Supporting Information

Host-guest sensing towards sodium cyclamate based on cationic pillar[6]arene reduced graphene nano-composite

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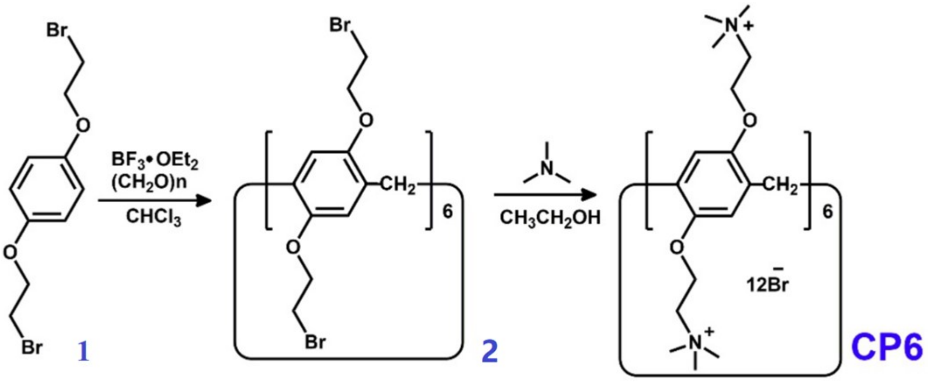
S1. Instruments

The obtained samples were characterized by Fourier transform infrared (FTIR) spectroscopy via the SCIENTIFIC Nicolet IS10 (Massachusetts, USA) FTIR impact 410 spectrophotometer with using KBr pellets at wavelength range of 4000–400 cm−1. Thermogravimetric analysis (TGA) with temperature range 25°C to 800 °C with heating rate of 10 °C min^{-1} at nitrogen atmosphere was carried out in the Q50 TGA (TA Instruments, New Castle, USA). The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) and with Al Ka X-ray radiation as the X-ray source for excitation. Fluorescent titrimetric experiment was performed on by the Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan). TEM images and the high resolution images were measured by a high resolution transmission electron microscope (HRTEM, JEM-2010). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DMX-400 spectrometer at 400 MHz.

S2. Reagents and methods

1,4-bis(2-bromoethoxy)benzene, chloroform, boron trifluoride diethyl etherate, trimethylamine, and paraformaldehyde were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. CP6 was synthesized according to the previous papers procedures.[S1-3] Carbonate beverage as a practical sample for the detection of SC, the detailed operation protocol is as follows: Fist of all, a solution of SC (100.0 μM) was obtained. The carbonate beverage was filtrated using filter membrane (0.45 μm). Then, The practical application of the fluorescence sensing system is further studied by standard addition method with carbonate beverage.

S3. Synthesis of cationic pillar[6]arene (CP6)



Scheme S1. Synthetic route of **CP6**.

Synthesis of 2: Boron trifluoride diethyl etherate ($BF_3·OEt_2$, 1.83 g, 11.5 mmol) was added to the mixed solution of paraformaldehyde (0.35 g, 11.5 mmol) and **1** (1.69 g, 5.75 mmol) in 1,2-dichloromethane (200 mL) under nitrogen atmosphere. The mixture was stirred at 25 °C for 2.5 h. The reaction mixture was then washed with water (3 × 120 mL) and dried with excess Na_2SO_4. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (*v*/*v* = 1:2) as the eluent to obtain a white powder of **2** (0.27 g, 14 %).

Synthesis of CP6: The mixture of compound **2** (0.25 g, 0.12 mmol) and trimethylamine (33 % in ethanol, 2 mL) in ethanol (10 mL) were stirred at 85 °C for 24 h under nitrogen atmosphere. Then the solvent was removed by evaporation, deionized water (25 mL) was added. The mixture was filtrated using filter membrane (0.45 μm), a clear solution was obtained. The water was removed by evaporation to obtain **CP6** as a colorless solid (0.32 g, 95 %). The ^{1}H NMR spectrum of **CP6** is shown in Figure S1. ^{1}H NMR (400 MHz, D_2O, rt) δ (ppm): 6.87 (s, 12H), 4.46 (s, 24H), 3.91 (s, 12H), 3.71 (s, 24H), 3.08 (s, 108H). The ^{13}C NMR spectrum of **CP6** is shown in Figure S2. ^{13}C NMR (100 MHz, D_2O, rt) δ (ppm): 149.76, 129.05, 116.19, 65.07, 63.36, 59.11, 30.10.

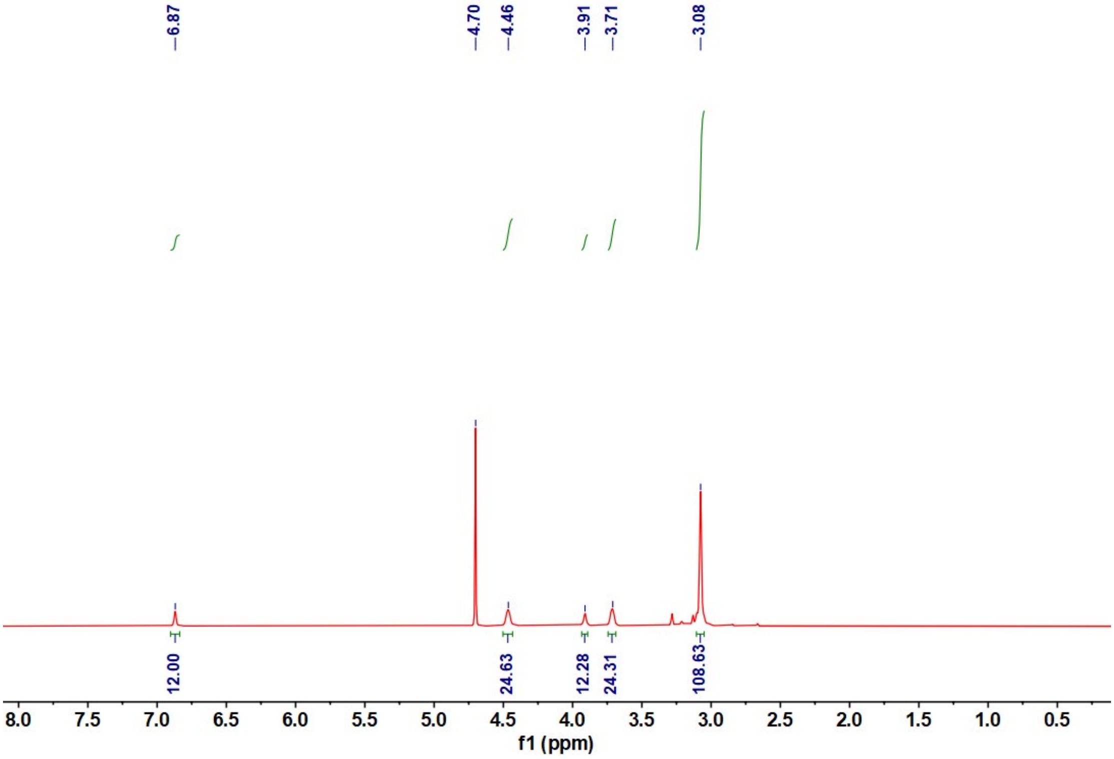


Figure S1. ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of **CP6**.

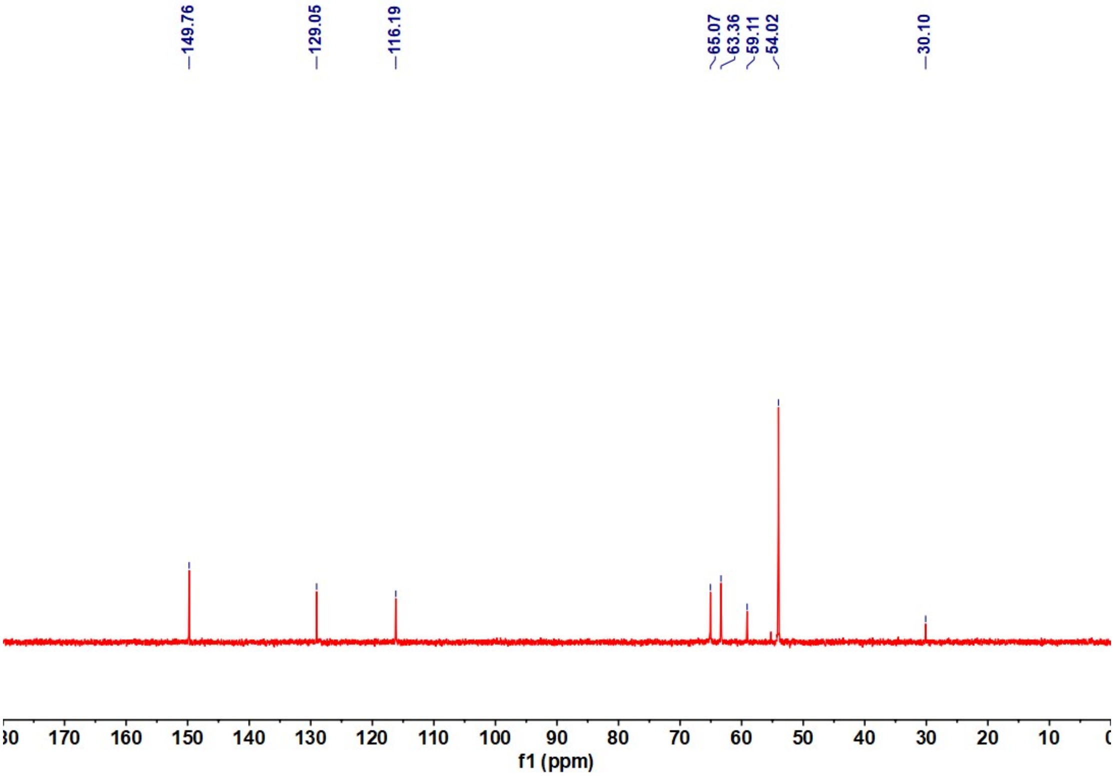


Figure S2. ^{13}C NMR spectrum (100 MHz, D_2O, 298 K) of **CP6**.

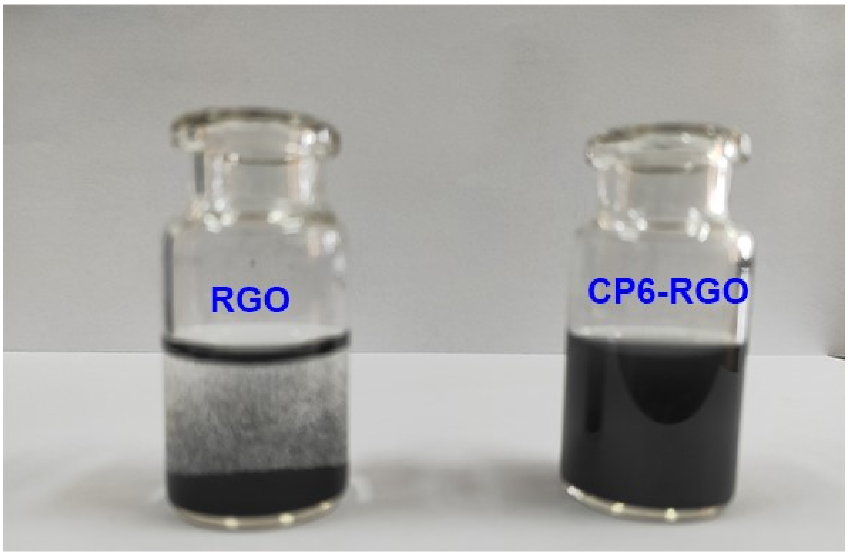


Figure S3. Actual photographs of RGO and CP6-RGO aqueous dispersions (1.0 mg mL^{-1}).

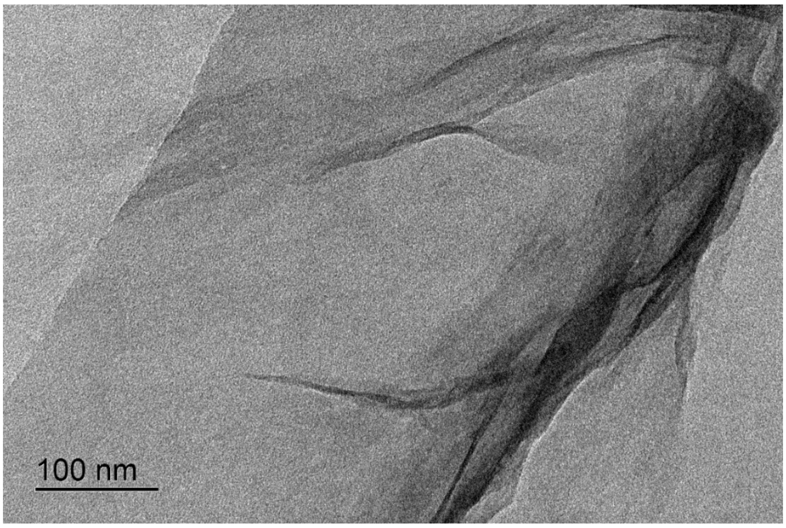


Figure S4. HRTEM image of CP6-RGO nano-composite.

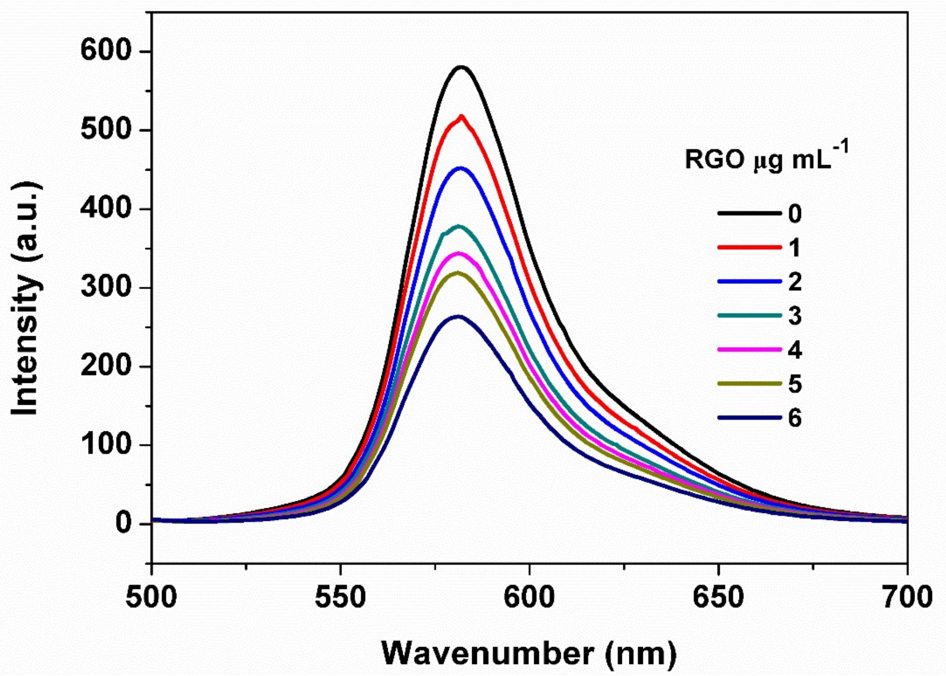


Figure S5. The effect of increasing concentrations of RGO (concentrations ranging from 0 to 6.0 µg mL^{-1}) on the fluorescence intensity of 10 µM RB.

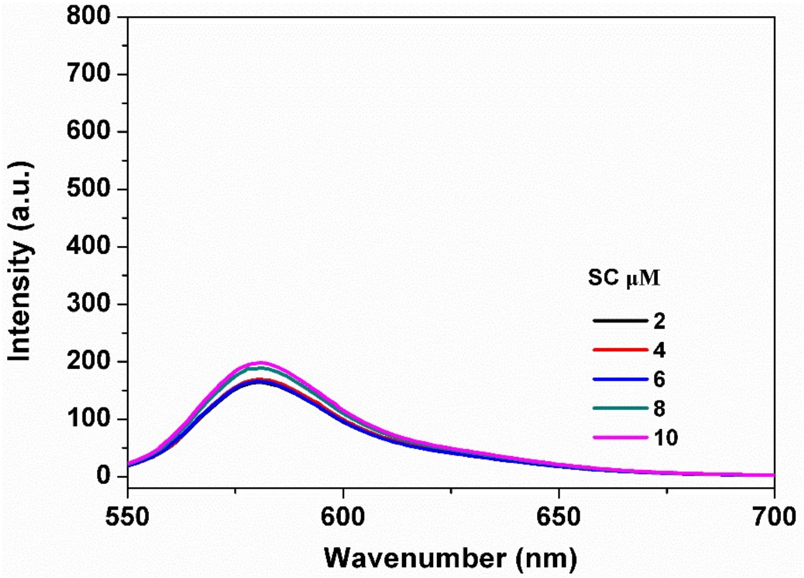


Figure S6. Fluorescence spectrum of the RB-RGO complexation *vs*. different concentrations of SC.

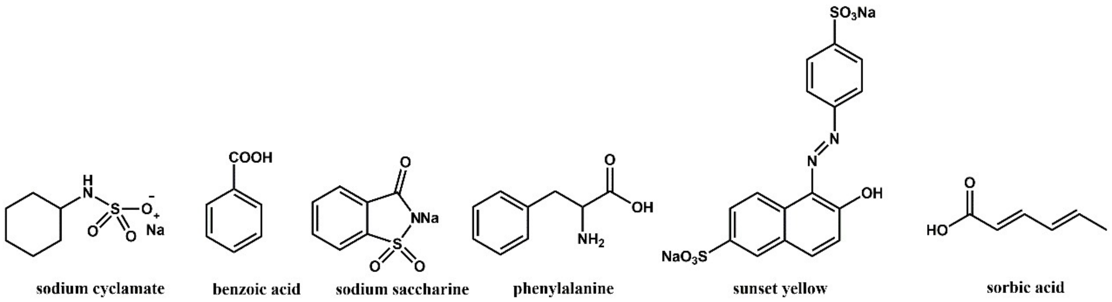


Figure S7. Chemical structures of sodium cyclamate, benzoic acid, sodium saccharine, phenylalanine, sunset yellow, and sorbic acid, respectively.

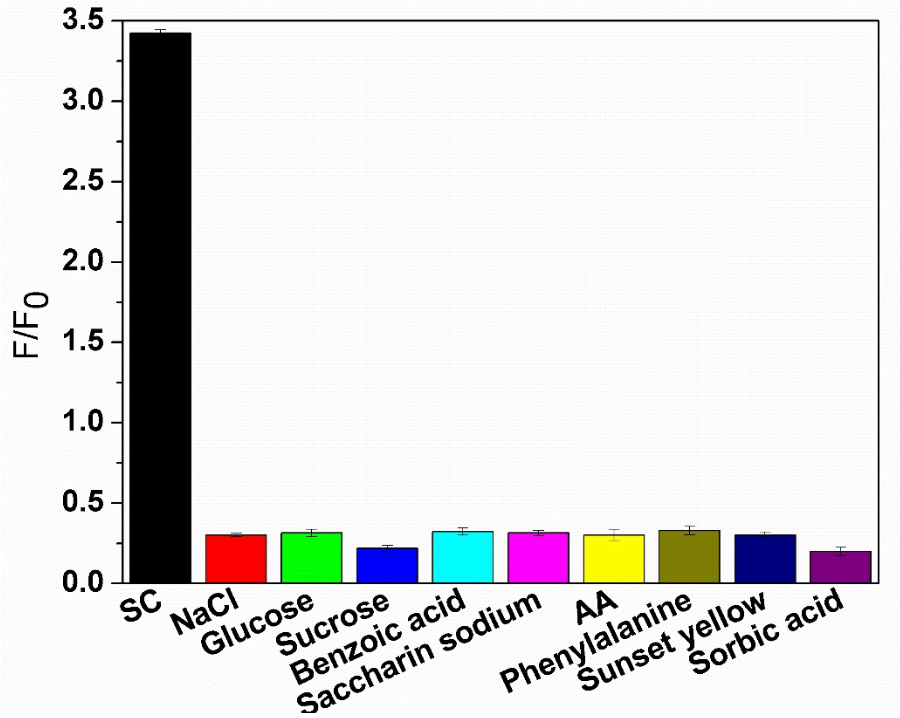


Figure S8. The relative fluorescence intensity of F/F0, and the F0 and F are the fluorescence intensity in the presence of 10.0 μM SC and 0.4 mM interferents.

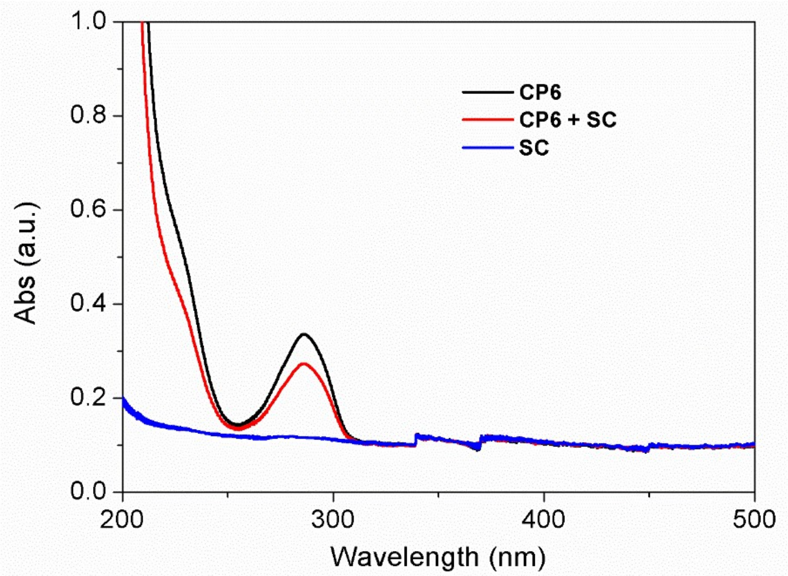


Figure S9. UV-vis adsorption of CP6 (10.0 μM), 10.0 μM mixture solution of CP6 and SC, and SC (10.0 μM), respectively.

Table S1. XPS elements analysis results of RGO (wt. %).

Elements	C	O
Assay	94.69	5.31

Table S2. XPS elements analysis results of CP6-RGO (wt. %).

Elements	C	N	O
Assay	90.17	2.06	7.77

Table S3. Determination of SC in carbonate beverage sample.

Sample	Added (μM)	Found (μM)	RSD (%)	Recovery (%)
carbonate beverage	0	0.00	–	–
	1.0	0.96 ± 0.04	4.1	96.0
	2.0	2.02 ± 0.11	5.4	101.0
	10.0	9.72 ± 0.19	1.9	97.2

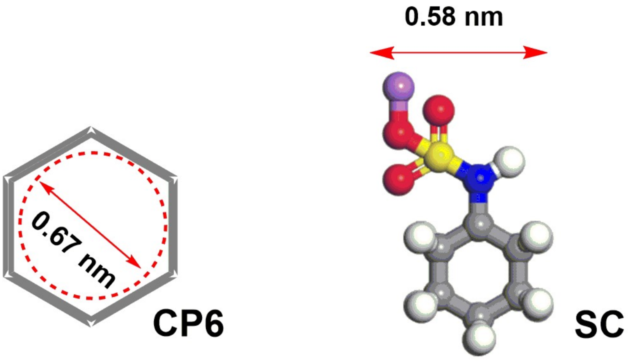


Figure S10. Cavity size of CP6 [S4]and molecular size of SC, respectively.

References

S1 Y. J. Ma, X. F. Ji, F. Xiang, X. D. Chi, C. Y. Han, J. M. He, Z. Abliz, W. X. Chen and F. H. Huang, *Chem. Commun.*, 2011, **47**, 12340–12342.

S2 R. Joseph, A. Naugolny, M. Feldman, I. M. Herzog, M. Fridman and Y. Cohen, *J. Am. Chem. Soc.*, 2016, **138**, 754–757.

S3 G. C. Yu, J. Zhou, J. Shen, G. P. Tang and F. H Huang, *Chem. Sci*., 2016, **7**, 4073–4078.

S4 C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org Lett*. 2010, 12 (2010) 4360−4363.