Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information:

Polyoxometalate-based Supramolecular Hydrogel Constructed through the Host-Guest Interactions

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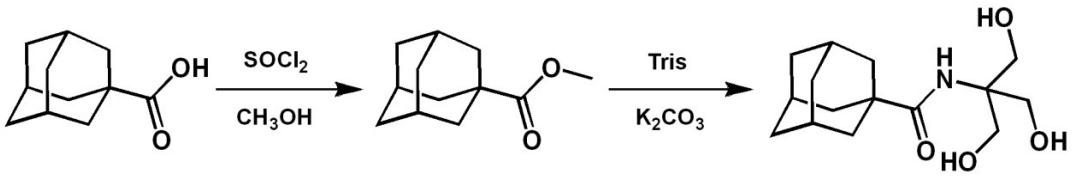
Synthesis of Tris-Adamantane:



Tris-Adamantane was synthesized according to reported methods.[1] 1-adamantanecarboxylic acid (3.6 g, 20 mmol) was dissolved in 15 mL of $SOCl_2$ in ice bath. The resulting clear solution was left for stirring overnight. After removal of the unreacted $SOCl_2$ under vacuum, dry methanol 20 mL was added and refluxed at 65 °C for 4 hours. Colorless needle crystals of 1-(methoxy- carbonyl)adamantane were separated and used without further purification after concentrated the above solution and recrystallized at 4 °C. 1-(methoxycarbonyl)- adamantane (900 mg, 4.6 mmol), Tris (560 mg, 4.6 mmol) and K_2CO_3 (700 mg, 5.0 mmol) were suspended in 20 mL dry DMSO and the resulting light yellow solution was stirred at room temperature for 24 hours under nitrogen. After removal the solvent, the solid obtained was washed with water and dried in air. The crude product was then dissolved in a minimum amount of ethanol and recrystallized at -20 °C. Yield: 73.2 %. ^{1}H NMR (DMSO-d_6, ppm): δ = 1.67 (t, 6H), 1.77 (d, 6H), 1.98 (m, 3H), 3.50 (d, 6H), 4.91 (t, 3H), 6.40 (s, 1H). ^{13}C NMR (DMSO-d_6, ppm): δ = 27.60, 35.98, 38.73, 40.48, 60.41, 61.21, 177.98. ESI-MS (methanol, positive mode): m/z = 284.33 ([M+H]$^+$), 306.30 ([M+Na]$^+$).

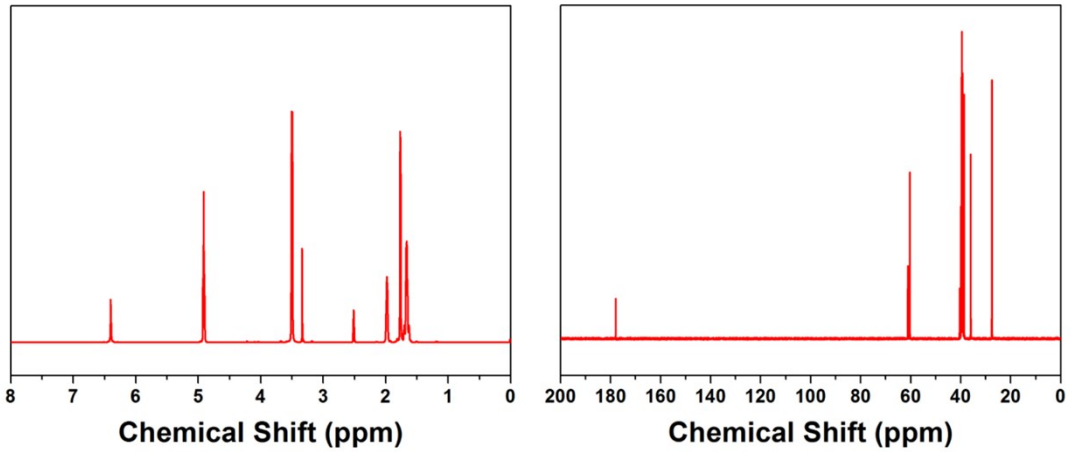


Fig. S1 ^{1}H NMR (left) and ^{13}C NMR (right) spectra of Tris-Adamantane.

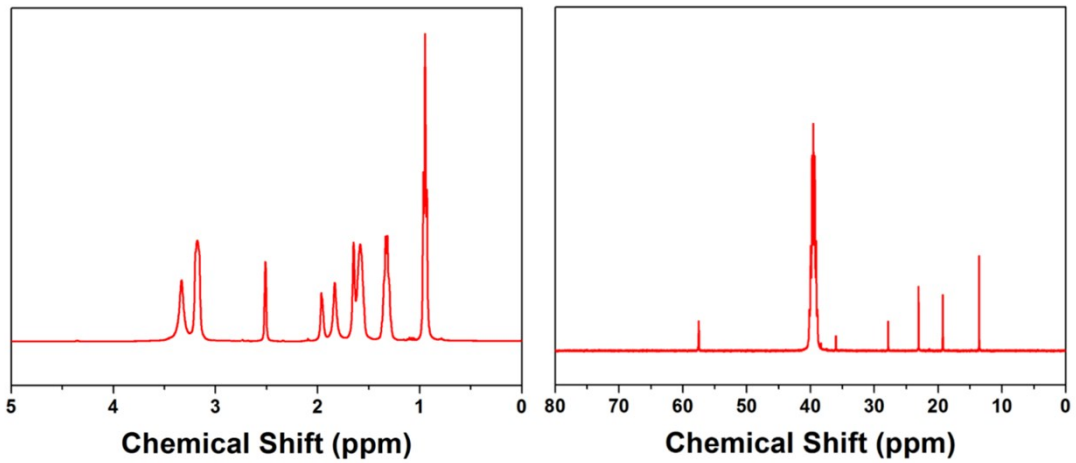


Fig. S2 ^{1}H NMR (left) and ^{13}C NMR (right) spectra of Anderson-Adamantane-TBA.

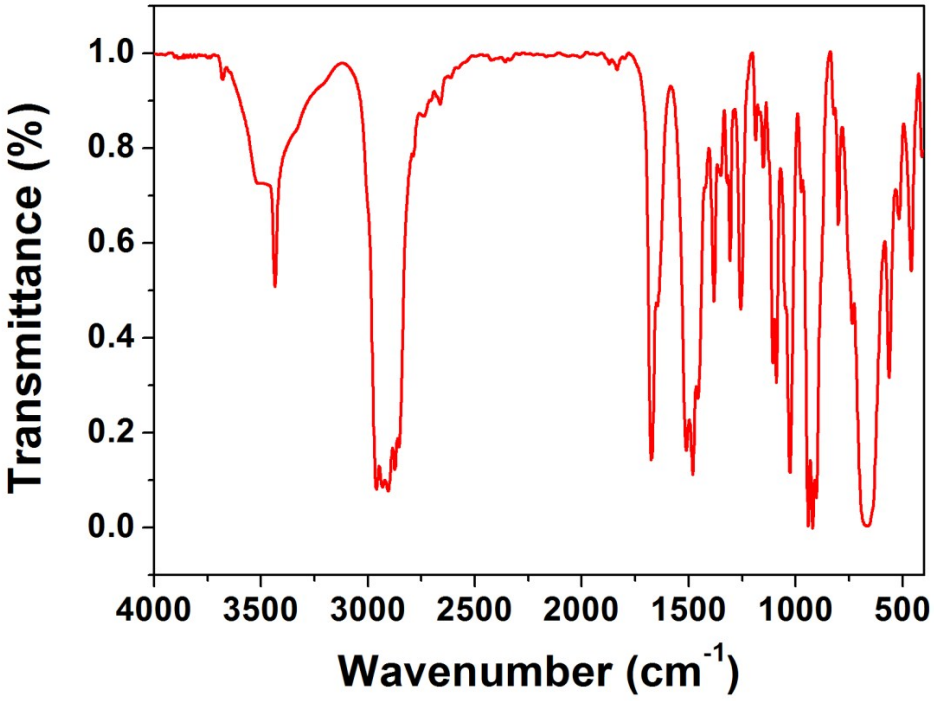


Fig. S3 FT-IR spectrum of Anderson-Adamantane-TBA.

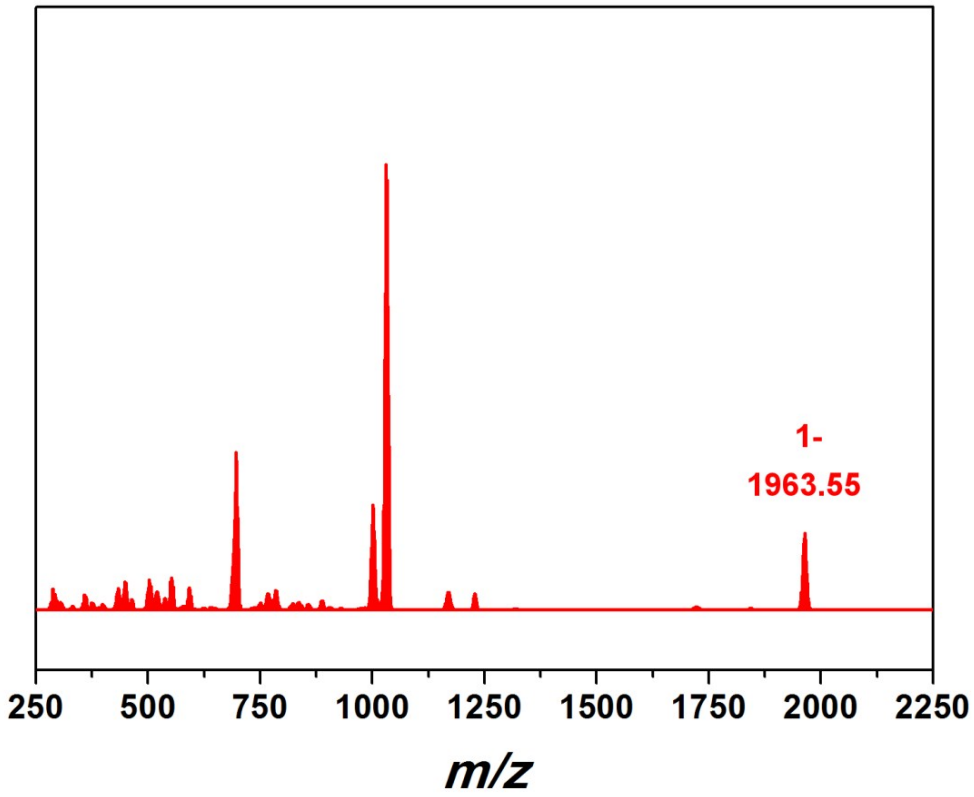


Fig. S4 ESI-MS spectrum of Anderson-Adamantane-TBA.

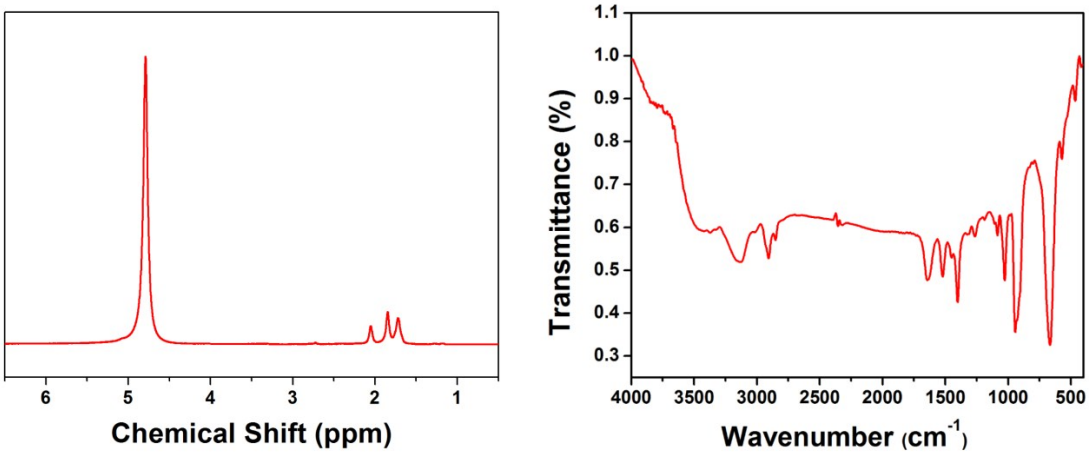


Fig. S5 ^{1}H NMR (left) and FT-IR (right) spectra of Anderson-Adamantane.

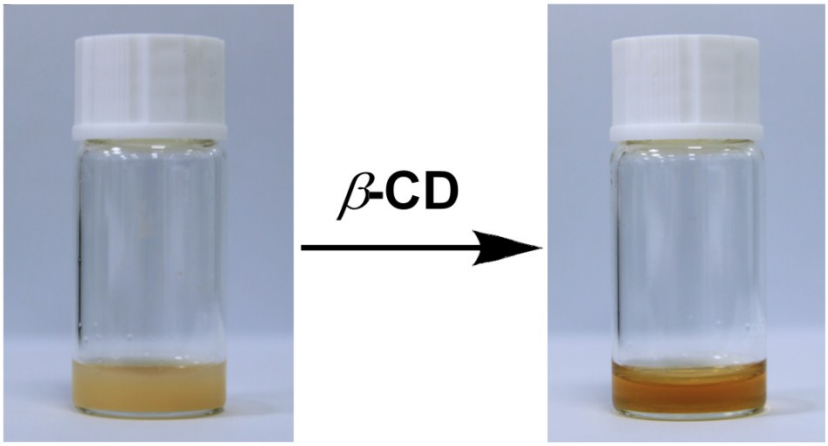


Fig. S6 The photographs of Anderson-Adamantane of in water upon addition of *β*-CD

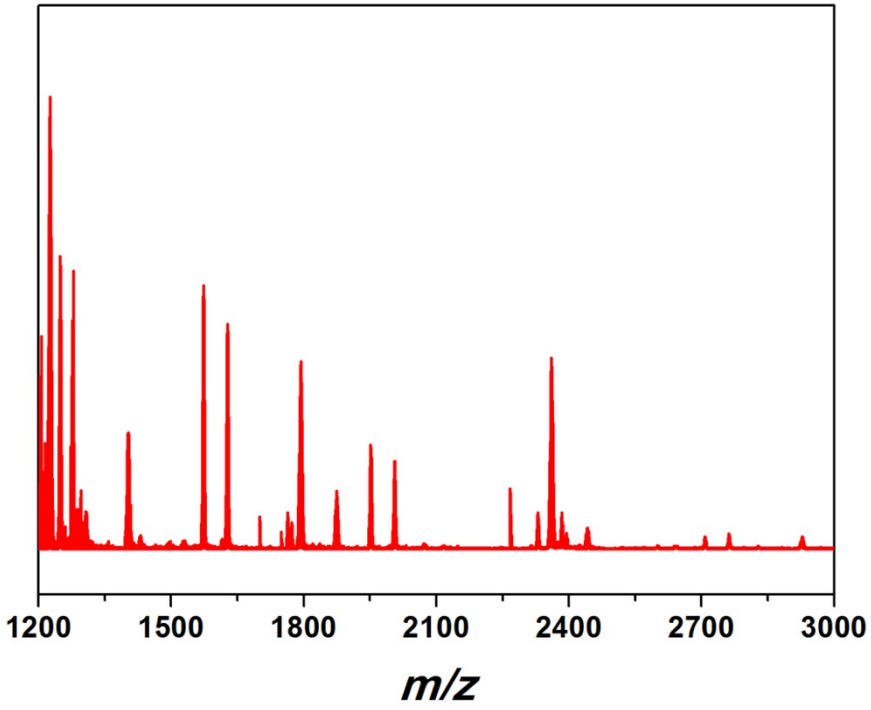


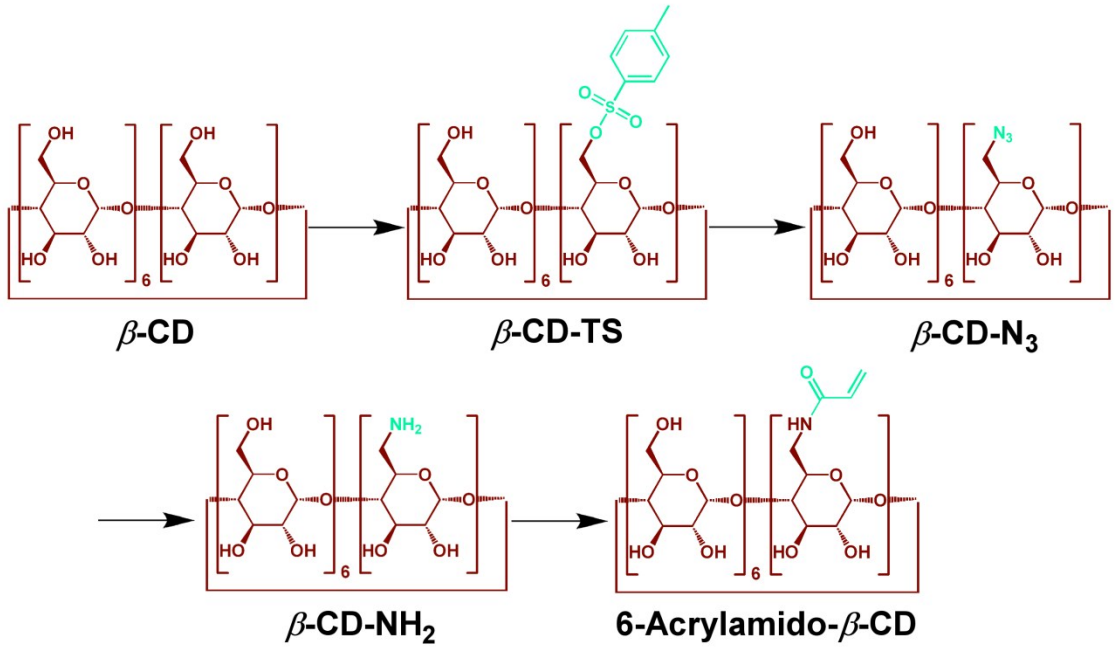
Fig. S7 ESI-MS spectrum of POM-CD complex in water (negative mode). The mole ratio of Anderson-Adamantane to *β*-CD used for ESI-MS is 1:6.

Table S1. Detailed assignment of the ESI-MS of POM-CD complex.

No.	Ion	*m/z* Calculated	*m/z* Observed
1	$4H_2O + [(\beta\text{-CD}) - H]^-$	1206.05	1205.96
2	$(\beta\text{-CD}) + [H(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{2-}$	1226.56	1226.57

3	$2(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{3-}$	1249.78	1249.41
4	$8H_2O + [(\beta\text{-CD}) - H]^-$	1278.11	1277.87
5	$15H_2O + [(\beta\text{-CD}) - H]^-$	1404.21	1403.69
6	$3(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{3-}$	1574.03	1573.68
7	$3(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{3-}$	1628.11	1627.69
8	$2(\beta\text{-CD}) + [H(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{2-}$	1794.06	1793.99
9	$2(\beta\text{-CD}) + [H(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{2-}$	1875.17	1875.00
10	$4(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{3-}$	1952.36	1952.28
11	$4(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{3-}$	2006.44	2006.29
12	$[2(\beta\text{-CD}) - 2H]^{2-}$	2267.98	2267.87
13	$5(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{3-}$	2330.69	2330.55
14	$3(\beta\text{-CD}) + [H(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{2-}$	2361.55	2361.39
15	$5(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{3-}$	2384.77	2384.55
16	$3(\beta\text{-CD}) + [H(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{2-}$	2442.67	2442.39
17	$6(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{3-}$	2709.02	2708.47
18	$6(\beta\text{-CD}) + [(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}_2]^{3-}$	2763.10	2762.47
19	$4(\beta\text{-CD}) + [H(MnMo_6O_{24})\{(CH_2)_3CNHCOC_{10}H_{15}\}\{(CH_2)_3CNH_2\}]^{2-}$	2929.05	2928.28

Synthesis of 6-Acrylamido-β-CD:



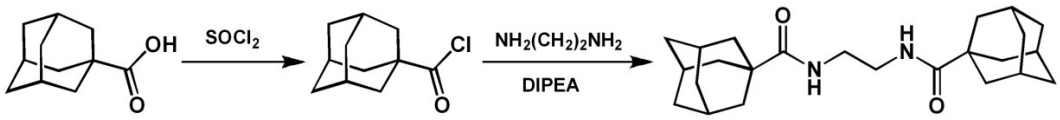
***β*-CD-TS** was prepared according to the literature.[2] Yield: 23%. ^{1}H NMR (DMSO-d_6, ppm) δ = 7.77 (d, 2H, CH of Ph), 7.45 (d, 2H, CH of Ph), 5.77-5.69 (m, 14H, OH-2 and HO-3 of CD), 4.86-4.77 (m, 7H, H-1 of CD), 4.53-4.46 (m, 6H, OH-6 of CD), 4.37-4.33 (m, 2H, H′-6 of CD), 4.22-4.18 (m, 1H, H′-5 of CD), 3.67-3.44 (m, 25H, H-3, H-5 and H-6 of CD) 3.37-3.30 (m, 14H, H-2 and H-4 of CD overlap with H_2O), 2.44 (s, 3H, Ph-CH_3). FT-IR (KBr, cm^{-1}): 3395, 2927, 1364, and 1030.

***β*-CD-N$_3$** was synthesized by converting ***β*-CD-TS** into the corresponding azido CD following a reported procedure.[2] Yield: 90%. ^{1}H NMR (DMSO-d_6, ppm) δ = 5.75-5.68 (m, 14H, OH-2 and OH-3), 4.89-4.84 (m, 7H, H-1), 4.56-4.47 (m, 6H, OH-6), 3.66-3.56 (m, 28H, H-3, H-5 and H-6), 3.36-3.30 (m, 14H, H-2 and H-4 overlap with H_2O). FT-IR (KBr, cm^{-1}): 3395, 2929, 2107, and 1031.

***β*-CD-NH$_2$** was synthesized according to the reported procedures.[3] Yield: 97.5%. ^{1}H NMR (DMSO-d_6, ppm) δ = 5.77-5.65 (m, 14H, OH-2 and OH-3), 4.90-4.81 (m, 7H, H-1), 4.46-4.43 (m, 6H, OH-6), 3.67-3.57 (m, 28H, H-5, H-3 and H-6), 3.43-3.35 (m, 14H, H-2 and H-4 overlap with H_2O). FT-IR (KBr, cm^{-1}): 3369, 2928, 1653, 1117, and 1031.

6-Acrylamido-*β*-CD was prepared following the previously reported literature.[4] Yield: 87%. ^{1}H NMR (DMSO-d_6, ppm) δ = 7.98 (s, 1H, NH), 6.30, 6.07 and 5.58 (3H, CH_2=CH-), 5.80-5.79 (14H, OH-2 and OH-3), 4.84(7H, H-1), 4.48 (6H, OH-6), 3.65-3.57 (28H, H-3, H-5 and H-6), 3.37-3.30 (14H, H-2, H-4, overlap with H_2O). FT-IR (KBr, cm^{-1}): 3372, 2929, 1662, 1558, and 1032.

Synthesis of *Bis*-adamantane:



Bis-adamantane was synthesized following a procedure in the literature.[5] Yield: 96.3%. ^{1}H NMR ($CDCl_3$, ppm) δ = 6.44 (s, 2H, NH), 3.41 (t, 4H, -CH_2-CH_2-), 2.07 (m, 6H, -CH-), 1.86 (d, 12 H, -CH_2-), 1.76 (t, 12H, -CH_2-).

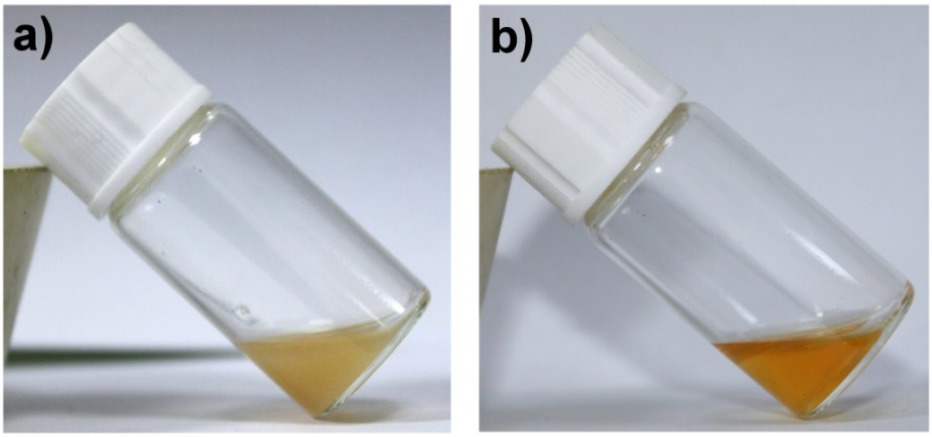


Fig. S8 The photographs of aqueous solution of the Anderson-Adamantane a) before and b) after adding of 6-Acrylamido-*β*-CD.

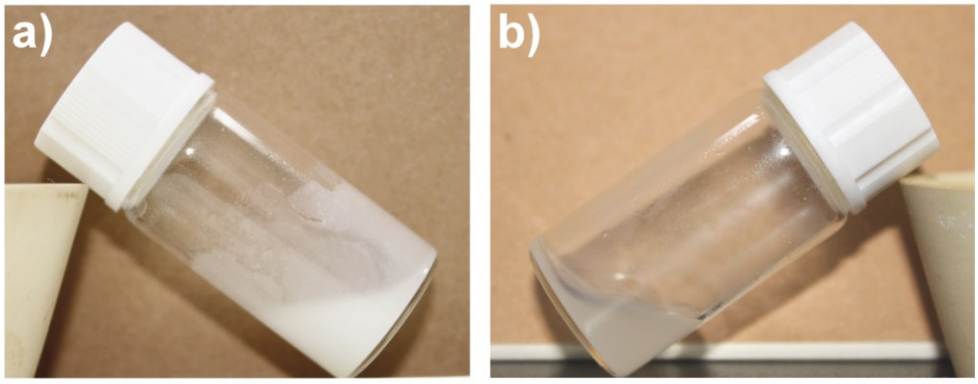


Fig. S9 The photographs of the aqueous solution of *bis*-adamantane/6-Acrylamido-*β*-CD a) before and b) after polymerization.

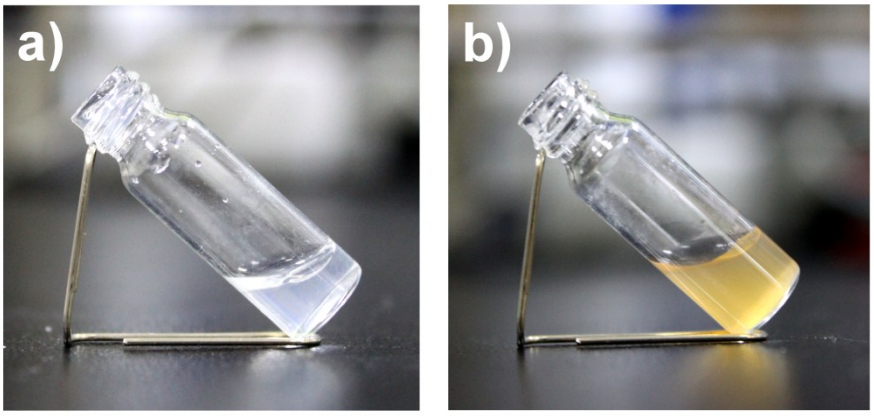


Fig. S10 The photographs of *β*-CD-containing host polymer a) before and b) after addition of the Anderson-Adamantane.

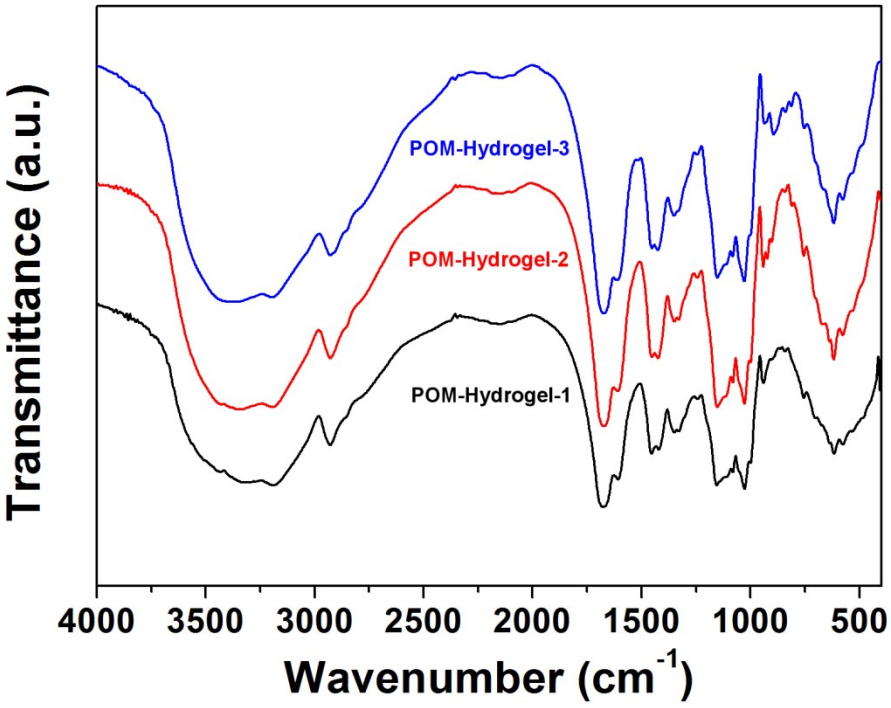


Fig. S11 FT-IR spectra of the freeze-dried POM-Hydrogels.

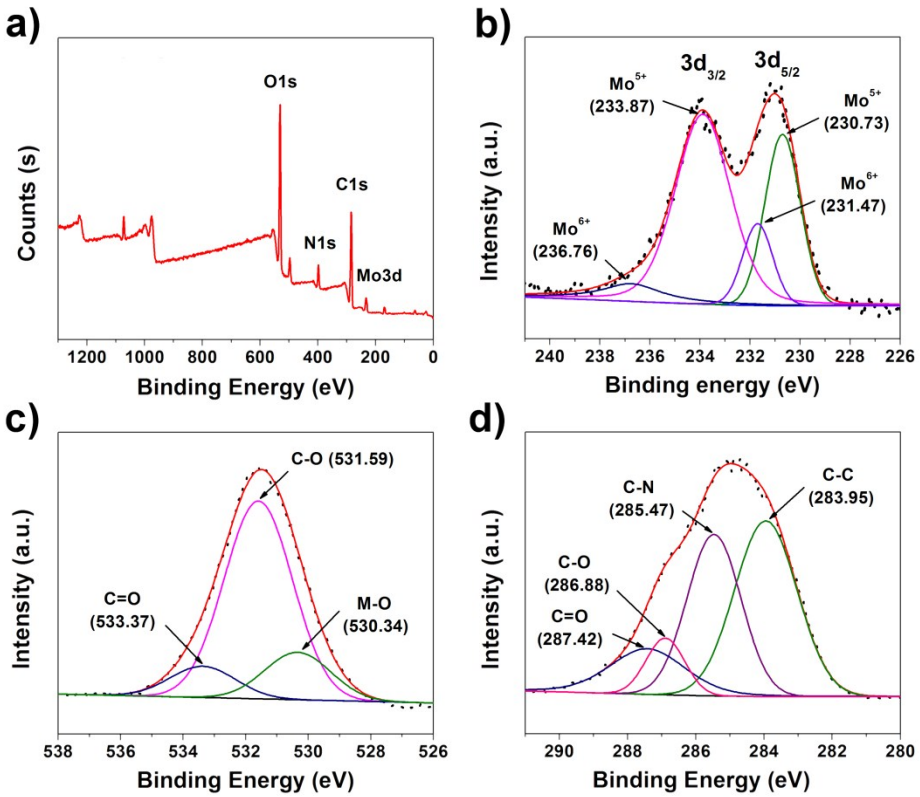


Fig. S12 a) XPS survey spectrum, b) XPS Mo3d spectrum, c) XPS O1s spectrum, and d) XPS C1s spectrum of freeze-dried POM-Hydrogel-1.

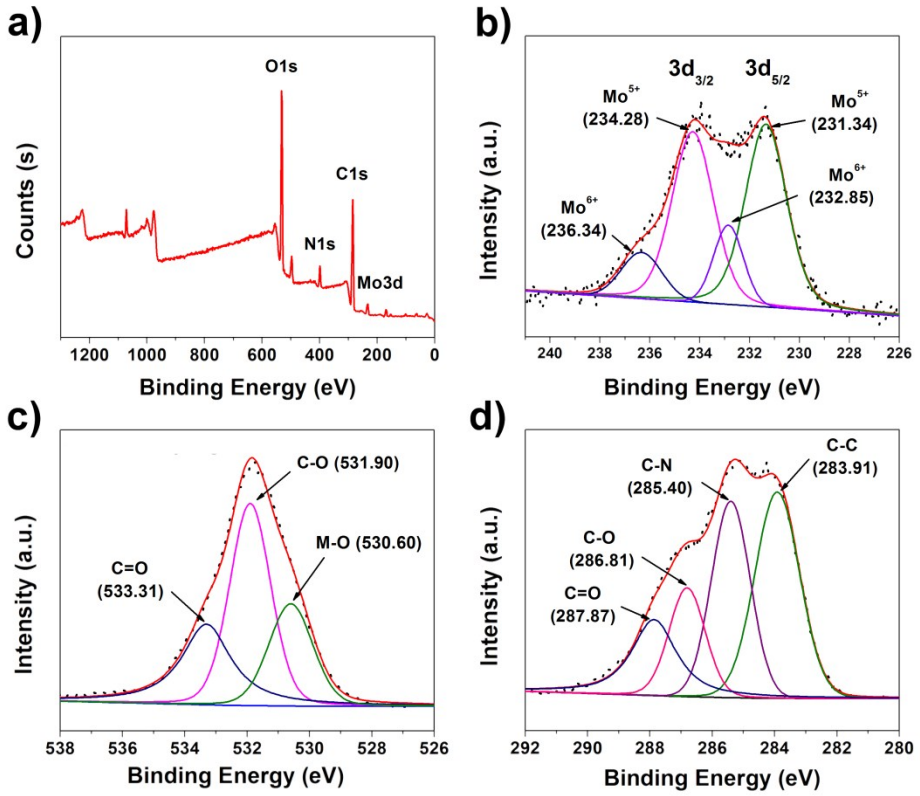


Fig. S13 a) XPS survey spectrum, b) XPS Mo3d spectrum, c) XPS O1s spectrum, and d) XPS C1s spectrum of freeze-dried POM-Hydrogel-2.

Reference:

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