Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015

Electronic Supplementary Information for

Self-assembly of polyoxometalate-cholesterol conjugate into microrods or nanoribbons regulated by thermodynamics

Hai-Kuan Yang,*[a,b] Li-Jun Ren,[c] Han Wu,[c] Wei Wang*[c]

[a]Department of Chemistry, North University of China, Taiyuan, Shanxi 030051, China. E-mail: haikuanyang@nuc.edu.cn

[b]Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

[c]Center for Synthetic Soft Materials, Key Laboratory of Functional Polymer Materials of Ministry of Education and Institute of Polymer Chemistry, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China. E-mail: weiwang@nankai.edu.cn

Details of experimental section

O-succinyl-cholesterol[1] (280 mg, 0.57 mmol) and 2-ethoxy-l-(ethoxycarbonyl)-l,2-dihydroquinoline (213 mg, 0.86 mmol) were dissolved in acetonitrile (125 mL) and the reaction was kept at 81.0 ^{O}C for 40 min, after that, the tetrabutylammonium (TBA) salt of the tris-modified Anderson-type POM cluster (Tris-POM-Tris)[2,3] $\{MnMo_6O_{18}[(OCH_2)_3CNH_2]_2\}^{3-}$ (416 mg, 0.22 mmol) was added to the solution and the mixture was refluxed for 36 h. The orange solution was cooled to room temperature, after evaporation of the acetonitrile under reduced pressure, the resulting concentrated solution was added dropwise to ethyl acetate (500 mL), collection of the light orange solid, and was dissolved in a minimum amount of acetonitrile (3 mL). After two days of slow evaporation in ether vapor at room temperature, afforded pure orange product (yield: 471 mg, 0.29 mmol, 76%). FT-IR (KBr pellet): bands at ν = 3340, 2957, 2938, 2871, 1730, 1684, 1541, 1509, 1468, 1376, 1333, 1252, 1234, 1168, 1115, 1066, 1028, 940, 921, 903, 667, 564 cm^{-1}; ESI-MS (negative mode, DMF): 1046.4 $g{\cdot}mol^{-1}$ $[M\text{-}3TBA+H]^{2-}$, 1064.7 $g{\cdot}mol^{-1}$ $[M\text{-}3TBA+K]^{2-}$; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.67 (s, 6H, $-CH_3$), 0.80-1.62 (m, 150H, -CH-, $-CH_2$-, $-CH_3$, 3TBA), 1.74-2.08 (m, 10H, -CH-, $-CH_2$-), 2.31 (d, 4H, $-C{=}C-CH_2$-), 2.42, 2.74 (m, 8H, $-(C{=}O)-CH_2-CH_2-(C{=}O)$-), 3.16 (m, 24H; TBA), 4.46-4.55 (m, 2H, -(C=O)-O-CH-), 5.37 (d, 2H, -C=C-H) 7.55 (s, 2H; NHCO), 63.83 (broad, $-CH_2$-) ppm; Elemental analysis (%) for $C_{118}H_{220}MnMo_6N_5O_{30}$ (2819.6 $gmol^{-1}$): calculated: C 50.26, H 7.86, N 2.48; found: C 49.91, H 7.98, N 2.45.

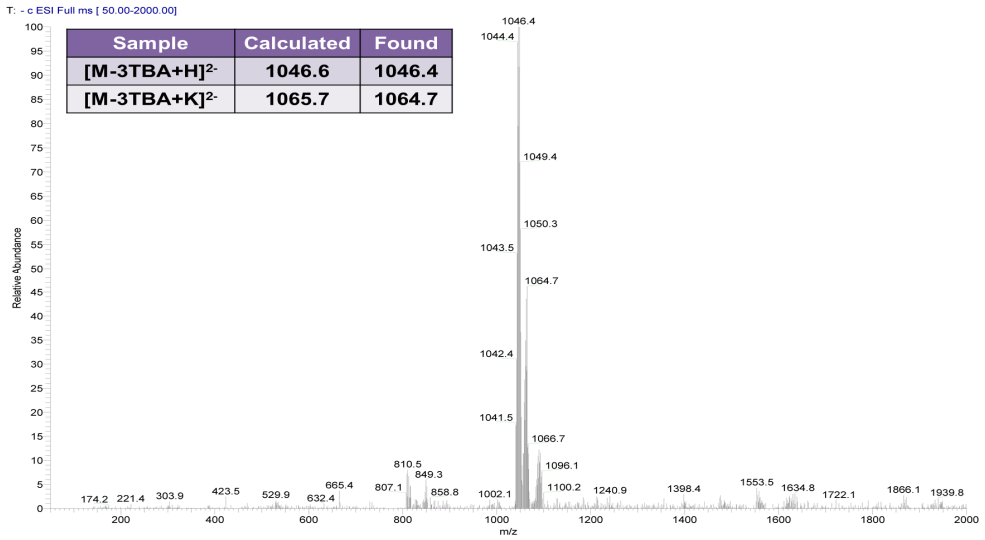

Figure S1 ESI-MS spectrum of the POM-cholesterol conjugate. ESI-MS (negative mode, DMF): 1046.4 g·mol^{-1} $[M\text{-}3TBA+H]^{2-}$, 1064.7 g·mol^{-1} $[M\text{-}3TBA+K]^{2-}$.

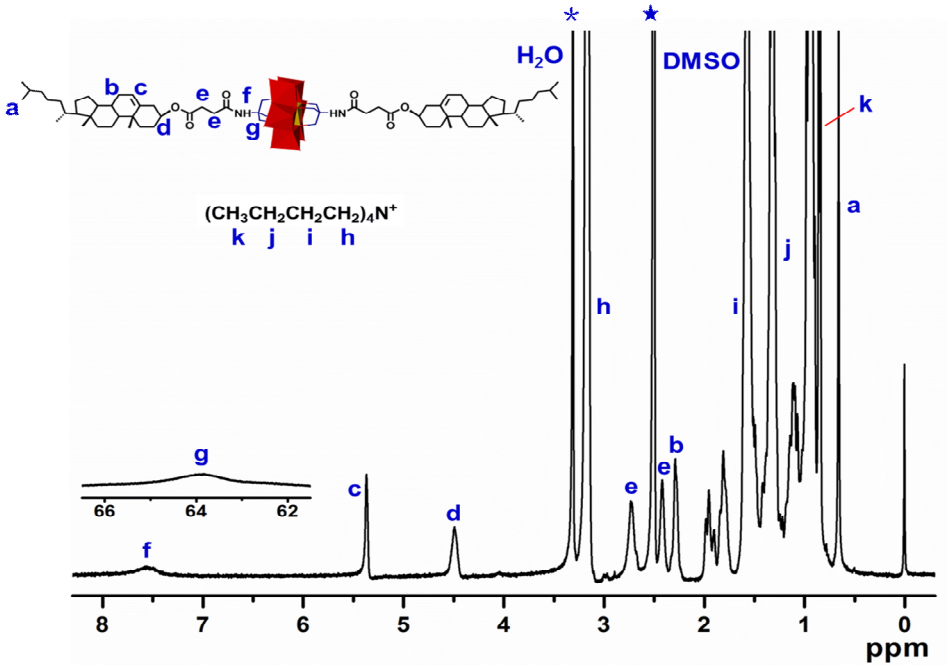

Figure S2 ^{1}H NMR spectrum of the POM-cholesterol conjugate in DMSO-d_6. (☆ the peak of DMSO, ⁎ the peak of H_2O).

Table S1 Self-assembly behavior of the POM-cholesterol conjugate (c = 15 mg mL^{-1}) in mixed DMF/toluene solvents at 20.0 ^{O}C[a].

Toluene/DMF (v/v%)	State	Toluene/DMF (v/v%)	State
1:0	S	1:7	G
1:1	S	1:8	G
1:2	S	1:9	G
1:3	S	1:10	G
1:4	S	1:11	G
1:5	S	1:12	G
1:6	G	0:1	G

[a]S = solution; G = gel.

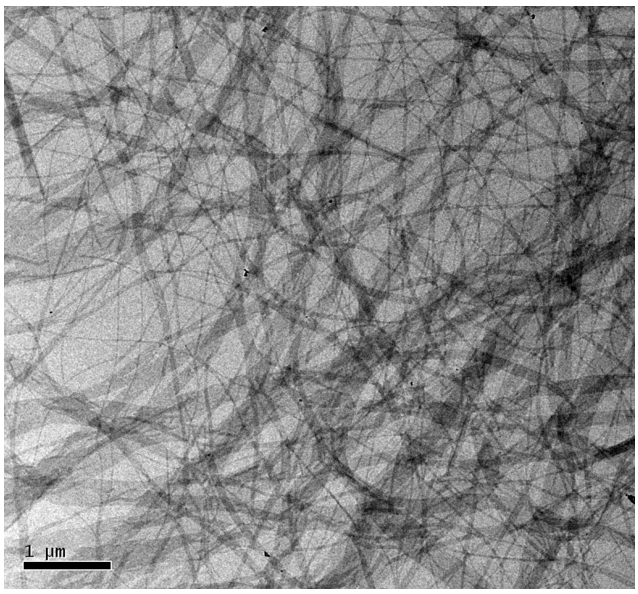

Figure S3 TEM image of dried gel sample (c = 15 mg mL^{-1}) formed in toluene at 20.0 ^{O}C.

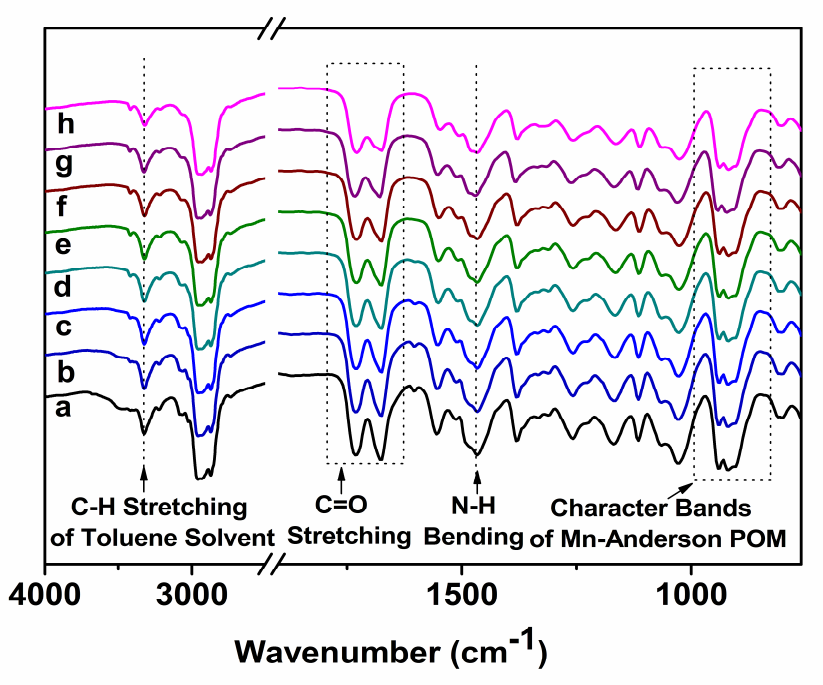

Figure S4 Temperature-dependent FT-IR spectra of the organogel formed in toluene (c = 15 mg mL^{-1}). (a) 20.0 ^{O}C; (b) 40.0 ^{O}C; (c) 60.0 ^{O}C; (d) 80.0 ^{O}C; (e) 100.0 ^{O}C; (f) 120.0 ^{O}C; (g) 140.0 ^{O}C; (h) 160.0 ^{O}C.

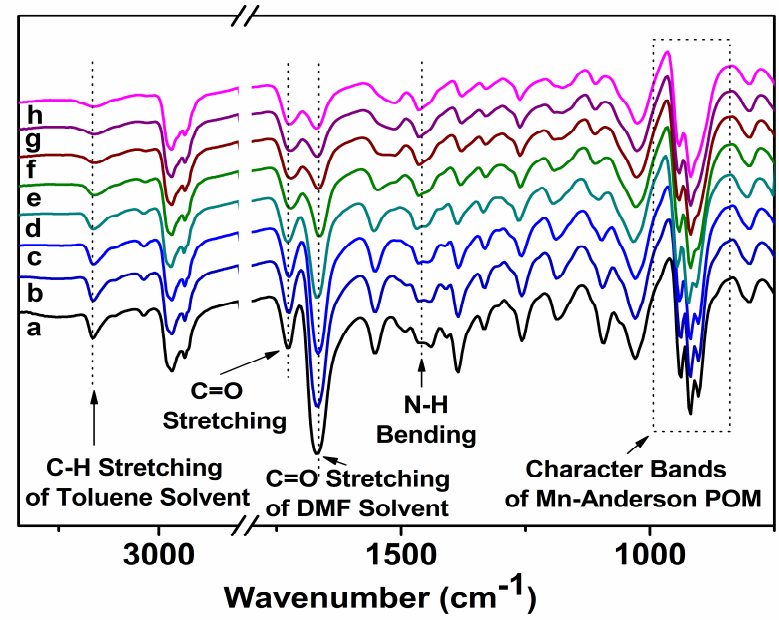

Figure S5 Temperature-dependent FT-IR spectra of the organogel formed in mixed DMF/toluene solvents (c = 15 mg mL^{-1}, v/v = 1:9). (a) 20.0 ^{O}C; (b) 40.0 ^{O}C; (c) 60.0 ^{O}C; (d) 80.0 ^{O}C; (e) 100.0 ^{O}C; (f) 120.0 ^{O}C; (g) 140.0 ^{O}C; (h) 160.0 ^{O}C.

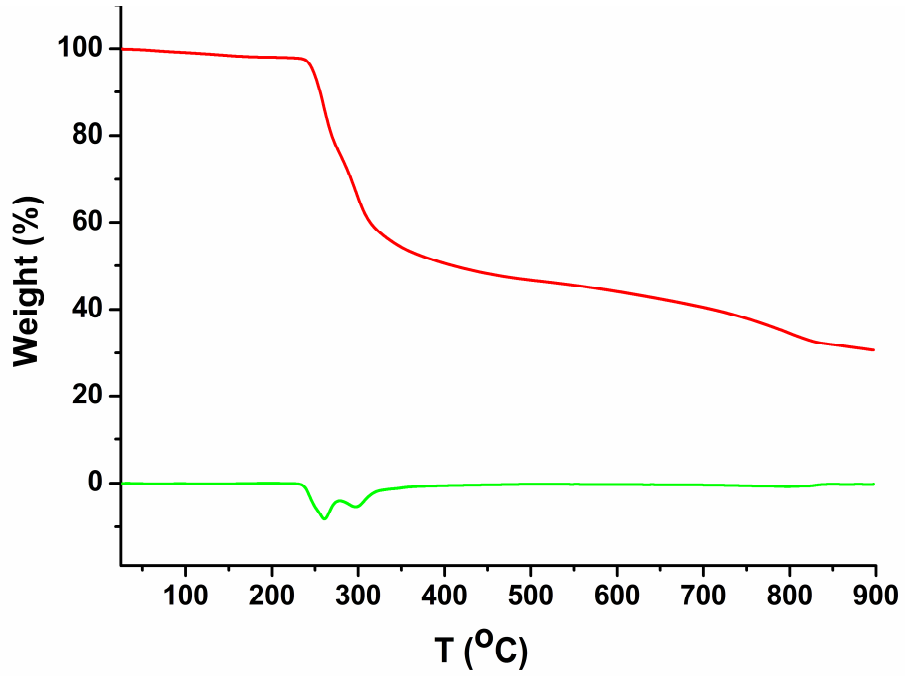

Figure S6 TGA thermogram of the xerogel in mixed DMF/toluene solvents at a 1/9 ratio (c = 15 mg mL^{-1}).

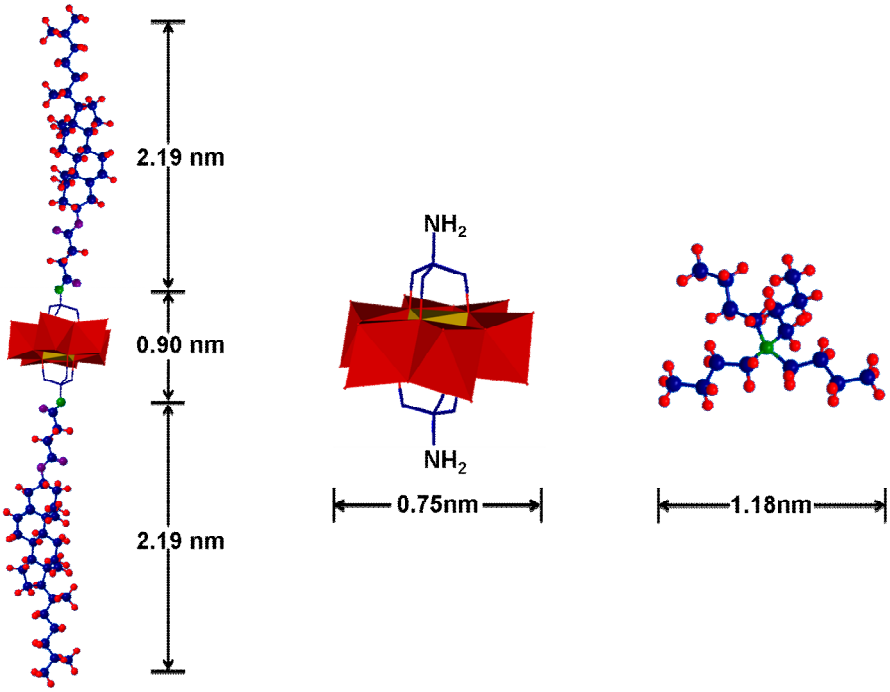

Figure S7 The molecular sizes of *o*-succinyl-cholesterol and tetrabutyl ammonium cation (Bu_4N^+) are simulated by Chem3D Ultra 10.0 and the Tris-POM-Tris is simulated according to the procedure reported in literature[4].

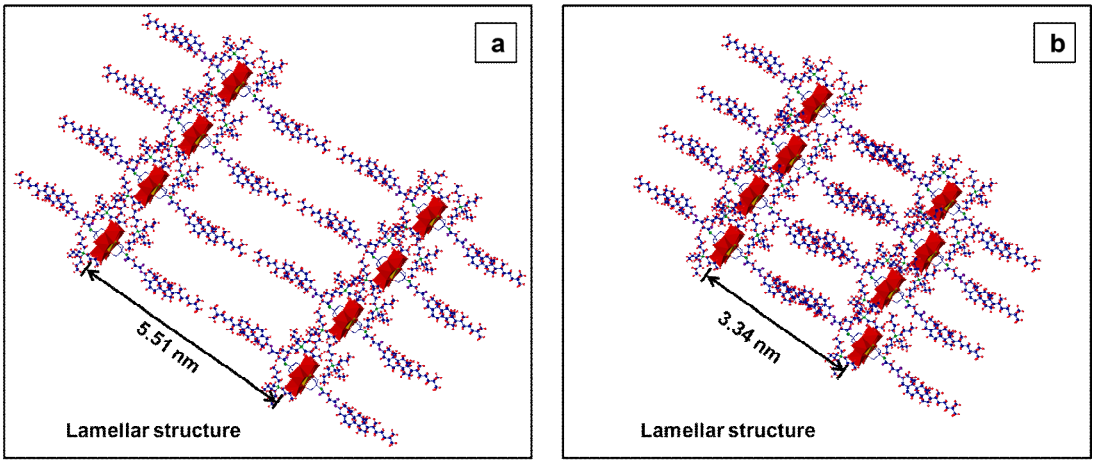

Figure S8 The schematic drawing of the lamellar structure. (a) the self-assembled structures in crystalline rods; (b) the self-assembled structures in the organogel.

References

1 P. Pescador, N. Brodersen, H. A. Scheidt, M. Loew, G. Holland, N. Bannert, J. Liebscher, A. Herrmann, D. Huster, A. Arbuzova, *Chem. Commun.,* 2010, *46*, 5358–5360.

2 B. Hasenknopf, R. Delmont, P. Herson, P Gouzerh, *Eur. J. Inorg. Chem*., 2002, 1081–1087.

3 P. R. Marcoux, B. Hasenknopf, J. Vaissermann, P. Gouzerh, *Eur. J. Inorg. Chem.,* 2003, 2406–2412.

4 C. M. Liu, Y. H. Huang, D Q.Zhang, S. Gao, F. C. Jiang, J. Y. Zhang, D. B. Zhu, *Crystal Growth & Design.,* 2005, *5*, 1531–1538.