**Supporting Information**

# Water-soluble pillar[5]arene modified graphdiyne functional material and its application towards ultrasensitive and robust electrochemical methylamphetamine determination

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***1 apparatus***

Materials were characterized by scanning electron microscope (SEM) (AMRAY 1000B) and transmission electron microscope (TEM) images that were performed using a JEM 2100 microscope (Japan). The atomic force microscopy (AFM) characterization was used to study the thickness of synthesized samples. Fourier transform infrared spectroscopy (FTIR) spectrum was obtained from a Thermo Nicolet Is10 spectrometer (America). X-ray photoelectron spectroscopy (XPS) was gotten by a Thermo K-Alphaþ spectrometer (America). Fluorescence spectra were investigated with Hitachi U-2900 and F-4600 (Japan). Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were recorded on a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) using a three-electrode system, including an WP5-GDY-modified glassy carbon working electrode (GCE), a platinum wire counter electrode (Pt), a saturated calomel reference electrode (SCE).

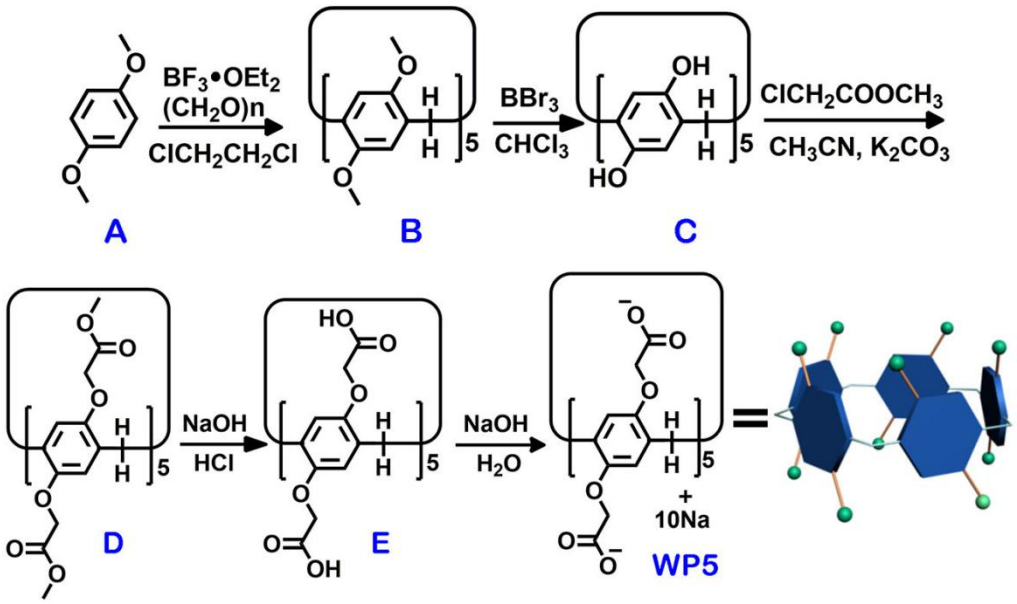
***2 Regents***

methylamphetamine (MA), methylenedioxy methamphetamine (MDMA) and urine were obtained from Kunming Medical University (Kunming, China). WP5 and GDY were synthesized by the reported procedure [S1,2] and the synthetic routes were illustrated in Scheme S1. Ultrapure water (18.25 MU cm), obtained from a Millipore Milli-Q water purification system, was utilized during the experiment process. Phosphate buffered saline (PBS, 0.1 M, pH 10.0) was prepared as electrolyte for CV and DPV measurements.

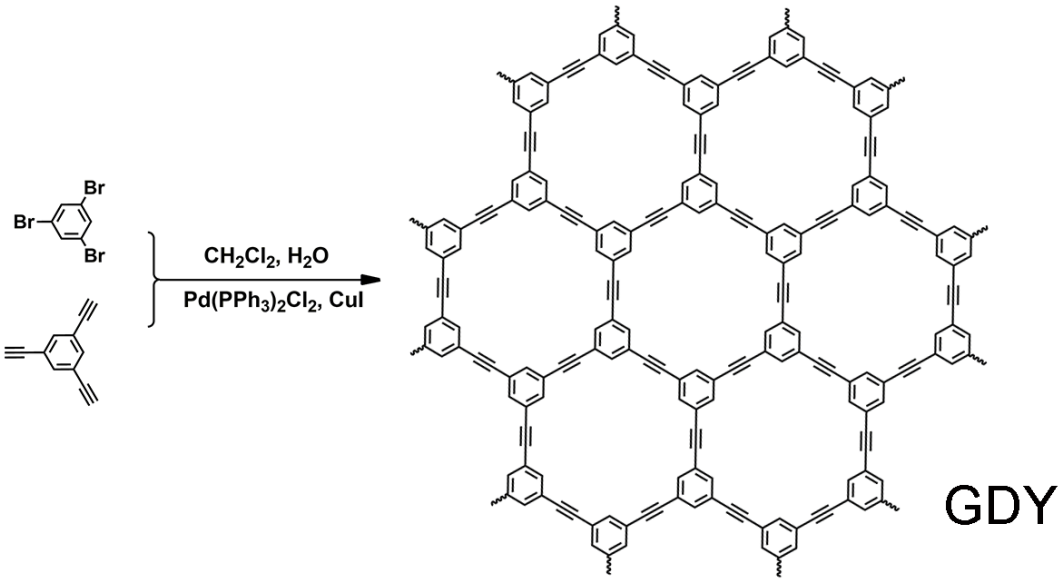
***3 Electrochemical determination of MA***

The clean bare glassy carbon electrodes (GCEs) were prepared by polishing and cleaning with aluminum oxide powder and DW, respectively. Modified GCE of WP5-GDY/GCE was prepared by dropping the dispersed solution of WP5-GDY in ethanol (6.0 μL) on the surface of the apinoid GCE and dried naturally. Other modified GCE of GDY/GCE was prepared in accordance with a similar procedure of WP5-

GDY/GCE, in which WP5-GDY/GCE was replaced by GDY. A differential pulse voltammetry (DPV) technique was carried out to detect MA with WP5-GDY/GCE at a working potential of 0.8 to 1.6 V in an aqueous solution of phosphate buffered saline (PBS, 0.1 M, pH 10.0) containing different concentrations of PQ. Then, the modified GCEs were studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in the solution of 2.0 mM $[Fe(CN)_6]^{3-/4-}$ containing 100.0 mM KCl as the supporting electrolyte and with a frequency range of $10^{-1}$ to $10^5$ Hz. To study the reproducibility and stability of the electrochemical sensing system of WP5-GDY/GCE, whole electrochemical tests were implemented at least six times. All electrochemical measurements were carried out by CHI660E electrochemical workstation.




**Scheme S1**. Synthetic route of WP5.




**Scheme S2**. Synthetic route of GDY.

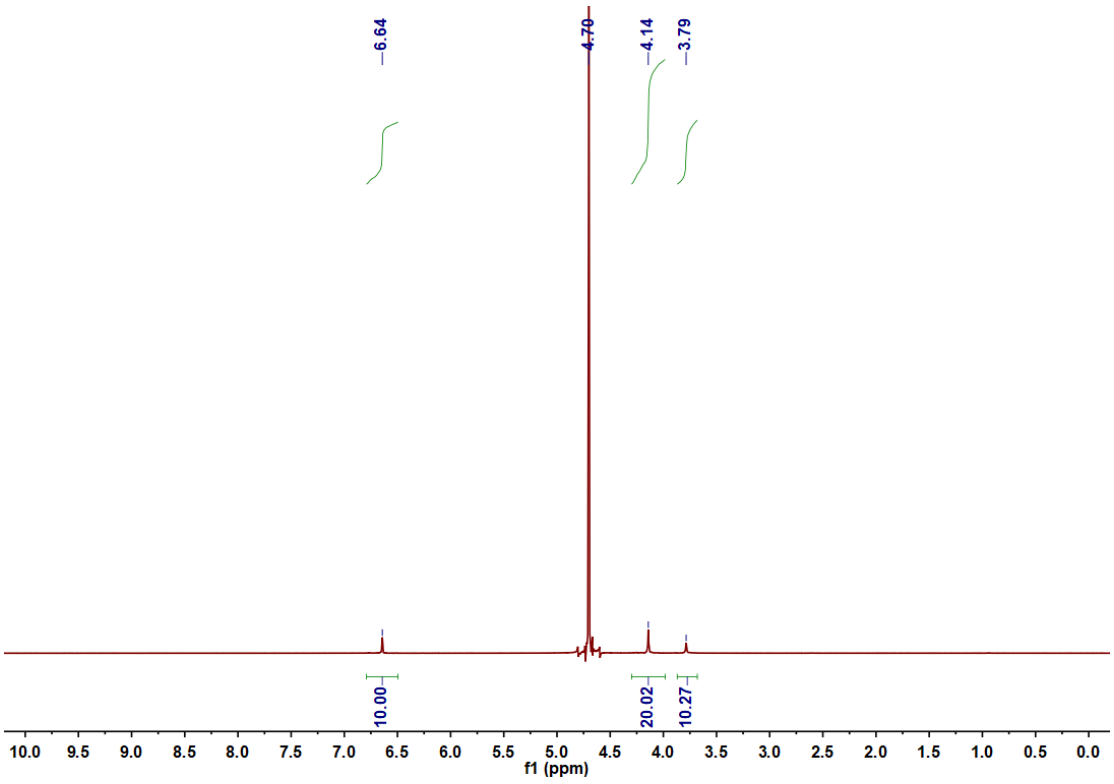



**Figure S1**. $^{1}$H NMR of WP5.

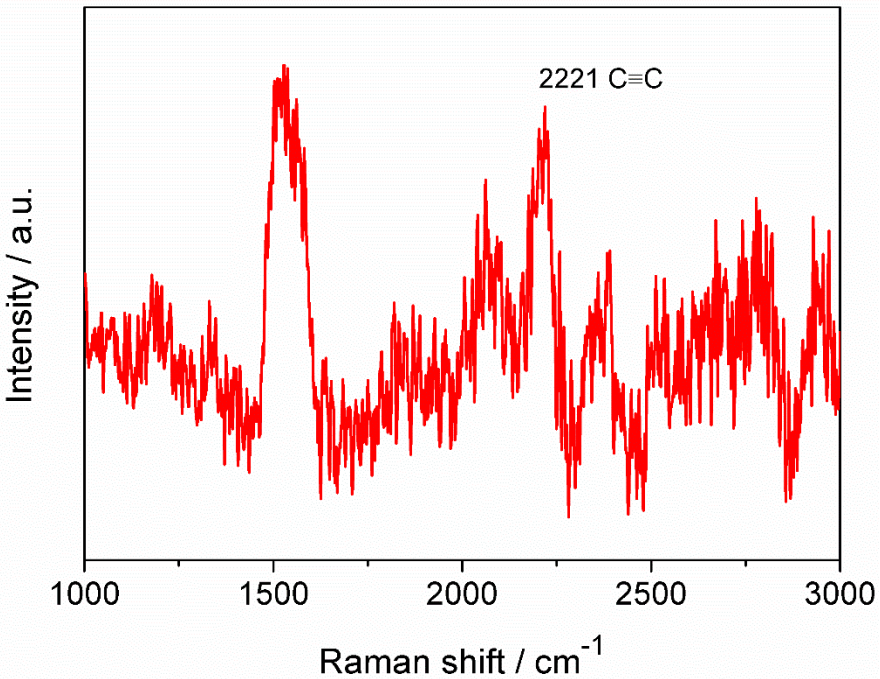



**Figure S2**. Raman spectrum of GDY.

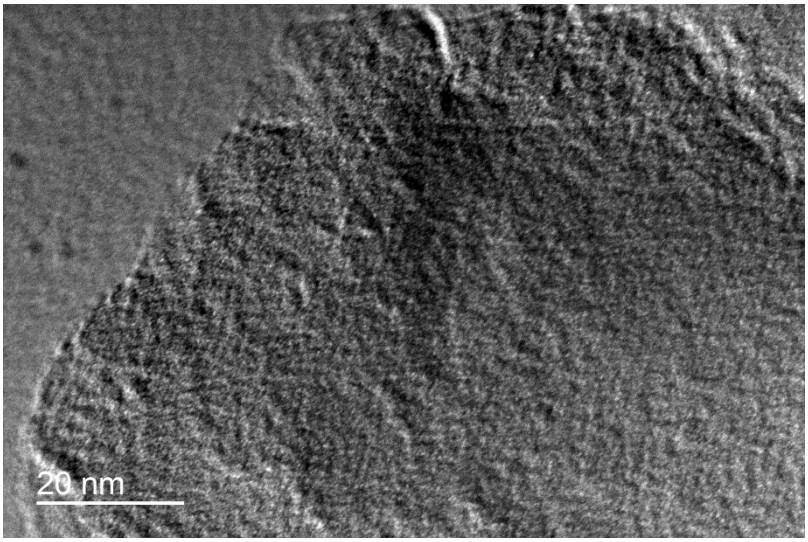



**Figure S3**. High resolution TEM image of GDY.

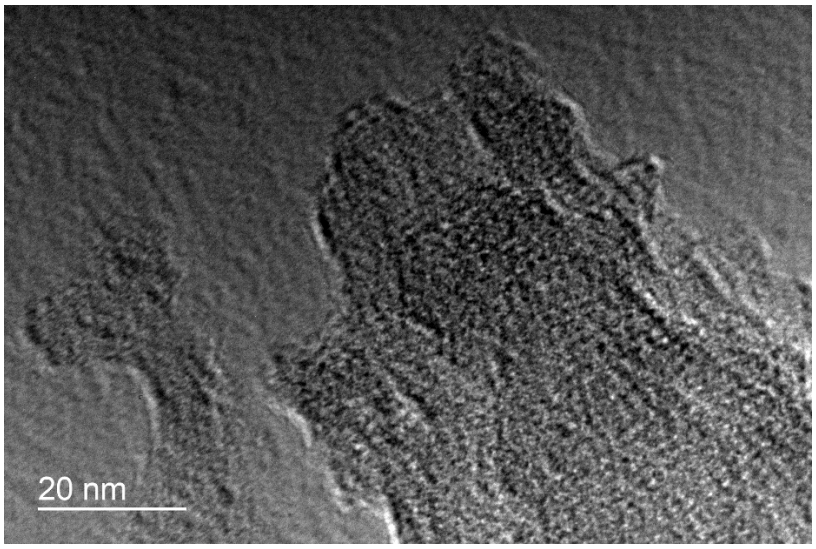
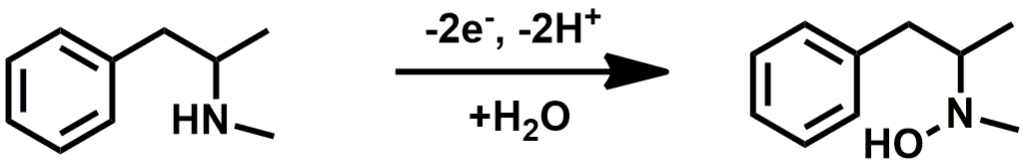



**Figure S4**. High resolution TEM image of WP5-GDY.




**Scheme S3**. Mechanism of electrochemical oxidation of MA.

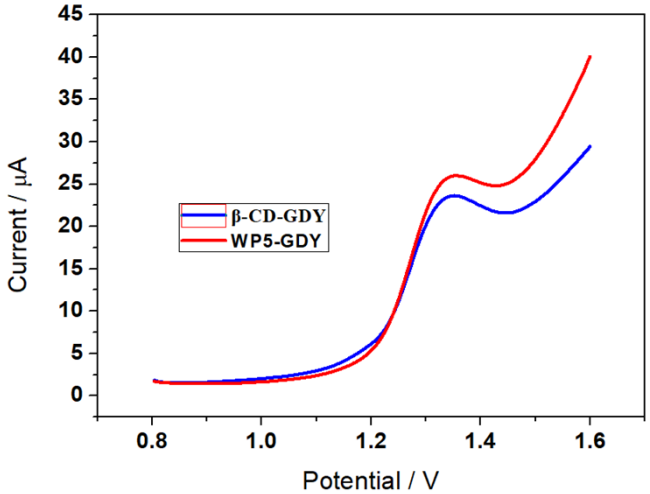



**Figure S5**. DPV curves of β-CD-GDY and WP5-GDY modified electrodes.

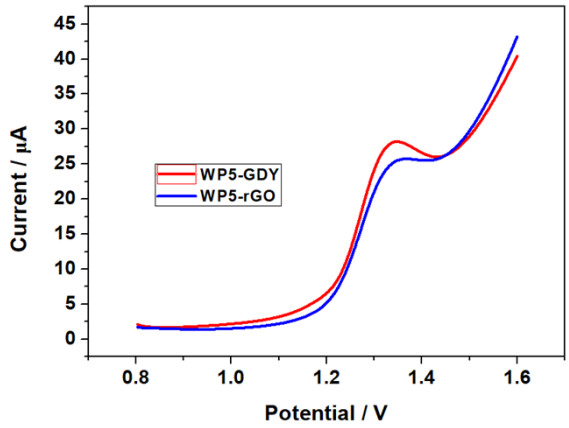



**Figure S6**. DPV curves of WP5-GDY and WP5-rGO modified electrodes.

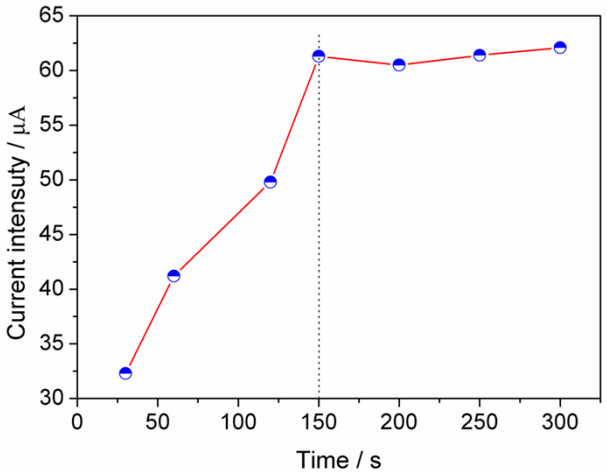



**Figure S7**. Effect of equilibrium time of MA-WP5-GDY/GCE.

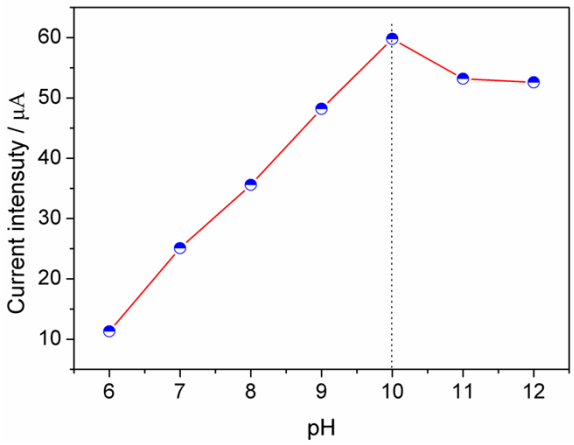



**Figure S8**. Effect of PBS pH of MA-WP5-GDY/GCE.

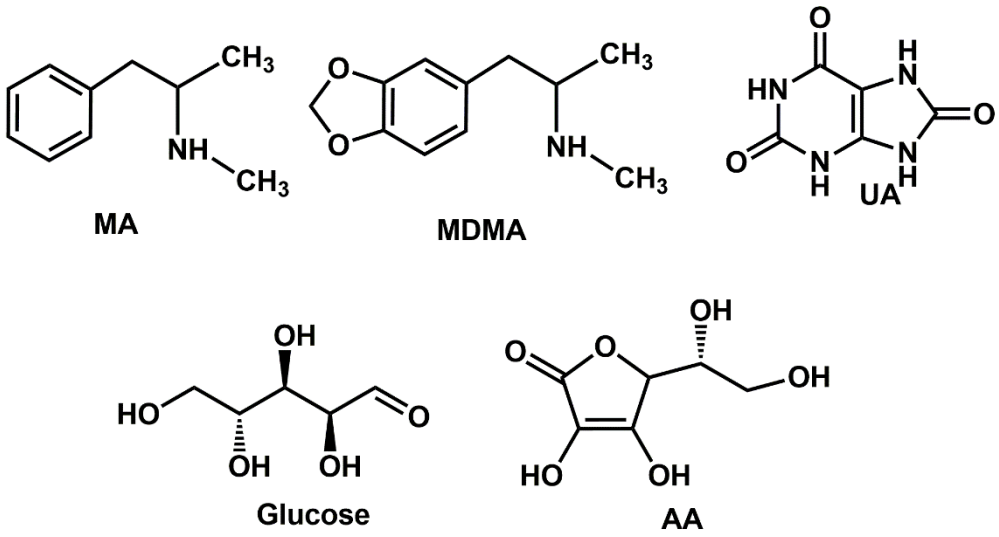



**Figure S9**. Chemical structure of MA, MDMA, UA, glucose and AA, respectively.

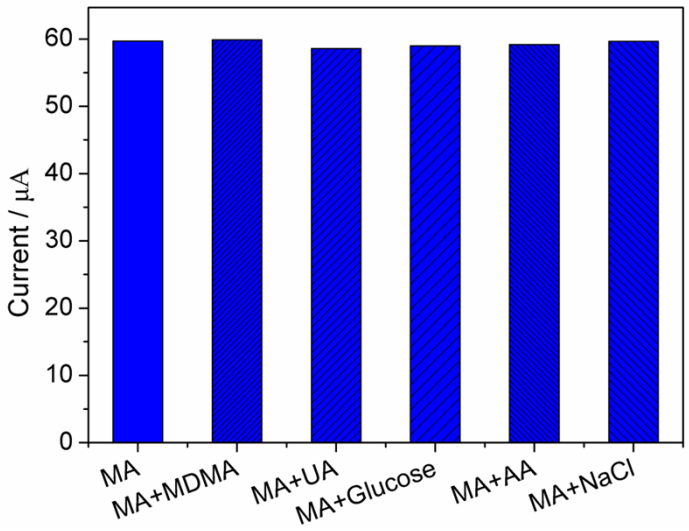



**Figure S10**. The peak current response of WP5-GDY/GCE toward 30.0 μM MA, 30.0 μM MA+MDMA, 30.0 μM MA+UA, 30.0 μM MA+glucose, 30.0 μM MA+AA, 30.0 μM MA+NaCl, respectively.

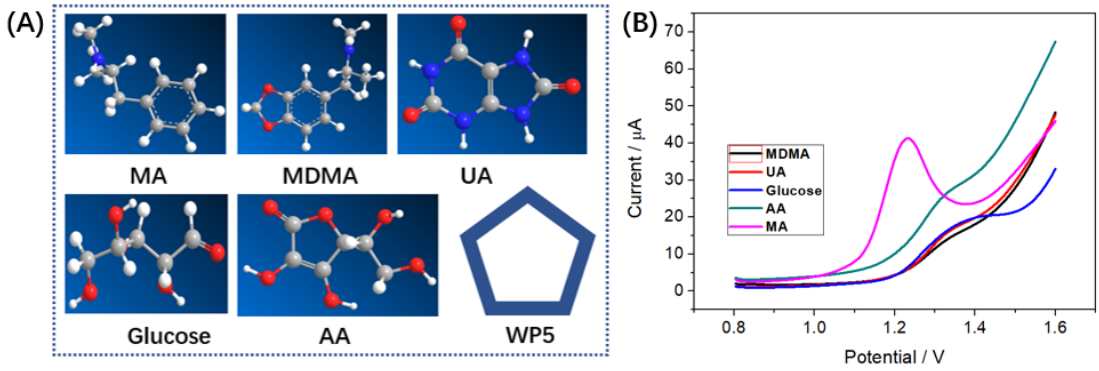



**Figure S11**. Chemical structure of MA, MDMA, UA, glucose, AA and WP5 (A) and DPVs for WP5-GDY/GCE toward various substances.

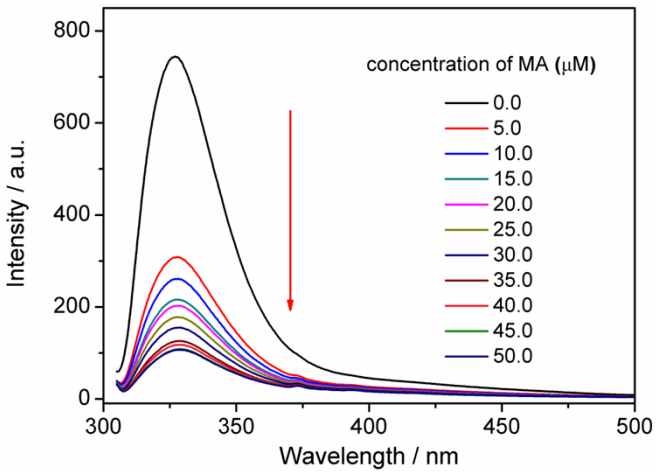



**Figure S12**. Fluorescence intensity changes of WP5 with various addition of MA.

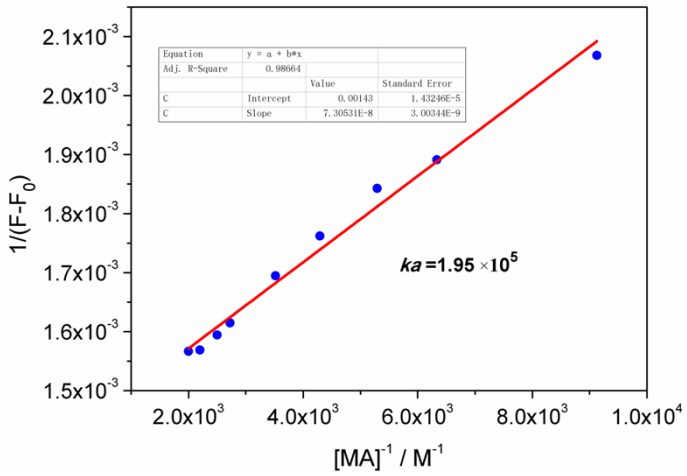



**Figure S13**. The plots of $1/(F-F_0)$ *vs*. 1/[MA] for WP5 **(B)** (λex = 290).

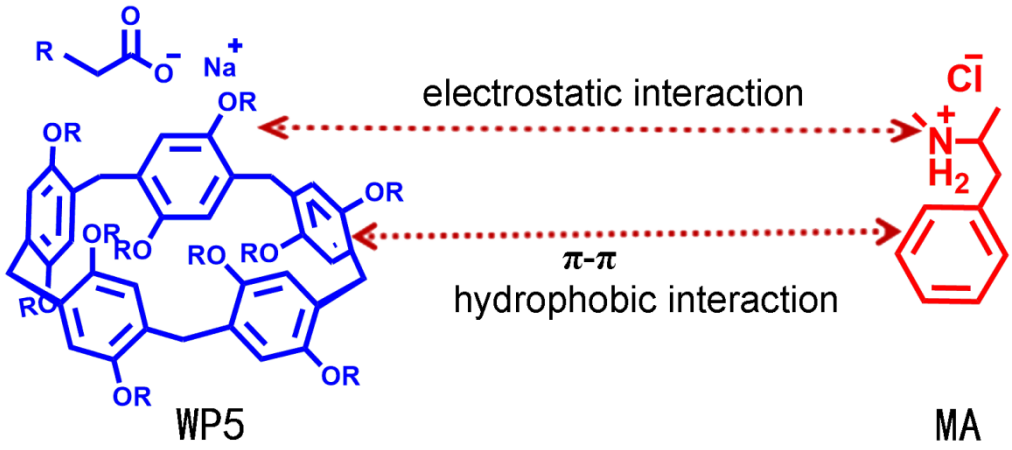



**Figure S14**. Host-guest interaction between WP5 and MA.

**Table S1**. The results of MA detection in urine sample (n=3) via the standard addition method.

| Added (μM) | Found (μM) | RSD% | Recovery% |
|---|---|---|---|
| 1.0 | 0.96 | 2.5 | 96.0 |
| 5.0 | 5.05 | 3.1 | 101 |
| 10.0 | 9.78 | 1.9 | 97.8 |
| 20.0 | 19.89 | 2.3 | 99.4 |

**Table S2**. Comparison of our material with other materials for determination of MA.

| **Material** | **Method** | **Linear range** (μM) | **LOD** (μM) | **Ref** |
|---|---|---|---|---|
| $Ru(bpy)_3^{2+}$/ Nafion/GCE | electrochemical luminescence | 0.05 ~ 100 | 0.005 | [S3] |
| SiN/Nafion/GCE | electrochemical luminescence | 0.1~ 10 | 0.026 | [S4] |
| BDDE | CV | 0.07 ~ 80 | 0.05 | [S5] |
| $G_4$HTD/PtNPs/CPE | DPV | 0.1 ~ 2 | 0.1 | [S6] |
| MWCNTs /AuNPs/SPE | stripping voltammetry | 0.02 ~ 50 | 0.006 | [S7] |
| **WP5-GDY/GCE** | DPV | 0.05 ~ 30 | 0.016 | This work |

Abbreviations: BDDE: boron-doped diamond electrode, SPE: screen printed electrode, GCE: glassy carbon electrode, MWCNTs: multi-walled carbon nanotube, AuNPs: gold nanoparticles, PtNPs: Pt nanoparticles.

**References**

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