

Electronic Supplementary Information for

Structure- and solvent-triggered influences in the self-assembly of polyoxometalate-steroid conjugates

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Details of experimental section

Synthesis of POM-Ca conjugate: The cholic acid (2.1 eq.) and 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (2.6 eq.) were dissolved in CH₃CN and the reaction was kept at 81 °C for 40 min, then the tetrabutylammonium (TBA) salt of the tris-modified Anderson-type POM cluster (POM-Tris)^{1,2} {MnMo₆O₁₈[(OCH₂)₃CNH₂]₂}³⁻ (1.0 eq.) was added to the solution and the mixture was refluxed for 36 h. The orange solution was cooled to room temperature and most acetonitrile was evaporated under reduced pressure. Some white precipitate was filtered off and then the orange filtrate was again concentrated to the minimum. The concentrated orange liquid was added dropwise to tetrahydrofuran to collect a light orange solid. The collected light orange solid was redissolved in a small amount of CH₃CN. After a three-day slow evaporation of the solution in ether vapor at room temperature, a pure orange product was received (yield: 76%). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 0.59 (s, 6H, H₃C-C(13)), 0.81 (s, 6H, H₃C-C(10)), 0.93 (t, 42H, H₃C-C(20), TBA), 1.57 (m, 24H, TBA), 3.16 (m, 26H, H-C(3), TBA), 3.61 (s, 2H, H-C(7)), 3.79 (s, 2H, H-C(12)), 3.99 (d, 2H, -OH), 4.09 (d, 2H, -OH), 4.29 (d, 2H, -OH), 7.31 (s, 2H, NHCO), 64.21 (broad, 12H, -CH₂-) ppm; FT-IR (KBr pellet): bands at ν = 3426, 3332, 2959, 2936, 2871, 1669, 1542, 1475, 1373, 1313, 1255, 1228, 1194, 1153, 1083, 1030, 941, 920, 902, 667, 564 cm⁻¹; ESI-MS (negative mode, DMF): 969 gmol⁻¹ [M-3TBA+H]²⁻.

Synthesis of POM-Dhca conjugate: The dehydrocholic acid (2.1 eq.) and EEDQ

(2.6 eq.) were dissolved in CH₃CN and the reaction was kept at 81 °C for 30 min, then the POM-Tris (1.0 eq.) was added to the solution and the mixture was refluxed for 18 h. The orange solution was cooled to room temperature and acetonitrile was evaporated under reduced pressure. Some white precipitate was filtered off and then the orange filtrate was again concentrated to the minimum. The concentrated solution was added dropwise to ethyl acetate to collect a light orange solid. The collected light orange solid was redissolved in a small amount of CH₃CN. After a three-day slow evaporation in ether vapor at room temperature, a pure orange product was received (yield: 82%). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 0.77 (d, 6H, H₃C–C(20)), 0.93 (t, 36H, TBA), 1.02 (s, 6H, H₃C–C(13)), 1.31 (m, 24H, TBA), 1.33 (s, 6H, H₃C–C(10)), 1.57 (m, 24H, TBA), 3.01 (dd, 4H, H₂–C(4)), 3.16 (m, 24H, TBA), 7.35 (s, 2H, NHCO), 64.91 (broad, 12H, –CH₂–) ppm; FT-IR (KBr pellet): bands at ν = 3350, 2961, 2939, 2874, 1709, 1652, 1537, 1464, 1379, 1341, 1273, 1204, 1184, 1100, 1045, 1024, 943, 922, 903, 667, 563 cm⁻¹; ESI-MS (negative mode, DMF): 963 gmol⁻¹ [M–3TBA+H]²⁻.

Synthesis of POM-Chol: The *o*-succinyl-cholesterol³ (2.1 eq.) and EEDQ (2.6 eq.) were dissolved in CH₃CN and the reaction was kept at 81 °C for 35 min, then the POM-Tris (1.0 eq.) was added to the solution and the mixture was refluxed for 24 h. The orange solution was cooled to room temperature and the acetonitrile was evaporated under reduced pressure. Some white precipitate was filtered off and then the orange filtrate was again concentrated to the minimum. The concentrated solution was added dropwise to ethyl acetate to collect a light orange solid. The collected light

orange solid was redissolved in a small amount of CH_3CN . After a two-day slow evaporation in ether vapor at room temperature, a pure orange product was received (yield: 78%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 0.67 (s, 6H, $-\text{CH}_3$), 0.80-1.62 (m, 150H, $-\text{CH}-$, $-\text{CH}_2-$, $-\text{CH}_3$, 3TBA), 1.74-2.08 (m, 10H, $-\text{CH}-$, $-\text{CH}_2-$), 2.31 (d, 4H, $-\text{C}=\text{C}-\text{CH}_2-$), 2.42, 2.74 (m, 8H, $-(\text{C}=\text{O})-\text{CH}_2-\text{CH}_2-(\text{C}=\text{O})-$), 3.16 (m, 24H, TBA), 4.46-4.55 (m, 2H, $-(\text{C}=\text{O})-\text{O}-\text{CH}-$), 5.37 (d, 2H, $-\text{C}=\text{C}-\text{H}$), 7.55 (s, 2H, NHCO), 63.83 (broad, 12H, $-\text{CH}_2-$) ppm; 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): 1047 gmol^{-1} $[\text{M}-3\text{TBA}+\text{H}]^{2-}$.

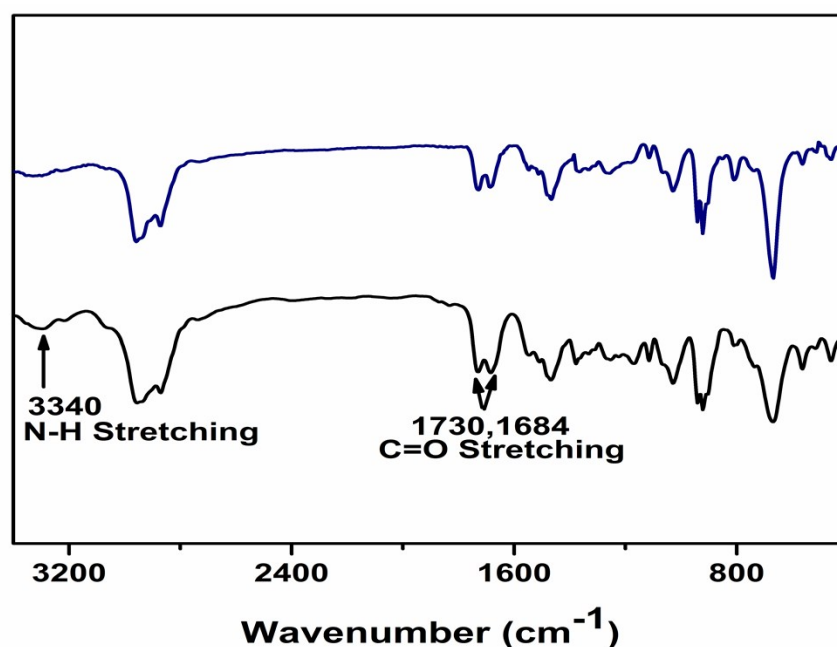


Figure S1 FT-IR spectra of the original powders and the dried sample of POM-Chol conjugate in toluene-DMF (5 : 1). Top: original powders; Bottom: dried sample.

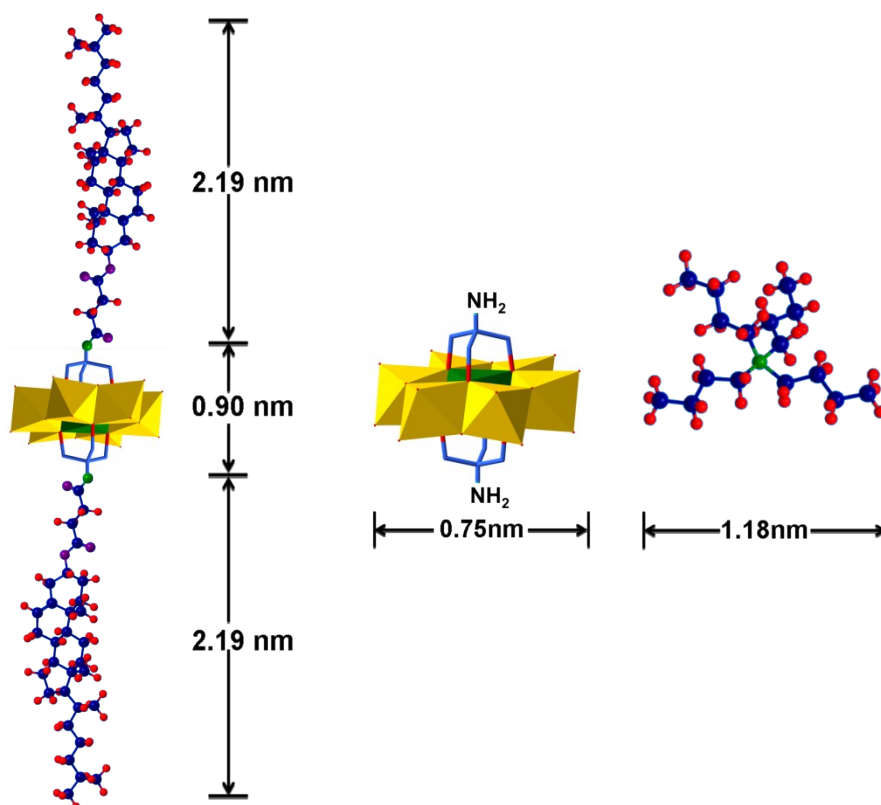


Figure S2 The molecular sizes of *o*-succinyl-cholesterol and tetrabutyl ammonium cation (Bu_4N^+) are simulated by Chem3D Ultra 10.0 and the Tris-POM-Tris is simulated according to the procedure reported in literature⁴.

Table S1 Dielectric constants, ϵ^e , of the various organic solvents⁵

Entry	Solvents	Dielectric constant
1	Toluene	2.57
2	CH_2Cl_2	9.08
3	Acetone	20.70
4	CH_3OH	32.70
5	DMF	36.71

References

- 1 B. Hasenknopf, R. Delmont, P. Herson, P. Gouzerh, *Eur. J. Inorg. Chem.*, 2002, 1081–1087.
- 2 P. R. Marcoux, B. Hasenknopf, J. Vaissermann, P. Gouzerh, *Eur. J. Inorg. Chem.*, 2003, 2406–2412.
- 3 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.
- 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.
- 5 J. A. Dean, Ed. *Lange's Handbook of Chemistry*, McGraw-Hill Book Company, 1985.