

Supporting Information

Pillar[6]arene modified gold nanoparticles grafted on cellulose nanocrystals for electrochemical detection of bisphenol A

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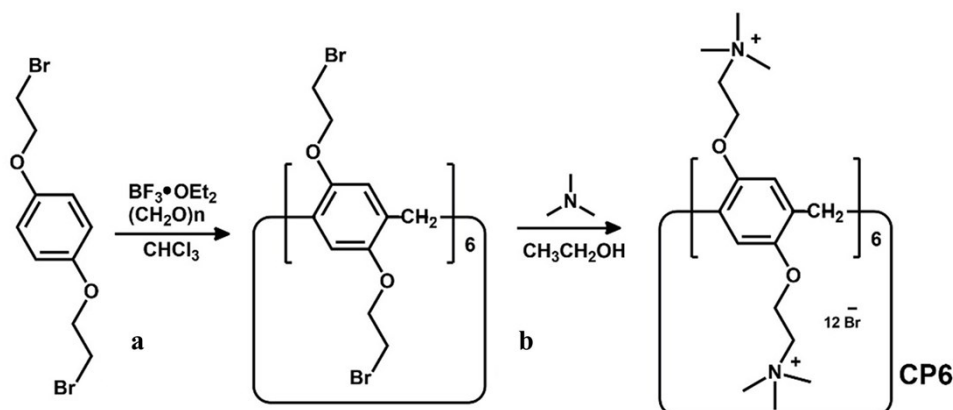
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S1. Instruments

The prepared samples were characterized by thermogravimetric analysis (TGA) with temperature range 25 to 800 °C with heating rate of 10 °C min⁻¹ at nitrogen atmosphere. 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. UV–visible spectroscopy was carried with a Shimadzu UV-3600 spectrophotometer from 200 nm to 800 nm region. EDS was carried out in the JEM 2100 transmission electron microscopy (TEM, Japan) equipped with an energy dispersive X-ray spectrometry. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) and with Al K α X-ray radiation as the X-ray source for excitation. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PAN analytical diffractometer for Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 1° min⁻¹ and a step size of 0.02° in 2θ . TEM images and the high resolution images were measured by a high resolution transmission electron microscope (HRTEM, JEM-2010). The nitrogen adsorption and desorption isotherms were measured at 77K using a Micromeritics ASAP 2020N system. The samples were outgassed at 198 °C for 8 h before the measurements. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance DMX-400 spectrometer at 400 MHz. Electrochemical measurements were obtained from a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) with conventional three-electrode system, including a modified glassy carbon working electrode (GCE), a saturated calomel reference electrode (SCE) and a Pt wire auxiliary electrode.

S2. Synthesis of pillar[6]arene (CP6) ^[1,2]



Scheme S1. The synthetic route of CP6.

Synthesis of compound b: Boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$, 6.52 g, 46.0 mmol) was added to the mixed solution of paraformaldehyde (0.698 g, 23 mmol) and **a** (6.74 g, 23 mmol) in 1, 2-dichloroethane (200 mL) under nitrogen atmosphere. Then the mixture was stirred at RT for 2 h. A green solution was obtained. The reaction mixture was then washed with water (2×100 mL) and dried with excess MgSO_4 . After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:2 v/v) as the eluent to get a white powder (2.97 g, 38 %).

Synthesis of CP6: Triethyl amine (5.0 mL, 36 mmol) was added to a solution of **b** (0.5 g, 0.297 mmol) in ethanol (20 mL), and the resulting mixture was refluxed for 48 h. After cooling to RT, diethyl ether (20 mL) was added to the mixture and precipitate was obtained. The precipitate was filtered, and was washed by acetone and diethyl ether to remove excess triethyl amine and obtained the colorless solid of CP6. ^1H NMR (400 MHz, D_2O , rt) δ (ppm): 6.88 (s, 12H), 4.48 (br, 24H), 3.92 (s, 12H), 3.73 (br, 24 H), 3.09 (s, 108H). ^{13}C NMR (100 MHz, D_2O , rt) δ (ppm): 149.96, 129.24, 116.68, 116.41, 65.18, 63.47, 59.80, 54.23, 30.29.

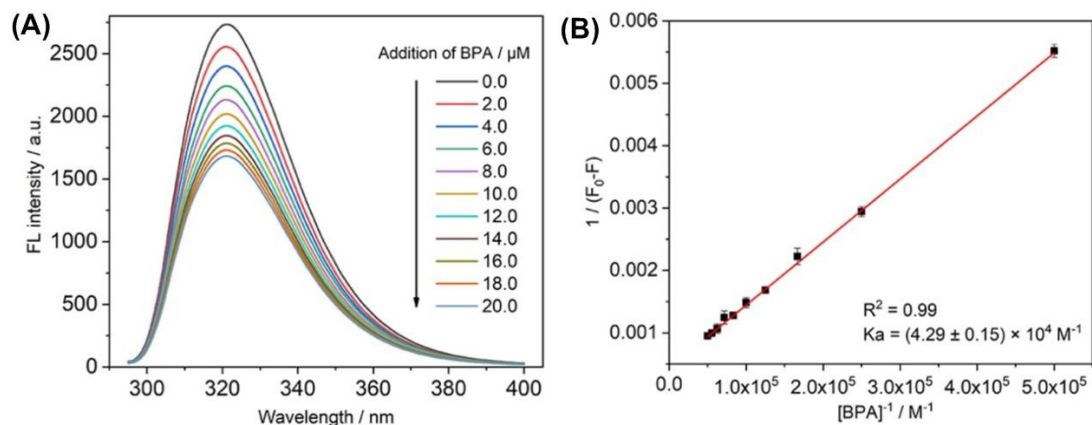


Figure S1. (A) Fluorescence titrations of CP6 (10 μM , $\lambda_{\text{ex}} = 290 \text{ nm}$) upon successive addition of BPA (up to 20 μM) in 0.1 M PBS (pH 7.0). (B) A double reciprocal plot of $1/(F_0 - F)$ versus $1/[\text{CP6}]$ for BPA to CP6 was obtained, indicating the existence of a 1 : 1 complex. From the plots the binding constant (K_a) for the 1 : 1 BPA/CP6 complex was calculated to be $4.29 \times 10^4 \text{ M}^{-1}$.

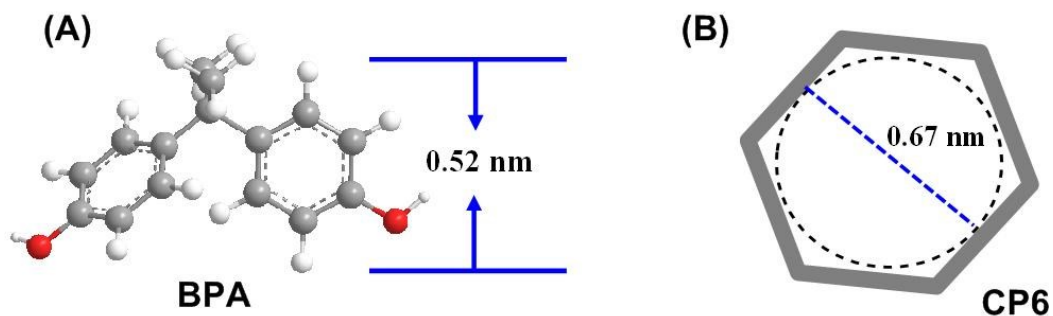


Figure S2. The molecular size of BPA and CP6.

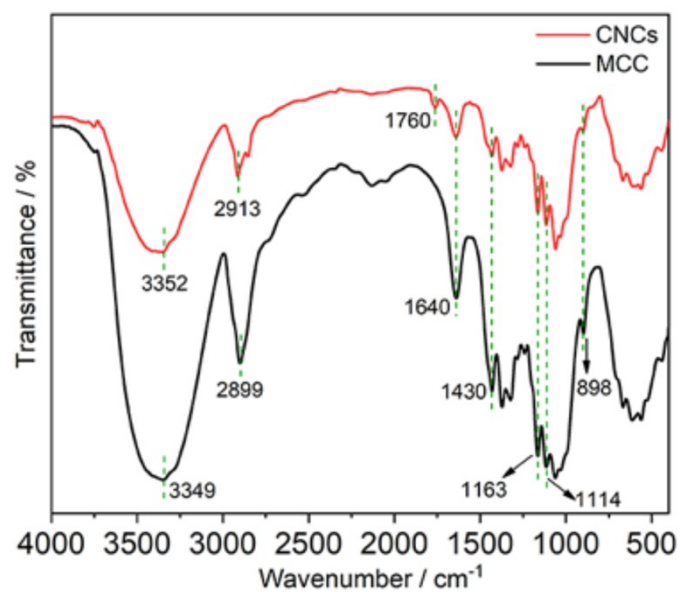


Figure S3. FTIR spectra of CNCs and MCC.

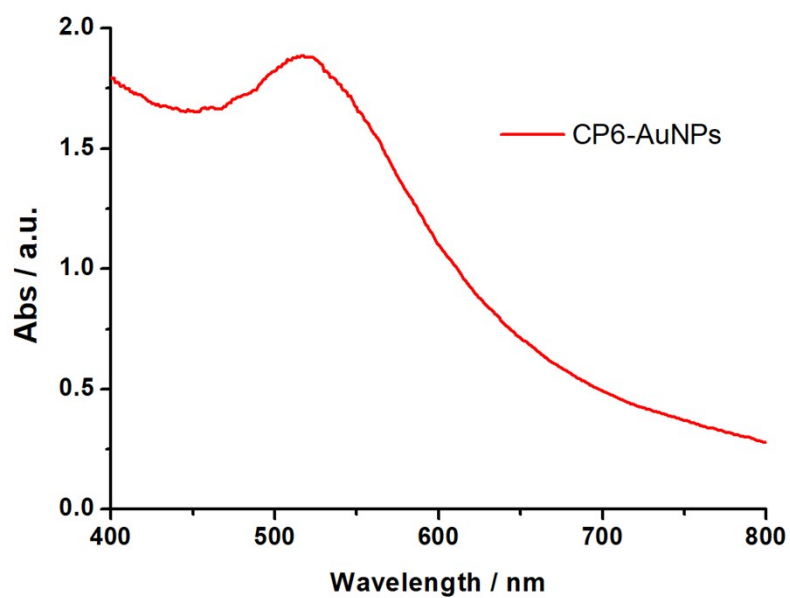


Figure S4. UV-vis absorption spectrum of CP6-AuNPs.

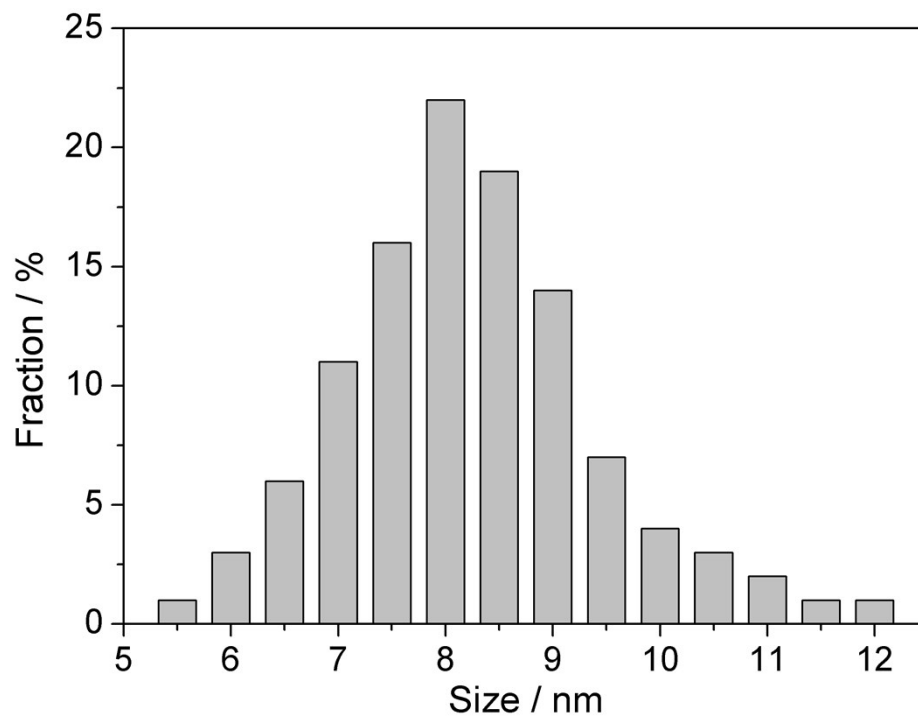


Figure S5. The size distribution histogram of the CP6-AuNPs.

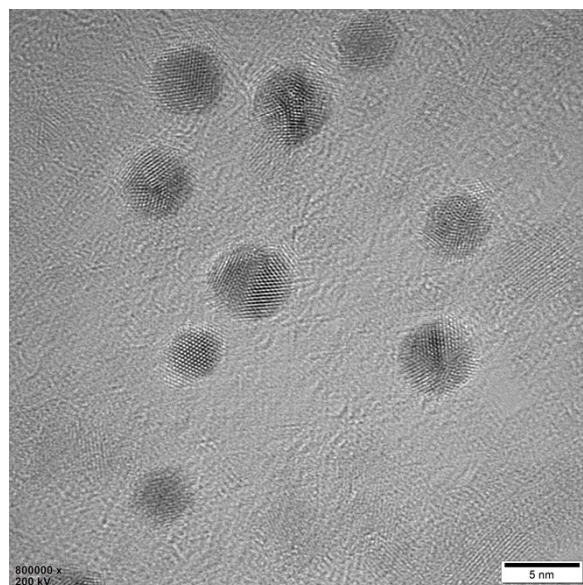


Figure S6. High-resolution image of CNCs@CP6-AuNPs.

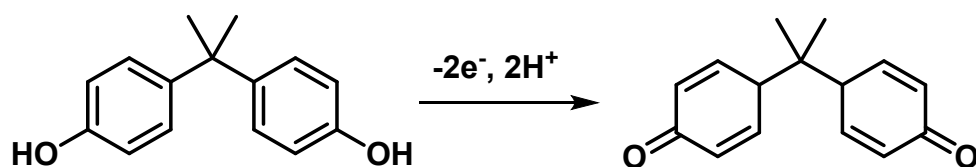


Figure S7. A scheme of possible BPA reduction processes on CNCs@CP6-AuNPs modified electrode. Each two-electron transfer may lead to the oxidation of BPA to 1,4-benzoquinone and formaldehyde [3].

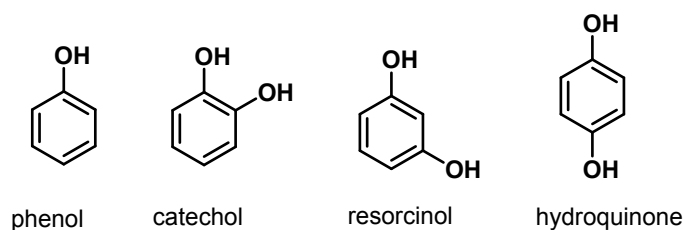


Figure S8. Chemical structures of phenol, catechol, resorcinol and hydroquinone, respectively.

References

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- S3 Jiang, L. Y.; Santiago, I.; Foord, J. A Comparative Study of Fouling-free Nanodiamond and Nanocarbon Electrochemical Sensors for Sensitive Bisphenol A Detection. *Carbon*, **2021**, *174*, 390–395.