Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

The chaotropic effect as an orthogonal assembly motif for multi-responsive dodecaborate-cucurbituril supramolecular networks

Wenjing Wang, Xiaoqiang Wang, Jin Cao, Jun Liu, Bin Qi, Xiaohai Zhou, Shuai Zhang, Detlef Gabel, Werner M. Nau, Khaleel I. Assaf* and Haibo Zhang*

Table of Content

1. Experimental section

Cesium *closo*-dodecaborate (Cs_2[*closo*-$B_{12}H_{12}$], 98%) was purchased from Strem Chemicals (Newburyport, USA). 1,8-dibromooctane and cesium fluoride (CsF) were purchased from Aladdin Industrial Corporation (Shanghai, China). Triethylamine hydrochloride (Et_3N•HCl) and methyltriphenylphosphonium bromide ($MePh_3PBr$) were purchased from Energy Chemical (Shanghai, China). MPEG2000-NH2 was purchased from Shanghai Ponsure Biotech,Inc (Shanghai, China). Tetrabutylammonium bromide (TBAB), K_2CO_3, KOH, NaOH, formic acid (88%), ammonium hydroxide, acetone, petroleum ether, ethyl acetate, acetonitrile, and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Deuterium oxide (D_2O, 99.9%), dimethyl-d6 sulfoxide (DMSO-d6, 99.8%, cont. 0.03 v/v% TMS) and chloroform-d ($CDCl_3$, 99.8%, cont. 0.03 v/v% TMS) were purchased from Ningbo Rotation Meditech Co., Ltd (Zhejiang, China). All the reagents were used as received. Cucurbit[7]uril (CB7)[1], 4-hydroxyazobenzene[2] and $Cs_2B_{12}H_{11}OH$[3] were synthesized according to published procedures.

^{1}H NMR spectra were recorded on a Bruker Advance 400M spectrometer at 400 MHz. Isothermal titration calorimetry experiments were carried out on a VP-ITC from Microcal, Inc., at 25 °C. Scanning electron microscopy (SEM) images were taken on a field-emission microscope (Zeiss Sigma) operated at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) was performed on a HITACHI H-7000FA electron microscope operating at 100 kV. The hydrodynamic diameter was determined by dynamic light scattering (DLS, Nano-ZS ZEN3600, Malvern Instruments). ESI-MS spectra were taken at room temperature on a mass spectrometer (Finnigan LCQ advantage; Thermo Fisher Scientific). Fourier transform infrared (FT-IR) spectra were collected on a Perkin-Elmer spectrophotometer (USA) using potassium bromide (KBr) pellets. Rheological measurements were conducted with a HAAKE RheoStress 600 (THermo ELECTRON CORPORATION). UV-Vis measurements were carried out on a Lambda 35 UV-Vis spectrophotometer (Perkin-Elmer).

Crystal data CB7/$B_{12}H_{11}OH^{2-}$, CB7/$B_{12}Cl_{12}^{2-}$ and CB6/$B_{12}H_{12}^{2-}$ were collected at 123.0(1) K on an Agilent Super-Nova diffractometer using mirror-monochromatized Cu-Kα (λ = 1.54184 Å) radiation. The crystals were mounted on a Hampton cryoloop with light oil to prevent water loss. The SHELX software package (Bruker) was used to

solve and refine the structures.[4] An empirical absorption correction was applied using the SADABS program.[5] The structures were solved by direct methods and refined by the full-matrix least-squares method ($\Sigma w(|F_o|^2 - |F_c|^2)^2$) with anisotropic thermal parameters for all heavy atoms included in the model. The hydrogen atoms of the organic groups were introduced in geometrically calculated positions. The hydrogens of the crystal waters were not located. It was not possible to locate all cations by X-ray diffraction, probably due to crystallographic disorder, which is a common problem in host-guest crystallography. The crystal data and structure refinement for CB7/$B_{12}H_{11}OH^{2-}$, CB7/$B_{12}Cl_{12}^{2-}$ and CB6/$B_{12}H_{12}^{2-}$ are summarized in Table S1. CCDC-1574822 (CB7/$B_{12}H_{11}OH^{2-}$), CCDC-1574912 (CB7/$B_{12}Cl_{12}^{2-}$) and CCDC-1574823 (CB6/$B_{12}H_{12}^{2-}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2. Synthesis of $Na_2B_{12}H_{12}$

Synthesis of $(Et_3NH)_2B_{12}H_{12}$: $Cs_2B_{12}H_{12}$ (4.08 g, 10 mmol) was dissolved in 30 mL hot water. Triethylamine hydrochloride (8.26 g, 60 mmol) was dissolved in 30 mL water and then added to the $Cs_2B_{12}H_{12}$ solution dropwise. The reaction was carried out at ambient temperature for 2 h. The precipitate was collected, washed with cold water, and dried under vacuum at 50 °C.

Synthesis of $Na_2B_{12}H_{12}$: $(Et_3NH)_2B_{12}H_{12}$ (2.77 g, 8 mmol) was suspended in 30 mL boiled water. NaOH (0.64 g, 8 mmol) was added. The reaction was boiled until all amine was released. Subsequently, the solvent was evaporated under reduced pressure. The solid product was dried under vacuum at 50 °C.

3. Binding affinities of the CB7/$B_{12}H_{12}^{2-}$ complex

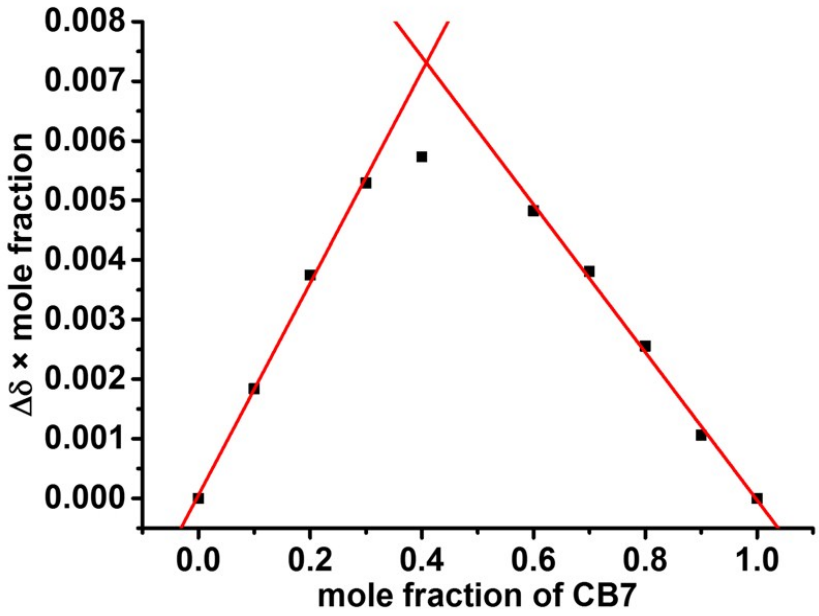

Fig. S1 Job plot for CB7 titrated with $B_{12}H_{12}^{2-}$. The data was collected by ^{1}H NMR (400 MHz, D_2O, 25 °C). The concentration of CB7 was kept fixed as 50 μM and the concentration of $Na_2B_{12}H_{12}$ was varied from 0 μM to 450 μM.

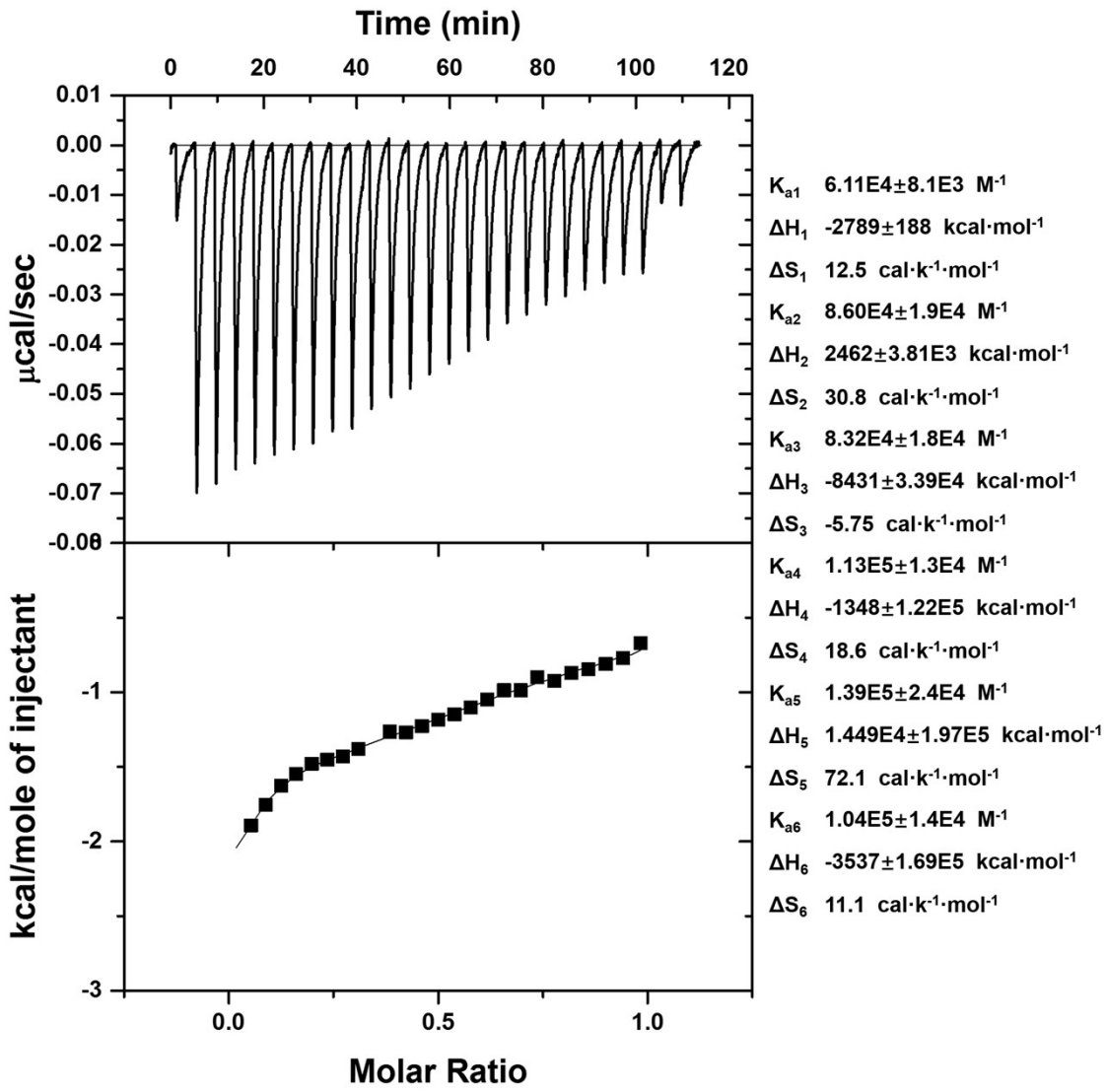

Fig. S2 ITC data for the complexation of CB7 (50 µM) with $B_{12}H_{12}^{2-}$ (250 µM) in aqueous solution at 25 °C: a) raw ITC data for sequential twenty-seven injections of $Na_2B_{12}H_{12}$ solution into CB7 solution, b) apparent reaction heats obtained from the integration of calorimetric traces.

4. X-ray crystallography

Single crystals of the CB7/$B_{12}Cl_{12}^{2-}$ complex were obtained by slow evaporation of a saturated aqueous solution of CB7 and $Na_2B_{12}Cl_{12}$. Single crystals of the CB7/$B_{12}H_{11}OH^{2-}$ and the CB6/$B_{12}H_{12}^{2-}$complexes were obtained by slow evaporation of a saturated aqueous solution of CB7 (or CB6) and $Cs_2B_{12}H_{11}OH$ (or $Cs_2B_{12}H_{12}$), adding a small amount of $CoCl_2$, concentrated hydrochloric acid and DMF.

In these structures as it was not possible to see clear electron-density peaks in

difference maps, which would correspond with acceptable locations for the various H atoms bonded to oxygen atoms, the refinements were completed with no allowance for these H atoms in the models.

The XRD structure of the CB7/$B_{12}Cl_{12}^{2-}$ complex shows that each CB7 unit interacts with six $B_{12}Cl_{12}^{2-}$ clusters, three on each hemisphere, giving rise to an overall star-shaped assembly (Fig. S3a). Short contacts between $B_{12}Cl_{12}^{2-}$ and CB7 were observed, specifically between the Cl atoms and the carbonyl-carbons (Cl---C=O: 3.3 Å) as well as the hydrogen atoms (Cl---H–C: 2.8 - 3.3 Å). Counter cations (Na^+) are coordinated to the carbonyl rims in all cases.

The XRD structure of the complex between CB6 and $B_{12}H_{12}^{2-}$ shows two types of complexation (Fig. S4). CB6 in two contiguous columns interacts with four $B_{12}H_{12}^{2-}$, two on each hemisphere (Fig. S4a,b). In every third column, the CB6 molecule is perpendicular to the CB6 molecules in adjacent columns, and interacts diagonally with only two $B_{12}H_{12}^{2-}$ clusters (Fig. S4c,d).

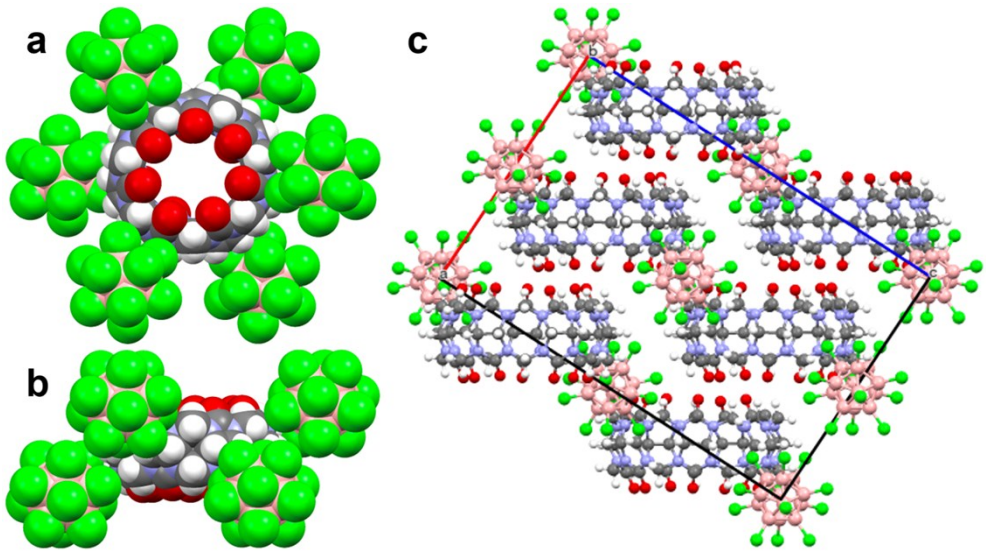

Fig. S3 Views of the CB7/$B_{12}Cl_{12}^{2-}$ complex XRD structure. The CB7 component has crystallographically-imposed twofold symmetry and that the $B_{12}Cl_{12}^{2-}$ component lies about an inversion centre.

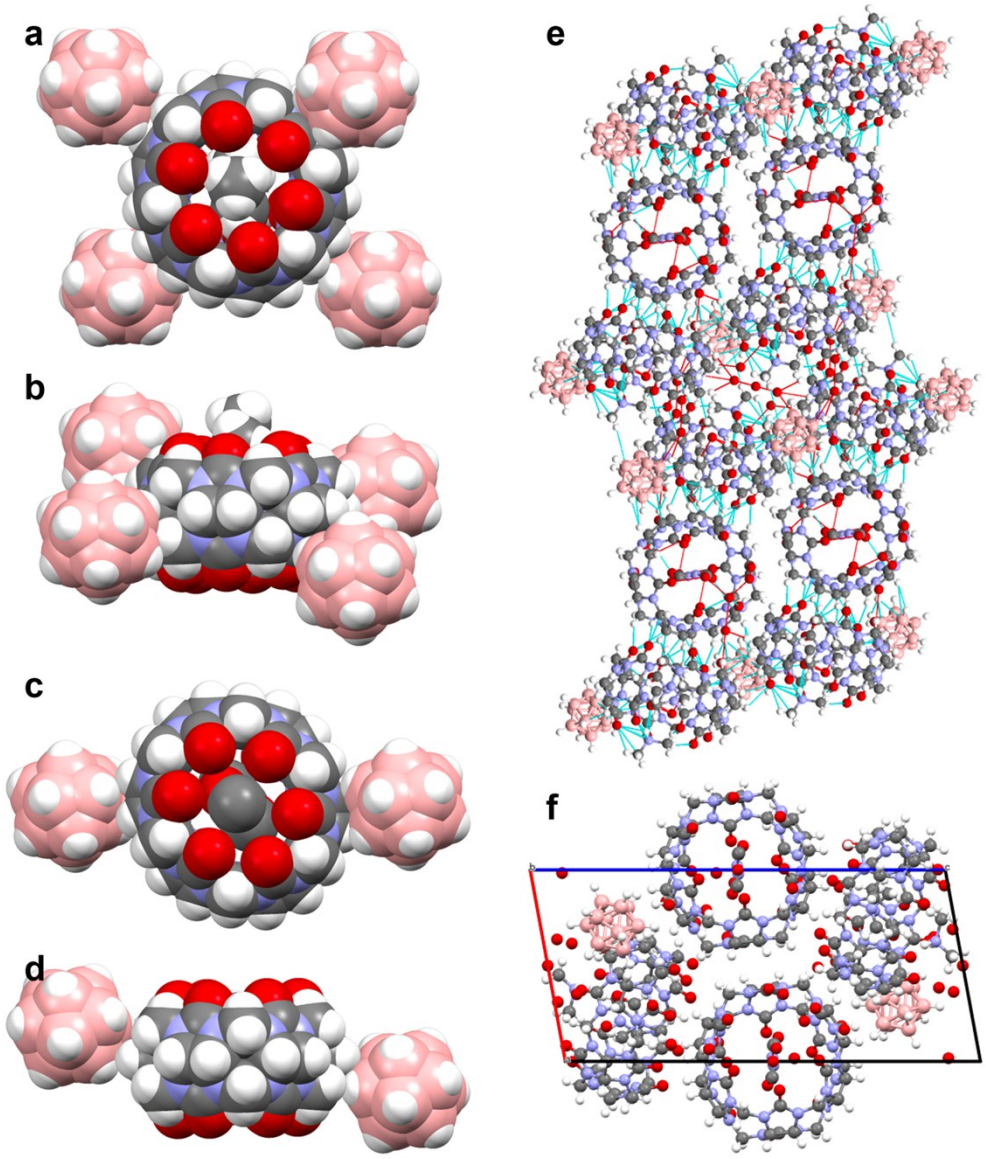

Fig. S4 Views of the CB6/$B_{12}H_{12}^{2-}$ complex XRD structure (DMF is entrapped inside the CB6 cavity). The asymmetric unit has a unit-occupancy $B_{12}H_{12}^{2-}$ component, a half CB6 component lying about an inversion centre (entrapping a disordered DMF molecule) and another full CB6 component in a general position (entrapping a full DMF molecule).

Table S1 Crystal data and structure refinement results.

compound*	Cucurbit[7]uril/$B_{12}H_{11}OH^{2-}$	Cucurbit[7]uril/$B_{12}Cl_{12}^{2-}$	Cucurbit[6]uril/$B_{12}H_{12}^{2-}$
Empirical formula	$C_{42}H_{42}N_{28}O_{14}+2B_{12}H_{12}O^{2-}$ $+4H^{+}+8H_2O$	$4C_{42}H_{42}N_{28}O_{14}+4B_{12}Cl_{12}^{2-}$ $+8Na^{+}+24H_2O$	$3C_{36}H_{36}N_{24}O_{12}+2B_{12}H_{12}^{2-}$ $+2H^{+}+2C_2H_8N^{+}+3C_3H_7NO$ $+18H_2O$
Sum formula	$C_{42}H_{86}B_{24}N_{28}O_{24}$	$C_{168}H_{216}B_{48}Cl_{48}N_{112}Na_8O_{80}$	$C_{121}H_{207}B_{24}N_{77}O_{57}$
Formula weight	1626.82	7488.92	3912.06

Temperature	293(2) K	100(2) K	293(2) K
Wavelength	1.54178 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Triclinic, *P*-1
Unit cell dimensions	*a* = 23.0662(16) Å, *α* = 90° *b* = 28.863(3) Å, *β* = 96.368(7)° *c* = 14.2661(10) Å, *γ* = 90°	*a* = 18.2093(6) Å, *α* = 90° *b* = 17.9662(5) Å, *β* = 90.792(2)° *c* = 27.6070(9) Å, *γ* = 90°	*a* = 12.6040(6) Å, *α* = 86.075(4)° *b* = 14.9311(6) Å, *β* = 79.443(4)° *c* = 26.8894(14) Å, *γ* = 87.306(3)°
Volume	9439.2(14) Å^3	9030.8(5) Å^3	4960.0(4) Å^3
Z, Calculated density	4, 1.145 Mg/m^3	1, 1.377 Mg/m^3	1, 1.310 Mg/m^3
Absorption coefficient	0.719 mm^{-1}	0.450 mm^{-1}	0.102 mm^{-1}
F(000)	3384	3792	2048
Crystal size	0.220 x 0.130 x 0.120 mm^3	0.130 x 0.120 x 0.060 mm^3	0.200 x 0.180 x 0.150 mm^3
Theta range for data collection	3.801-57.998°	3.499-24.712°	3.331-25.000°
Limiting indices	-25<=*h*<=25, -30<=*k*<=31, -11<=*l*<=15	-21<=*h*<=21, -21<=*k*<=21, -32<=*l*<=32	-14<=*h*<=14, -17<=*k*<=17, -26<=*l*<=31
Reflections collected / unique	10740 / 6318 [*R*(int) = 0.1488]	109409 / 7672 [*R*(int) = 0.0992]	35213 / 17249 [*R*(int) = 0.0723]
Completeness to theta = 57.998°	95.7 %	99.7 %	98.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.869	0.973 and 0.943	0.985 and 0.980
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6318 / 108 / 605	7672 / 210 / 604	17249 / 1010 / 1367
Goodness-of-fit on F^2	1.062	1.004	1.066
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.1904, wR_2 = 0.3572	R_1 = 0.1119, wR_2 = 0.2674	R_1 = 0.1593, wR_2 = 0.3507
R indices (all data)	R_1 = 0.3133, wR_2 = 0.4271	R_1 = 0.1509, wR_2 = 0.2795	R_1 = 0.2079, wR_2 = 0.3731
Extinction coefficient	0.00149(10)	n/a	n/a
Largest diff. peak and hole	0.705 and -0.427 e Å^{-3}	2.820 and -0.574 e Å^{-3}	1.536 and -0.862 e Å^{-3}

*All three compounds are hydrates and the compound names and formula information altered accordingly. The composition of the three compounds were calculated based on the SXRD data.

5. Morphology of CB7/$B_{12}Cl_{12}^{2-}$ complex

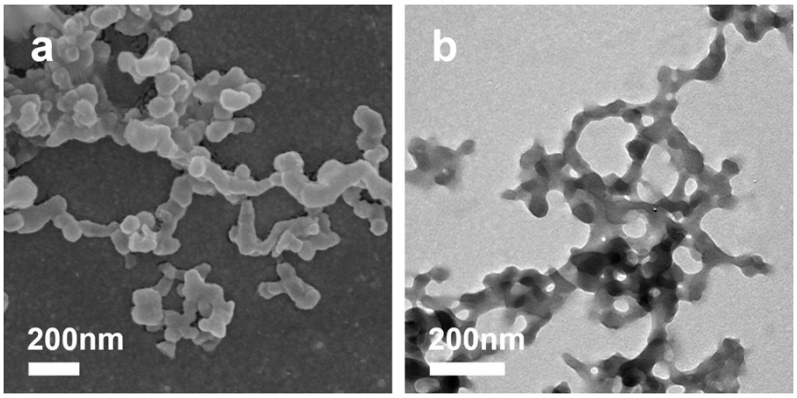

Fig. S5 a) SEM and b) TEM images of the CB7/$Na_2B_{12}Cl_{12}$ aggregate in aqueous solution, the solution was aged for one day.

6. Morphology of CB7/$B_{12}H_{12}^{2-}$ complex

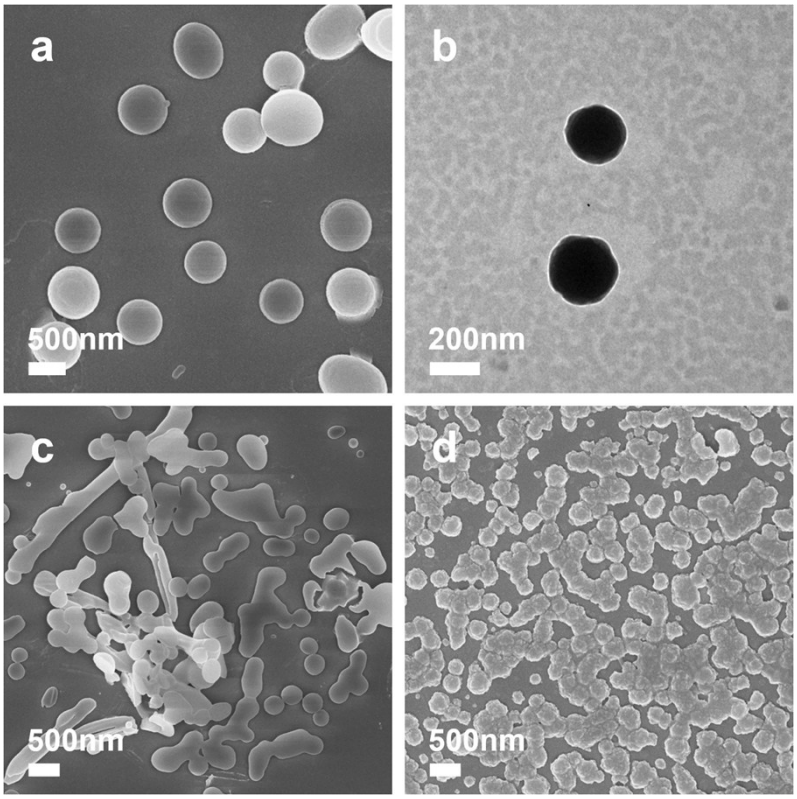

Fig. S6 a) SEM and b) TEM images of the CB7/$Na_2B_{12}H_{12}$ aggregate in formic acid solution (88%). c) SEM image of CB7/$Na_2B_{12}H_{12}$ when formic acid was diluted to half the concentration. d) SEM image of CB7/$Na_2B_{12}H_{12}$ when formic acid was neutralized by ammonium hydroxide.

7. Synthesis of G1

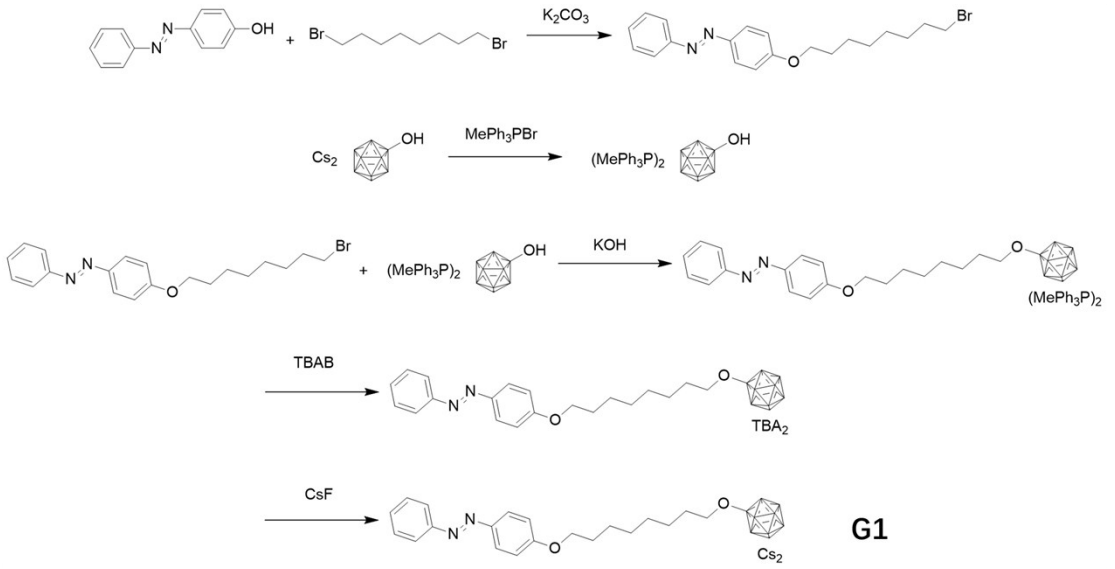

Fig. S7 Synthetic route for the preparation of **G1**.

Synthesis of Ph-N=N-Ph-O-$(CH_2)_8$-Br: 1,8-dibromooctane (13.60 g, 50 mmol) and K_2CO_3 (1.38 g, 10 mmol) were suspended in 30 mL acetone under reflux. 4-Hydroxyazobenzene (1.00 g, 5 mmol) was dissolved in 10 mL acetone and added to the former acetone solution dropwise. The reaction was carried out at reflux for 24 h. After cooling, the salts were filtered off and the solution was concentrated. The solid residue was purified by silica-gel column chromatography; first petroleum ether was used to reclaim unreacted 1,8-dibromooctane, followed by ethyl acetate: petroleum ether 1:4 to purify the product. The product was obtained as a yellow powder (1.89 g, yield: 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.91 (m, 4H); 7.48 (m, 3H); 7.01 (d, 2H); 4.05 (t, 2H); 3.42 (t, 2H); 1.90-1.38 (m, 12H).

Synthesis of $(MePh_3P)_2B_{12}H_{11}OH$: $Cs_2B_{12}H_{11}OH$ (4.24 g, 10 mmol) was dissolved in 10 mL boiling water. $MePh_3PBr$ (21.43 g, 60 mmol) was dissolved in 20 mL water and added to the $Cs_2B_{12}H_{11}OH$ solution dropwise. The reaction was carried out at ambient temperature for 2 h. The resulting precipitate was collected, washed with cold water, and dried under vacuum at 50 °C to give the product as a white powder (0.77 g, yield: 11%).

Synthesis of $Cs_2B_{12}H_{11}$-O-$(CH_2)_8$-O-Ph-N=N-Ph (G1): Ph-N=N-Ph-O-$(CH_2)_8$-Br (0.39g, 1 mmol), $(MePh_3P)_2B_{12}H_{11}OH$ (1.42 g, 2 mmol) and KOH (0.56 g, 10 mmol) were suspended in 200 mL acetonitrile and stirred at reflux for 24 h. After cooling to room temperature, the mixed solution was dried under reduced pressure. The residue was

suspended in 300 mL boiled water, tetrabutylammonium bromide (3.87 g, 12 mmol) dissolved in 10 mL water was added, and the solution was stirred at ambient temperature for 2 h. The resulting precipitate was filtered, washed with cold water, and dried under vacuum at 50 °C. The residue was subsequently dissolved in 250 mL methanol, and CsF (0.76 g, 5 mmol) dissolved in 20 mL methanol was added and stirred at room temperature for 2 h. The precipitate was filtered, washed with small amount of cold methanol, and dried under vacuum at 50 °C to give the product as a yellow powder (0.43 g, yield: 59%). ^{1}H NMR (400 MHz, dimethyl-d6 sulfoxide): δ= 7.87 (m, 4H); 7.54 (m, 3H); 7.14 (d, 2H); 4.09 (t, 2H); 3.33 (t, 2H); 1.76-0.00 (m, 23H). ESI-MS m/z $[M-2Cs+H+H_2O]^-$ calcd for **G1** 485.27, found 485.65; $[M-2Cs+H+CH_3OH]^-$ calcd for **G1** 499.29, found 500.33; $[M-Cs+3H_2O]^-$ calcd for **G1** 653.20, found 653.45. IR υ (C–O–C) 1034.35 cm^{-1}, υ (B–B) 2493.41cm^{-1}.

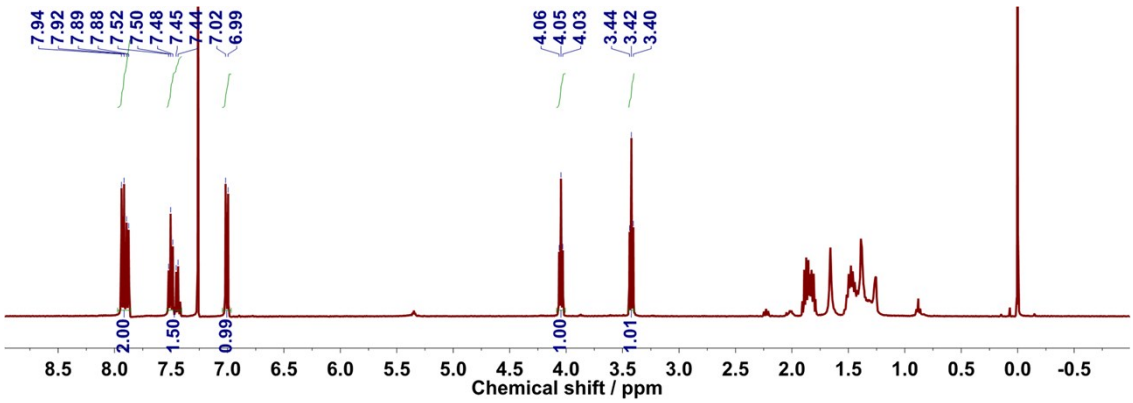

Fig. S8 ^{1}H NMR spectrum of Ph-N=N-Ph-O-$(CH_2)_8$-Br (400 MHz, $CDCl_3$, 25 °C).

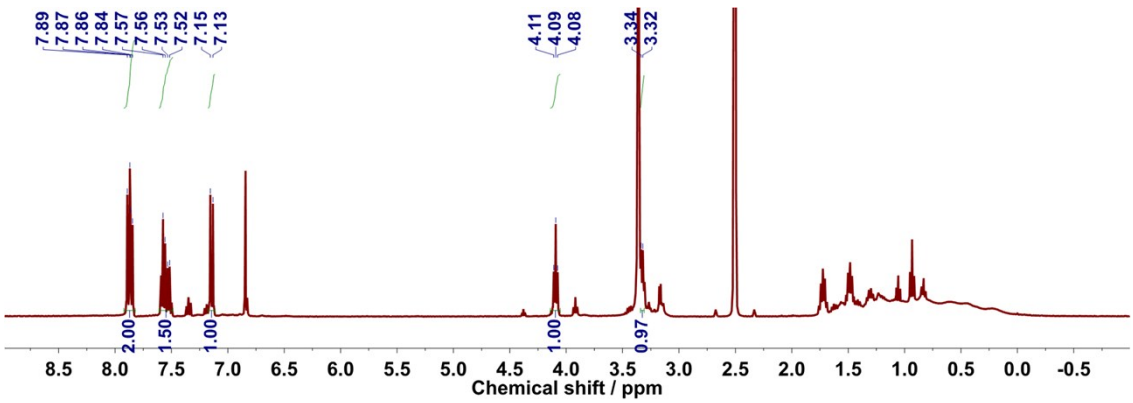

Fig. S9 ^{1}H NMR spectrum of **G1** (400 MHz, dimethyl-d6 sulfoxide, 25 °C).

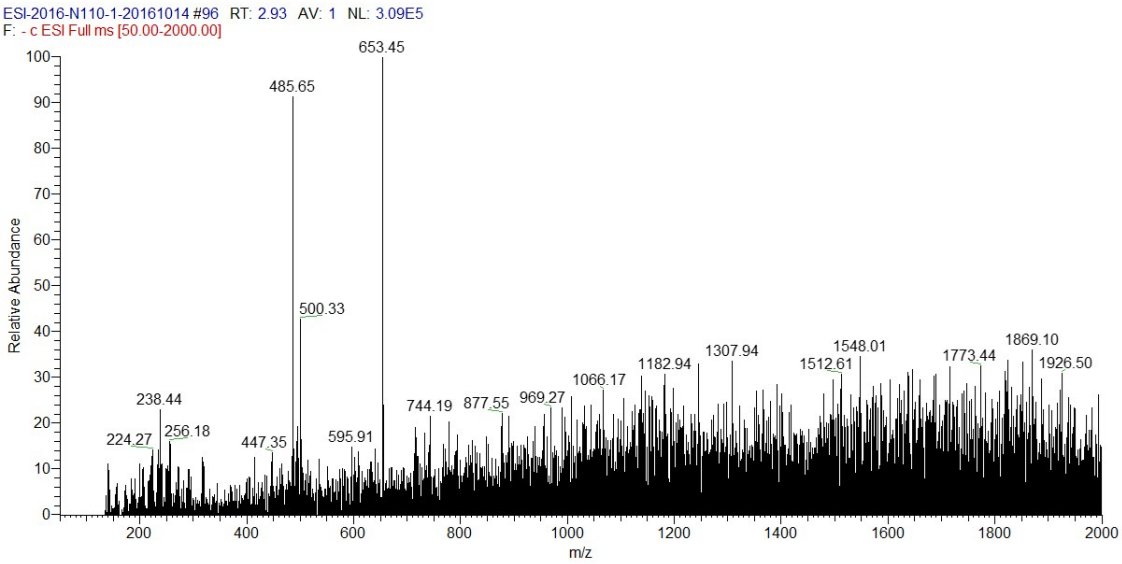

Fig. S10 ESI-MS spectrum of **G1** in aqueous solution.

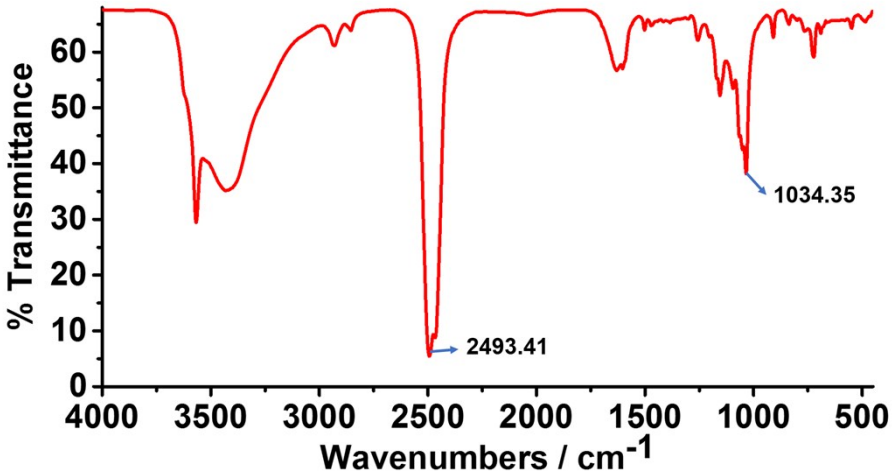

Fig. S11 IR spectrum of **G1**.

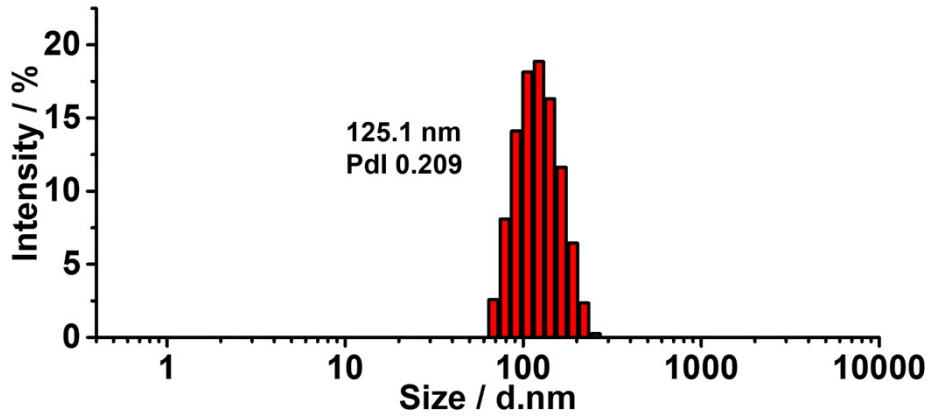

Fig. S12 DLS result of **G1** in aqueous solution.

8. Binding affinities of the CB7/G1 complex

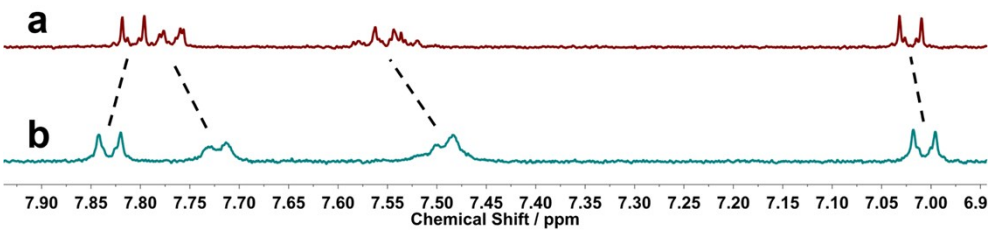

Fig. S13 ^{1}H NMR spectra of a) 4-Phenylazophenol, b) CB7/4-Phenylazophenol (400 MHz, 1% Dimethyl-d6 sulfoxide/D_2O, 25 °C).

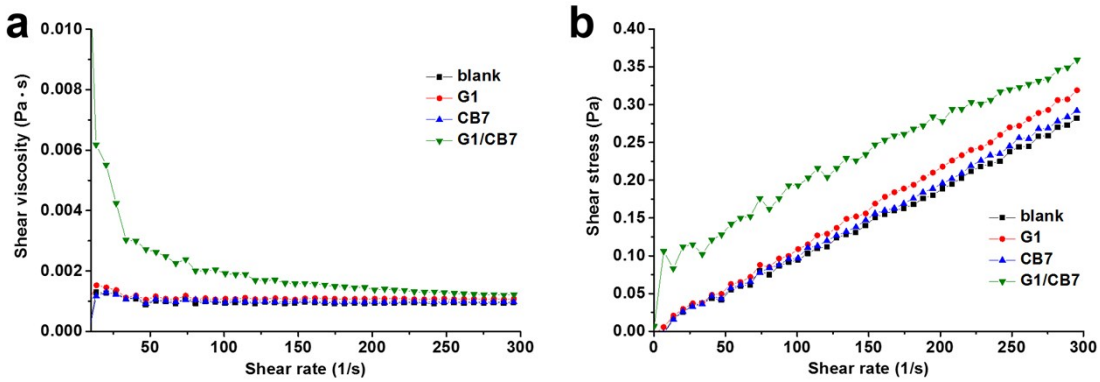

Fig. S14 Variations of a) the shear viscosity and b) the shear stress with shear rate for blank, **G1**, CB7 and CB7/**G1** complex in aqueous solution at 25 °C. The concentrations of **G1**, CB7 and CB7/**G1** complex were 1 mM. The data of CB7/**G1** complex were collected 75 s after the two moieties were mixed.

9. Photo-switching of the CB7/G2 complex

As an additional, independent line of evidence for the retained photoactivity of the **G1** and CB7/**G1** complex, we have now prepared a highly water-soluble model compound (**G2**), which combines amino functionalized methoxyl polyethylene glycol (mPEG-NH_2) with azobenzene. UV-Vis spectra before and after irradiation (Fig. S15) confirmed that the isomerization is happening with and without CB7.

Synthesis of MPEG2000-NH_n-Ph-N=N-Ph (G2): Ph-N=N-Ph-O-$(CH_2)_8$-Br (19.46 mg, 0.05 mmol), NH_2-PEG (100 mg, 0.05 mmol) and Na_2CO_3 (10.60 mg, 0.1 mmol) were

suspended in 12.5 mL acetonitrile and stirred at reflux for 24 h. After cooling to room temperature, the salts were filtered off and the solution was concentrated. The solid residue was dried under vacuum at 50 °C.

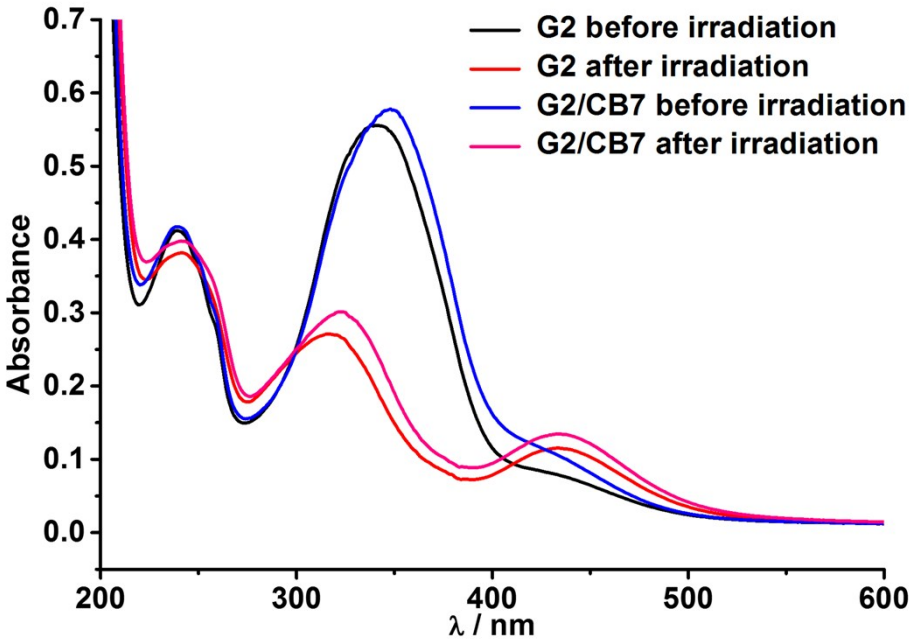

Fig. S15 UV-Vis spectra of **G2** and CB7/**G2** before and after UV irradiation in water (*λ* = 350 nm).

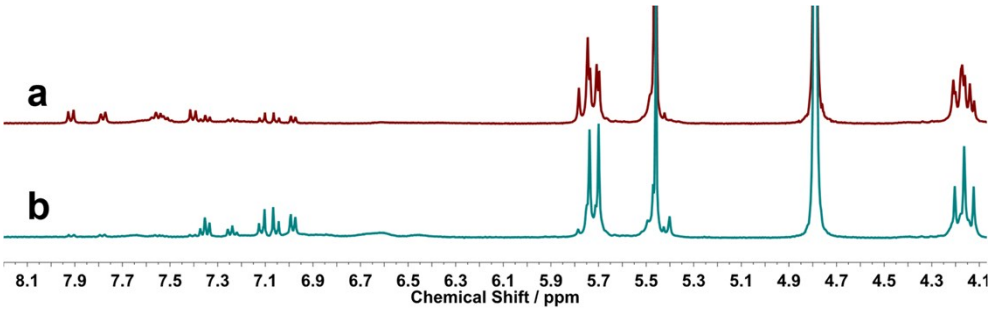

Fig. S16 ^{1}H NMR spectra (400 MHz, D_2O, 25 °C) of CB7/**G2** complex a) before and b) after UV irradiation *(λ* = 350 nm).

10.Stimuli-response of the CB7/G1 complex

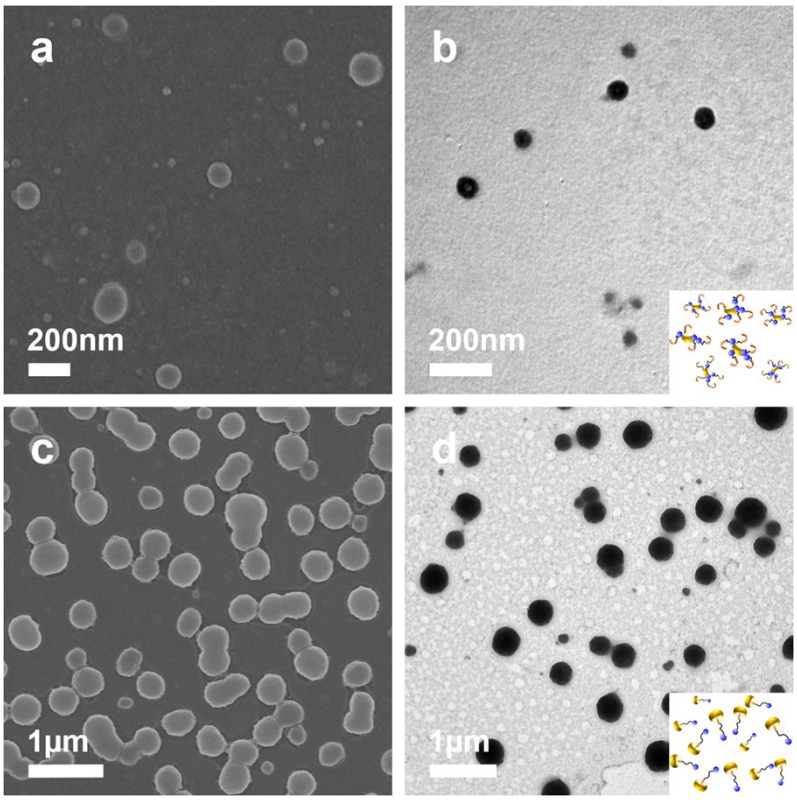

Fig. S17 a) SEM and b) TEM images of the CB7/**G1** aggregates upon irradiation with UV light for 30 min. c) SEM and d) TEM images of CB7/**G1** aggregates in formic acid (88%).

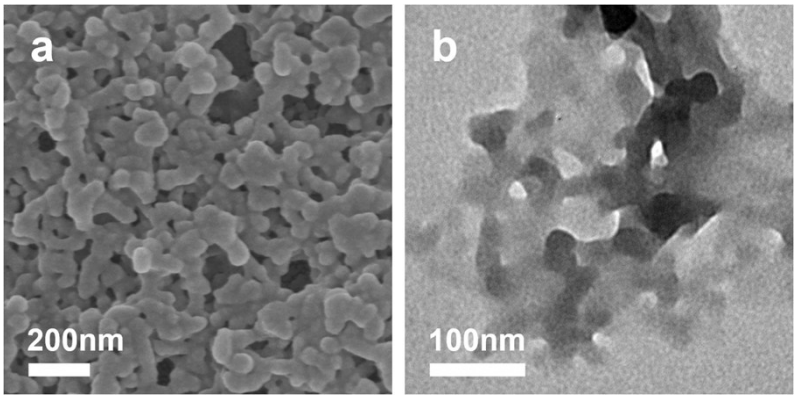

Fig. S18 a) SEM and b) TEM images of CB7/**G1** assembly exposing to visible light after irradiated with UV light for 30 min.

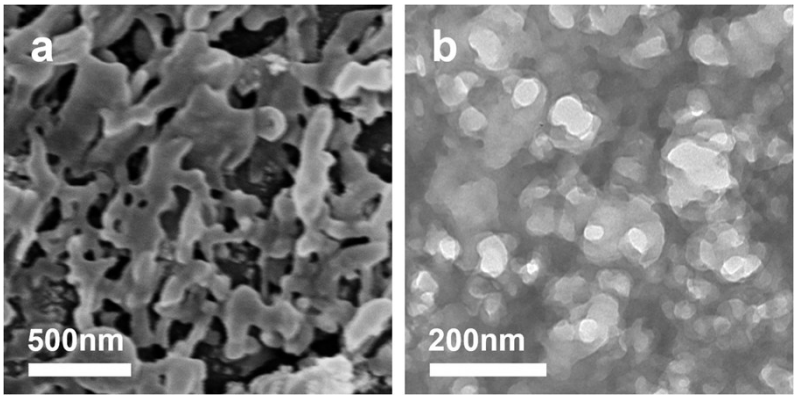

Fig. S19 a) SEM and b) TEM images of CB7/**G1** assembly heated at 60 °C after irradiated with UV light for 30 min.

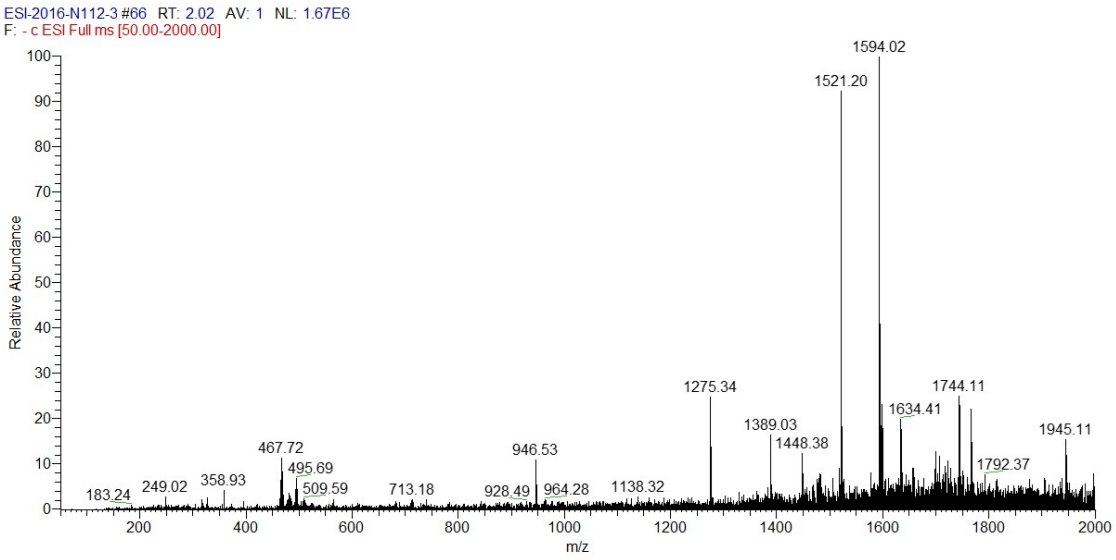

Fig. S20 ESI-MS spectrum of CB7/**G1** multi-responsive assembly in 88% formic acid. ESI-MS m/z $[M\text{-}B_{12}H_{11}+CH_3OH]^-$ calcd for CB7/**G1** 1520.43, found 1521.20; $[M\text{-}B_{12}H_{11}+CH_3OH+2HCl]^-$ calcd for CB7/**G1** 1593.35, found 1594.02.

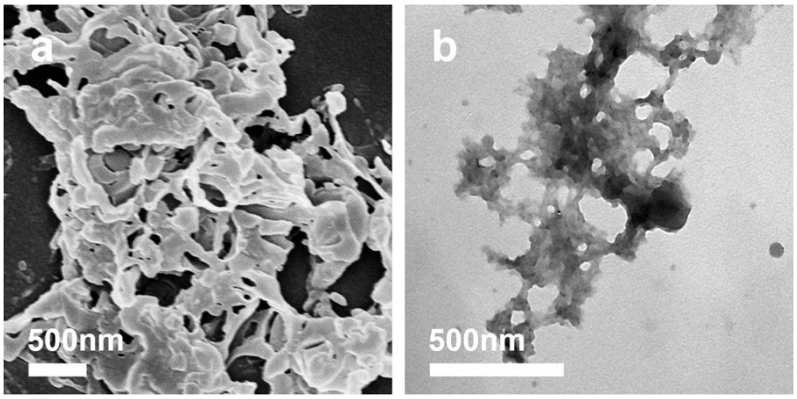

Fig. S21 a) SEM and TEM images of CB7/**G1** reassembled in diluted formic acid solution.

11. References

1 J. Kim and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540.

2 D. Zhou and X. Sun, *Chem. Commun.*, 2015, **51**, 10656.

3 T. Peymann and M. F. Hawthorne, *Inorg. Chem.*, 2000, **39**, 1163.

4 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **A64**, 112–122.

5 G. M. Sheldrick, *SADABS, Program for Empirical X-ray AbsorptionCorrection*, Bruker-Nonius, Madison, WI, 1990.