Supporting Information for:

Wettability Recognition for Isomeric Phenyleneamine by Nitro-Calix[4]arene Clicking

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1. Experiments.

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1. Experiments.

1.1 Experiments of wettability measurements.

The wettability property (the CA values all refer to static CAs) was performed with a water droplet (1.000 μL) and side-view photographs were obtained after 5 min of adding the water droplet to stable state. The successfully modified gold surface of **C4N2** was firstly performed by contact angle as control experiment. **C4N2** SAMs were dipped into solutions containing the four recognizing guests (0.1 mL, 1.0 mM) for 10 min, respectively and then were flushed by little water, dried by nitrogen and then measured.

1.2 Experiments of impedance.

Impedance spectroscopy (EIS) was performed on a conventional three-electrode system with platinum wire as auxiliary electrode, saturated calomel electrode (SCE) as reference and the treated gold 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 (rms). The impedance experiments were carried: hexacyanoferrate (II)/(III) (5 mM) as redox probe, KNO_3 (100 mM) as electrolyte in aqueous solution at room temperature and the four guests (0.10 mM) being in solutions respectively.

1.3 Infrared spectrum (IR) assay.

Firstly, prepare even mixture of **C4N2** (8.2 mg) and $\mathbf{a_o}$ guest (1.1 mg) in $CHCl_3$ (1 mL); then the mixture was interacted by ultrasonic wave for 3 min; at last the mixture was made to dry by wrotatory evaporator and then are irradiated by infrared light for some minitues. IR characterizes **C4N2**, OPD guest and the dry mixture.

1.4 Synthesis of compound 2

Compound **1**[8] (2.0 g, 2.2 mmol) and acetic acid (20 mL, CH_3COOH) were dissolved in CH_2Cl_2 (40 mL) in ice-salt bath, HNO_3 (3.8 mL, 65%) was added in the reaction container in condition of constant pressure drops. Then, to remove redundant HNO_3 with saturated $NaHCO_3$ solution, and washed with saturated salt solution. The evaporated crude product was then purified by column chromatography to give 1.17g (1.32mmol, 60%) of a red brown powder **2**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 (s, Ar*OH*, 2H), 8.06 (s, Ar*H*, 4H), 6.92 (s, Ar*H*, 4H), 4.25 and 4.23 (d, *J* = 13.3 Hz, ArCH_2Ar,4H), 4.06 (s, OCH_2, 4H), 3.63 (s, OCH_2CH_2 4H), 3.51 and 3.49 (d, *J* = 13.3 Hz, ArCH_2Ar,4H), 2.30 and 2.28 (d, *J* = 7.4 Hz, CH_2CH_2Br, 4H), 2.24 and 2.23 (d, *J* = 7.3 Hz, CH_2CH_2Br, 4H), 1.03 (s, $C(CH_3)_3$, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ159.3, 149.5, 148.7, 139.8, 130.9, 128.6, 126.3, 126.1, 124.5, 124.2, 34.2, 33.2, 31.5, 30.6, 29.3, 28.7; ESI(+)MS calcd. for $C_{44}H_{52}Br_2N_2O_8$ 894.2, found: m/z = 895.4 $[M+H]^+$; Anal. calcd for $C_{44}H_{52}Br_2N_2O_8$: C, 58.94; H, 5.85; N, 3.12; found: C, 58.73; H, 6.01; N, 2.97.

1.5 Synthesis of C4N2

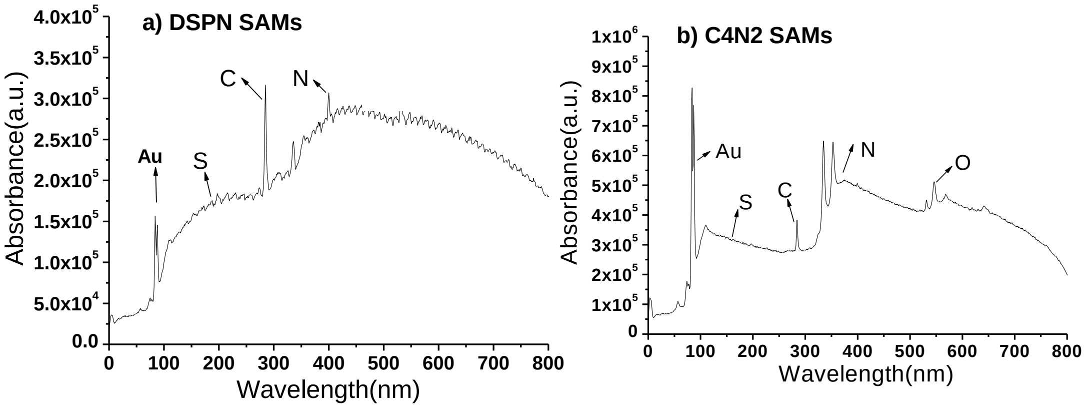
The obtained **2** (1.17g, 1.32mmol) interacted with NaN_3 for 1 h in DMSO, after stopping reaction add 30mL H_2O to vessel, then extract three times by ethyl acetate and washed with saturated NaCl solution five times. Then, the crude product was evaporated to dryness to give 1.03g (1.25mmol, 95%) of white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.05 (s, Ar*OH*,2H), 8.06 (s, Ar*H*, 4H), 6.93 (s, Ar*H*, 4H), 4.26 and 4.23 (d, *J* = 13.2 Hz, ArCH_2Ar, 4H), 4.05 (s, OCH_2, 4H), 3.52-3,49 (m, OCH_2CH_2 and ArCH_2Ar, 8H), 2.15 and 2.14 (d, *J* = 7.4 Hz, CH_2CH_2Br, 4H), 2.02 and 2.01 (d, *J* = 7.3 Hz, CH_2CH_2Br, 4H), 1.04 (s, $C(CH_3)_3$, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ159.4, 149.6, 148.7, 139.9, 131.0, 128.7, 126.4, 126.2, 124.5, 124.2, 51.3, 51.1, 34.2, 30.7, 27.3, 25.8; ESI(+)MS calcd for $C_{44}H_{52}N_8O_8$ 820.3, found: m/z = 821.4 $[M+H]_+$; Anal. calcd for $C_{44}H_{52}N_8O_8$: C, 64.37; H, 6.38; N, 13.65; found: C, 64.49; H, 6.22; N, 13.19.

1.6 Preparation of C4N2 modified gold electrode

Au electrode was polished with alumina powder slurry (0.3 down to 0.05 μm, Buehler) and rinsed with water, ethanol and then water for 3 min, respectively. Then, the substrate gold electrode was soaked in piranha solution (H_2SO_4: 30% H_2O_2 = 3:1) for 30 min to eliminate the adsorbed organic substances and then rinsed with water. Finally, it was sonicated for 5 min in ethanol and water, respectively. The clean electrode was dried under nitrogen. The electrode was cycled between 0 and +1.5 V at 100 $mV{\cdot}s^{-1}$ in 0.5 M H_2SO_4 solution until a stable cyclic voltammogram was obtained. The obtained activated gold electrode can be used in the following experiments. SAMs of DSPN (DSPN SAMs) were prepared by dipping the gold beads into the mix-solution of CS_2 (1.0×10^{-3} M) and allylene amino (1.0×10^{-3} M) for 24 h in CH_3CN. And SAMs of nitro-calix[4]arene (**C4N2** SAMs) were obtained by click chemistry. The DSPN SAMs, which was washed by acetonitrile and then dried by nitrogen to excepting the free DSPN molecules, immerged into the solution containing 5 mM Cu^+ and 1 mM **C4N2** dimethylformamide (DMF) solution for 24 h. The treated gold beads were immerged into DMF for 10 min to wash off the free **C4N2** on the surface and then dried under a stream of N_2 and at last **C4N2** SAMs were obtained.

According to the same method and processes of constructing **C4N2** SAMs, **C4N2** modified gold film surfaces including the smooth and micro – nano surfaces were obtained again. At first, the gold surfaces immerge into acetone for 6 h in order to remove organic impurities pollutants and then the gold surfaces were respectively washed by ehtanol and water for three times until the gold surfaces completely cleaned. At last, the **C4N2** SAMs synthesis processes are the same as the **C4N2** SAMs electrode surfaces.



SAMs	C	N	S	O
C4N2	57.92	12.86	11.92	11.89
DSPN	36.94	11.52	49.01	0

Figure S1. XPS characterization the kinds of elements and their content.

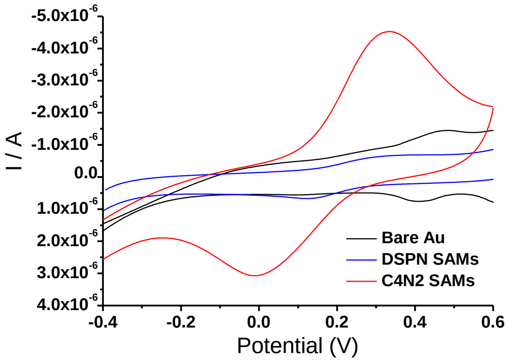


Figure S2. Characterization of cyclic voltammetry for gold electrode, DSPN SAMs and **C4N2** SAMs.

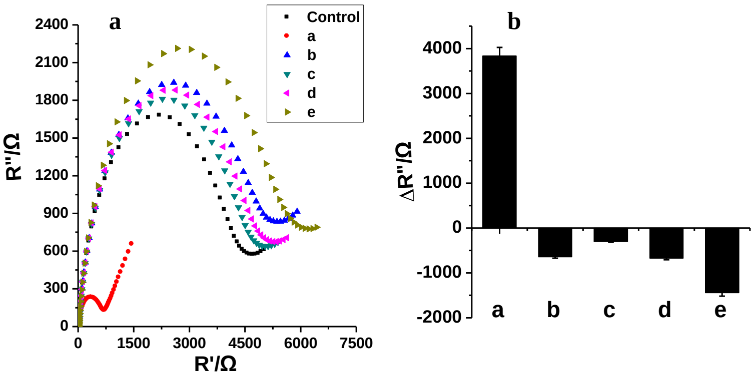


Figure S3. a) Impedance selectivity for OPD; b) histogram showing impedance value variations, indicating that **C4N2** modified on gold electrode can recognize *o*-phenylenediamine from the isomers and the derivatives of aniline.

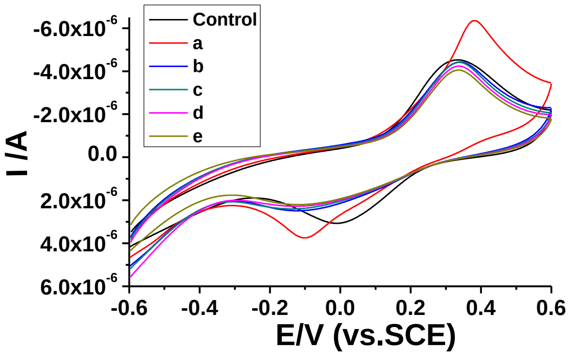


Figure S4. Cycle voltammetry (CV) selectivity for OPD of the five guests (a_o, b, c d, e).

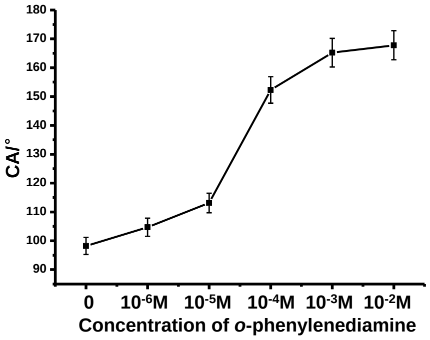


Figure S5. CAs with various concentrations of OPD (0.05 ± 0.01 mL, 1.0×10^{-6} – 1.0×10^{-2} M).

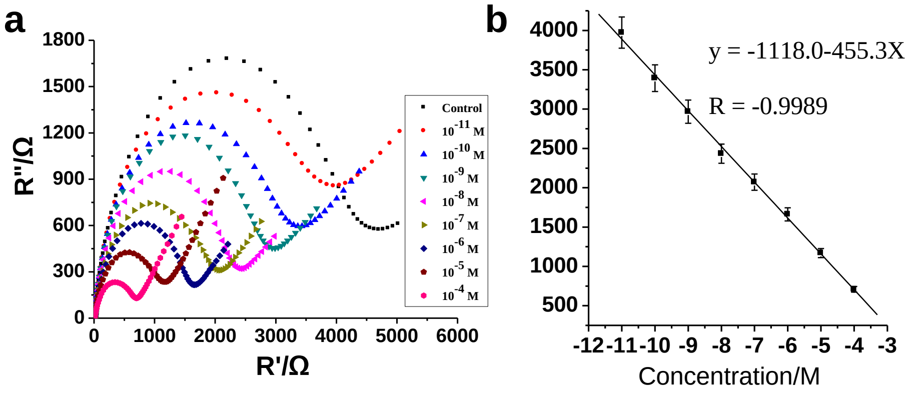


Figure S6. Impedance response with various concentrations of o-phenymine from 1.0×10^{-11} to 1.0×10^{-4} M, which present excellent linear relationship and high sensitivity with 10 pM.

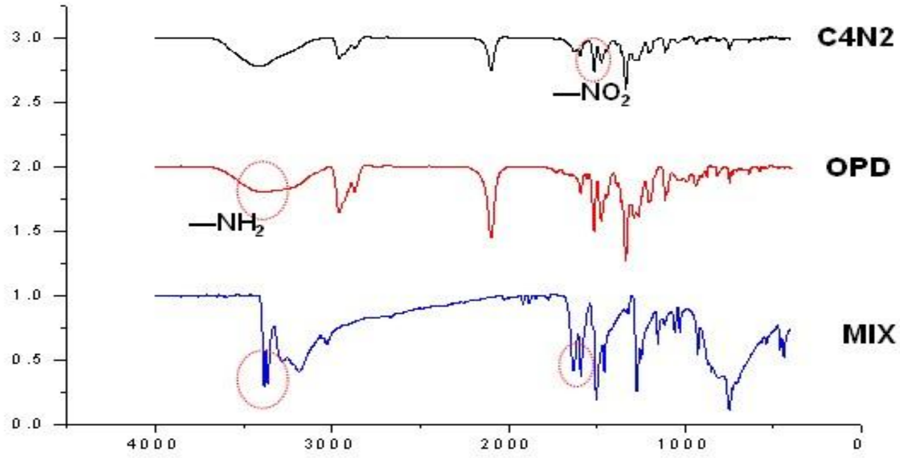


Figure S7. IR of the guest of OPD, the host of **C4N2** and the mix-solution of the guest and the host molecule.

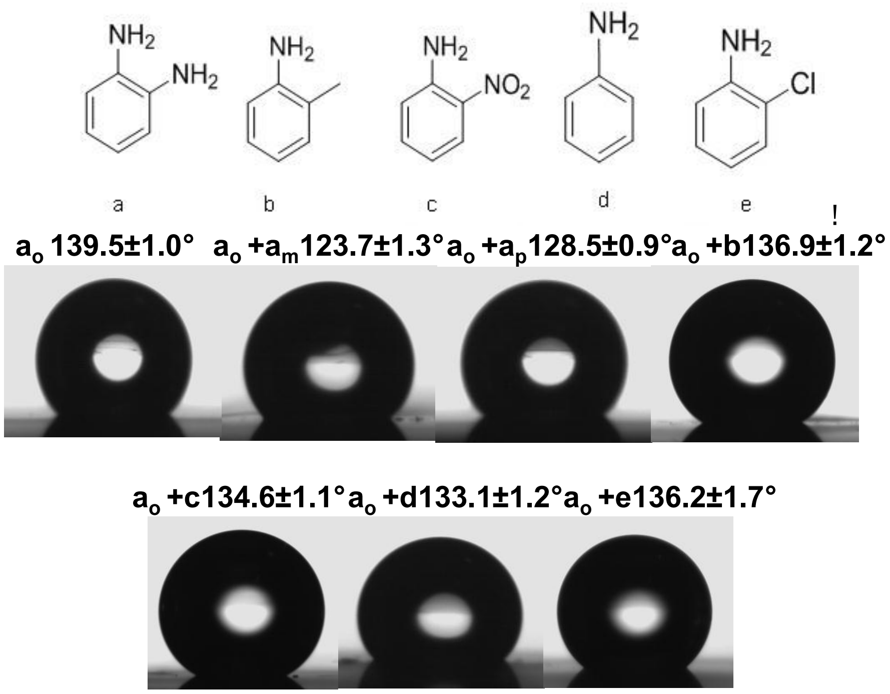


Figure S8. CA relationship images of **C4N2** SAMs responding to a_o in presence and absence of solutions of a_p, a_m, b, c and d respectively. The result of experiments indicates that the guests of a_p, a_m, b, c and d can not obviously affect contact angle of **C4N2** SAMs when it exposes into the solution of a_o.

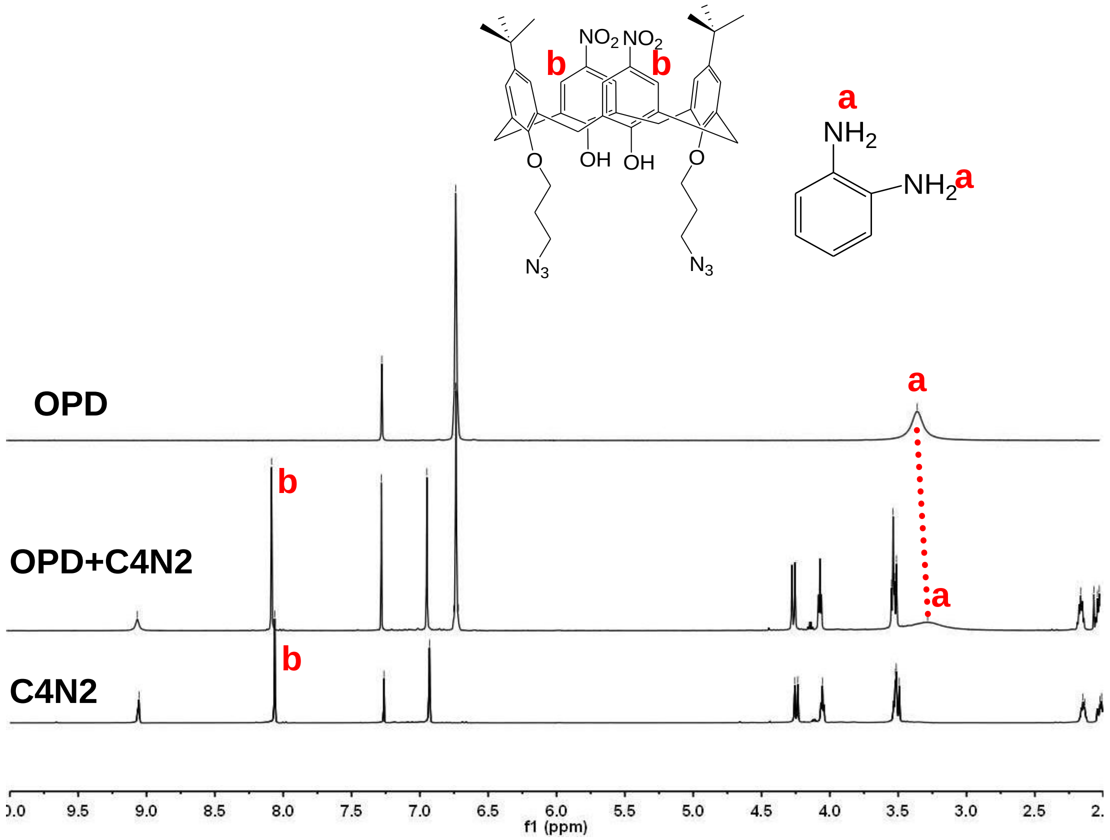


Figure S9. ^{1}H NMR of the guest of a (A), the host of calix[4]arene (B) and the mix-solution of the guest and the host (C) in $CDCl_3$.

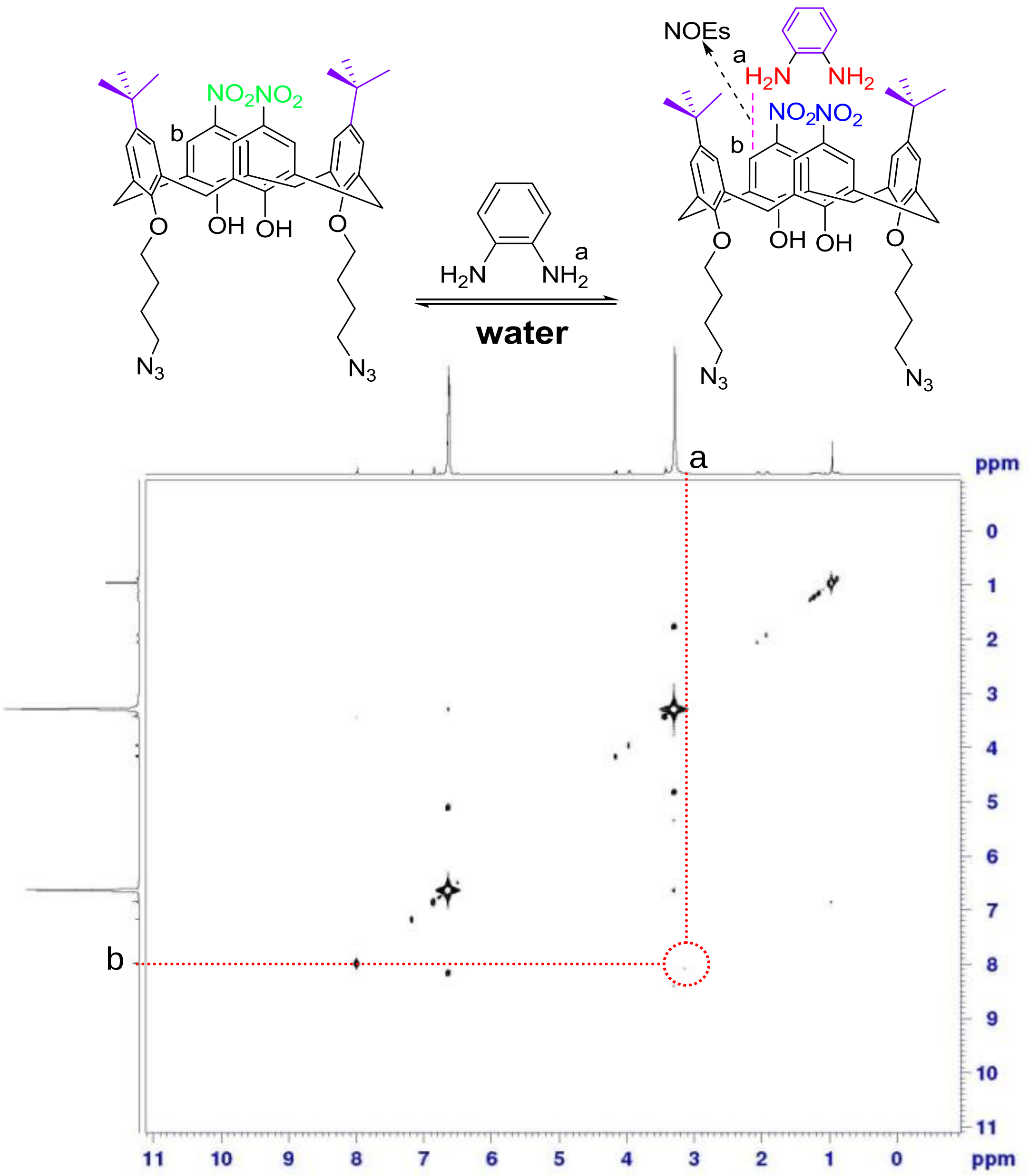
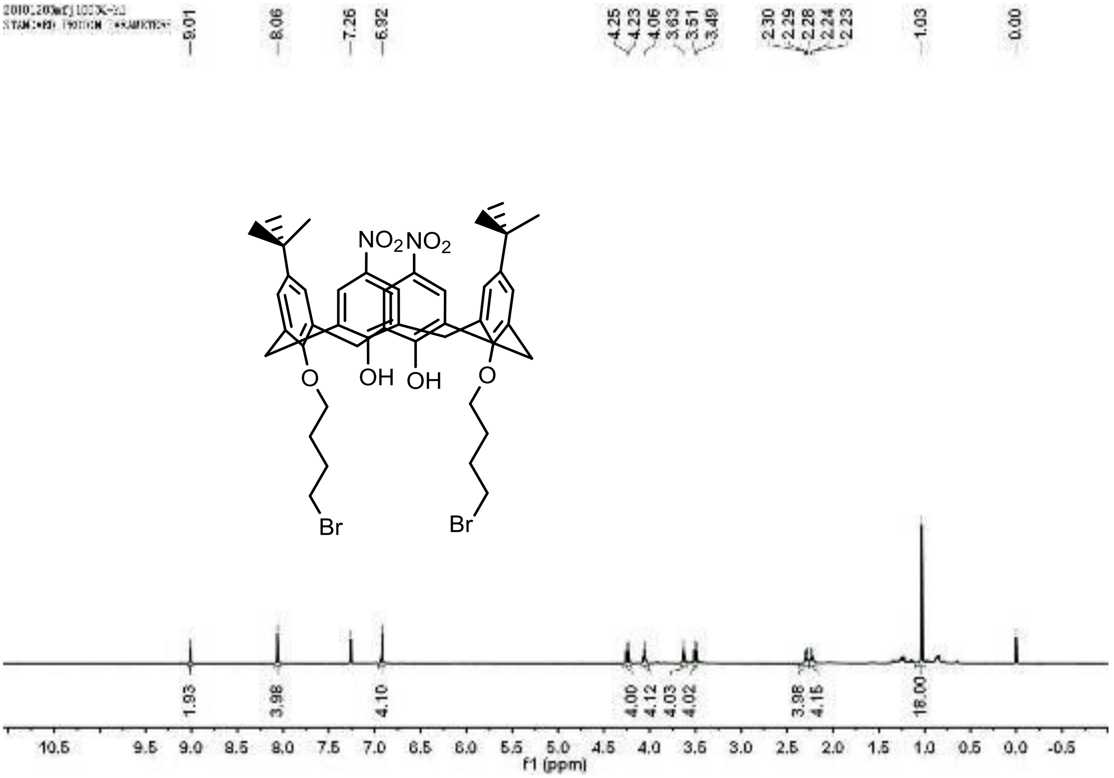
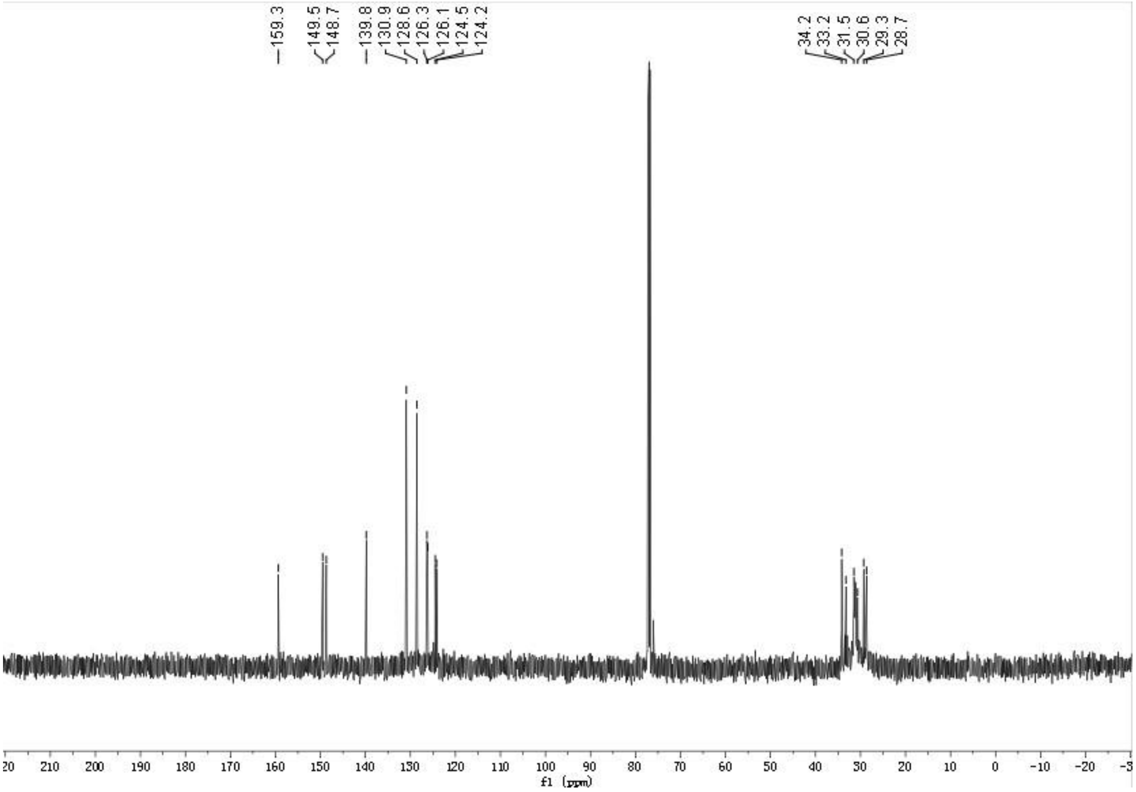


Figure S10. NOESY spectra ($CDCl_3$, 600 MHz, 298 K) of **C4N2,** mix-solution of **C4N2**@OPD, and OPD.


STANDARD PROTON PARAMETERS
9.01
8.06
7.26
6.92
4.25
4.23
4.06
3.63
3.51
3.49
2.30
2.29
2.28
2.24
2.23
1.03
0.00
NO2 NO2
OH OH
O
O
Br
Br
1.93
3.98
4.10
4.00
4.12
4.03
4.02
3.98
4.15
18.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.3
149.5
148.7
139.8
130.9
128.6
126.3
126.1
124.5
124.2
34.2
33.2
31.5
30.6
29.3
28.7
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

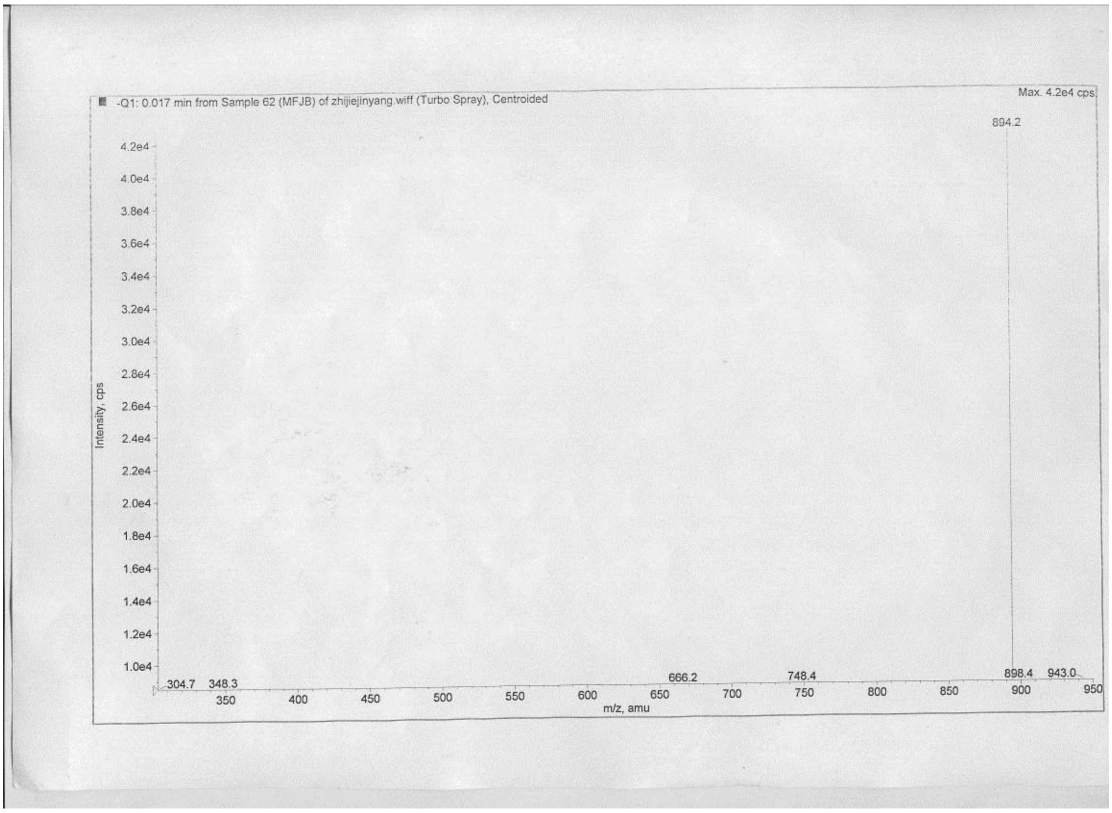
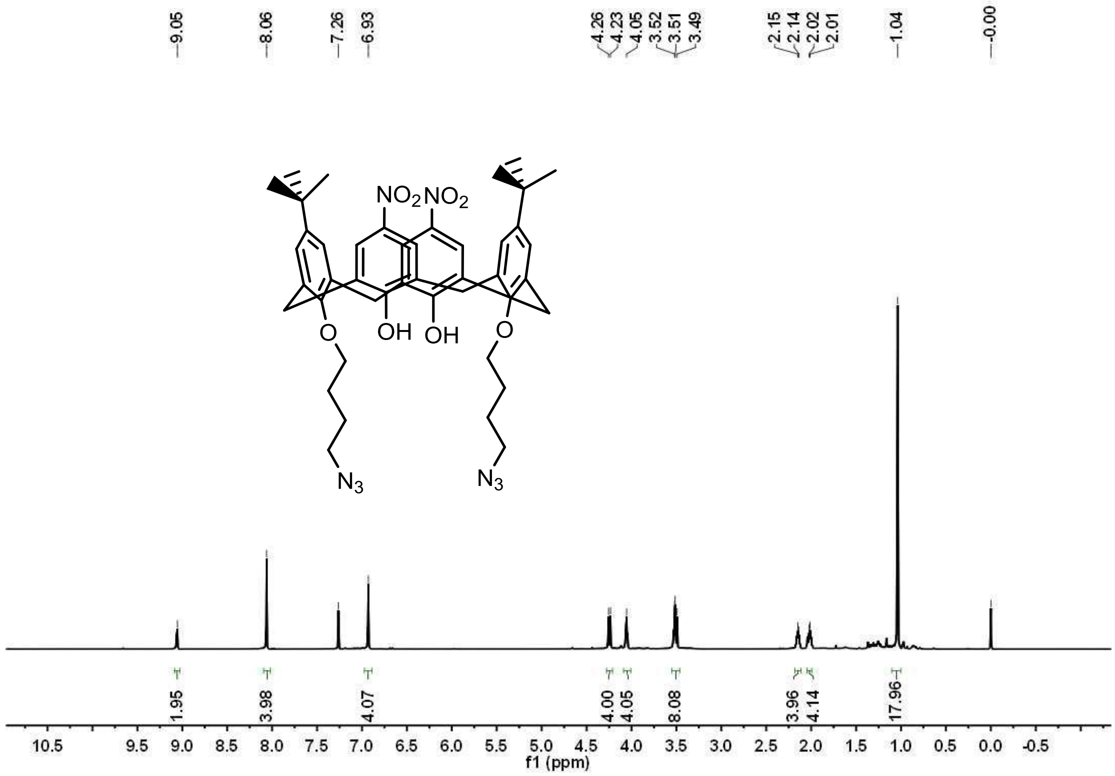
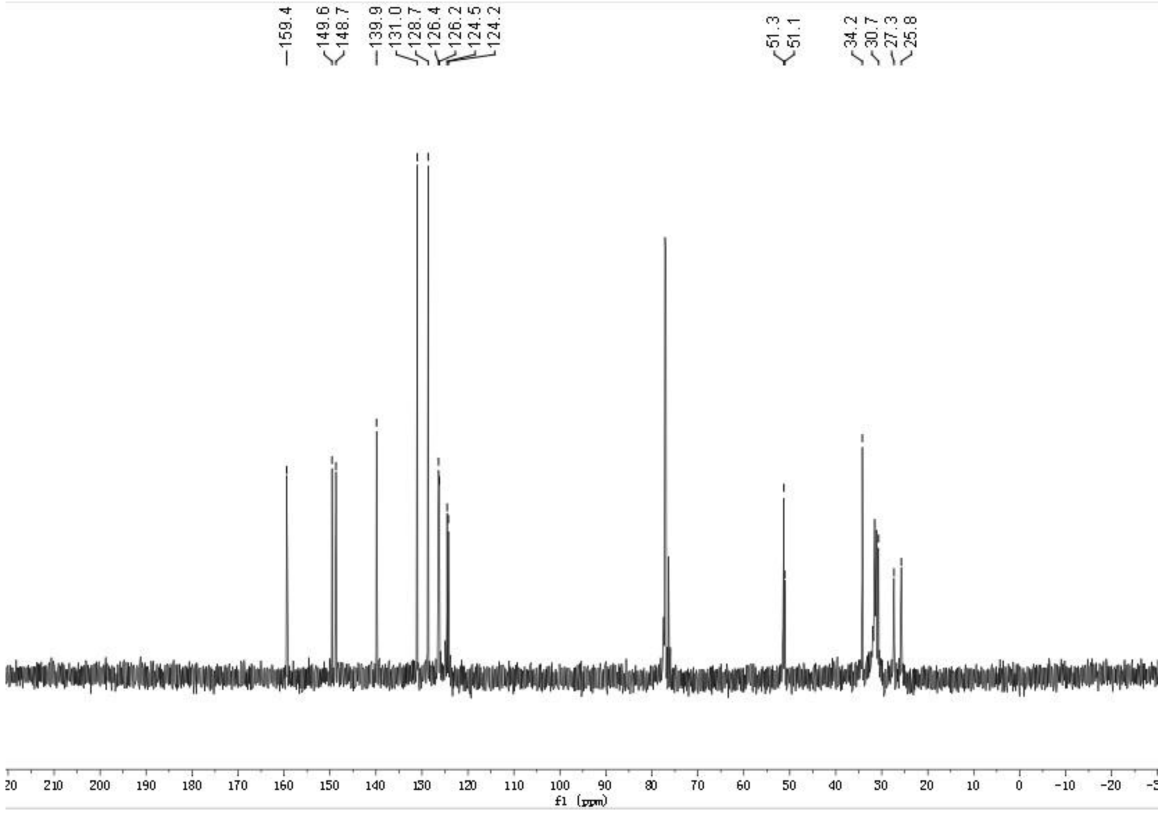


Figure S11. ^{1}H NMR, ^{13}C NMR and MS of compound **2**.


9.05
8.06
7.26
6.93
4.26
4.23
4.05
3.52
3.51
3.49
2.15
2.14
2.02
2.01
1.04
-0.00
NO2 NO2
OH OH
O
O
N3
N3
1.95
3.98
4.07
4.00
4.05
8.08
3.96
4.14
17.96
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.4
149.6
148.7
139.9
131.0
128.7
126.4
126.2
124.5
124.2
51.3
51.1
34.2
30.7
27.3
25.8
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

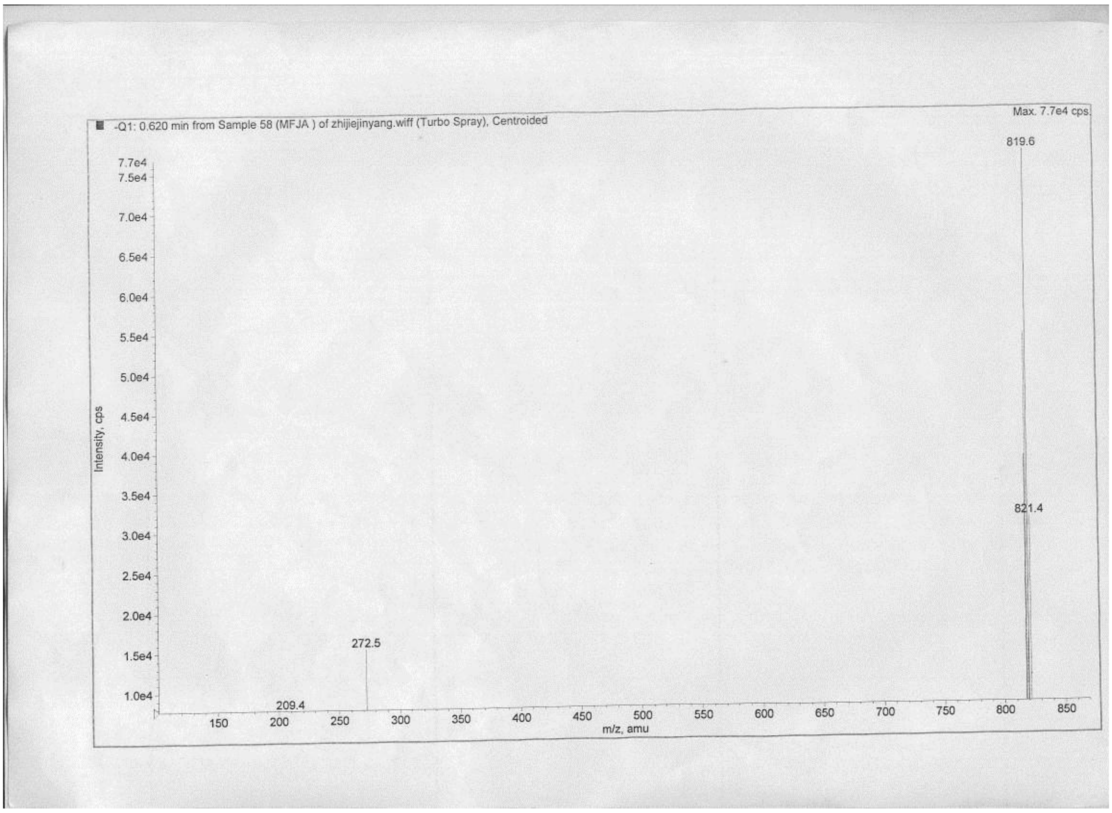


Figure S12. ^{1}H NMR, ^{13}C NMR and MS of **C4N2**.