Supporting information

of

Photoresponsive Glyco-Nanostructures Integrated from Supramolecular Metallocarbohydrates for the Reversible Capture and Release of Lectins

Feihu, Bi,[a ∇] Changwei Zhang, [b, ∇] Guang Yang,*[, a, c] Jie Wang,[a] Wei Zheng,[b] Zan Hua,[a] Xiaopeng Li,[d] Zhongkai Wang,[a] Guosong Chen,*[,c]

[a]Biomass Molecular Engineering Center and Department of Materials Science and Engineering, School of Forestry and Landscape Architecture, Anhui Agricultural University, Hefei, Anhui 230036, China

[b] The State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai 200433, P. R. China

[c] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, P. R. China

[d]Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

[∇]These authors contributed equally to this work

Email: * guangyang@ahau.edu.cn

* guosong@fudan.edu.cn

i. General information

Concanavalin A (ConA) and peanut agglutinin (PNA) protein were purchased from Alladin and used as received. All the reagents and solvents were utilized as received.

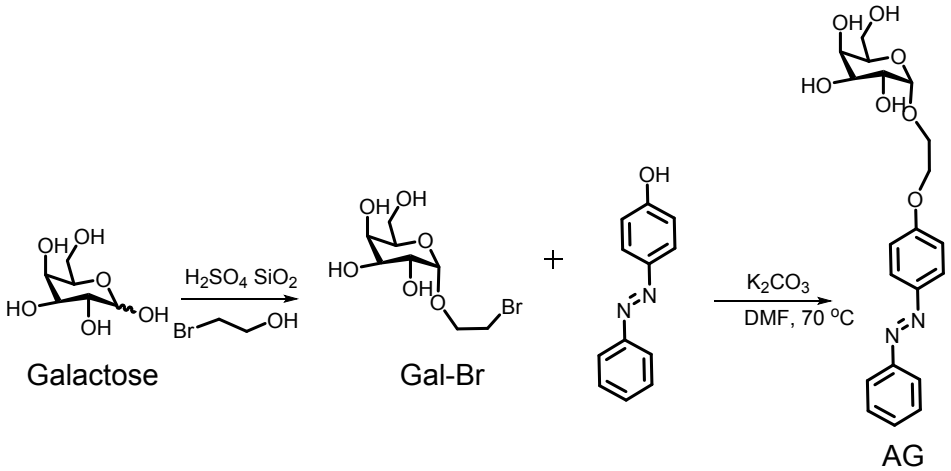
NMR and MS experiments. NMR data were collected on AVANCE III HD 400 MHz from Bruker BioSpin International. ^{31}P NMR chemical shifts are referenced to an internal standard of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are named in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet. Mass spectra were collected on Bruker Compact ESI-Q-TOF-HRMS.

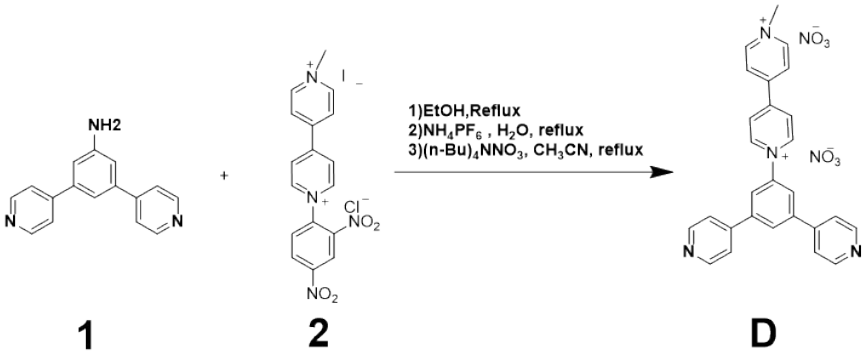
Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) Studies. TEM micrographs were acquired from various magnifications by a Tecnai G2 20 TWIN (FEI), operated at 200 kV. The samples for TEM measurement were prepared by dropping 4 μL the sample solution onto a carbon-coated copper grid. all carbon films on copper grids were handled for hydrophilicity by glow-discharge. Preparation procedures of TEM samples were as follows: 4 uL solution was dropped onto the hydrophilic treated carbon film. After keeping *ca.* 1 min, the liquid was absorbted by filter paper. Dynamic light scattering (DLS) was carried out on a Zetasizer Nano ZS90 from Malvern Instruments.

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) Experiments. SEM images were acquired on Ultra 55 of Zeiss. The SEM samples were prepared on clean silicon wafer substrates. AFM micrographs were pictured on a multimode 8 (Bruker) through scanasyst mode. AFM samples were prepared by depositing 10 μL solution on the freshly cleaved mica. Samples solution was keeping on mica surface *ca.* 2 min and then 200 mL water was utilized to wash the mica surface carefully. Then the washed samples were dried at ambient condition.

Isothermal titration calorimetry (ITC) studies. ITC experiments were carried on a MicroCal VP-ITC system at 25.00 ± 0.01□C.

UV-vis Absorption Spectra. UV-Vis experiments were conducted in a quartz cell (light path 1 cm) on a Cary 50 Bio UV-Vis spectrophotometer. UV-vis spectra were collected in a quartz cell (light path 1 cm) on a UV-2550 spectrophotometer from Shimadzu, Japan. The turbidity experiments were carried out by mixing PNA or ConA and **2-Gal** or **3-Gal** at in HEPES buffer with final concentration of PNA or ConA 0.15 mg/ mL and galactose 0.1 mM on metallacycles.





Scheme S1. Synthetic procedures of **AG** and **D**.

Synthesis of AG. Gal-Br was synthesized according to our previous report.[1] 0.5 g **Gal-Br** (1.8 mmol) and 0.4 g (2 mmol) 4-phenylazophenol and 7 mg tetramethylammonium iodide (0.035 mmol) were mixed into 20 mL DMF. Then, the solution was kept at 65 ℃ for 24 h. The final product **AG** (0.52g, yield: 73%) was purified by the chromatography column utilizing the mixture methanol and DCM (volume 1:8) as eluting agent. ^{1}H NMR (400 MHz, CD_3OD, 298 K, Fig. S37) δ 7.93-7.86 (m, 4H), 7.56-7.46 (m, 3H), 7.16-7.12 (m, 2H), 4.97-4.96 (d, 1H), 4.35-4.31 (m, 2H), 4.15-4.10 (m, 1H), 3.96-3.88 (m, 3H), 3.79-3.73 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD, 298 K, Fig. S38) δ 161.61, 152.68, 130.22, 128.79,124.33, 122.33, 122.10, 114.66, 99.38, 71.09, 70.04, 69.69, 68.84, 67.34, 66.19, 61.35.

Synthesis of dipyridyl donor ligand D. A solution of compound **1** (200 mg, 0.81 mmol) and compound **2** (380 mg, 0.74 mmol) in ethanol (5 mL) was heated at 90 ºC for 12 h. The resulted red solid was filtered and washed with dichloromethane. Then the solid was solved in hot water and the KPF_6 was added with continuous stirring (5 min). The resulted solid was filtered and washed with water. Then the solid was solved in hot acetonitrile and the tetrabutylammonium nitrate was added with continuous stirring (5 min) to precipitate the product. Yield: 360 mg, 93.1%. ^{1}H NMR (500 MHz, D_2O, Fig. S39a) δ 9.17 (dd, J = 17.7, 6.2 Hz, 4H), 8.65 (dd, J = 18.6, 6.4 Hz, 4H), 8.36 (d, J = 4.4 Hz, 4H), 7.97 (s, 2H), 7.85 (s, 1H), 7.52 (d, J = 4.3 Hz, 4H), 4.58 (s, 3H). ^{13}C NMR (126 MHz, D_2O, Fig. S39b) δ 151.43, 149.28, 148.91, 146.51, 145.23, 144.71, 143.11, 140.30, 127.93, 127.11, 126.77, 122.57, 121.71, 48.47. ESI-TOF-MS of **D** (Fig. S40): calcd for $[M\text{-}HNO_3\text{-}NO_3^-]^+$: 401.1755, found: 401.1768.

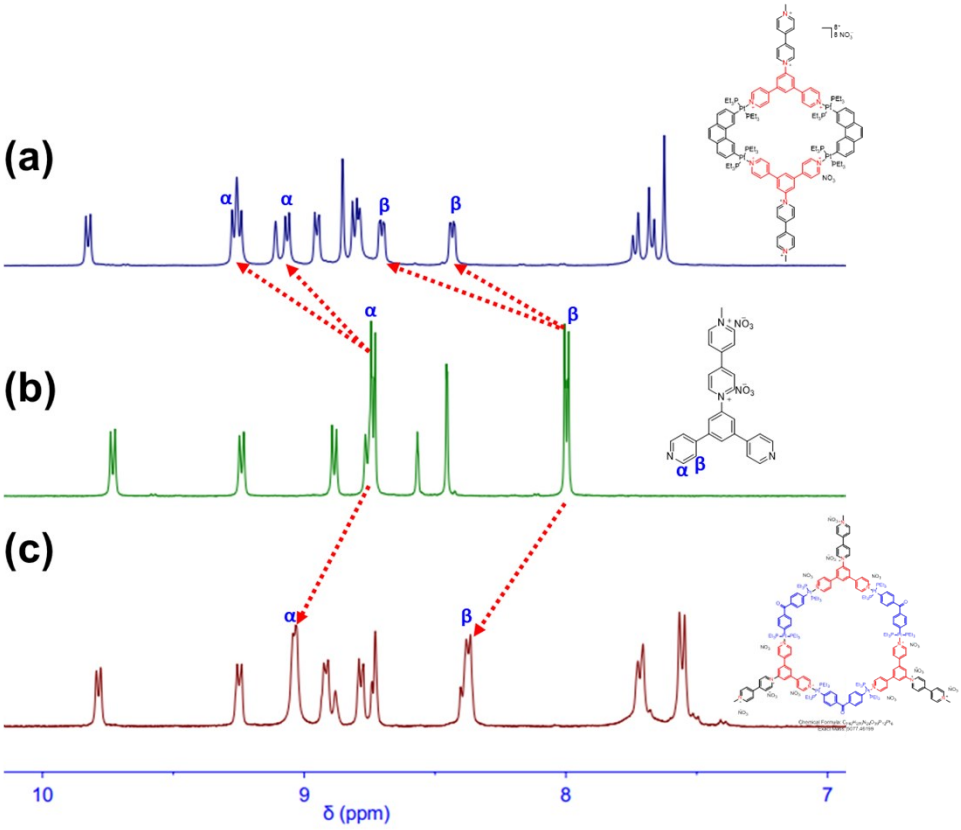


Fig. S1 Partial ^{1}H NMR spectra (400 MHz, in CD_3OD, 298K) of rhomboid [2+2] (a), donor D (b), self-assembled hexagonal [3+3] (c).

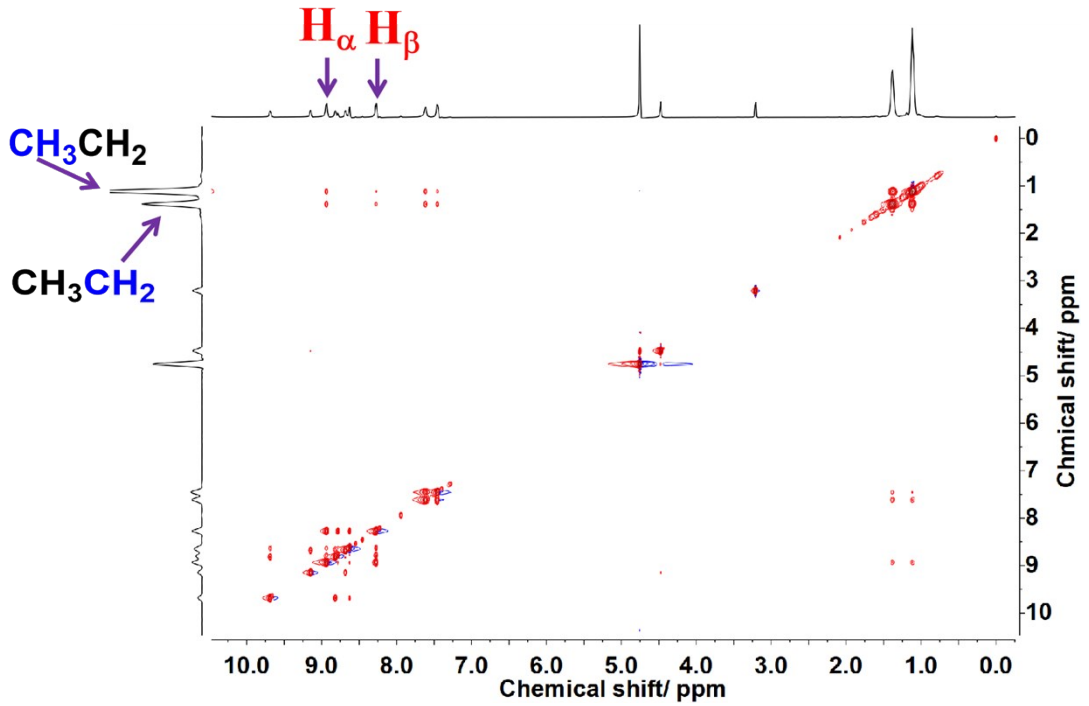


Fig. S2 ^{1}H-^{1}H NOESY spectrum of [2+2] in CD_3OD at 298 K.

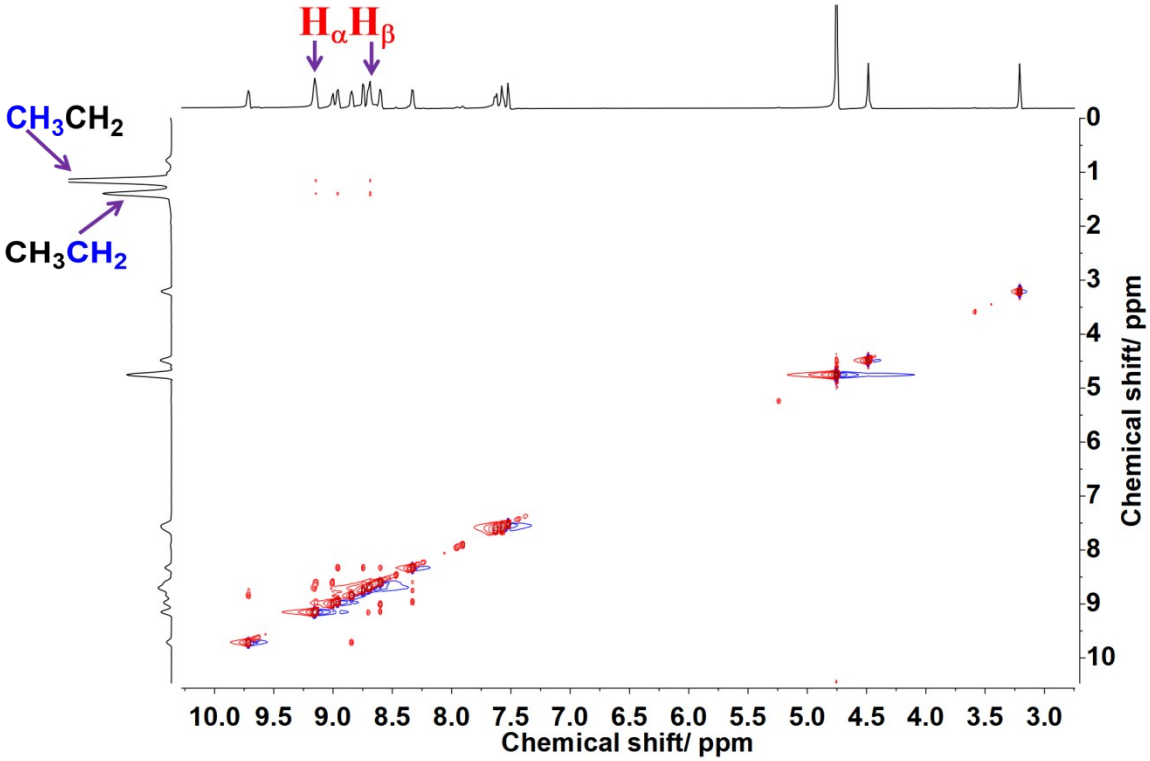


Fig. S3 ^{1}H-^{1}H NOESY spectrum of [3+3] in CD_3OD at 298 K.

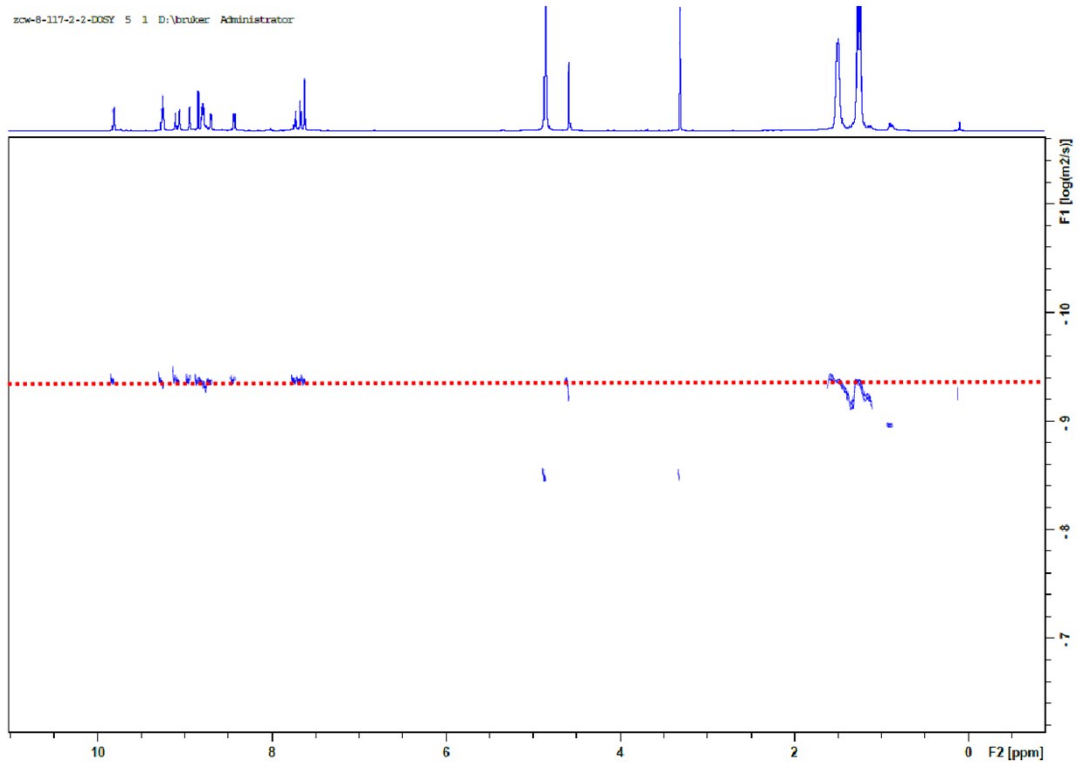


Fig. S4 2D DOSY spectrum of [2+2] in CD_3OD at 298 K.

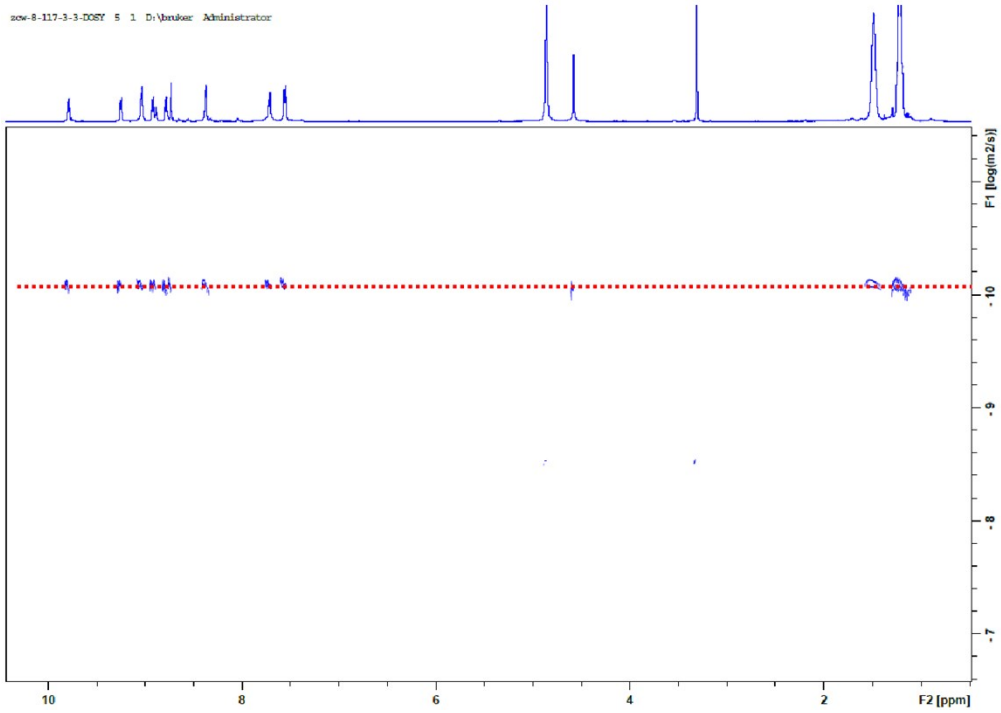


Fig. S5 2D DOSY spectrum of [3+3] in CD_3OD at 298 K.

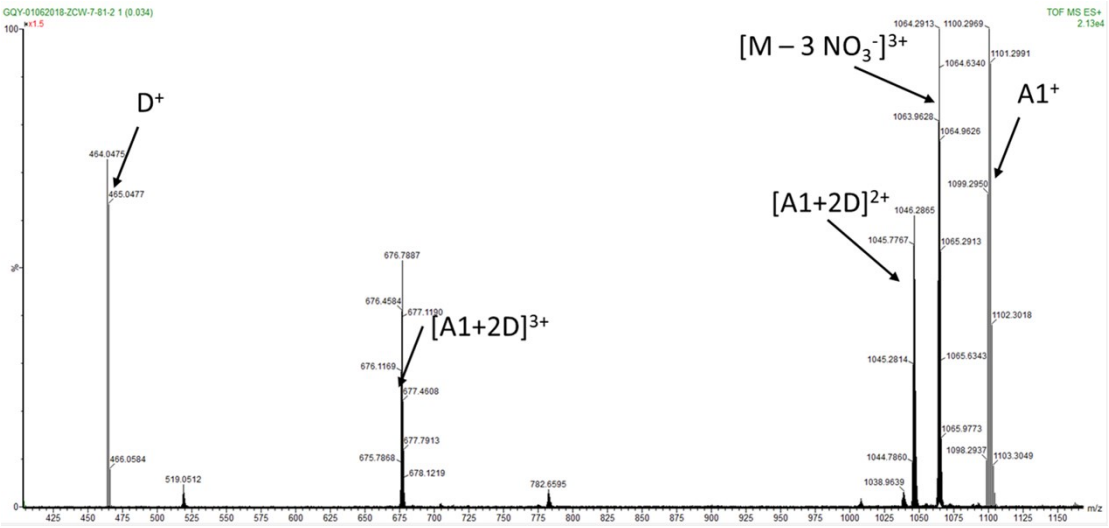


Fig. S6 ESI-TOF-MS full spectrum of [2+2].

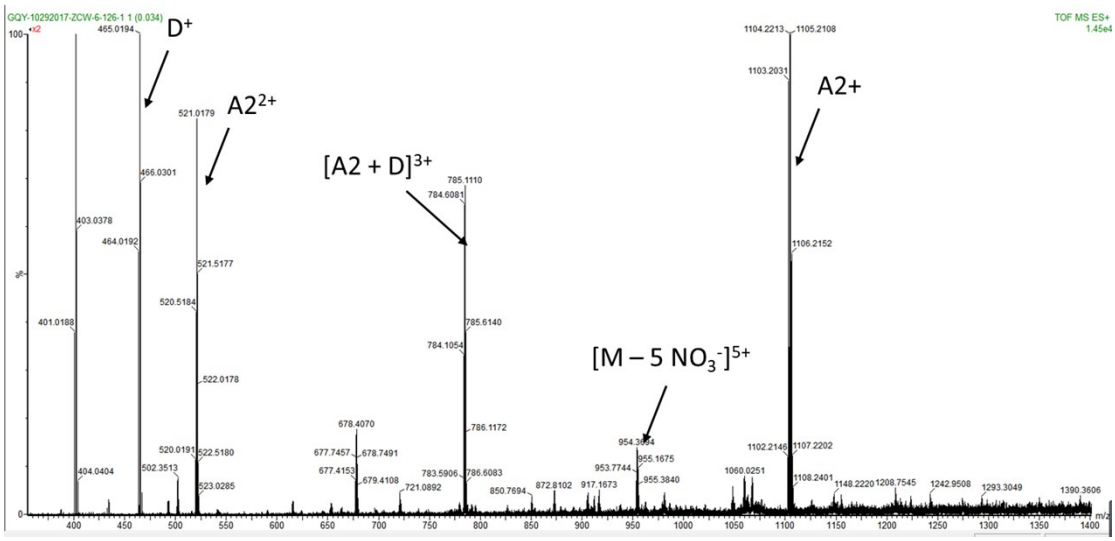


Fig. S7 ESI-TOF-MS full spectrum of [3+3].

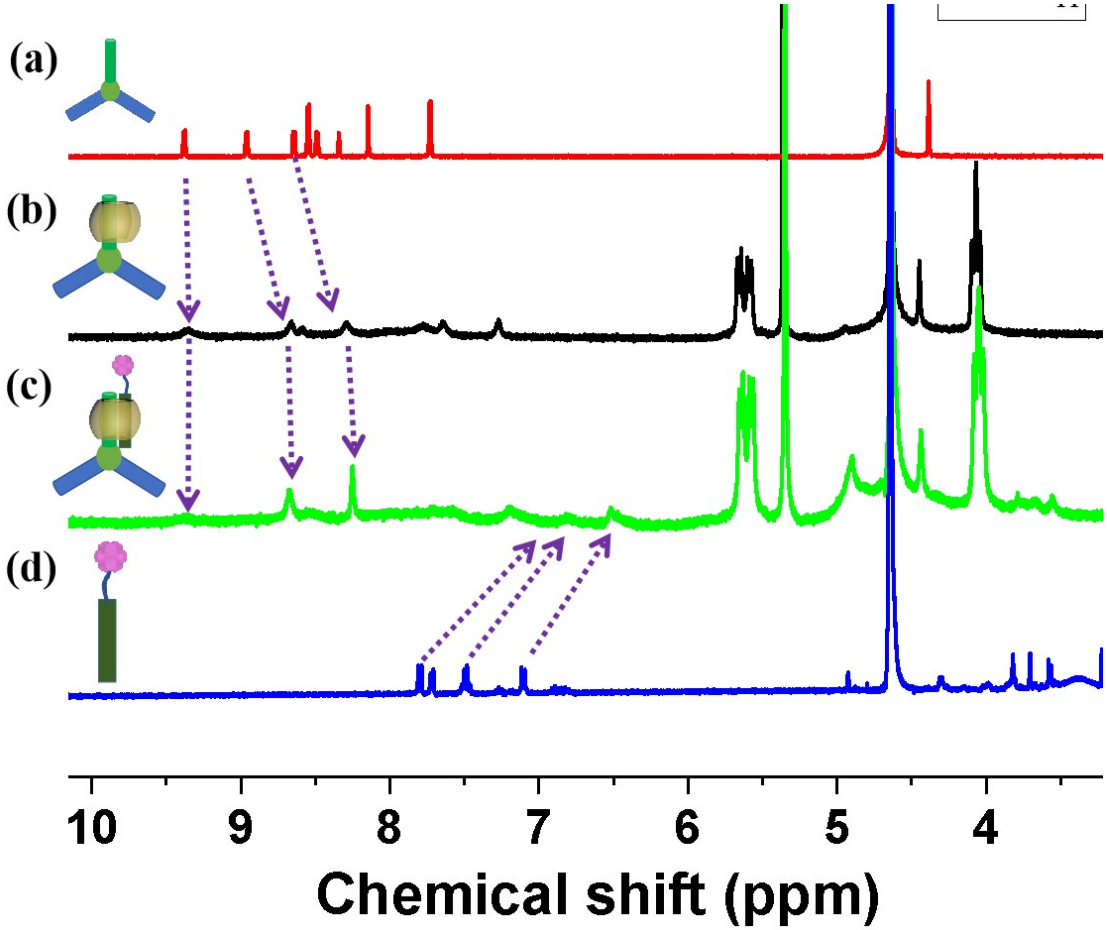


Fig. S8 ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of D (a), D and CB[8] mixture with 1:1 molar ratio (b) , D, CB[8] and AG mixture with 1:1:1 molar ratio (c), AG (d).

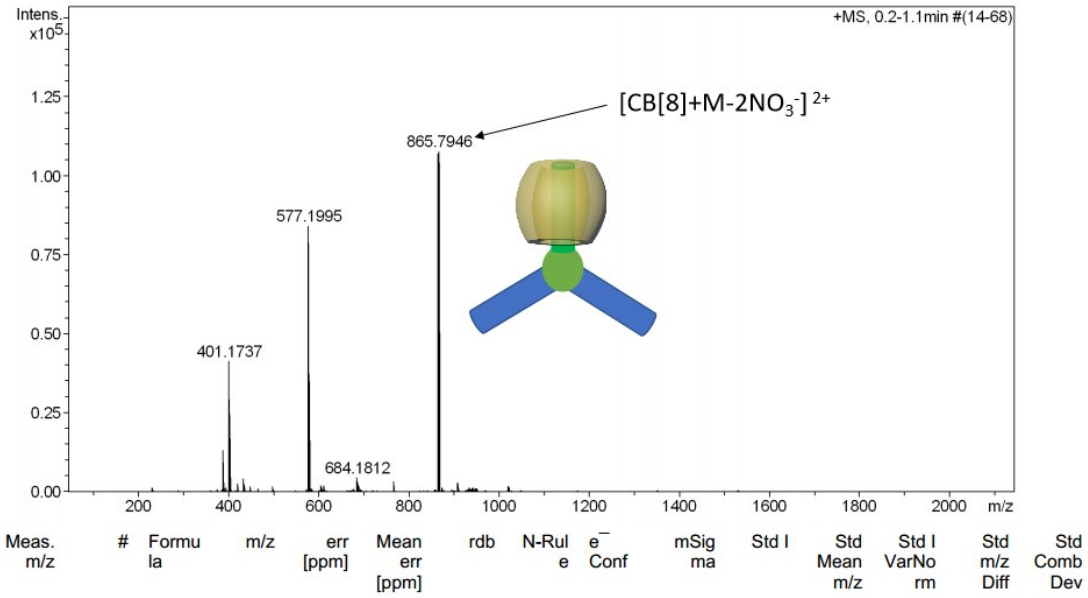


Fig. S9 ESI-MS spectrum of the mixture of D and CB[8] mixture with 1:1 molar ratio.

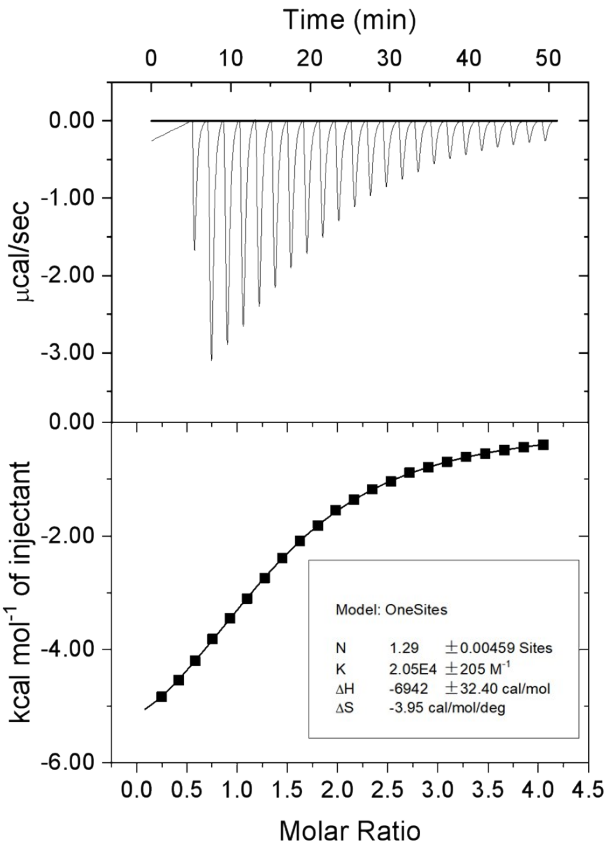


Fig. S10 ITC analysis of AG (1.5 mM) to D/CB[8] mixture (0.1 mM).

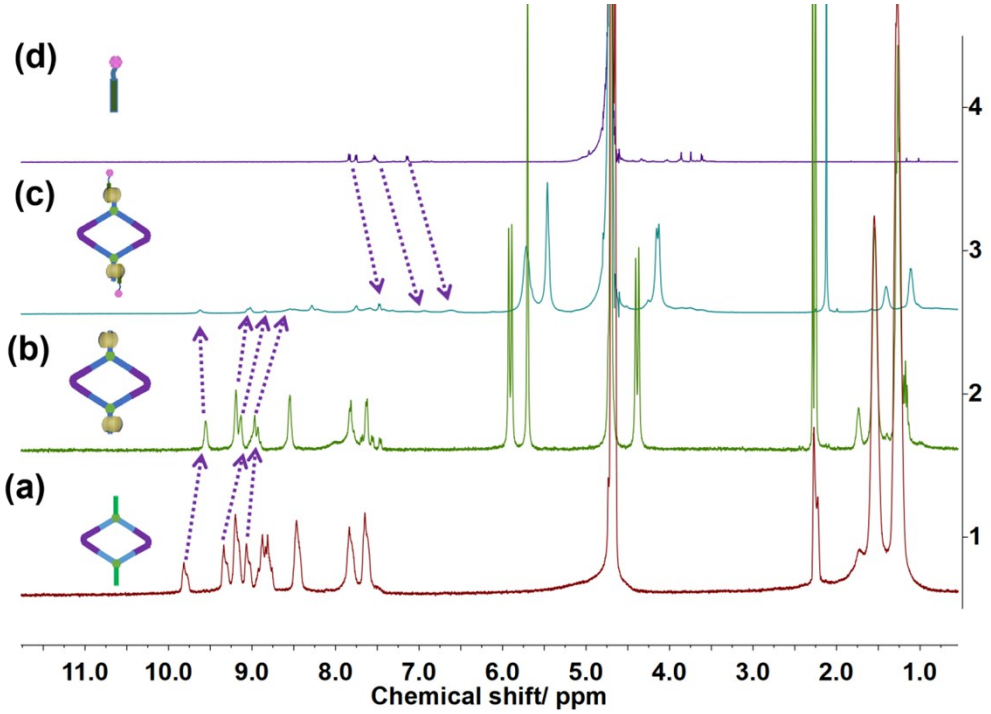


Fig. S11 ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of [2+2] (a), [2+2] and CB[8] mixture (The molar ratio of [2+2] and CB[8] is 1 : 2) (b), the mixture of [2+2], CB[8] and AG (The molar ratio of [2+2] : CB[8]: AG is 1 : 2 : 2) (c), AG (d).

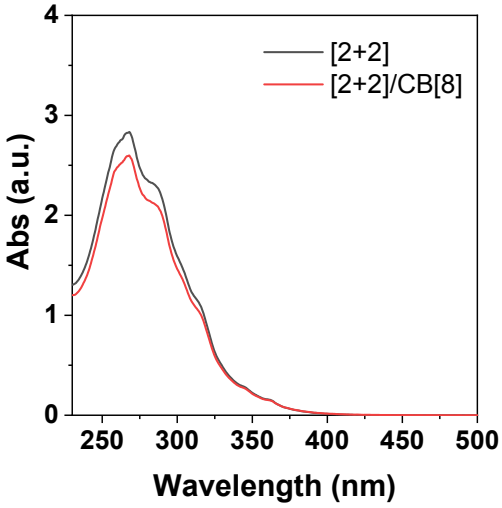


Fig. S12 UV-vis spectra of [2+2] (0.05 mM, black line), the mixture of [2+2] (0.05 mM) and CB[8] (0.1 mM) (red line).

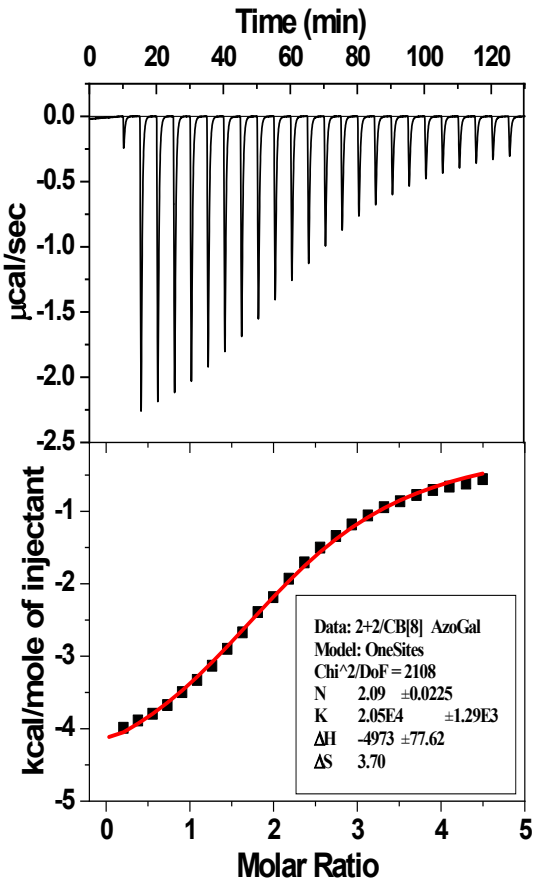


Fig. S13 ITC analysis of AG ([AG]:1.5 mM) to [2+2]/CB[8] mixture ([[2+2]]: 0.05 mM, [CB[8]]: 0.1 mM).

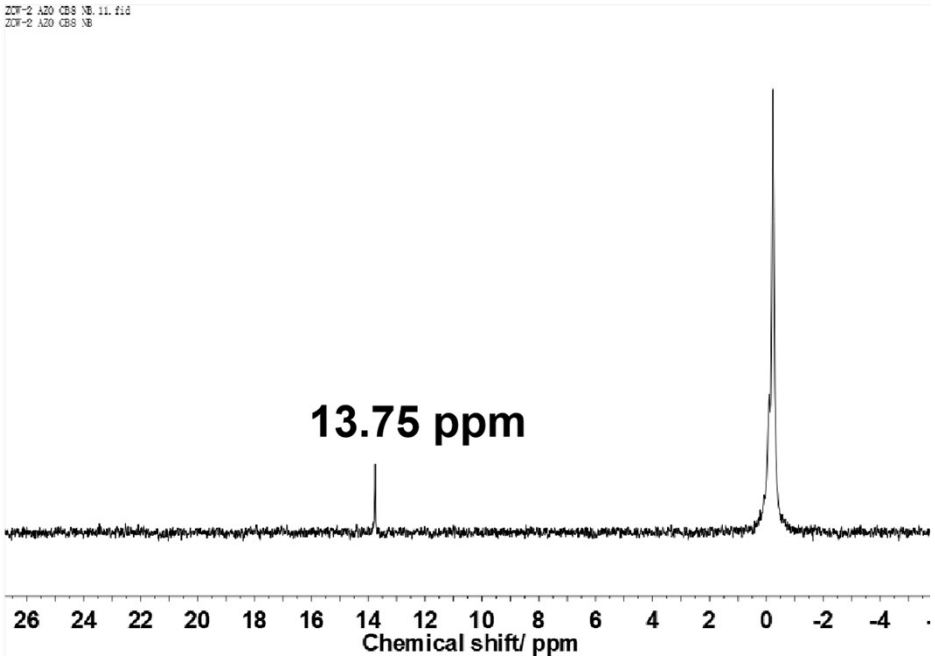


Fig. S14 ^{31}P NMR spectra (161.9 MHz, in D_2O, 298K) of self-assembled rhomboid **2-Gal**.

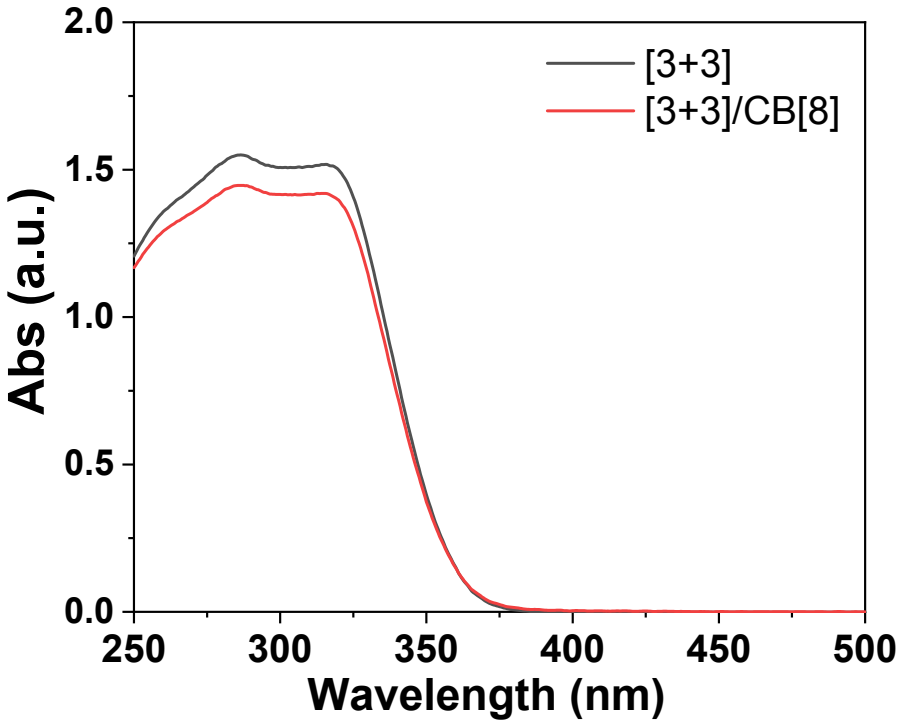


Fig. S15 UV-vis spectra of [3+3] (0.02 mM, black line), the mixture of [3+3] (0.02 mM) and CB[8] (0.06 mM) (red line).

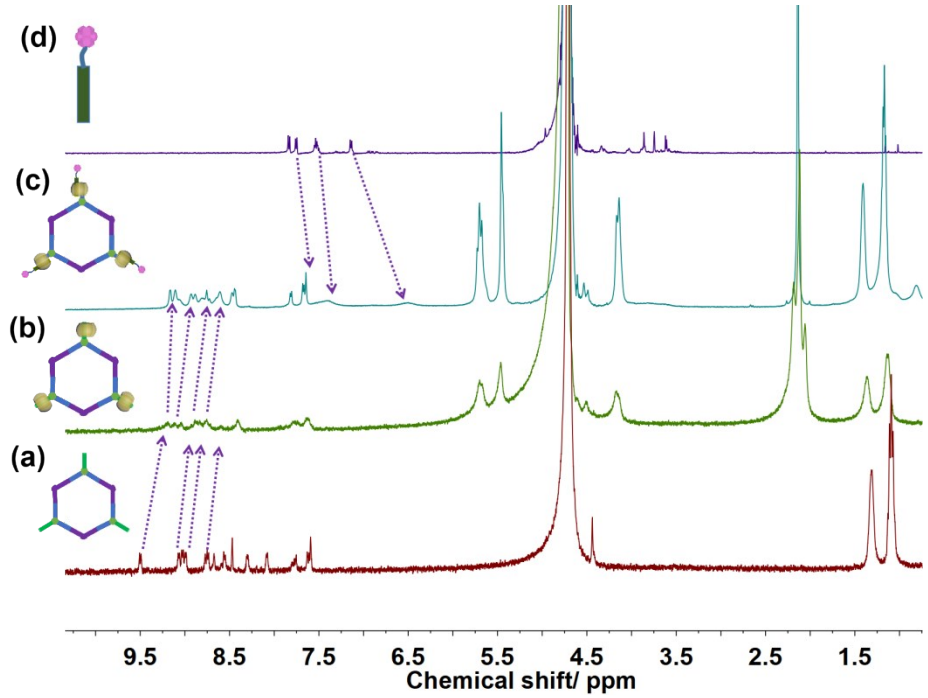


Fig. S16 ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of [3+3] (a), [3+3] and CB[8] mixture (The molar ratio of [3+3] and CB[8] is 1 : 3) (b), the mixture of [3+3], CB[8] and AG (The molar ratio of [2+2]

: CB[8]: AG is 1 : 3 : 3) (c), AG (d).

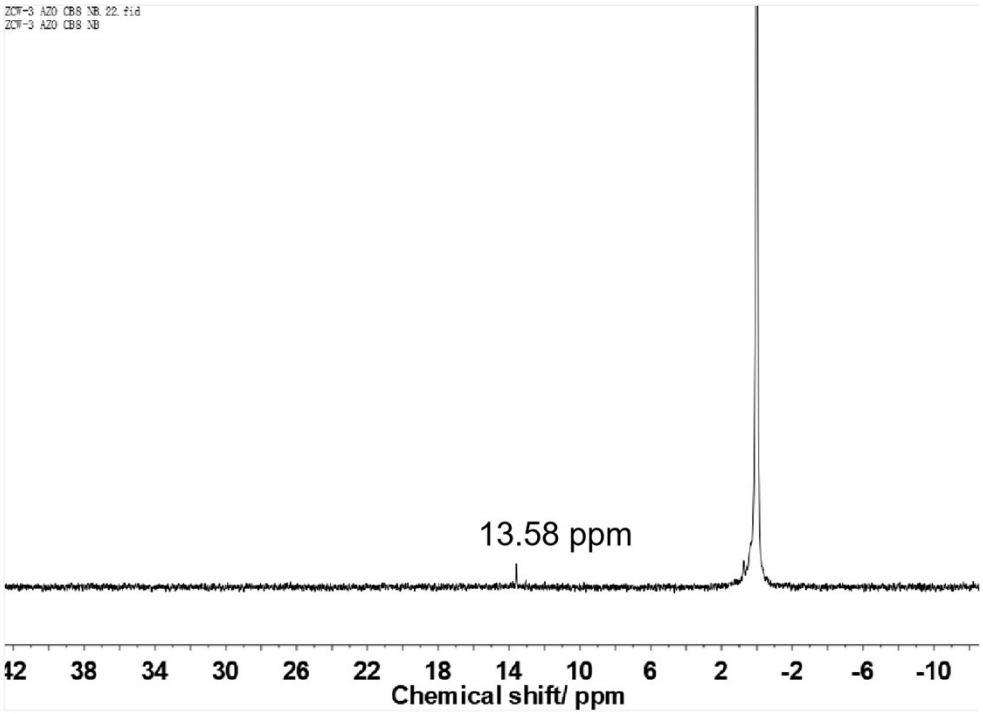


Fig. S17 ^{31}P NMR spectra (161.9 MHz, in D_2O, 298K) of self-assembled hexagonal **3-Gal**.

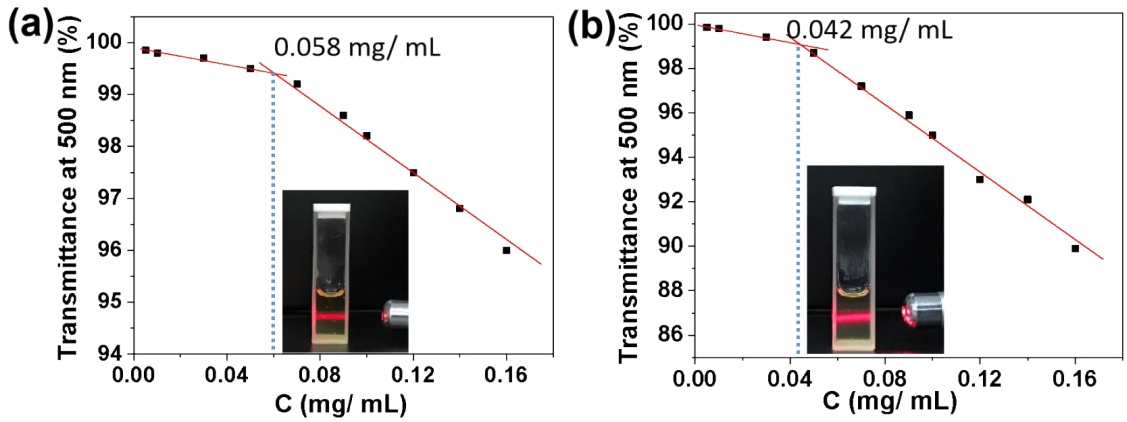


Fig. S18 Concentration-dependent optical transmittance of (a) **2-Gal** and (b) **3-Gal** in water. The insets are the Tyndall effect of (left) 2-Gal and (right) 3-Gal. [**2-Gal**] = [**3-Gal**] = 0.3 mg/ mL.

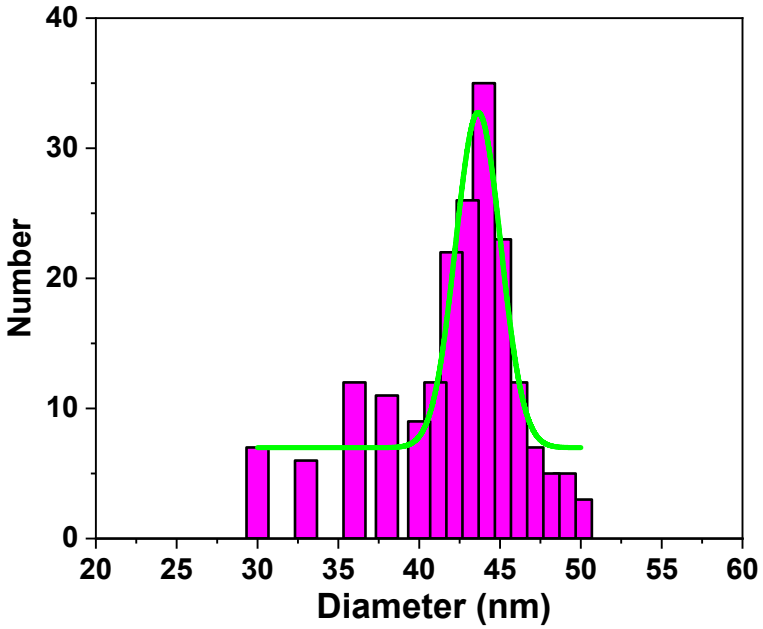


Fig. S19 Diameter distribution measured from TEM images of multi-layered vesicles of **2-Gal** in water.

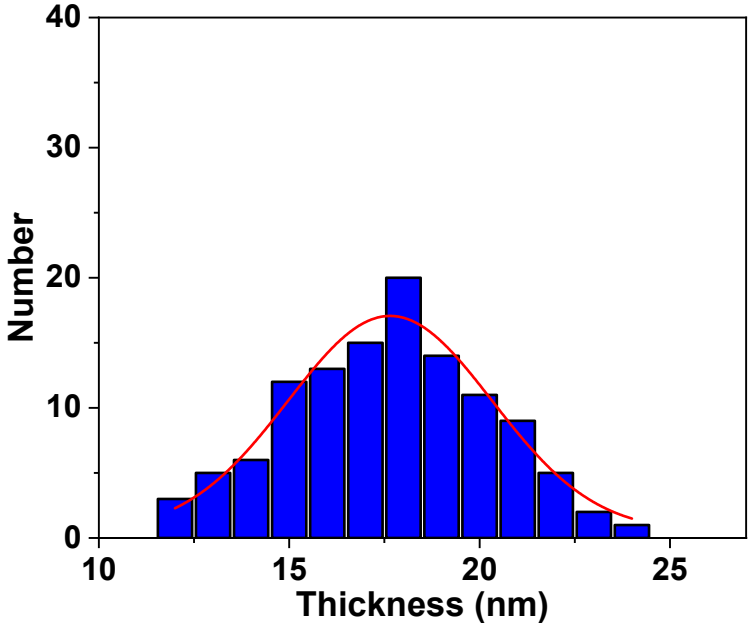


Fig. S20 Wall thickness distribution measured from TEM images of multi-layered vesicles of **2-Gal** in water.

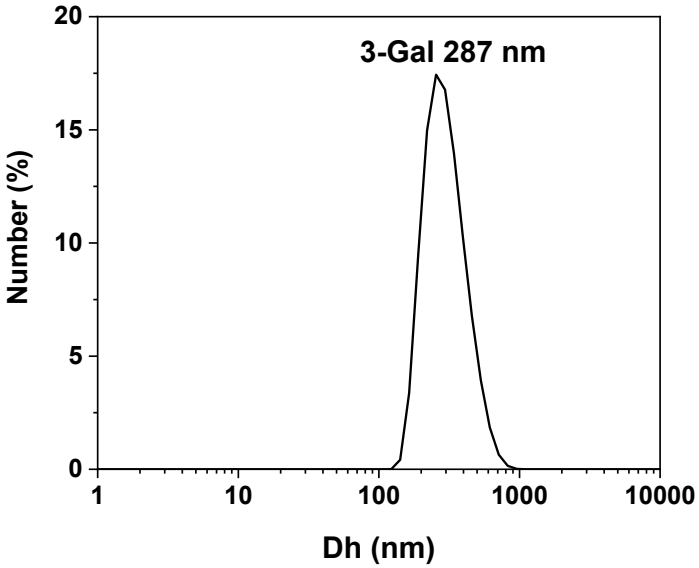


Fig. S21 DLS analysis of **3-Gal** (0.3 mg/ mL) in water.

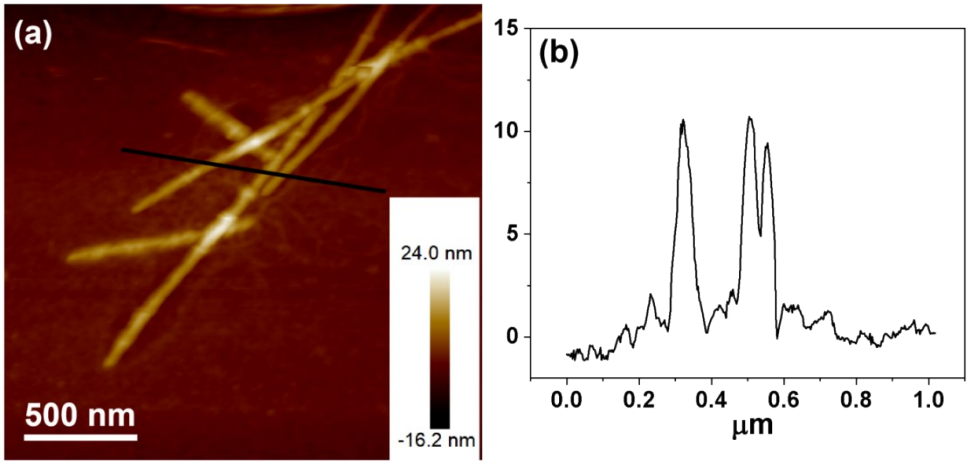


Fig. S22 (a) AFM image of glyco-rods from **3-Gal** (0.3 mg/ mL) in water. (b) The height distribution of the glyco-rods along the black line in image of figure S22a.

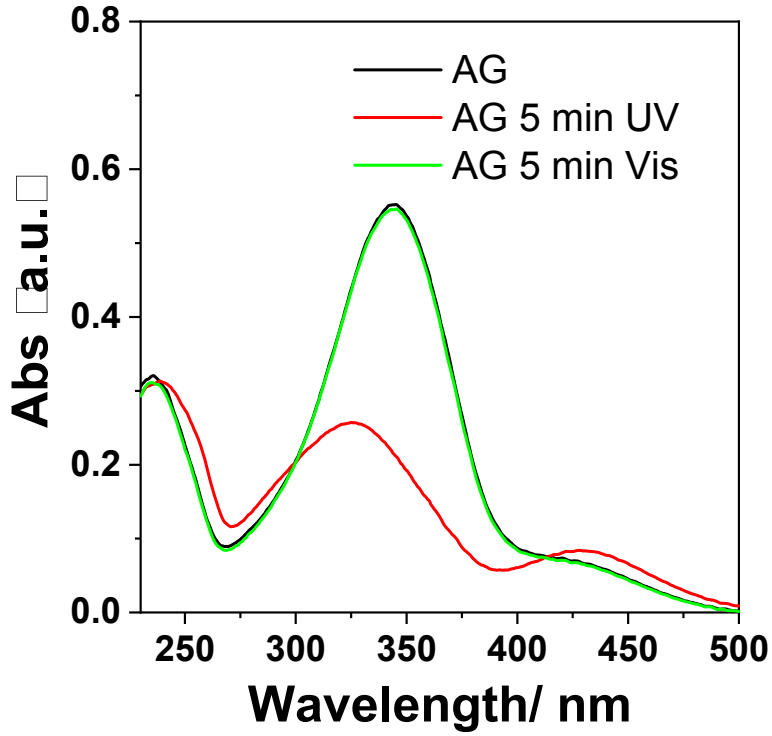


Fig. S23 UV-vis spectra of AG (0.1 mM) before 365 nm irradiation (black line), after 365 nm irradiation (red line), after 365 nm 5 min and subsequent 420 nm irradiation (green line).

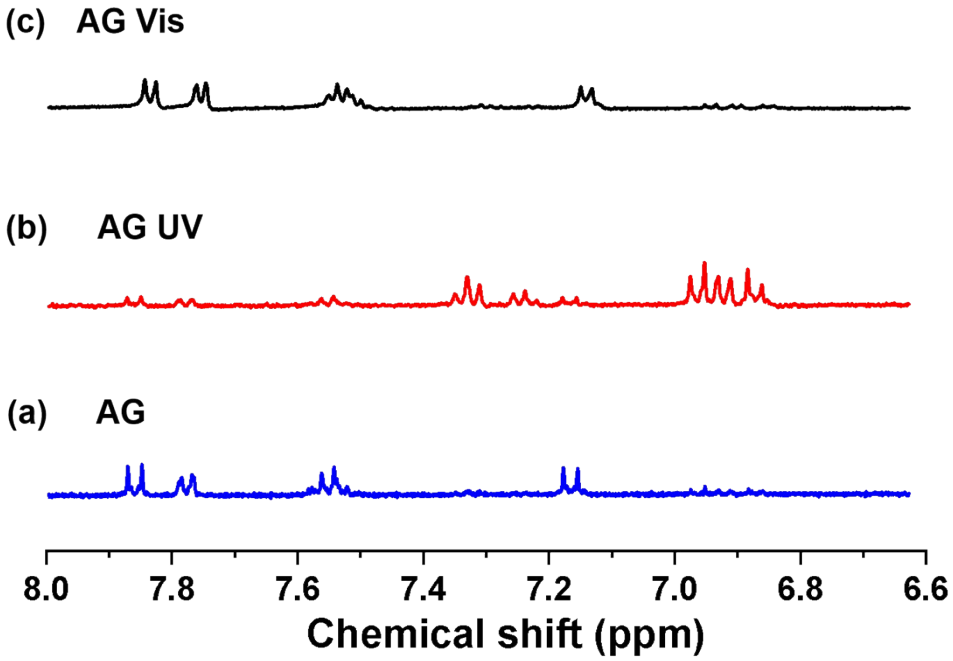


Fig. S24 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of AG before 365 nm irradiation (a), after 365 nm irradiation (b), after 365 nm 5 min and subsequent 420 nm irradiation (c).

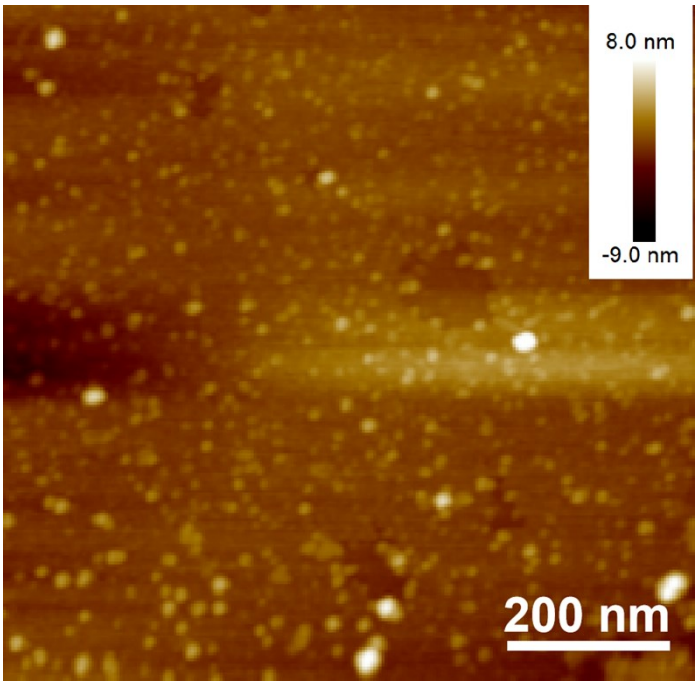


Fig. S25 AFM image of **2-Gal** after 15 min UV irradiation.

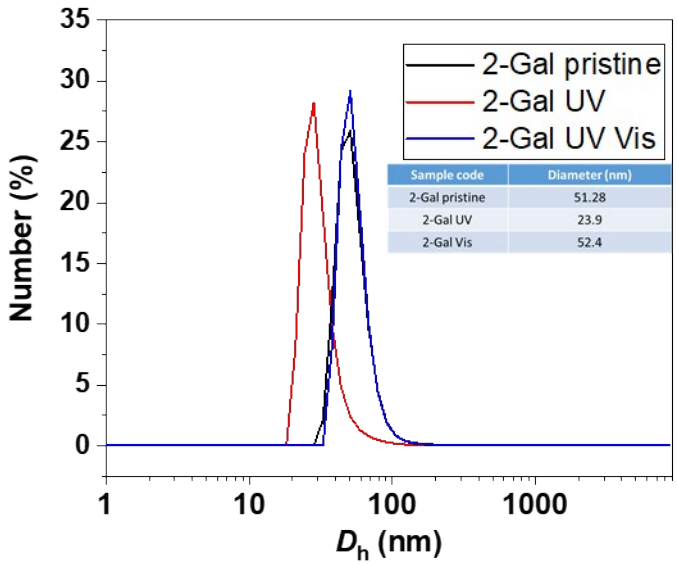


Fig. S26 DLS analysis of **2-Gal** in water before 365 nm irradiation (black line), after 365 nm irradiation for 15 min (red line), after 365 nm for 15 min and subsequent 420 nm irradiation for 15 min (blue line). The inset table was the corresponded diameter values.

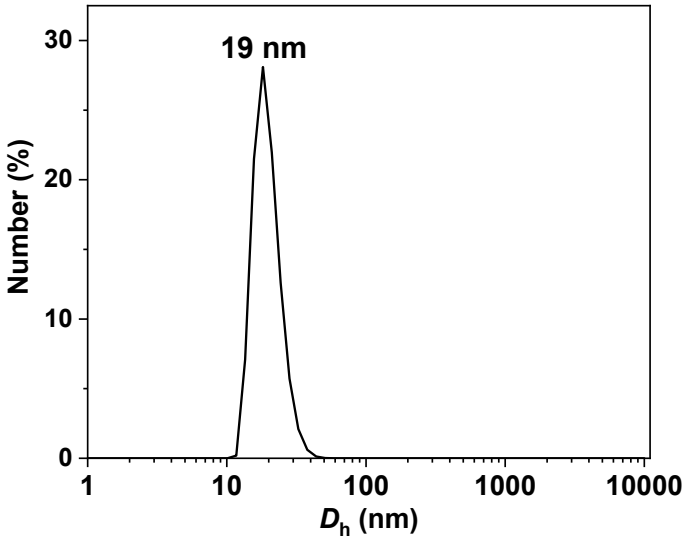


Fig. S27 DLS analysis of **2-Gal** in water after the addition of 10 equivalent Ada.

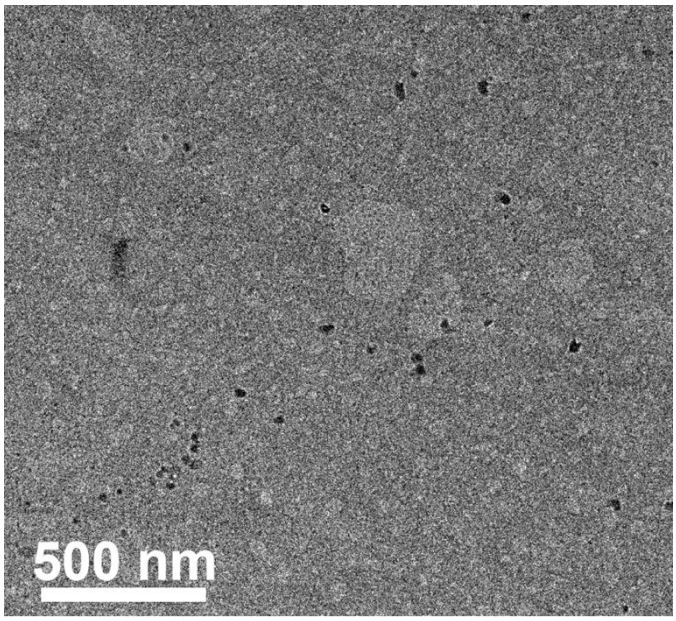


Fig. S28. TEM image of **2-Gal** in water after the addition of 10 equivalent Ada.

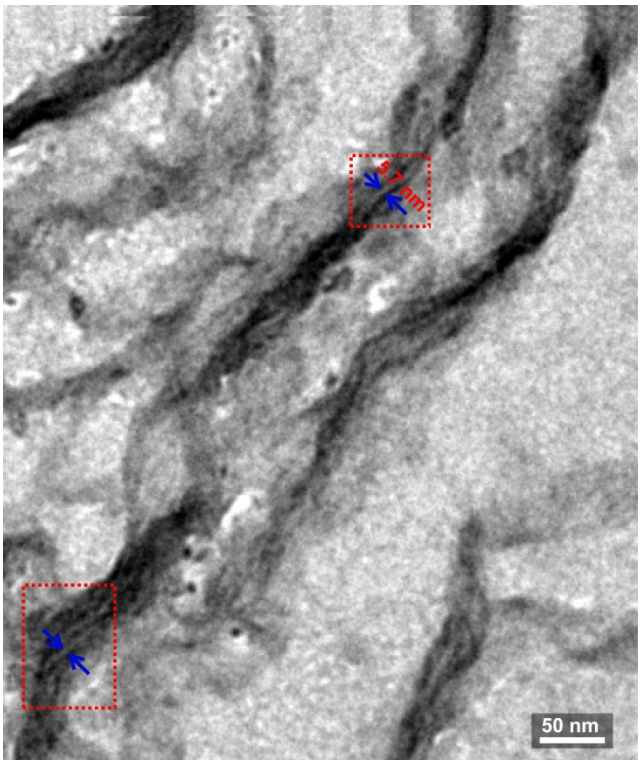


Fig. S29 Enlarged TEM image of **3-Gal** after 365 nm irradiation for 15 min.

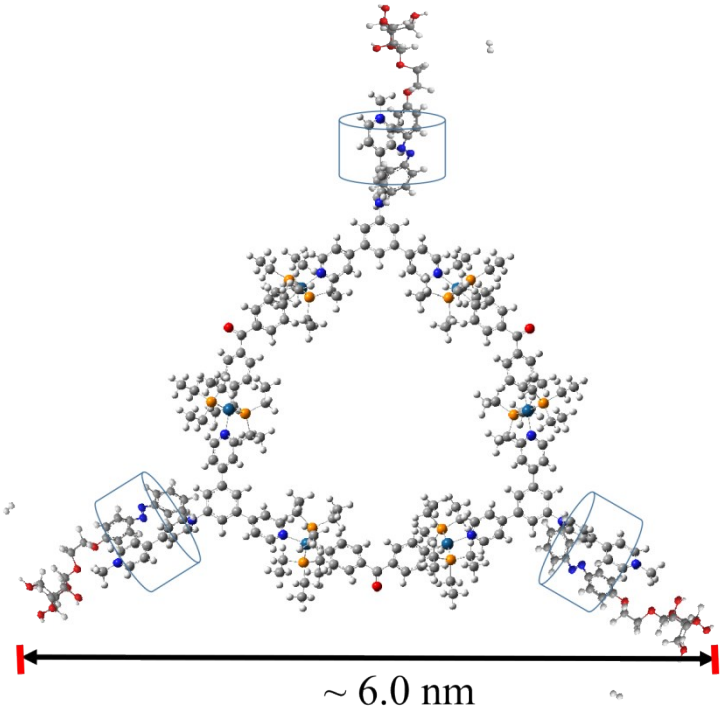


Fig. S30 Geometrical structures of **3-Gal**.

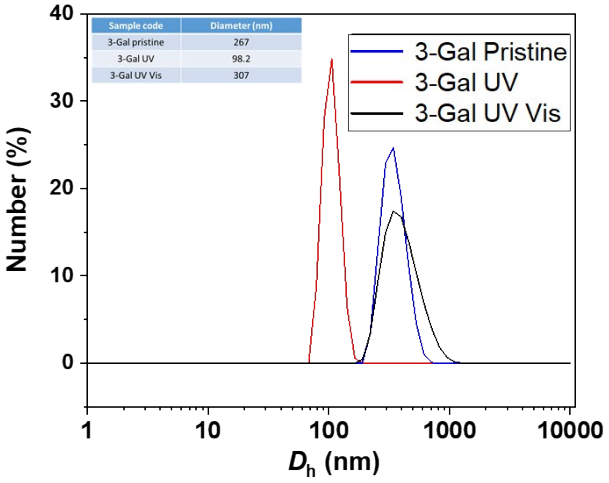
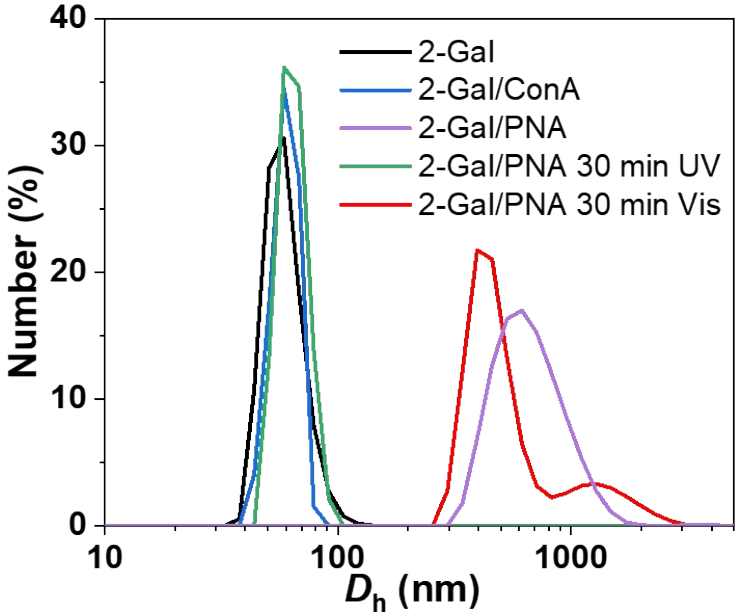


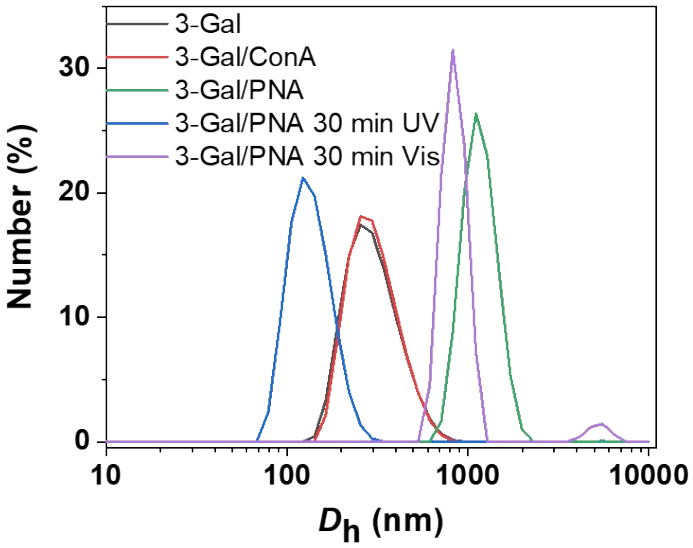
Fig. S31 DLS analysis of **3-Gal** in water before 365 nm irradiation (black line), after 365 nm irradiation for 30 min (red line), after 365 nm for 30 min and subsequent 420 nm irradiation for 30 min (blue line). The inset table was the corresponded diameter values.



Sample code	Diameter (nm)
2-Gal	53.8
2-Gal/ConA	60.1
2-Gal/PNA	647
2-Gal/PNA 30 min UV	65.7
2-Gal/PNA 30 min Vis	477

Fig. S32 DLS analysis of the supramolecular complex of **2-Gal**/PNA in water at room temperature. Conditions: [**2-Gal**] = 0.05 mM, [PNA]=[ConA] = 0.15 mg/ mL. The following table was the

corresponded diameter values.



Sample code	Diameter (nm)
3-Gal	290
3-Gal/ConA	289
3-Gal/PNA	1034
3-Gal/PNA 30 min UV	141
3-Gal/PNA 30 min Vis	812

Fig. S33 DLS analysis of the supramolecular complex of **3-Gal**/PNA in water at room temperature. Conditions: [**3-Gal**] = 0.033 mM, [PNA]=[ConA] = 0.15 mg/ mL. The following table was the corresponded diameter values.

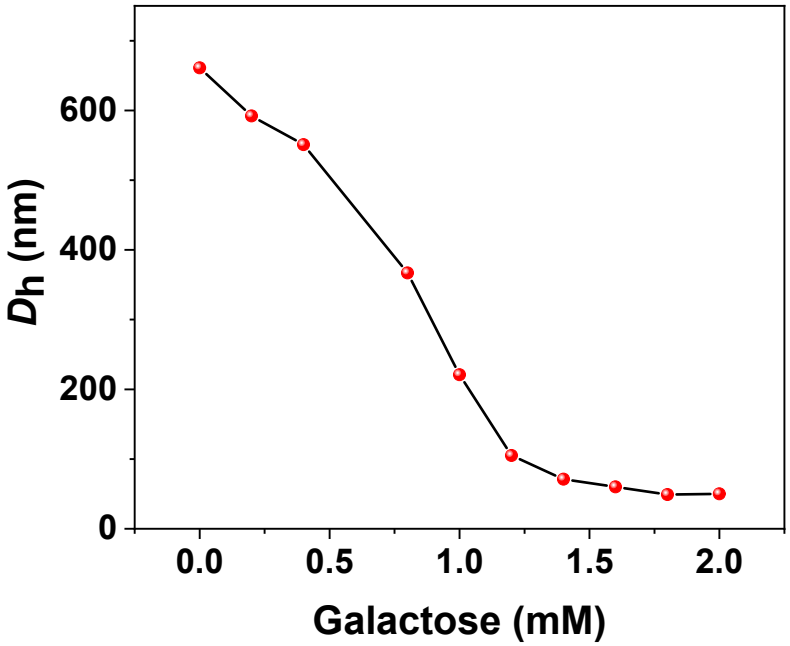


Fig. S34 hydrodynamic diameter change upon the gradual addition of free galactose from 0.2 mM

to 2 mM in water.

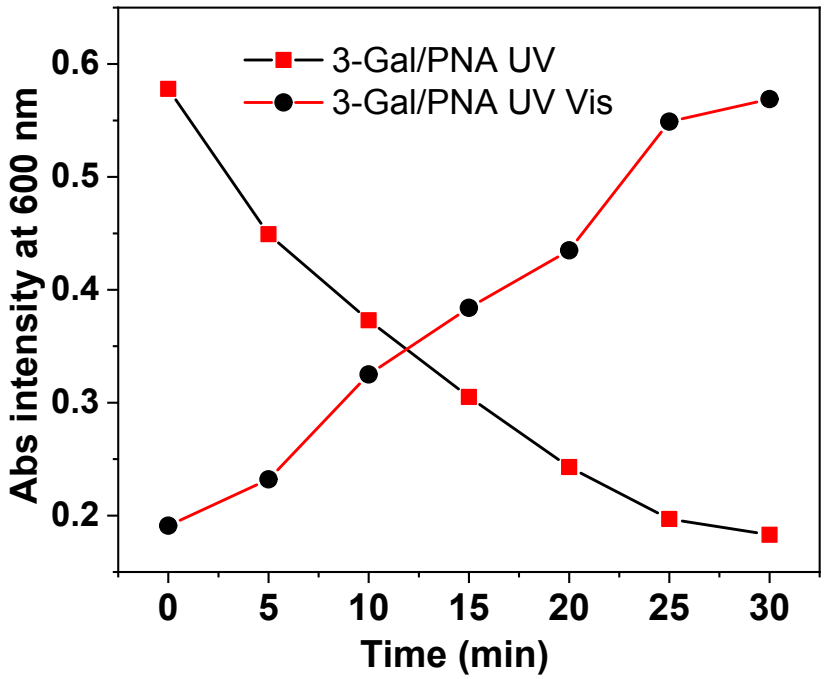


Fig. S35 Time dependent absorption intensity of **3-Gal**/PNA monitoring at 600 nm after the Uv irradiation and subsequent Vis irradiation.

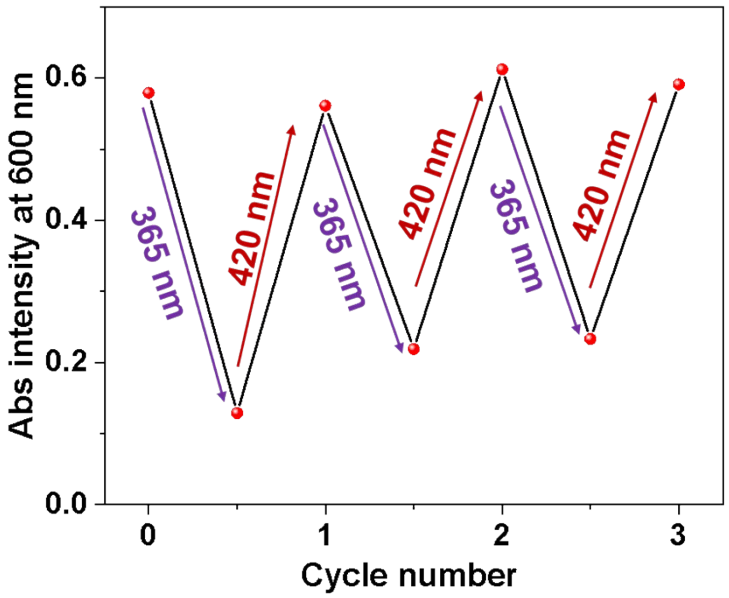


Fig. S36 repeated cycles of photo-reversible assembly and disassembly of **3-Gal**/PNA.

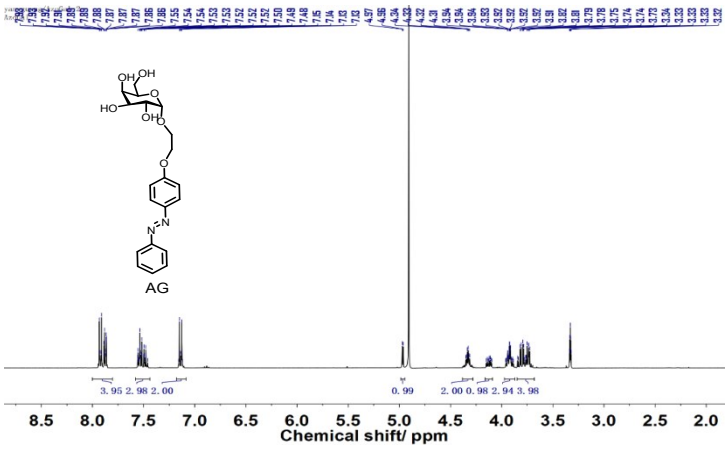


Fig. S37 ^{1}H NMR spectrum of **AG** in CD_3OD at 298K.

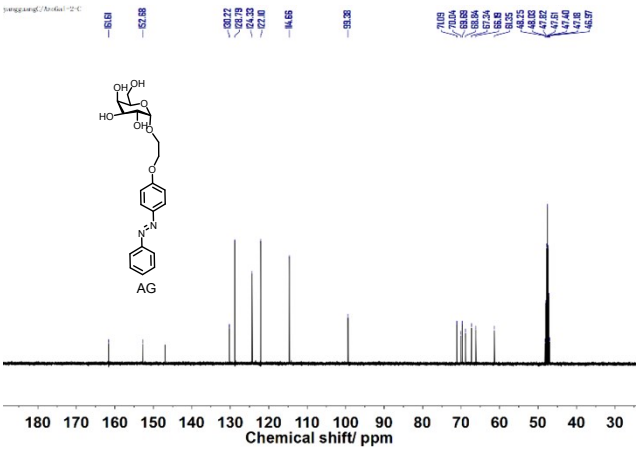
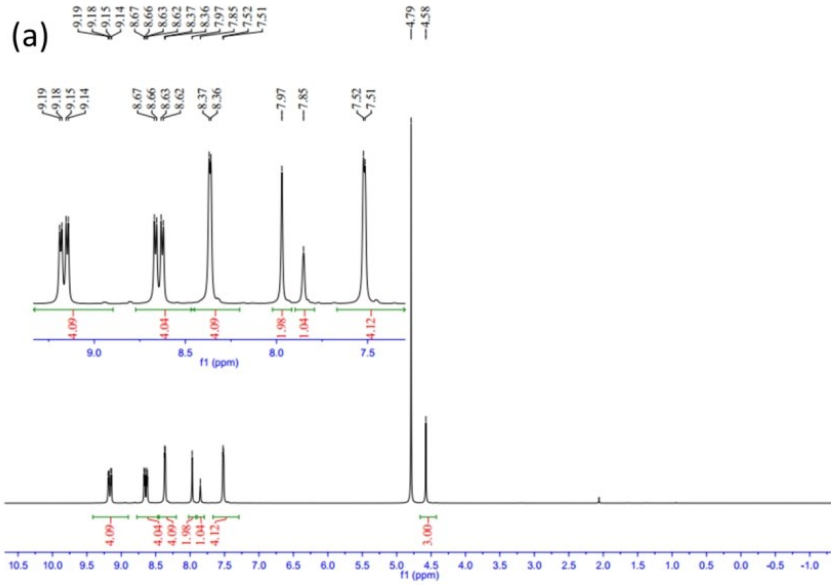


Fig. S38 ^{13}C NMR spectrum of **AG** in CD_3OD at 298K.



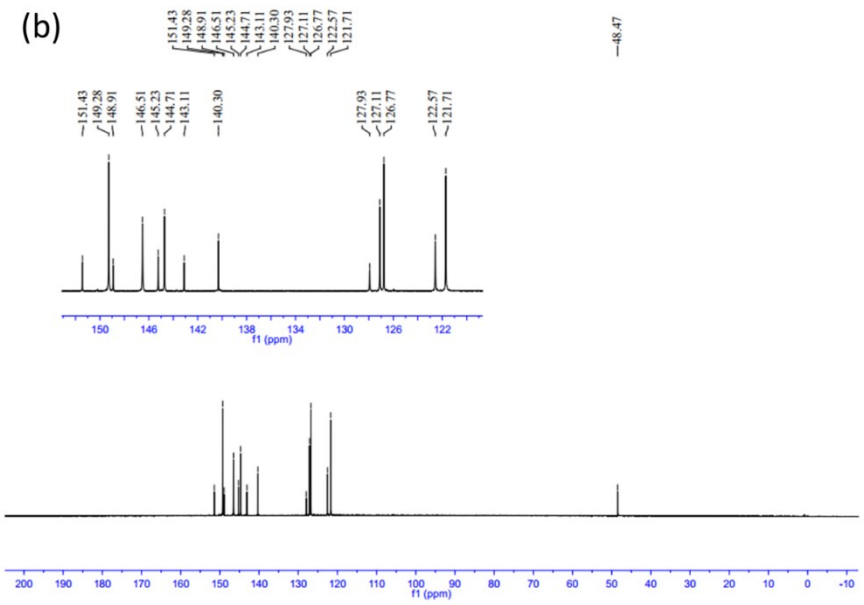


Fig. S39 (a) ^{1}H and (b) ^{13}C NMR spectra of **D** in D_2O at 298K.

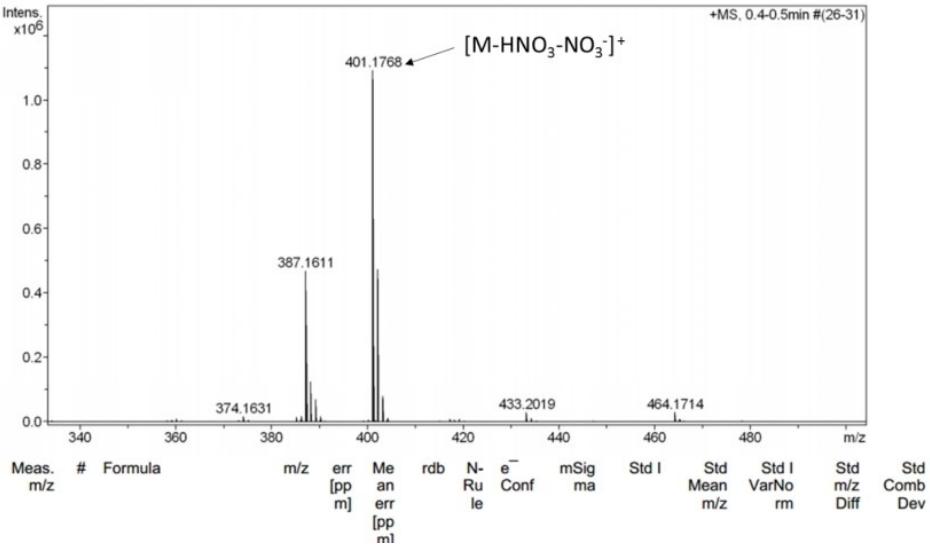


Fig. S40. Experimental ESI-TOF-MS spectra of **D.**