Nanoscope IIIa equipped with a cantilever (NCH-10V) at room temperature in air. X-ray diffraction (XRD) measurement of the xerogel was carried out on a Rigaku RINT 2500 diffractometer using monochromated Cu Ka radiation. Magnetic susceptibilities were measured using a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer. An analogous nonradical compound, N-carbobenzyloxy-L-isoleucylaminooctadecane (ZI18) as a reference, at 0.1 M concentration were measured at an applied magnetic filed of 1 T. The net χ_M values of the fibrous aggregates of 1 in the dodecane were obtained by subtracting the diamagnetic contribution of amino acid scaffold of 1, dodecane and cells as a background. The ESR spectrum for a benzene solution at 2.0×10^{-6} M spin concentration were recorded on a JEOL JESRE1X X-band spectrometer at room temperature with a center field of 323 mT, sweep time of 1 minute, sweep width of 25 mT, a microwave frequency of 9 GHz, modulation width of 0.1 mT, and a power of 1 mW. Manganese oxide was used as an external standard.

2. Synthesis of 1

Ethyl (4-TEMPO-oxy) acetate: A mixture of 4-hydroxy-TEMPO (0.59 g, 3.43 mmol), NaH (0.29 g, 12.08 mmol), and dry THF (20 mL) was stirred for 1 hour. Then ethyl bromoacetate (0.90 g, 5.39 mmol) was added, and the reaction mixture was stirred for 20 h at room temperature. The reaction mixture was dissolved in ethyl acetate and washed with saturated NaCl aq. The organic phase was dried with MgSO₄, filtrated and the solvent was evaporated. The crude material was purified by silica gel column chromatography using an eluent of hexane/ethyl acetate (3:1). Yield: 0.52 g (59 %). IR (KBr): *v* 2983, 2939, 1753, 1377, 1359, 1244, 1204, 1129, 1032 cm⁻¹. Anal. Calcd. for $C_{13}H_{24}NO_4$ · (258.33): C, 60.44; H, 9.36; N, 5.42. Found: C, 60.22; H, 9.46; N, 5.29. MS (MALDI-TOF): calcd, 260.18 (M+2); found, 260.30 (M+2).

(4-TEMPO-oxy) acetic acid: A mixture of ethyl (TEMPO-oxy) acetate (0.26 g, 1.0 mmol), KOH (0.56 g, 10.0 mmol), ethanol (20 mL), and water (7 mL) was refluxed for 1 h. The reaction mixture was acidified with 5 % hydrochloridic acid, dissolved in chloroform, and washed with water. The organic phase was dried with MgSO₄, filtrated and the solvent was evaporated. Yield: 0.20 g (87 %). IR (KBr): v 2985, 2948, 1755, 1734, 1470, 1377, 1365, 1243, 1172, 1132 cm⁻¹. MS (MALDI-TOF): calcd, 232.14 (M+2); found, 232.15 (M+2).

N-(**4-TEMPO-oxymethyl-carbonyl**)-*L*-isoleucylaminooctadecane: A mixture of (4-TEMPO-oxy)acetic acid (0.11 g, 0.48 mmol), *L*-isoleucylaminooctadecane (0.18 g, 0.47 mmol), EDC (0.13 g, 0.68 mmol), DMAP (0.007 g, 0.06 mmol), and dichloromethane (10 mL) was stirred at room temperature for 48 h. The reaction mixture was dissolved in chloroform and washed with saturated NaCl aq. The organic phase was dried with MgSO₄, filtrated and the solvent was evaporated. The crude material was purified by silica gel column chromatography using an eluent chloroform/methanol (10:1), followed by GPC. Yield: 0.22g (79%). mp: 310.4 K. UV (CHCl₃): λ 240nm. IR (KBr): ν 3281, 3097, 2975, 2920, 2850, 1641, 1466, 1378, 1241, 1178, 1127 cm⁻¹. Anal. Calcd. for C₃₅H₆₈N₃O₄· (594.93): C, 70.66; H, 11.52; N, 7.06. Found: C, 70.43; H, 11.71; N, 6.90. MS (MALDI-TOF): calcd, 596.93 (M+2); found, 596.75 (M+2).



Scheme S1. Synthetic scheme of 1. Reagents and conditions: (a) ethyl bromoacetate, NaH, THF, r.t., (b) KOH, ethanol/water, reflux, (c) EDC, DMAP, dichloroethane, r.t.

3. FT/IR spectrum of the gel of 1



Figure S1. FT-IR spectrum of a dodecane gel of 1 at room temperature.

4. UV-vis absorption spectrum of the gels of 1



Figure S2. UV-Vis spectrum of a dodecane gel at 0.05 M concentration.

5. X-ray diffraction pattern of the xerogel of 1



Figure S3. XRD pattern of the xerogel of **1** at room temperature. The *d*-values of six main diffraction peaks $(2\theta = 2.0^{\circ}, 3.5^{\circ}, 5.7^{\circ}, 9.7^{\circ}, 19.4^{\circ}, 21.5^{\circ})$ are described. The dodecane gel of **1** (0.1 M) was spreaded on a glass plate and dried in air at room temperature for 3 h to give the xerogel. Dodecane was slowly evaporated although the boiling point is 214-218 °C.

6. Special set up for SQUID measurement of 1



Picture of the cell

Figure S4. Schematic illustration of set up for SQUID measurement of **1** in dodecane. To prevent the evaporation of the solvent, all samples were encapsulated in an appropriately designed copper cell and the cell was sealed with an epoxy resin.

7. One-dimensional chain model of Bonner-Fisher model

Based on the Bonner-Fisher model, the molar susceptibility is given by the Equation (1):

$$\chi_{M} = \frac{Ng^{2}\beta^{2}}{kT} \frac{0.25 + 0.074975x + 0.075235x^{2}}{1 + 0.9931x + 0.172135x^{2} + 0.757825x^{3}}$$
(1)

where x = |J|/kT and J is the exchange coupling parameter describing the magnetic interactions.

8. Analysis of the SQUID data by a simple Curie-Weiss model



Figure S5. Thermal variation of the χ_{M}^{-1} for the radical aggregates of **1** at 2–240 K. The solid line is the best fit to the Curie-Weiss law.

9. Special set up for SQUID measurement of solvent-free system



Figure S6. Schematic illustration of set up for SQUID measurement of solvent-free system (xerogels). To prepare solvent-free system, dodecane was slowly evaporated at room temperature and ambient pressure. After that, the χ_M was measured.

10. Thermal variation of the $\chi_{\rm M}T$ product for the xerogels



Figure S7. Thermal variation of the $\chi_{\rm M}T$ product for the xerogels. The red solid line is the best fit to the antiferromagnetic S = 1/2 chain based on the Bonner-Fisher model with $J = -0.94 \text{ cm}^{-1}$, g = 2.00, and $R = 6.0 \times 10^{-4}$ (*R* is the agreement factor defined as $R = \Sigma[(\chi_{\rm M})_{\rm obs} - (\chi_{\rm M})_{\rm calc}]^2 / \Sigma[(\chi_{\rm M})_{\rm obs}]^2$).