

# Supporting Information

## In-situ Formation of Phosphorescent Molecular Gold (I) Cluster in a Macroporous Polymer Film to Achieve Colorimetric Cyanide Sensing

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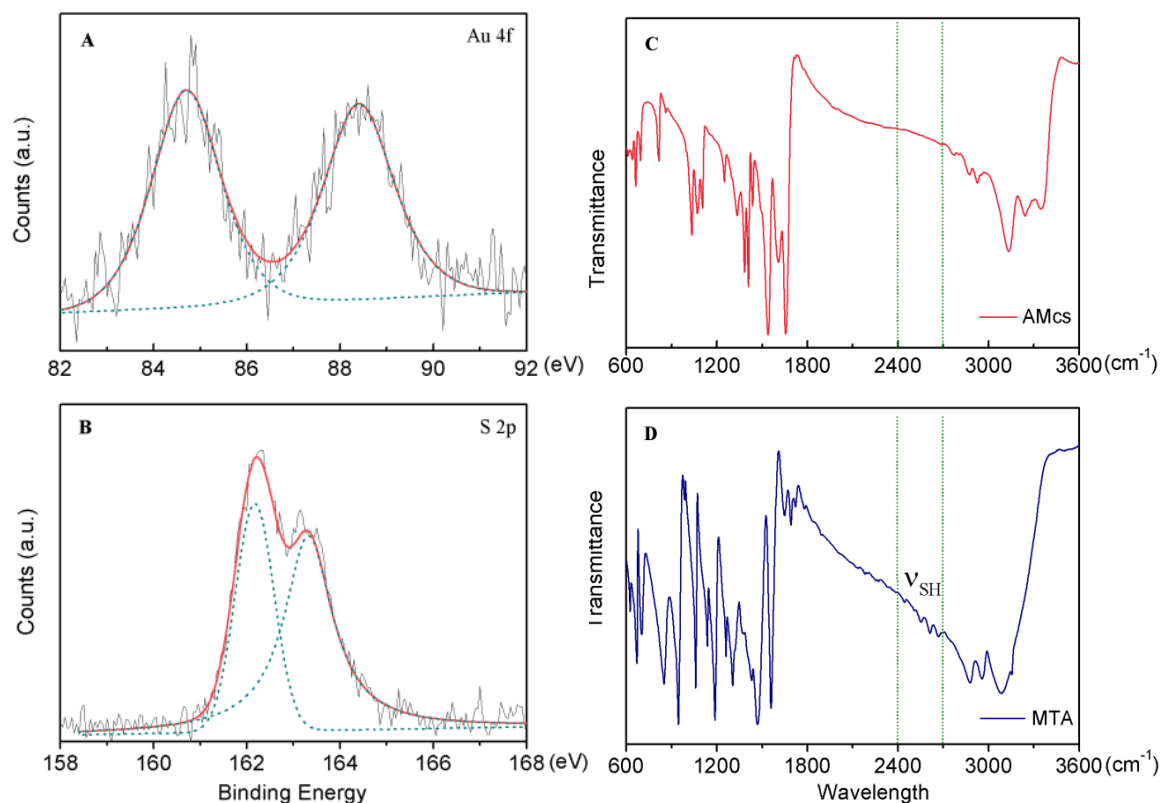
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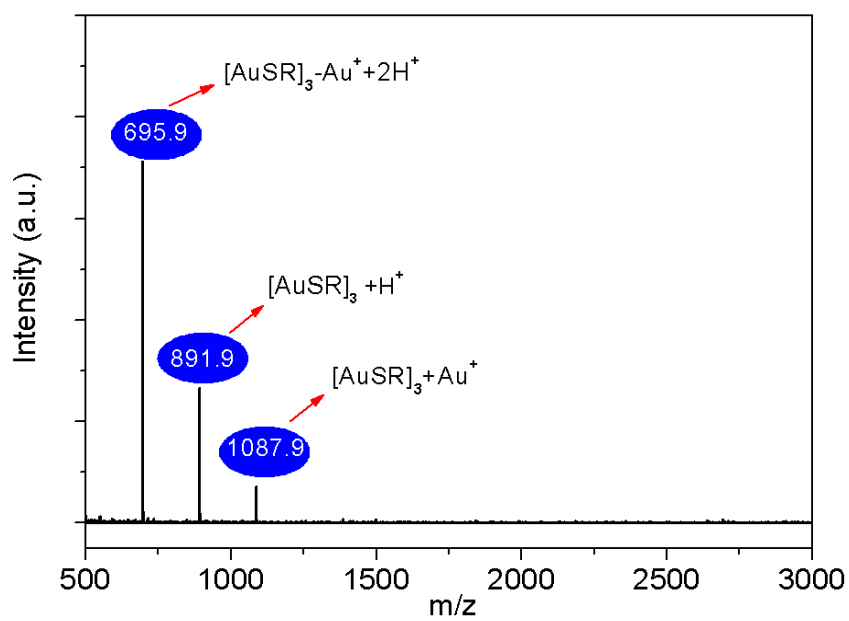
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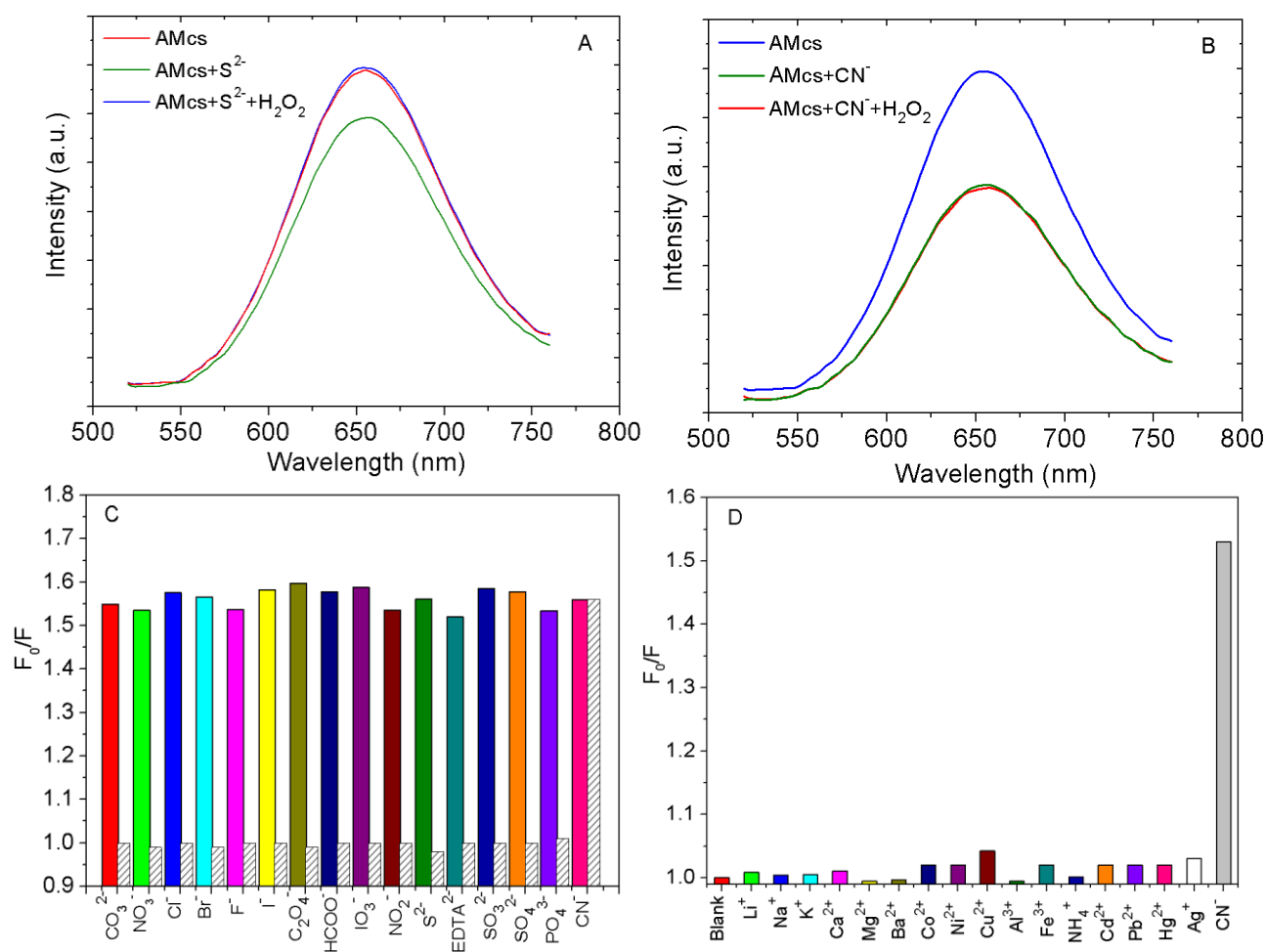
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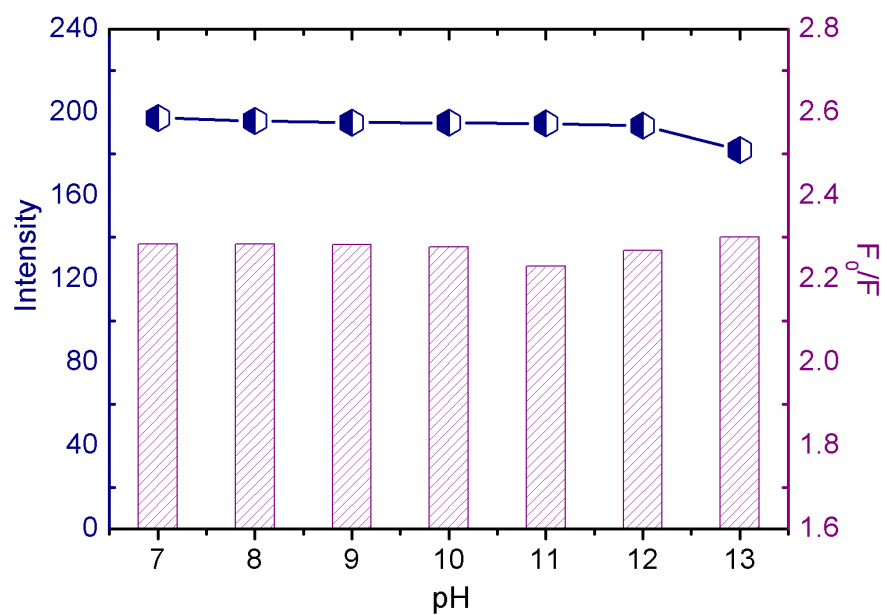
**Figure S1.** (A) Au 4f and (B) S 2p XPS spectrum of the AMcs. (C) FTIR spectra of the as-prepared AMcs and (D) the MTA ligand. The absence of the absorption band at ca. 2565 cm<sup>-1</sup> ( $\nu_{S-H}$ ) in AMcs indicates the ligation of the MTA ligand, which is in agreement with the XPS spectra.<sup>1</sup>



**Figure S2.** MALDI-TOF mass spectrum for the as-prepared AMcs by using 2, 5-dihydroxy-benzoic acid (DHB) as matrix (R represents the triazole group).



**Figure S3.** (A) Phosphorescence response of the AMcs toward  $S^{2-}$  (10  $\mu$ M) with and without the addition of  $H_2O_2$  (0.2 mM). (B) Phosphorescence response of the AMcs toward  $CN^-$  (10  $\mu$ M) in the absence and in the presence of  $H_2O_2$  (0.2 mM). (C) Selectivity of the AMcs for  $CN^-$  over other anions (the concentrations of the detected anions were all 10  $\mu$ M) and (color bar) phosphorescence response of the AMcs toward  $CN^-$  in the presence of 20  $\mu$ M interfering anions ( $H_2O_2$  was used as the making agent in the case of  $S^{2-}$ ). (D) Relative phosphorescence intensity changes toward 1  $\mu$ M of common metal ions in the presence of 0.01 mM EDTA, 0.2 mM GSH. In fact, the possible interferences of the metal ions could be effectively overcome by using the sensing film-based sensing strategy.

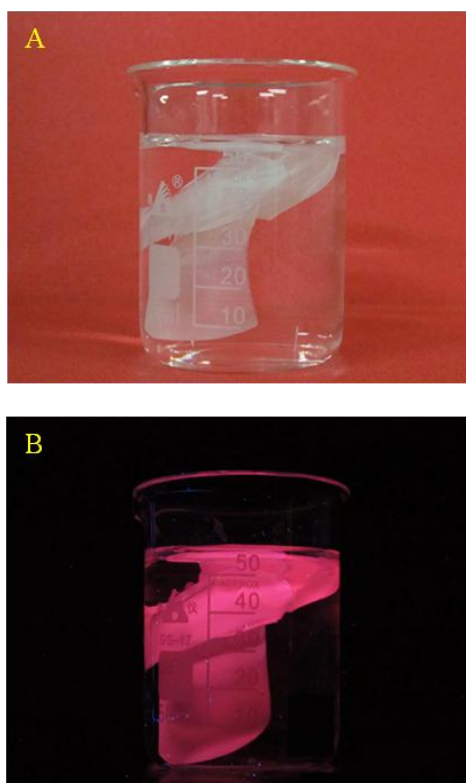


**Figure S4.** Phosphorescence response of the AMCs toward 20  $\mu\text{M}$   $\text{CN}^-$  in different pH solution and the corresponding phosphorescence intensity changes of the AMCs upon addition of different pH solution alone.

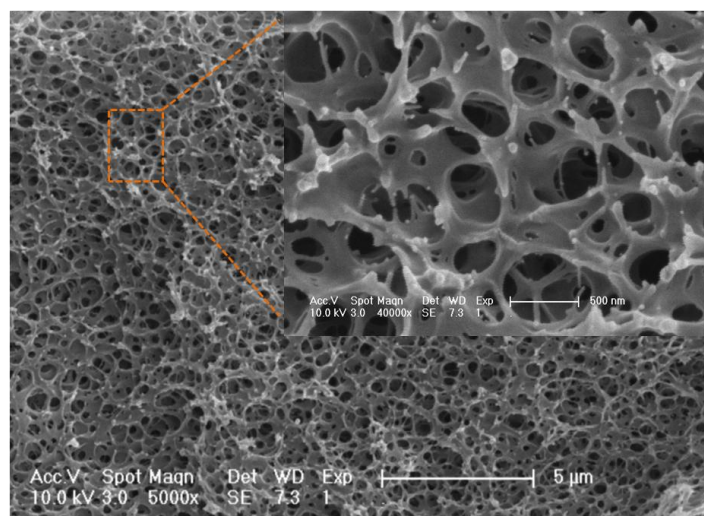
**Table S1.** Structural parameters extracted from quantitative EXAFS curve-fitting

<b>Sample</b>	<b>Bond</b>	<b><math>R</math> (Å)</b>	<b><math>N</math></b>	<b><math>\sigma^2</math></b>	<b><math>\Delta E</math>(eV)</b>	<b><math>R</math>-factor</b>
<b>AMcs</b>	Au-S	1.93	2	0.005	5.2	0.014
<b>CN1</b>	Au-S/C	1.92/1.55	1/1	0.003	4.3	0.044
<b>CN2</b>	Au-C	1.92	1.8	0.002	5.0	0.041

$R$ (Å): inter-atomic distance,  $N$ : coordination number,  $\sigma^2$ : mean-square relative displacement (Debye–Waller factor),  $\Delta E$ : shift of  $E_0$  value,  $R$ -factor is a measure of the misfit distribution over both data sets (%).



**Figure S5.** Photographs of the porous film after stored in ethanol for 5 month (A) under day light and (B) under UV illumination.



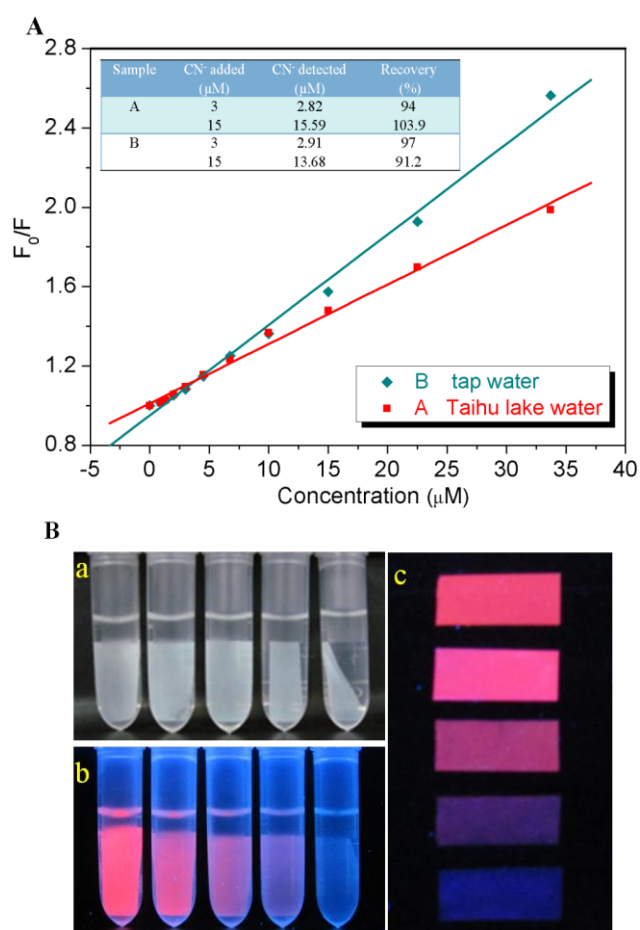
**Figure S6.** SEM image of the porous film after the detection procedure.



## Additional Analytical Applications

### 1) Detection of cyanide in real water sample:

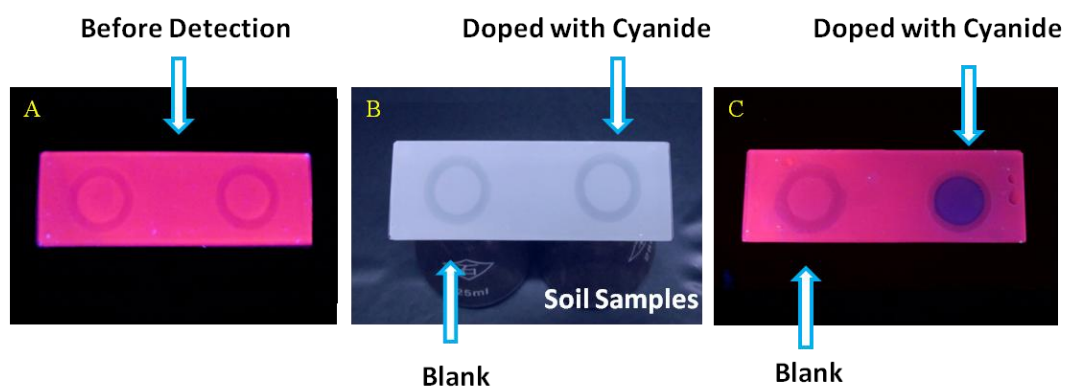
The as-prepared molecular gold (I) cluster can also be applied to detect cyanide in real water samples such as tap water and Taihu lake water and excellent linear correlations are obtained in both cases. The recoveries of these measurements are 91.2-97% and 94-103.9% for tap water and Taihu lake water, respectively. More importantly, the molecular gold (I) cluster-based porous film can be immersed directly into Taihu lake water samples spiked with cyanide to transform the real-time cyanide concentration into ratiometric signals as shown in Figure S7.



**Figure S7.** (A) Phosphorescence response of the AMCs solution toward  $\text{CN}^-$  in tap water and Taihu lake water. Inset showed the corresponding recovery data. (B) Visual detection of cyanide in Taihu lake water spiked with increasing amount of cyanide: 0, 2.5  $\mu\text{M}$ , 10  $\mu\text{M}$ , 30  $\mu\text{M}$ , 60  $\mu\text{M}$ .

## 2) Detection of cyanide in real soil sample:

Due to their wide industrial use, accidental cyanide leaks do occur (For example, on 26<sup>th</sup> Feb, 2013, a snow plough had mistakenly hit a tank containing cyanide liquid waste in northern Japan, causing five tons of liquid waste containing 125,000 lethal doses of cyanide seeped out). The leaked cyanide could seep in soil, which would result in serious contamination of the ground water and even drinking water. In this connection, the porous sensing film is further applied to screening cyanide in soil. As shown in Figure S8. It is worth noting that the porous film does not directly contact with the soil samples, and therefore, the quencher is solely the leaked HCN vapor that penetrates through the soil and the sensing film.



**Figure S8.** Additional application of the porous film in screening cyanide in soil.

## Reference

- (1)Shibu, E. S.; Muhammed, M. A. H.; Tsukuda, T.; Pradeep, T. *J. Phys. Chem. C* **2008**, *112*, 12168–12176.