

**Supporting Information For**

**Exploiting Metal-Organic Coordination Polymers  
as Highly Efficient Immobilization Matrices of  
Enzymes for Sensitive Electrochemical  
Biosensing**

**Yingchun Fu,<sup>†</sup> Penghao Li,<sup>†</sup> Lijuan Bu,<sup>†</sup> Ting Wang,<sup>†</sup> Qingji Xie,<sup>†,\*</sup> Jinhua  
Chen,<sup>‡</sup> and Shouzhuo Yao<sup>†,‡</sup>**

<sup>†</sup> Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research  
(Ministry of Education), College of Chemistry and Chemical Engineering, Hunan Normal  
University, Changsha 410081, P. R. China

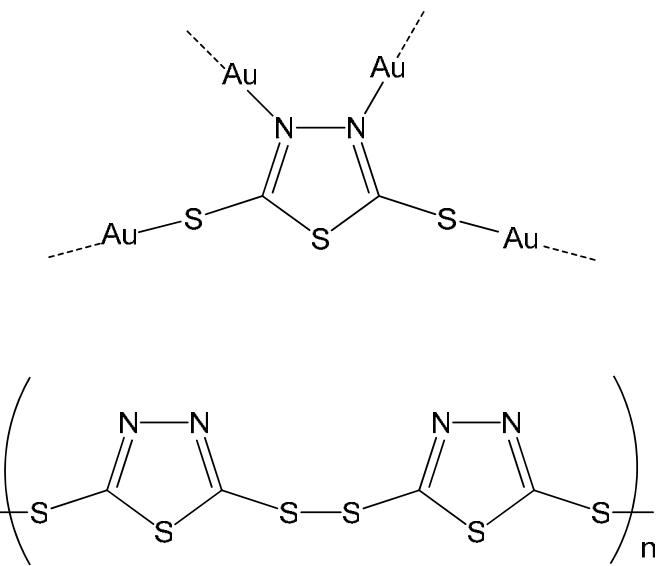
<sup>‡</sup> State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry  
and Chemical Engineering, Hunan University, Changsha 410082, P. R. China

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\*Corresponding author. Tel./Fax: +86 731 88865515. E-mail: xiejq@hunnu.edu.cn.

<sup>†</sup>Hunan Normal University.

<sup>‡</sup>Hunan University



**Scheme S-1.** Illustration of the possible structures of a MOCPs **1**'s unit (top) and PDMcT<sub>c/e</sub> (bottom).

**Table S-1.** Optimization of the experimental variables

Experimental variable	Testing range	Optimized value
$c_{\text{DMcT}}$ (mg mL <sup>-1</sup> )	0.25-2.5	0.5
$c_{\text{GOx}}$ (mg mL <sup>-1</sup> )	2-8	4
$c_{\text{NaAuCl}_4}$ (mM)	0.5-8	4
$c_{\text{Na}_2\text{PtCl}_6}$ (mM)	1.2-4.8	2.4
Cast-coating volume of MEBCs <b>1's</b> suspension (μL)	0.5-4.5	1
pH of detection solution	5-9	7
Detection potential (V)	0.4-0.9	0.7

**Table S-2.** Comparison of the performance of the proposed biosensors with analogues for detection of catechol

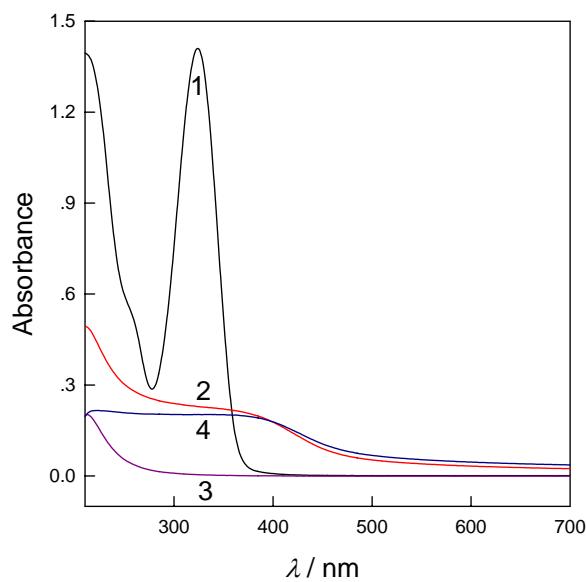
Biosensors	Sensitivity ( $\mu\text{A mM}^{-1} \text{cm}^{-2}$ )	LDR	LOD (nM)
Nano-hydroxyapatite/chitosan /tyrosinase-modified Au electrode <sup>1</sup>	2110	10 nM to 7 $\mu\text{M}$	5
Colloidal gold nanoparticles/graphite-Teflon/tyrosinase <sup>2</sup>	407	0.01 to 8 $\mu\text{M}$	20
polyacrylamide microgels/tyrosinase-modified glassy carbon electrode <sup>3</sup>	469	0.5 to 24 $\mu\text{M}$	300
Nano- $\text{CaCO}_3$ -polyphenol oxidase biocomposite modified glassy carbon electrode <sup>4</sup>	6992	6 nM to 0.2 $\mu\text{M}$	0.44
Molecularly imprinted polymers-tyrosinase modified Gold slides <sup>5</sup>	274	0.228 to 144 $\mu\text{M}$	228
chitosan/tyrosinase-modified screen printed carbon electrode <sup>6</sup>	2590	10 nM to 15 $\mu\text{M}$	10
MEBCs 3/Au	6780	0.2 nM to 15 $\mu\text{M}$	0.2
MEBCs 4/Au	1430	2.5 nM to 44 $\mu\text{M}$	1.9

### References (only for Table S-2)

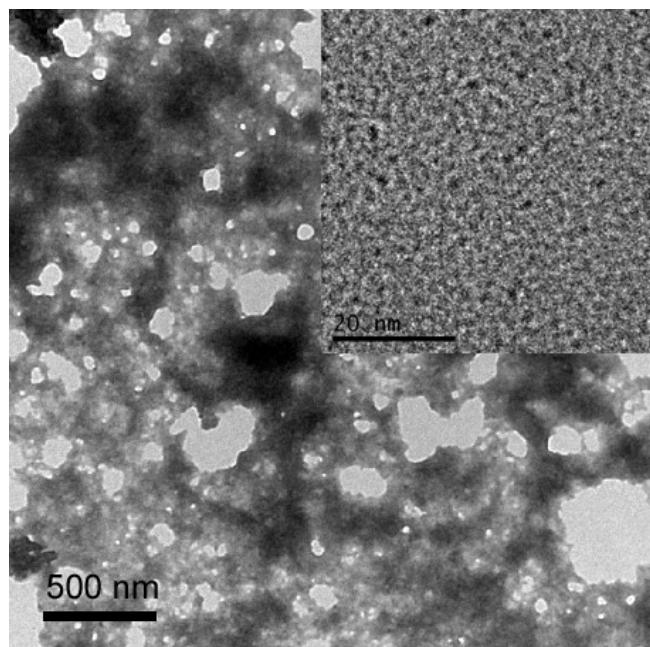
- (1) Lu, L.; Zhang, L.; Zhang, X.; Huan, S.; Shen, G.; Yu, R. *Anal. Chim. Acta*, **2010**, *665*, 146-151.
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- (3) Pérez, J. P. H.; López, M. S. P.; López-Cabarcos, E.; López-Ruiz, B. *Biosens. Bioelectron.* **2006**, *22*, 429-439.
- (4) Shan, D.; Zhu, M.; Han, E.; Xue, H.; Cosnier, S. *Biosens. Bioelectron.* **2007**, *23*, 648-654.
- (5) Lakshmi, D.; Bossi, A.; Whitcombe, M. J.; Chianella, I.; Fowler, S. A.; Subrahmanyam, S.; Piletska, E. V.; Piletsky, S. A. *Anal. Chem.* **2009**, *81*, 3576-3584.
- (6) Zhang, Y.; Ji, C. *Anal. Chem.* **2010**, *82*, 5275-5281.

**Table S-3.** Determination of catechol in river water using the MEBCs **3**/Au electrode (three parallel determinations for each).

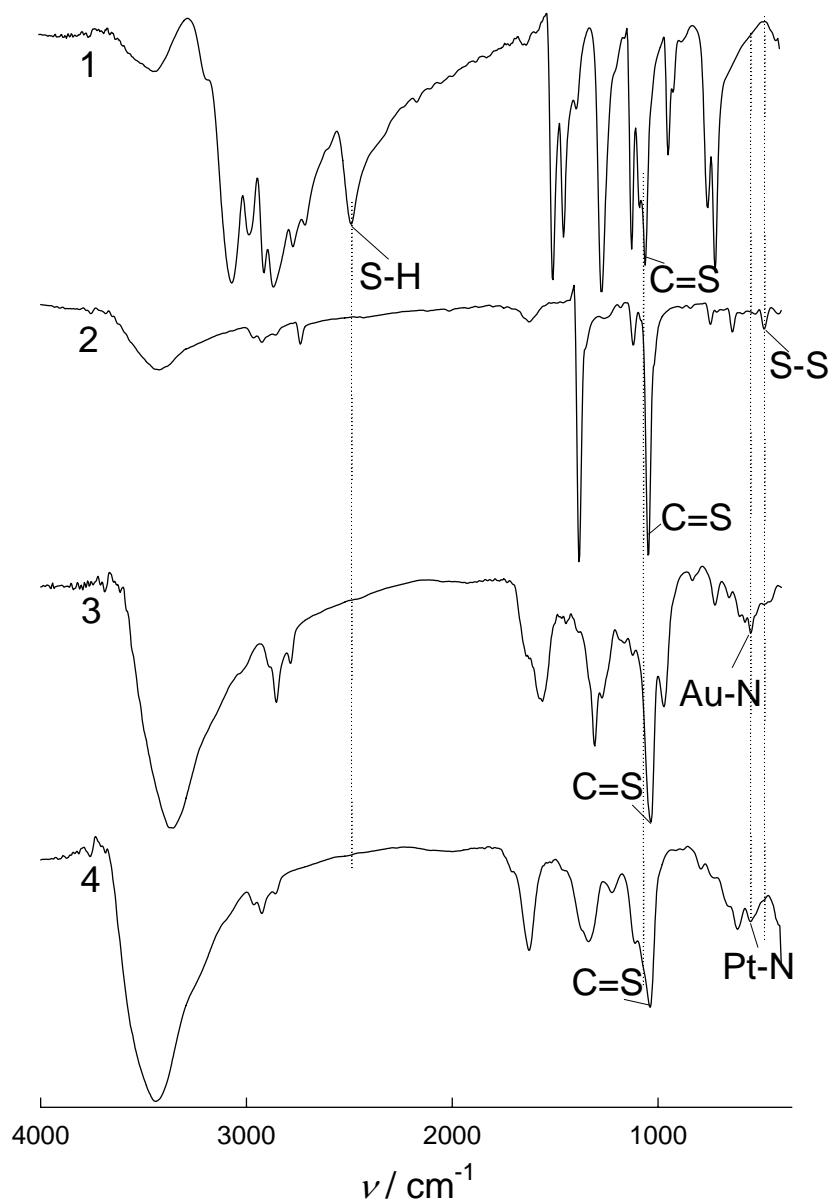
Added / $\mu\text{M}$	Found / $\mu\text{M}$	RSD / %	Recovery / %
0.20	0.19	5.7	95
0.50	0.53	6.5	106
1.00	0.97	3.3	97
2.86	2.89	6.0	101
4.29	4.51	4.1	105
8.58	9.1	3.7	106



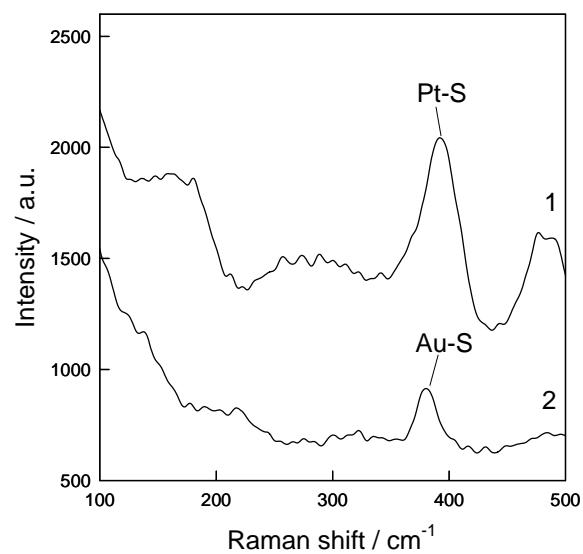
**Figure S-1.** UV-Vis spectra of DMcT (1), the MEBCs **1**'s suspension before centrifugation (2), the centrifugation-isolated supernatant of MEBCs **1**'s suspension (3), and the suspension of rinsed MEBCs **1** (4). PBS was used thoroughly.



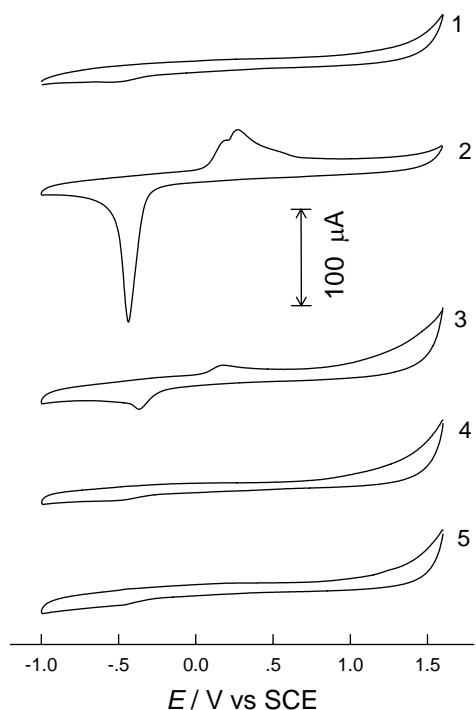
**Figure S-2.** TEM images of MEBCs 1.



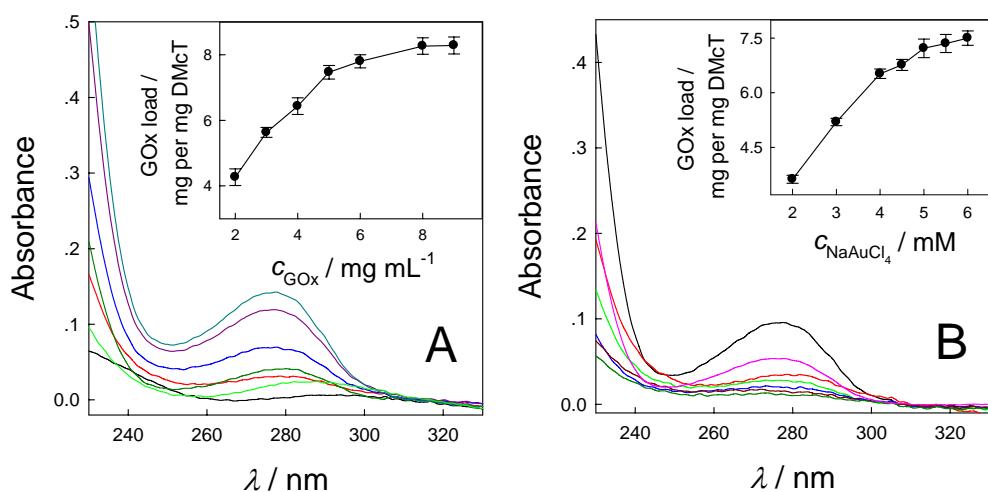
**Figure S-3.** FT-IR spectra of DMcT (1), PDMcT<sub>c</sub> (2), MOCPs **1** (3), and MOCPs **2** (4).



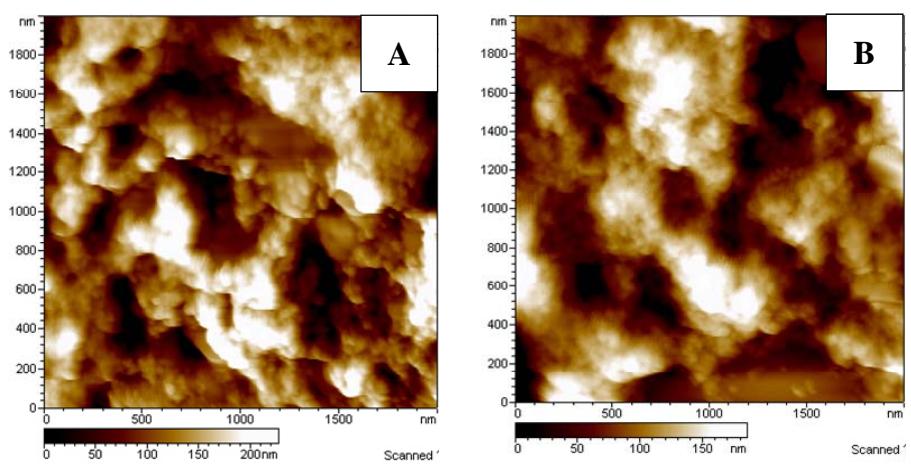
**Figure S-4.** Raman spectra of MOCPs **1** (2) and MOCPs **2** (1).



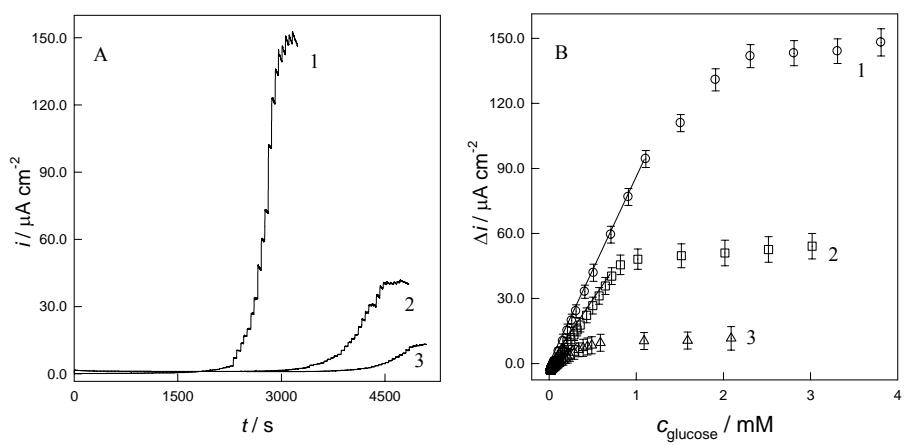
**Figure S-5.** The cyclic voltammetric curves of bare glassy carbon electrode (GCE) in 0.1 M pH 7.0 PBS in the absence (1) and presence (2) of 0.5 mg mL<sup>-1</sup> DMcT, as well as PDMcT<sub>c</sub> (3), MOCPS **1** (4), and MOCPs **2** (5) films modified GCE via cast-coating method in 0.1 M pH 7.0 PBS. Scan rate: 0.1 V s<sup>-1</sup>.



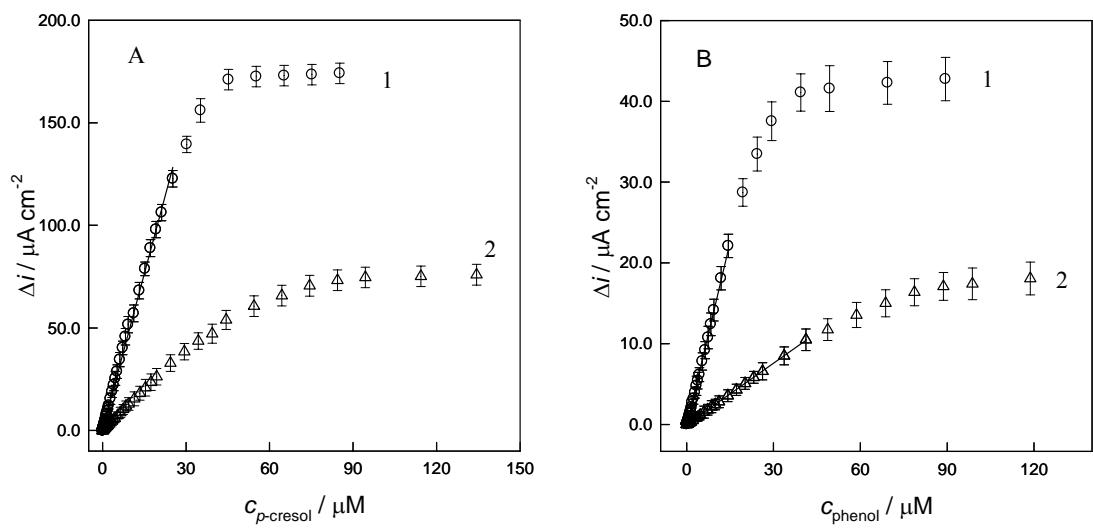
**Figure S-6.** (A) UV-vis spectra for centrifugation-isolated supernatants of the suspension of MEBCs **1** prepared in the presence of 2, 3, 4, 5, 6, 8, or 9  $\text{mg mL}^{-1}$  GOx (curves from bottom to top), as well as the GOx load (versus mass of DMcT) in the MEBCs **1** (Insert). The concentrations of DMcT and  $\text{NaAuCl}_4$  were 0.5  $\text{mg mL}^{-1}$  and 4 mM, respectively. (B) UV-vis spectra for centrifugation-isolated supernatants of the suspension of MEBCs **1** prepared in the presence of 2, 3, 4, 4.5, 5, 5.5, or 6 mM  $\text{NaAuCl}_4$  (curves from top to bottom), as well as the GOx load (versus mass of DMcT) in the MEBCs **1** (Insert). The concentrations of DMcT and GOx were 0.5  $\text{mg mL}^{-1}$  and 4  $\text{mg mL}^{-1}$ , respectively.



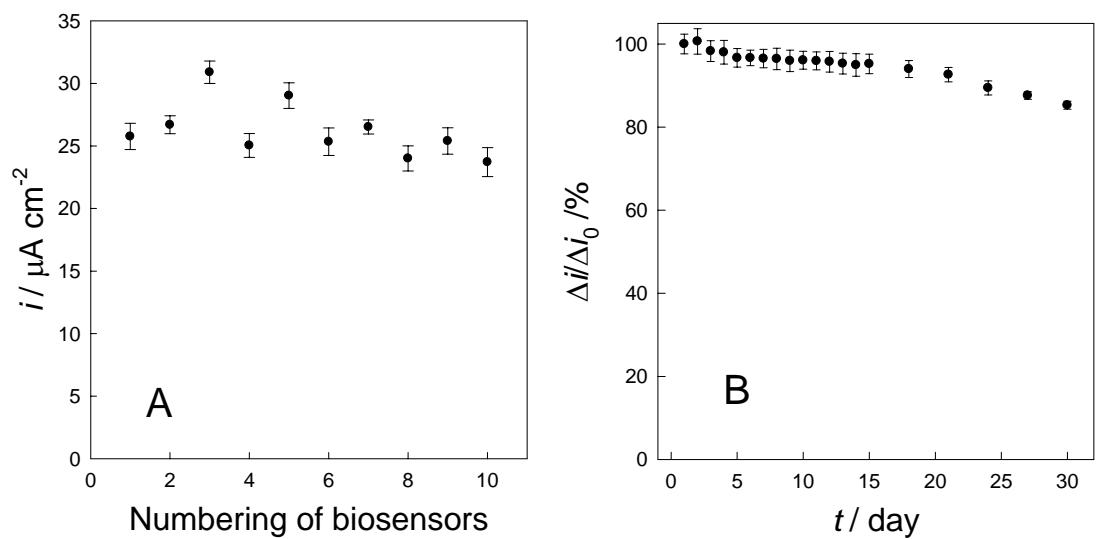
**Figure S-7.** The AFM images of MEBCs **1**/Au (A) and MEBCs **2**/Au (B) electrode surfaces.



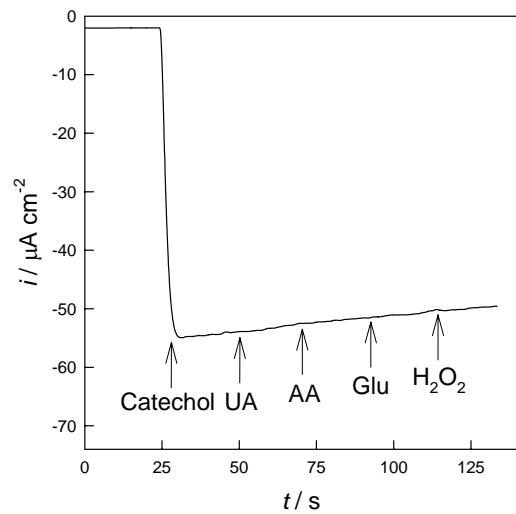
**Figure S-8.** Chronoamperometric responses (A) and calibration curves (B) of the MEBCs 1/Au (1), MEBCs 2/Au (2), and PDMcT<sub>c</sub>-GOx/Au (3) electrodes to successive additions of glucose at 0.7 V in pH 7.0 PBS. The PDMcT<sub>c</sub>-GOx/Au electrode was prepared by addition of H<sub>2</sub>O<sub>2</sub> to suspension of DMcT and GOx to yield PDMcT<sub>c</sub>-GOx composites followed by its cast coating on an Au electrode.



**Figure S-9.** Calibration curves of the MEBCs **3**/Au (1) and MEBCs **4**/Au (2) electrodes to successive additions of *p*-cresol (A), and phenol (B) at -0.1 V in pH 7.0 PBS.



**Figure S-10.** The fabrication reproducibility (A) and storability (B) of the MEBCs **3/Au** electrodes (three parallel determinations for each).



**Figure S-11.** Chronoamperometric responses of the MEBCs **3**/Au electrode to successive additions of 10  $\mu\text{M}$  catechol, 0.2 mM uric acid (UA), 0.1 mM ascorbic acid (AA), 10 mM glucose (Glu), and 0.5 mM  $\text{H}_2\text{O}_2$  at -0.1 V in pH 7.0 PBS.