### **Electronic Supplementary Information (ESI)**

# A highly selective and sensitive recyclable colorimetric Hg<sup>2+</sup> sensor based on porphyrin-functionalized polyacrylonitrile fiber

Xiaoxing Liu,<sup>*a,b*</sup> Xiaojuan Liu,<sup>*a,b*</sup> Minli Tao<sup>\**a,b*</sup> and Wenqin Zhang<sup>\**a,b*</sup>

<sup>a</sup>Department of Chemistry, School of Sciences, Tianjin University, Tianjin, 300072, P. R. China.

<sup>b</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China.

E-mail: mltao@tju.edu.cn and zhangwenqin@tju.edu.cn; Fax: +86-22-27403475; Tel: +86-22-27890922

#### 1. Synthesis of 5,10,15-Tris(4-aminophenyl)-20-phenylporphyrin (T<sub>A</sub>PP)

Tetraphenylporphyrin (TPP) was prepared according to literature procedure.<sup>1</sup> The T<sub>A</sub>PP was prepared by a reported method.<sup>2</sup> Tetraphenylporphyrin (TPP) (3.0 g, 4.88 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (300 mL) under a nitrogen atmosphere, then fuming nitric acid (6.0 mL, 132.75 mmol) was added dropwise over a period of 30 min at 0-5 °C. The reaction mixture was stirred for another 2 h and then quenched with aqueous ammonia solution slowly. The organic layer was washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel eluted with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:1 v/v) to give 5,10,15-Tris(4-nitrophenyl)-20-phenylporphyrin (T<sub>N</sub>PP, 1.9 g, 51.9%).

The  $T_NPP$  (2.0 g, 2.67 mmol) was dissolved in concentrated HCl (80 mL) under nitrogen,  $SnCl_2 \cdot 2H_2O$  (6.0 g, 26.59 mmol) was added and stirred for 1 h at 65 °C. The

reaction mixture was cooled and poured into ice-water (300 mL) and then was extracted with  $CH_2Cl_2$  after adjusting the pH to 8 using aqueous ammonia solution. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and purified by column chromatography on silica gel eluted with ethyl acetate/ $CH_2Cl_2$  (2:1 v/v) to give 1.1 g of the T<sub>A</sub>PP with a yield of 62.4%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (s, 6H), 8.85 (d, *J* = 4.7 Hz, 2H), 8.25 (d, *J* = 6.0 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 6H), 7.83-7.75 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 6H), 4.04 (s, 6H), -2.67 (s, 2H). MALDI-TOF (*m/z*): calcd M<sup>+</sup>: 659.2797; found [M+H]<sup>+</sup>: 660.2679.

## 2. Synthesis of 5,10,15-Tris[4-(3,5-dichlorotriazinyl)aminophenyl]-20phenylporphyrin (CT<sub>A</sub>PP)

T<sub>A</sub>PP (1.0 g, 1.52 mmol) dissolved in THF (60 mL) was added into a solution of cyanuric chloride (0.85 g, 4.60 mmol) and triethylamine (TEA) (0.55 g, 5.44 mmol) in THF (30 mL) at 0 °C. After stirring for 30 min, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (2:1 v/v) to give the CT<sub>A</sub>PP (1.5 g, 89.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.90 (s, 8H), 8.26 (t, *J* = 9.8 Hz, 8H), 8.08 (s, 3H), 7.99 (d, *J* = 8.4 Hz, 6H), 7.35 (s, 3H), -2.76 (s, 2H). MALDI-TOF (*m/z*): calcd M<sup>+</sup>: 1100.0971; found [M+3H]<sup>3+</sup>: 1103.2770.

#### 3. Acid exchange capacity of the produced fiber

Dried PAN<sub>A</sub>F (0.200 g) was immersed into 20 mL of 0.100 mol/L HCl for 6 h. The neutralized fiber was then filtered and the concentration of the remaining solution was determined by titration with 0.100 mol/L NaOH. The exchange capacity was calculated based on the consumption of the acid.<sup>3</sup>

#### 4. Functionality of CT<sub>A</sub>PP-PAN<sub>A</sub>F

The functionality (mmol/g) can be used to illustrate the extent of modification. Functionality =  $(W_2-W_1)/(W_1 \times M) \times 1000$ . For the immobilization step,  $W_1$  and  $W_2$  are the weights of PAN<sub>A</sub>F and CT<sub>A</sub>PP-PAN<sub>A</sub>F, respectively; M is the relative molecular mass increased after the immobilization.

Functionality = 
$$\frac{(0.35 \text{ g} - 0.30 \text{ g})}{994.3 \text{ g mol}^{-1} \times 0.35 \text{ g}} \times 1000 = 0.14 \text{ mmol g}^{-1}$$

#### 5. Sensitivity study

Two methods are used to investigate the sensitivity of the sensor: One way is to keep the total mole number of  $Hg^{2+}$  unchanged by increasing the volume of solutions to ensure that there is sufficient amount of  $Hg^{2+}$  to be complexed by  $CT_APP-PAN_AF$ ; Another way is to decrease the total mole number of  $Hg^{2+}$  in solutions gradually with fixed volume.

In the first method, 8 mg of  $CT_APP-PAN_AF$  is used. The corresponding functionality of the fiber is 0.14 mmol g<sup>-1</sup> (see ESI† 4), so there are  $1.1 \times 10^{-6}$  mol porphyrin functional groups. Along with the gradient decrease of the concentration of  $Hg^{2+}$ , the volume required is increased accordingly. Take the concentration of  $1 \times 10^{-7}$  mol L<sup>-1</sup> as an example, the required volume of the solution must be more than 11 L. In order to afford sufficient  $Hg^{2+}$ , the volume of the solution was set as 50 L. In this case, the colorimetric detection limit is  $1 \times 10^{-7}$  mol L<sup>-1</sup> based on the naked-eye observation.

Concentration	Volume of solution	Response time
10 <sup>-4</sup> mol L <sup>-1</sup>	50 mL	15 min
10 <sup>-5</sup> mol L <sup>-1</sup>	500 mL	1 h
10 <sup>-6</sup> mol L <sup>-1</sup>	5 L	5 h
10 <sup>-7</sup> mol L <sup>-1</sup>	50 L	24 h

In the second method, the volume of solutions is fixed at 1 L, and the mole number of Hg<sup>2+</sup> in the solutions decreases gradually. In this case, the visual detection limit is  $1 \times 10^{-6}$  mol L<sup>-1</sup> (The dosage of CT<sub>A</sub>PP-PAN<sub>A</sub>F is also 8 mg).

Concentration	Volume of solution	Response time
10 <sup>-4</sup> mol L <sup>-1</sup>	1 L	15 min
10 <sup>-5</sup> mol L <sup>-1</sup>	1 L	1 h
10 <sup>-6</sup> mol L <sup>-1</sup>	1 L	15 h

#### References

- 1 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
- 2 W. J. Kruper Jr, T. A. Chamberlin and M. Kochanny, J. Org. Chem., 1989, 54, 2753-2756.
- A. A. Shunkevich, Z. I. Akulich, G. V. Mediak and V. S. Soldatov, *React. Funct. Polym.*, 2005, **63**, 27-34.