Supporting Information

The macroscopic wettable surface : fabricated by calix[4]arene-based host-guest interaction and chiral discrimination of glucose

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Contents of supporting information

1. General methods

Synthetic method and characterization of S-MC4.

Reagents were commercially available and used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H and ^{13}C NMR spectra were recorded on a Mercury-Plus spectrometer (400 MHz). MALDI-TOF-TOF were recorded on a Synapt G2 HDMS system (Waters, USA). Elemental analyses were performed on a Perkin-Elmer 240 C analyzer.

Materials

The static water contact angle was measured at 25 °C by means of an OCA 20 contact angle system (Dataphysics, Germany). The static water contact angle was measured at 25 °C by means of an OCA 20 contact angle system (Dataphysics, Germany). XPS was recorded on a KRATOS XSAM800 Electron spectrometer (FRR mode).

2. The synthesis and characterization of compound S-MC4
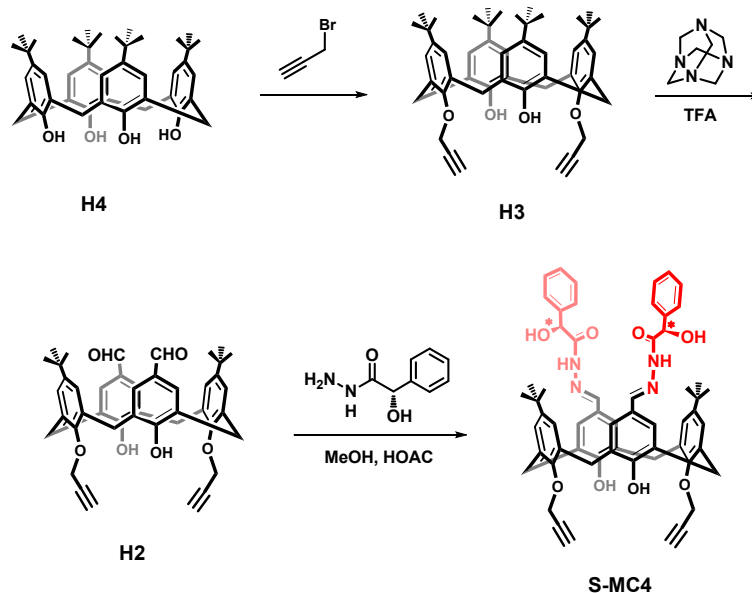
Scheme S1. The synthesis route of chiral host S-MC4.

Synthesis of compound H3: The H4 was synthesized according to the literature.[S1] Potassium carbonate (4.6 mmol, 0.64 g) and propargyl bromide (4.6 mmol, 0.5 mL) were added to the solution of tert-butyl calix[4]arene (1.54 mmol, 1 g) in anhydrous acetone (60 ml). After stirring at 60 °C for 12 h under nitrogen atmosphere, the potassium carbonate was washed by water in room temperature. Then removed the solvent and residue was subject to column chromatography (silica gel, petroleum ether/ethyl acetate, 8:1), yielding of compound H3 as a white powder (0.7 g, 67%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.04 (s, 4H), 6.69 (s, 4H), 6.43 (s, 2H), 4.71 (s, 4H), 4.37 (d, 4H), 3.33(d, 4H), 2.51 (s, 2H), 1.30 (s, 18H), 0.89 (s, 18H) ppm. ^{13}C NMR (150 MHz, 293K, CDCl$_3$): δ 150.16, 149.29, 146.99, 141.38, 132.39, 127.86, 125.37, 124.86, 78.75, 76.34, 63.27, 33.92, 32.12, 31.80, 31.12, 32.12, 31.80, 31.14, 30.92 ppm.

Synthesis of compound H2: The compound H3 (0.15 mmol, 0.11 g) and hexamethylenetetramine (6.17 mmol, 0.86 g) were taken in trifluoroacetic acid (50 mL). The reaction mixture was refluxed until the starting materials had disappeared (TLC). And the mixture was quenched with ice cold water and extracted with chloroform. The organic layer was washed with water and dried (Na$_2$SO$_4$). The

solvent was evaporated under reduced pressure, and the residue was purified as mentioned to yield the desired bisformyl calix[4]-arene product (H2). ^{1}H NMR (600 MHz, CDCl$_3$): δ 9.85 (s, 2H), 7.77 (s, 2H), 7.67 (s, 4H), 6.79 (s, 4H), 4.78 (s, 4H), 4.39 (s, 4H), 3.52 (d, $J = 18.0$, 4H), 2.63 (s, 2H), 0.93 (s, 18H) ppm. ^{13}C NMR (150 MHz, 293K, CDCl$_3$): δ 191.71, 191.11, 159.11, 149.41, 148.48, 131.48, 130.69, 128.95, 128.60, 126.03, 125.97, 78.08, 64.57, 63.47, 34.07, 31.88, 31.11, 30.89 ppm.

Synthesis of compound S-MC4: In a 50 mL flask, calix[4]arene (H2) (0.16 g, 0.25 mmol) was dissolved in ethanol (20 mL) under a nitrogen atmosphere. And then S-mandelic acid hydrazide (0.12 g, 0.51 mmol) was added into the mixture. The solution was stirred for 30 min at ambient temperature. Subsequently, catalytic amount of HOAc was added. The mixture was further stirred for 10h. After evaporation of the solvent, the crude product was dissolved in CHCl$_3$, washed with brine for three times, and dried with anhydrous Na$_2$SO$_4$. The residue was recrystallized to yield the white solid (0.13 g, 48%). ^{1}H NMR (400 MHz, 297K, CD$_3$COCD$_3$) δ (ppm): 10.34 (d, $J = 28.0$ Hz, 2H), 8.27 (s, 1H), 8.16-8.11 (m, 2H), 7.84 (s, 1H), 7.55-7.51 (m, 8H), 7.32-7.30 (m, 4H), 7.09 (d, 4H), 5.89 (s, 1H), 5.34 (s, 1H), 5.18 (s, 1H), 4.89 (m, 4H), 4.57 (d, 1H), 4.49-4.42 (m, 4H), 3.61-3.58 (m, 4H), 3.26 (s, 2H), 1.01-0.96 (m, 18H); ^{13}C NMR (100 MHz, 297K, CD$_3$COCD$_3$) δ (ppm): 167.86, 155.56, 149.74, 148.80, 147.87, 141.14, 132.47, 128.30, 128.04, 127.63, 127.15, 126.57, 126.10, 78.46, 77.66, 73.73, 70.67, 63.36, 33.78, 31.64, 30.54, 30.46; MALDI-TOF mass spectrum calcd for m/z=987.422, found m/z= 986.980 [M+Na]$^{+}$. Anal. Calc. for :C, 74.84; N, 5.82; H, 6.03. Found: C, 74.68; N, 5.69; H, 6.01.

3. The ¹H NMR titration of S-MC4 and D-/L-Glu

To determine the stoichiometry and association constant (K_a) between S-MC4 and D-/L-Glu. ¹H NMR titrations were done with solutions which had a constant concentration of S-MC4 (8 mM) and varying concentrations of glucose. Using the nonlinear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation:[S2, S3]

$$\Delta\delta = (\Delta\delta/[H]_0)\ (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5\ ([G]_0^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$$

Where is the chemical shift change of Ha of amide in S-MC4 at $[G]_0$, is the chemical shift change of H_a when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host S-MC4, and $[G]_0$ is the varying concentrations of guest glucose.
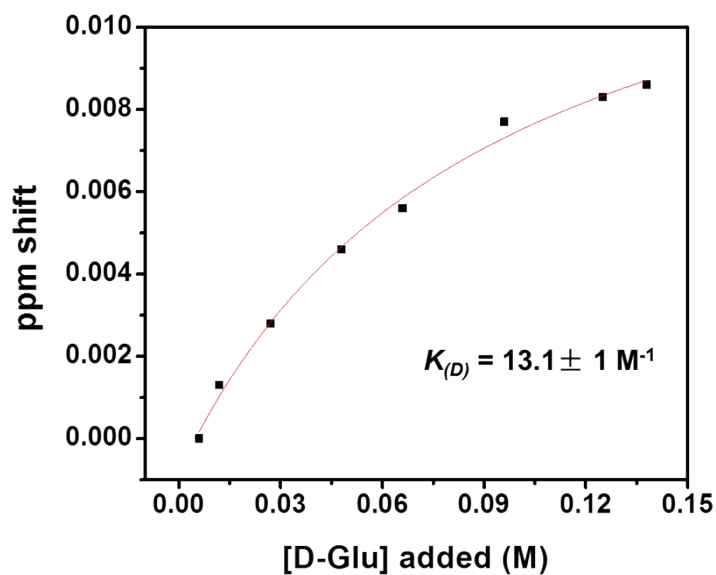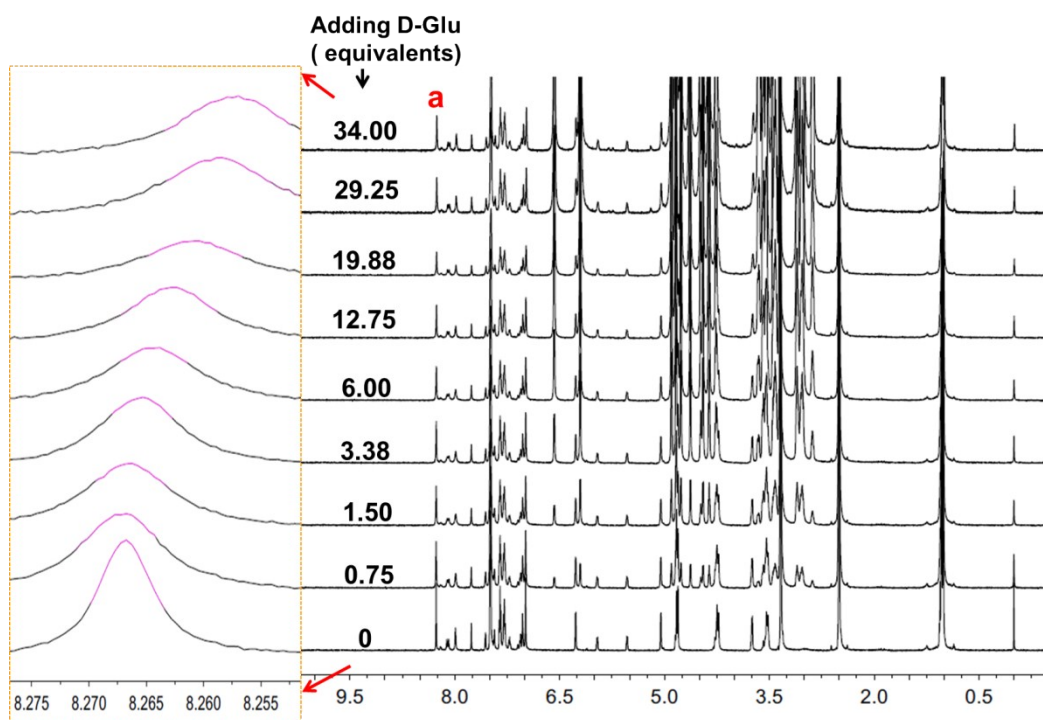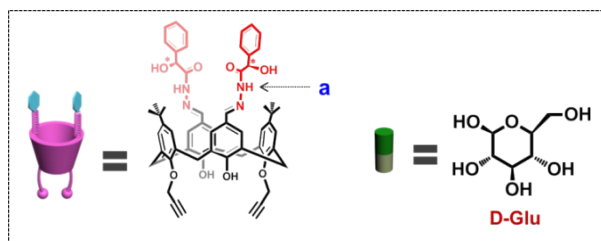
Figure S1. Experimental values for the ^{1}H NMR (400 MHz) binding study of S-MC4 vs D-Glu in DMSO.
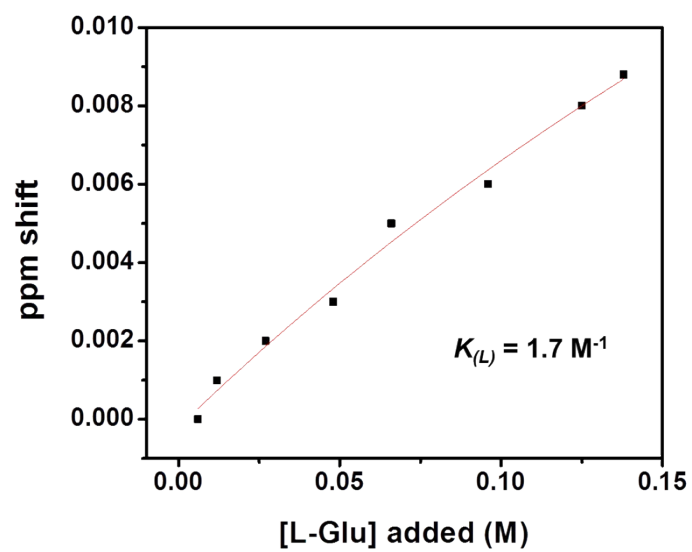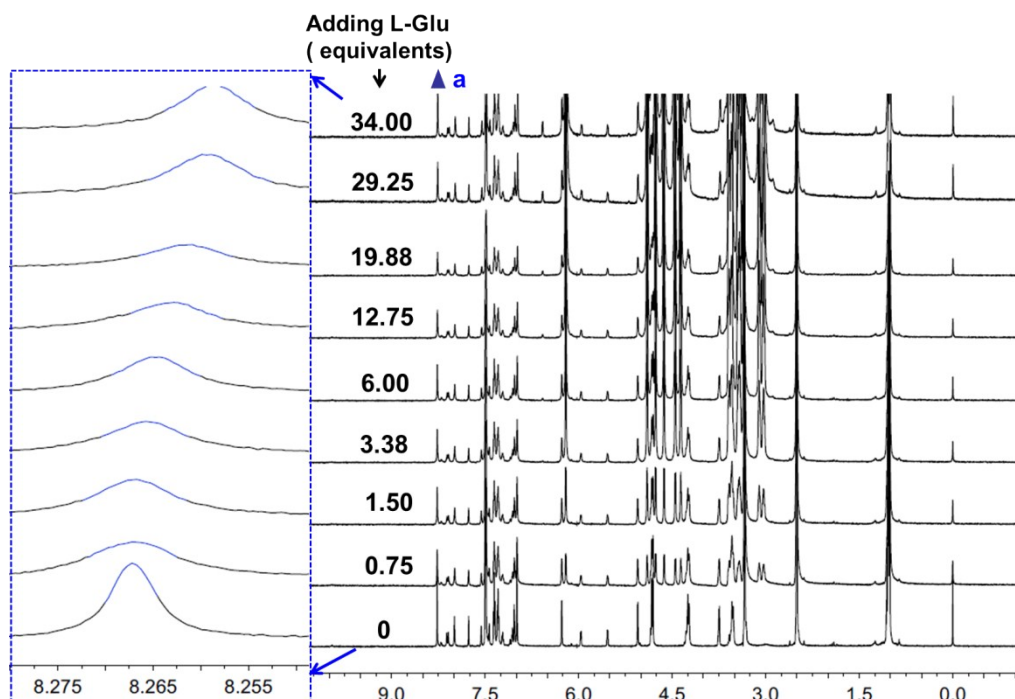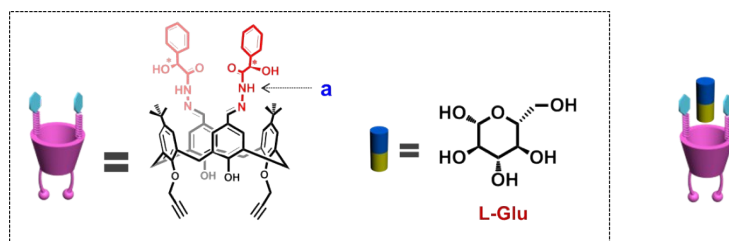
Figure S2. Experimental values for the ^{1}H NMR (400 MHz) binding study of S-MC4 vs L-Glu in DMSO.

4.   Procedures of functionalization gold surface using S-MC4

The silicon wafer was used directly as the smooth substrate. The structured silicon substrate was fabricated by the combination of the photolithography and an inductively coupled plasma (ICP) deep-etching technique. The photolithography and ICP technique were used to obtain the patterned silicon micropillar structure on silicon wafer. And the Au-coated Si interface was obtained through spraying Au at a thickness of 1–2 nm (See the following picture). The S-MC4 modified surface was prepared by dipping the micro–nano Au wafer into the S-MC4 solution (10^{-3} M) for 24 h in DMSO. And then gently washing the functional surface with EtOH, dried under argon. The successfully modified Au surface of S-MC4 was firstly performed by contact angle as control experiment. S-MC4 gold surface were dipped into solutions containing the D-/L-glucose (0.1 mL, 1.0 mM) for 5 min, respectively and then were flushed by little water, dried by nitrogen and then measured. The wettability property was performed with a water droplet (1.000 μL) and side-view photographs were obtained after 5 second of adding the water droplet.

Figure S3. The process of the fabricating micro–nano Au interface.
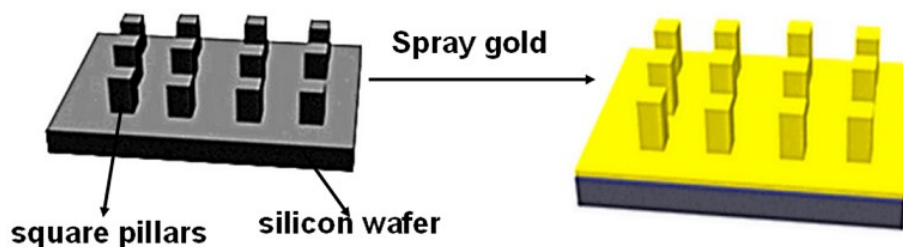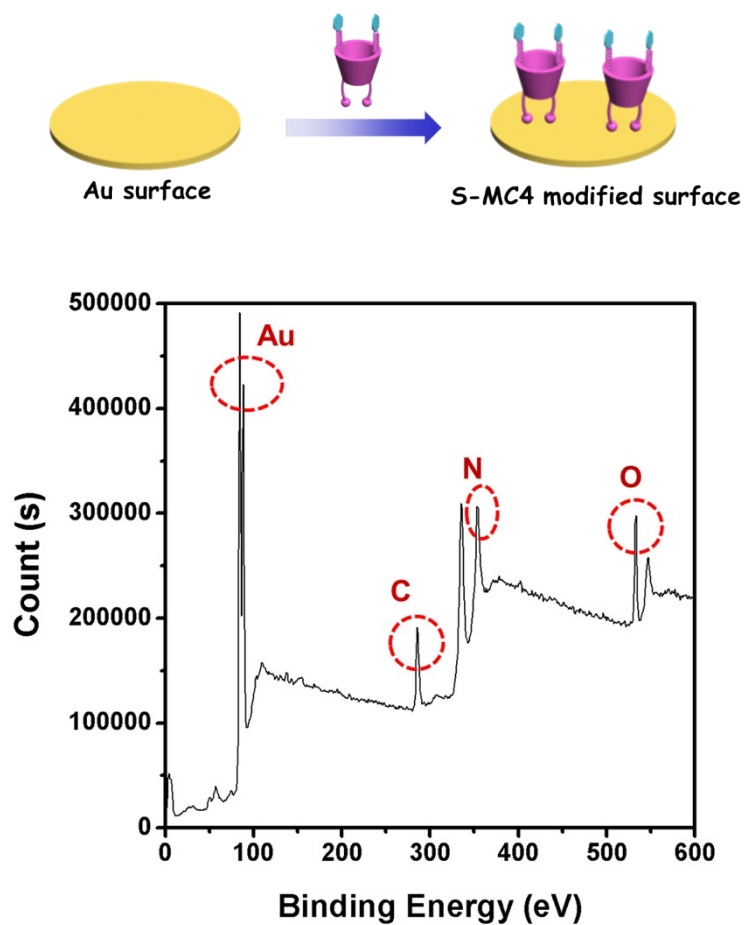
5. S-MC4-modified interface by XPS

Figure S4. X-ray photoelectron spectra S-MC4 modified Au substrate. These showed the concentration of Oxygen, Carbon and Nitrogen had a significant appear in the XPS-derived atomic concentration analysis for the SAMs after the self-assembly. We concluded that the S-MC4-modified Au substrate was constructed perfectly.

Table S1. Element content analysis of bare Au surface (A); and S-MC4 modified surface (B).

(A) Bare Au surface

Element	Au_{4f}	C_{1s}	N_{1s}	O_{1s}	Si_{2s}
Assay	46.15	12.34	1.03	2.16	15.13

(B) S-MC4 modified surface

Element	Au_{4f}	C_{1s}	N_{1s}	O_{1s}	Si_{2s}
Assay	27.06	48.05	3.55	26.92	4.92

From the above the data, we attempt to estimate the surface coverage of S-MC4 on the Au substrate by XPS experiments. As showing in the table S1, the increasing mass of N is 2.52 %. We may get the amount of substance (S-MC4) (2.52% / 56). The amount of substance Au is 27.06% / 197. Thus, the mole ratio of chiral S-MC4 and Au surface is about 0.46. That is to say, per-mole Au surface was modified with about 0.46 mole S-MC4.

6. S-MC4 modified interface by SEM

A rough surface introduced geometrical structures with patterned square pillars on a flat silicon wafer, 20 mm high, 4 mm long, and with a spacing of 6 mm between the silicon pillars. (SEM picture)
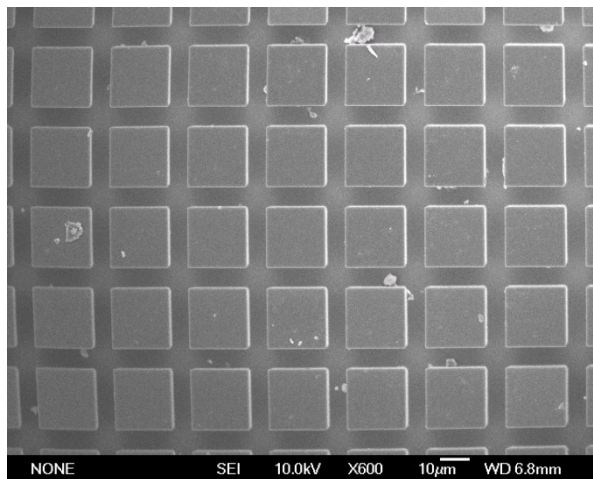

Figure S5. SEM images of the functional micro–nano Au interface.

7. ESI of the interaction between S-MC4 and D-/L-Glu on the micro Au interface

EIS was performed on a conventional three-electrode system with platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as reference, and the treated Au electrode as the working electrode in a one-compartment three-electrode cell. The impedance spectra were recorded over the frequency range of 1–100000 Hz, a potential of +0.200 V, and excitation amplitude at 10 mV (root mean square (rms) values). The impedance experiments were performed by using hexacyanoferrate(II)/(III) (5 mm) as redox probe, KCl (100 mm) as electrolyte in aqueous solution at room temperature, and the glucose enantiomers (0.10 mm) in solutions, respectively.

An Au electrode was soaked in mixture solution ($H_2SO_4 : H_2O_2$ (30%) = 7:3 v/v) for 1 hour to eliminate the adsorbed organic substances and then rinsed with water. Subsequently, Au electrode was sonicated for 5 min in ethanol and water, respectively, and the electrode was dried under argon. Finally, the Au electrode was exposed to a DMSO solution of S-MC4 (10^{-3} M) for 24 h at room temperature. And then gently washing the functional electrode with EtOH, dried under argon.
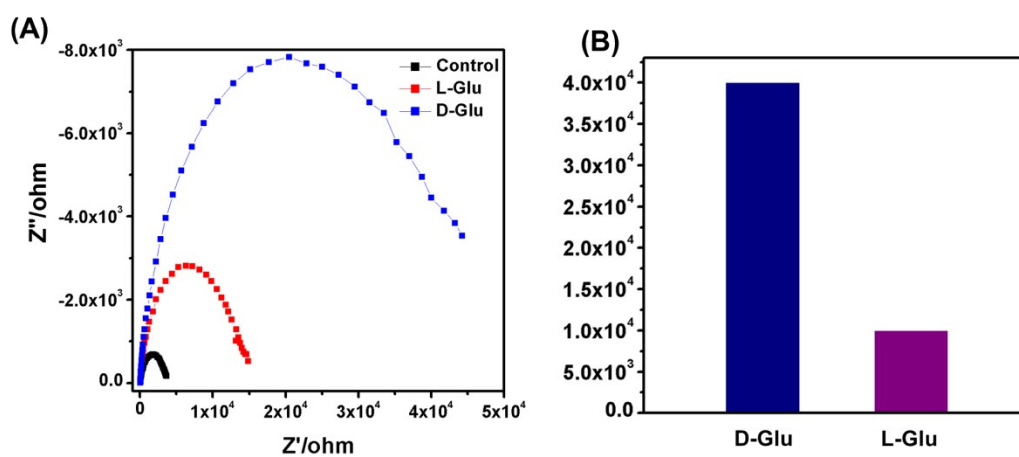
Figure S6. (A) Electrochemical impedance (EIS) for chiral recognition of glucose (10^{-4} M); (B) Histogram shows the electrochemical impedance (EIS) of the difference in value change. More clearly, it showed highly selective recognition for D-Glu.

8. Different concentrations of D-/L-Glu with S-MC4 EIS diversification after interaction
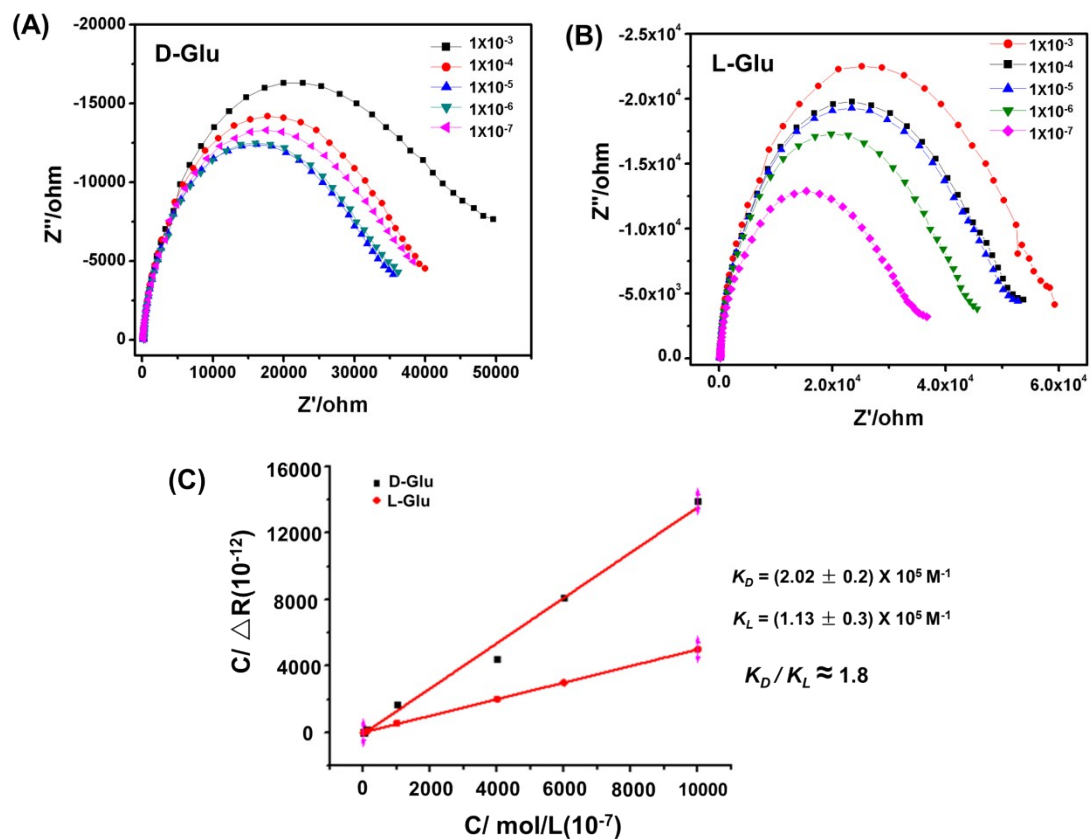
Figure S7. (A) and (B) the S-MC4 SAMs interact with different concentration($1.0 \times 10^{-3} \sim 1.0 \times 10^{-7}$ M) of D-/L-glucose; (C) Fitting out corresponding binding constant.

9. The time-dependent enantiomer discrimination capability of the S-MC4 modified surface
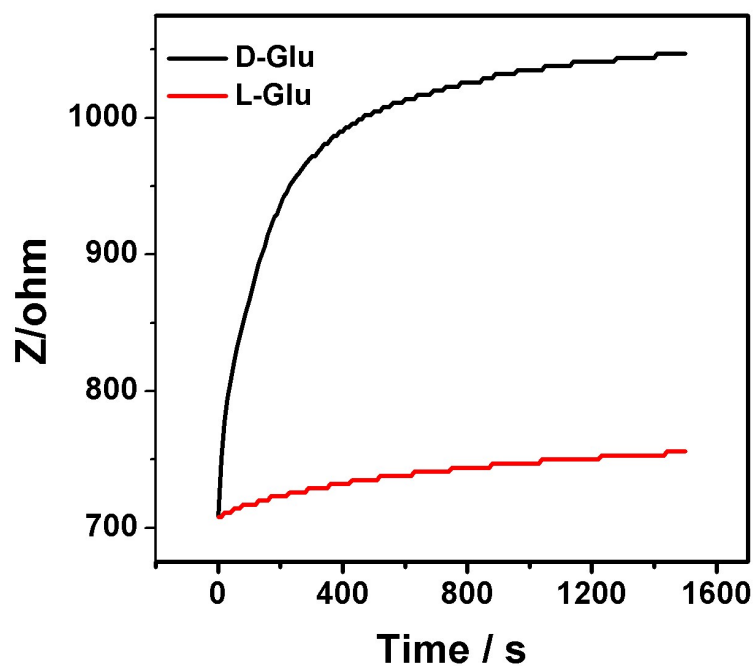
Figure S8. The time-dependent enantiomer discrimination capability of the S-MC4 modified surface (D/L-Glu, 0.1 mM). From the dynamic process of interaction between the chiral surface and glucose enantiomer, there are distinctly different on the balance time.

10. Gauss calculation and three-dimensional coordinates of D-/L-Glu and S-MC4

The binding of S-MC4 and D-/L-Glu were examined by computational calculations at b3Lyp/6-31G(d) levels by using Gaussian 03.

Figure S9. Energy-minimized complex of S-MC4 with D-Glu (left) or L-Glu (right), optimized at the B3LYP/6–31G* level. This result shows that S-MC4 prefer to bind D-Glu.

Computational model of S-MC4 binding D-Glu

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S-MC4-D-Glu

0 1

Cartesian Co-ordinates (XYZ format)

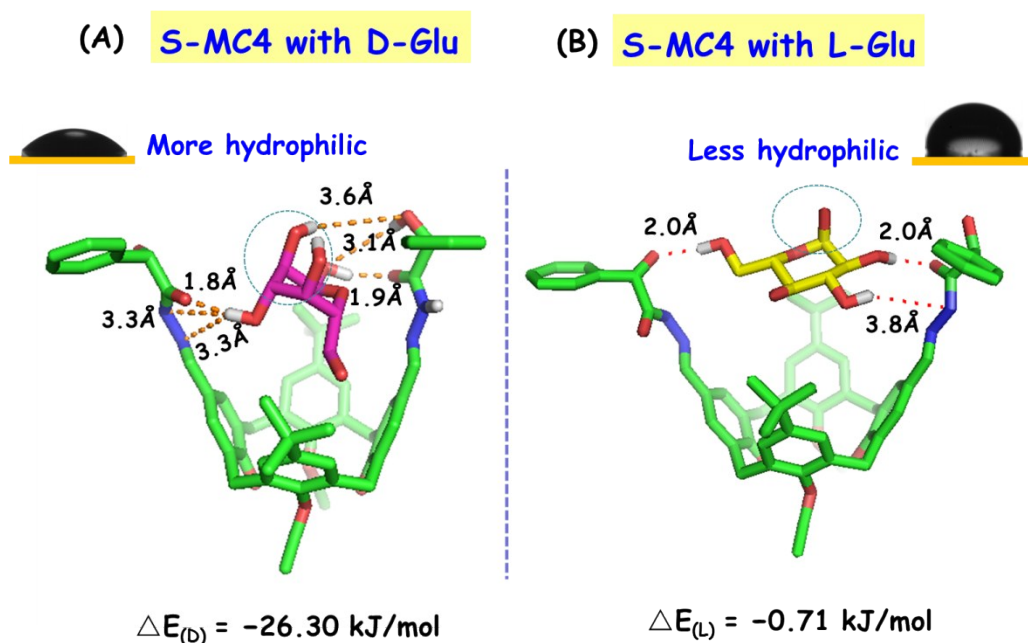|			
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Computational model of S-MC4 binding L-Glu

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S-MC4-L-Glu

0 1

Cartesian Co-ordinates (XYZ format)

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C	1.27353900	-0.44640800	4.19503600
C	-1.13927900	-0.34537700	4.81582500
C	0.55312600	0.85208900	6.23012700
C	0.80879800	-1.06621100	-3.91479100
C	0.53816300	0.12805700	-6.12044400
C	2.47269100	4.11899700	-0.13591400
O	-2.00687300	4.97127700	-0.23077900
C	-1.46892800	-0.70251100	-4.87853000
C	-0.07148600	-0.07627200	-4.71169300
C	0.03125900	1.76418300	3.96036400
C	1.16919000	2.50048200	3.59932700
C	1.10954500	3.71221600	2.90322700
C	2.89647200	3.67868600	1.13421900
C	3.70331200	2.54591500	1.21052300
C	4.06795000	1.81720300	0.06985500
C	3.64055800	2.28586600	-1.18073800
C	2.86003100	3.43064500	-1.30956700
C	-4.40711900	1.59222300	0.04447900
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C	-2.71184800	4.01014200	2.48448400

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C	-0.16709400	4.20960900	2.62890500
C	-1.32062000	1.91733200	-3.64594300
O	1.70737600	5.24331000	-0.15782700
C	-2.77094000	3.86333600	-0.08011200
C	-3.17785600	3.22892000	-1.27816400
C	-2.71288000	3.76823700	-2.62719200
C	-1.36801000	3.19107700	-3.05908600
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C	-1.21126800	2.28432200	3.58263400
C	-1.33785000	3.51084900	2.91912500
C	-0.12272700	1.28663100	-3.99680900
C	2.40499600	3.87334700	-2.69880800
C	-0.14687500	3.83459200	-2.86078200
C	1.06965000	1.95865400	-3.68989500
C	1.08710300	3.22810400	-3.11053200
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O	-5.54038700	-2.76694400	-2.31783200
C	-7.26775200	-3.69454200	-0.91380900

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H	-2.71492800	5.10247100	2.41075400
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H	1.18309300	5.30887000	-0.97688800
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C	7.98723000	-3.62482100	0.30242000
C	10.12477800	-3.67054900	-0.84079300
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H	-6.38581000	-4.53214800	-2.38490500
C	0.79066300	-3.81483300	-0.25345500
C	-0.03094700	-2.97326400	0.73114700
C	-1.49127600	-3.40421500	0.65540100
C	-2.01681000	-3.29932200	-0.77284500
C	-1.09888800	-4.09591000	-1.71848000
O	0.24105700	-3.65448900	-1.57602200
C	2.25700100	-3.42346300	-0.30715700
O	-2.23692000	-2.57248900	1.54425700
O	-1.24610600	-5.46581000	-1.43855400
O	-3.36137100	-3.75167100	-0.75372200
O	0.48006200	-3.16087700	2.04671500
O	2.96138100	-4.42807800	-1.02109800
H	0.72986200	-4.86834600	0.04551800
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H	-1.96846300	-2.24552400	-1.08362000

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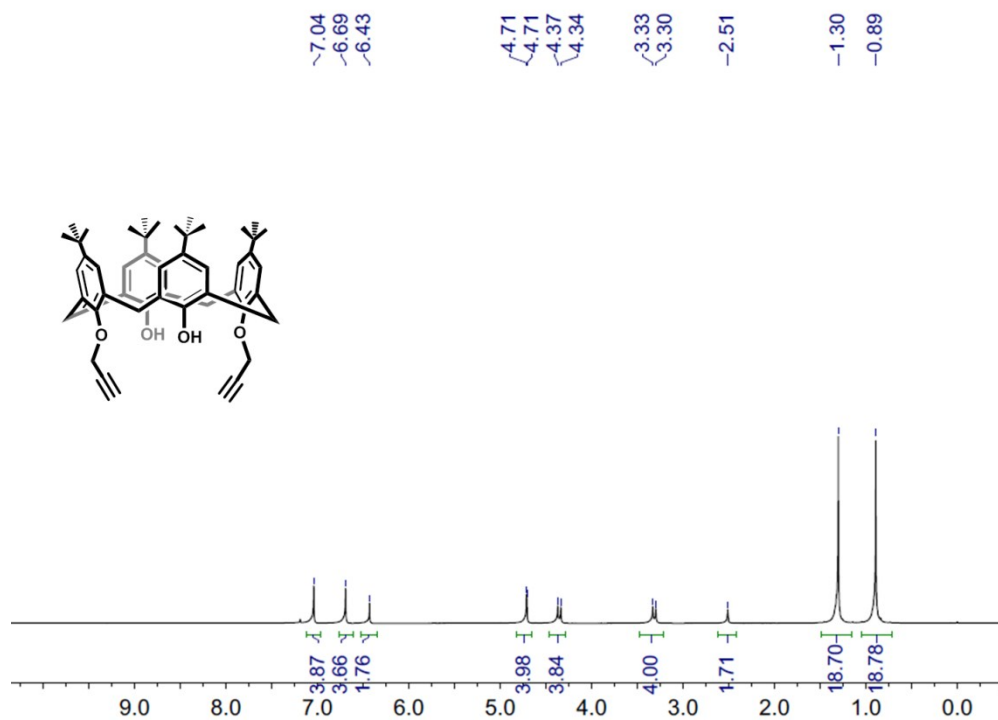| H | -1.34213900 | -3.87870600 | -2.76813200 |
H	2.34758800	-2.43649100	-0.78916700
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H	-0.61156500	-5.93422400	-2.00590300
H	-3.85213300	-3.36981000	-1.50492500
H	-0.20800200	-2.82860700	2.64721600
H	3.90882700	-4.20507500	-1.00171800

11. ¹H NMR, ¹³C NMR and MS for the main compounds

Figure S10. ¹H NMR spectrum (400 MHz) of compound H3 in CDCl₃.
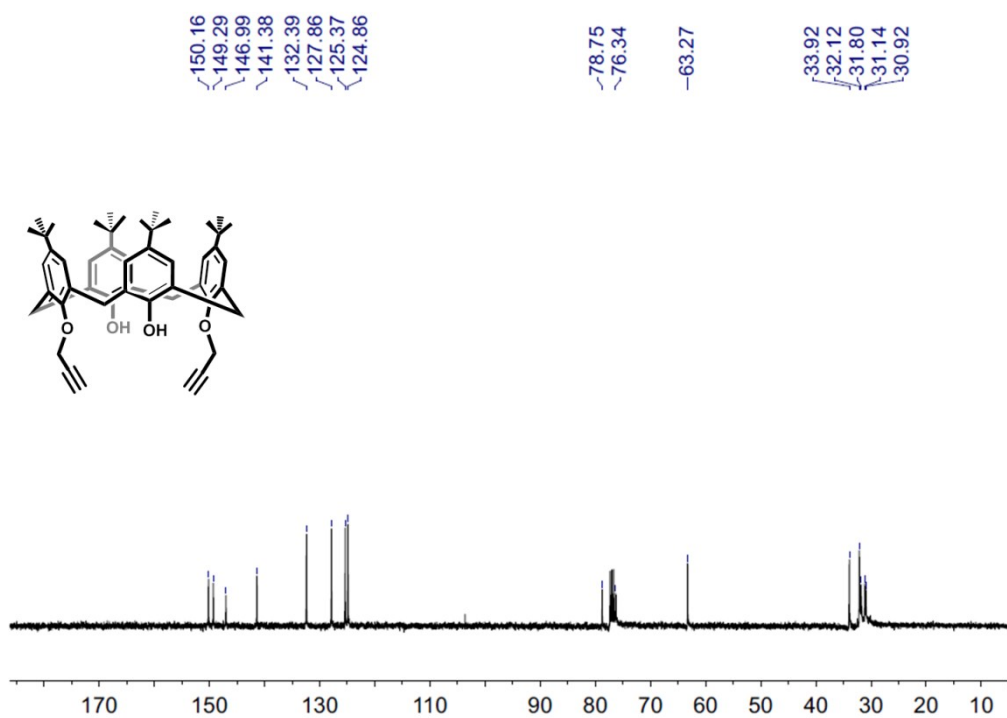
Figure S11. ^{13}C NMR spectrum (100 MHz) of compound H3 in CDCl$_3$.
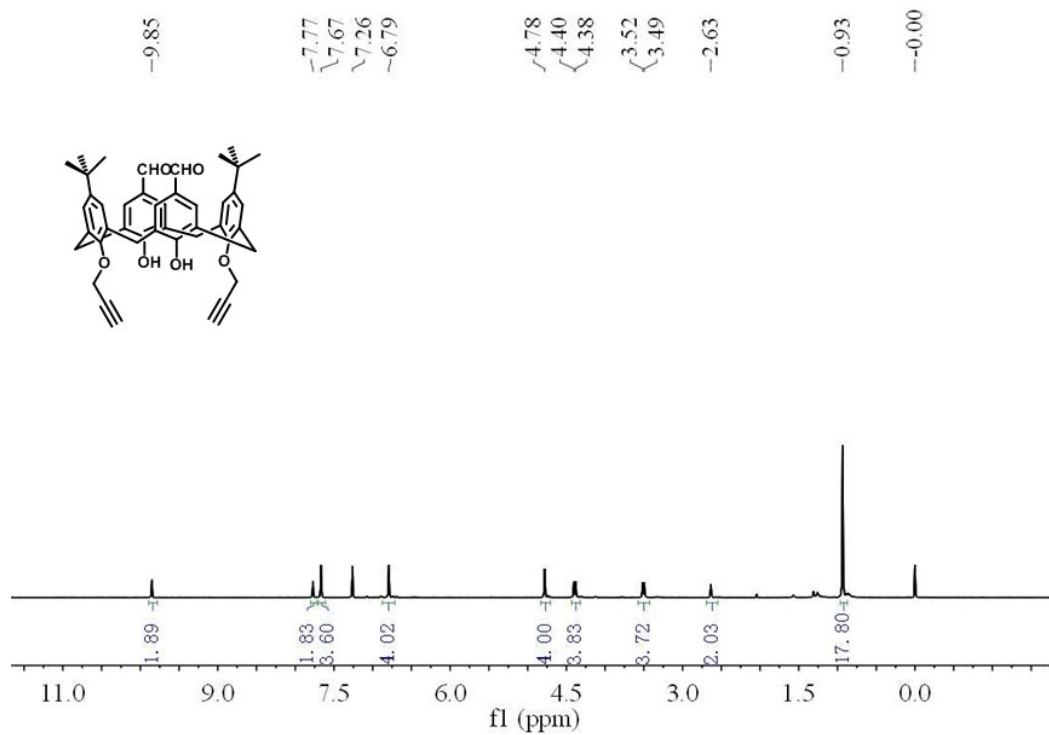
Figure S12. ^{1}H NMR (400 MHz, CDCl$_3$) of compound H2.
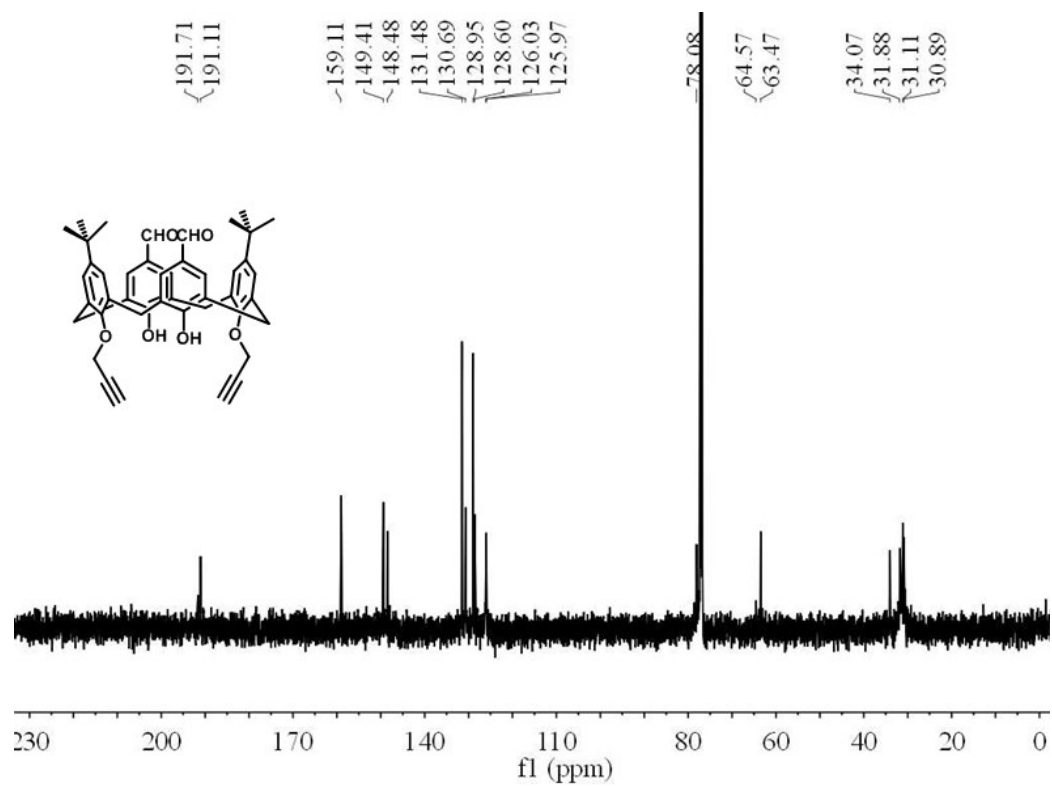
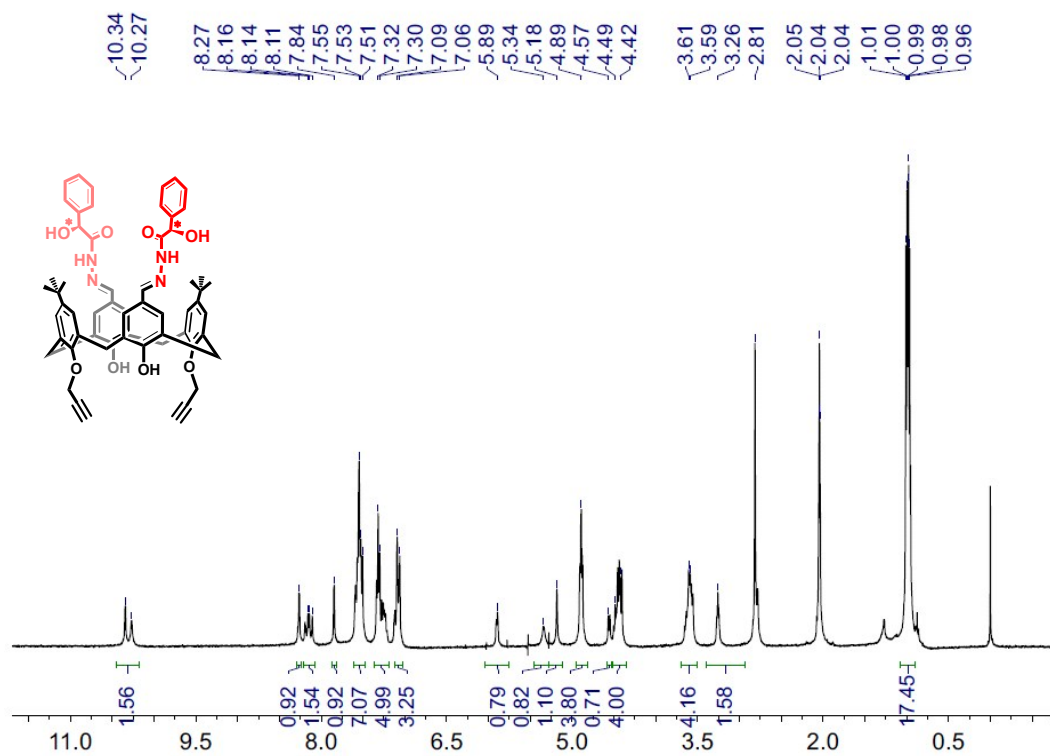**Figure S13.** ^{13}C NMR spectrum (100 MHz) of compound H2 in CDCl$_3$.

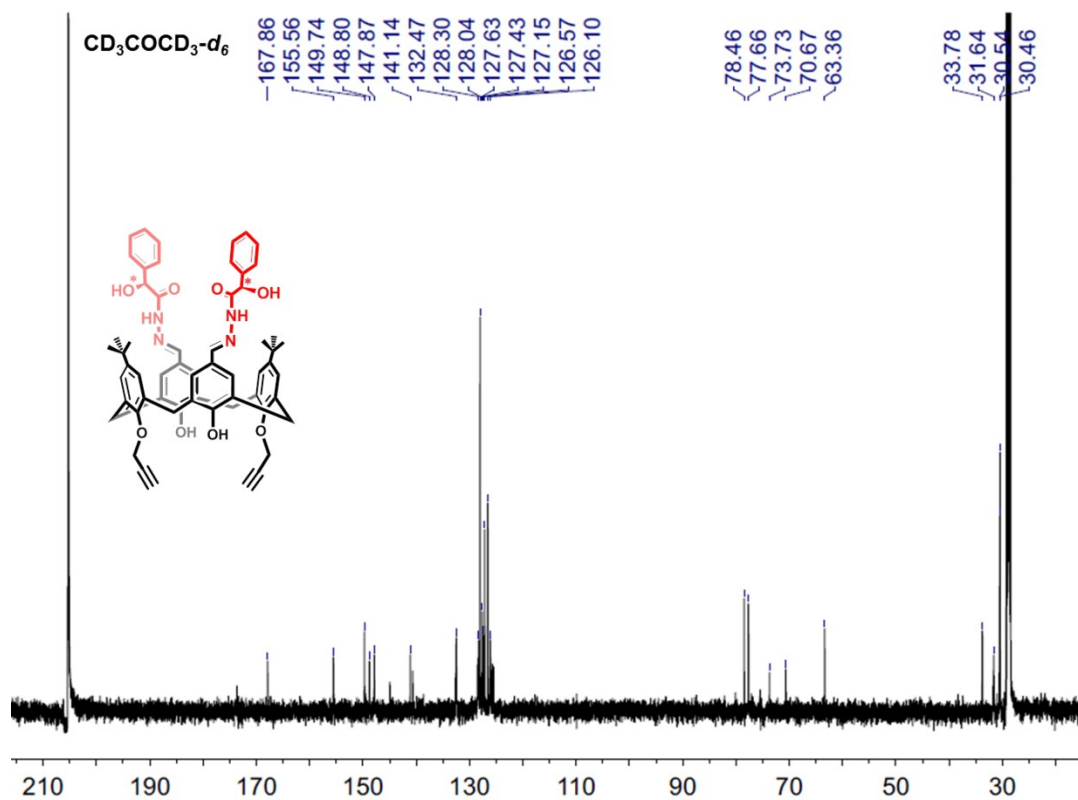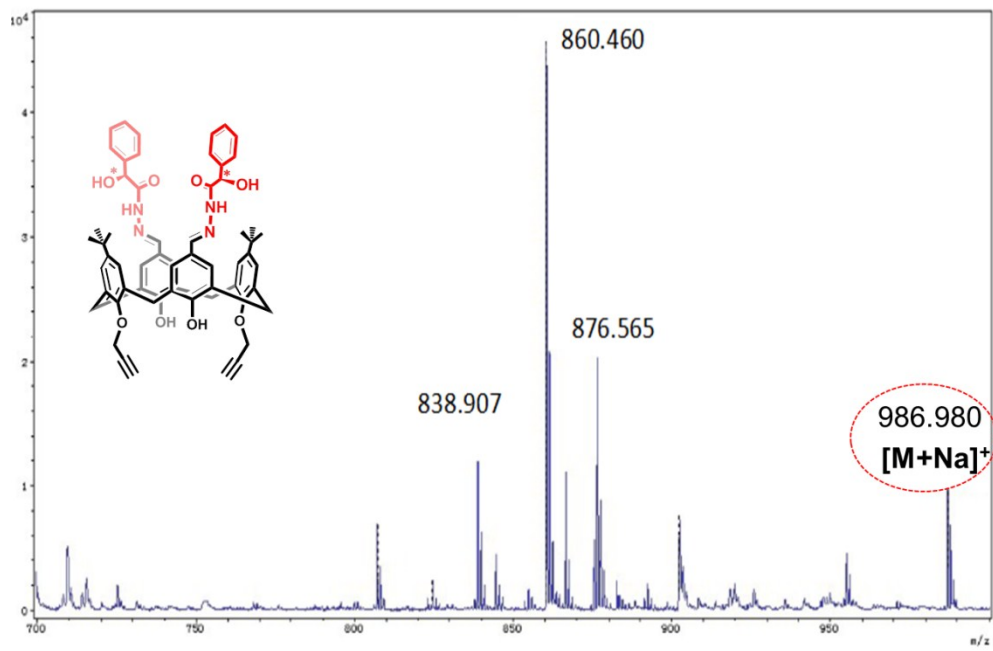**Figure S14.** ^{1}H NMR (400 MHz, CD$_3$COCD$_3$) of compound S-MC4.

Figure S15. ^{13}C NMR (100 MHz, CD$_3$COCD$_3$) of compound S-MC4.

Figure S16. MALDI-TOF mass spectrum of S-MC4.

12.References

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2. C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun*., 2010, **46**, 9016.

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