Supplementary Data

Self-Assembled Tetraphenylethylene Macrocycle Nanofibrous Materials for the Visual Detection of Copper (II) in Water Solution

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Measurements:

$^1$H NMR and $^{13}$C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in CDCl$_3$. Infrared spectra were recorded on BRUKER EQUINAX55 spectrometer. Absorption spectra were recorded on a Hewlett Packard 8453 UV–Vis spectrophotometer. Mass spectrum was measured on an IonSpec 4.7 Tesla FTMS instrument. Field emission scanning electron microscopy (FE-SEM) images were taken on a FEI Sirion 200 electron microscope operating at 10 kV. Cyclic voltammetry (CV) was measured on a Chenghua CHI 830C. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K. The fluorescence spectra for AIE effect were measured after water was added and let the mixture stand for 4 h at 298 K. For measuring change of fluorescence intensity with copper ion or other metal ions, all mixtures of tetraphenylethylene (TPE) Schiff base macrocycle 3 and metal ions were left standing for 8 h at 298 K before their fluorescence spectra were measured.

UV-Vis titration was carried out by gradual addition of concentrated solution of copper ions into solution of the probe 3 in H$_2$O/THF 2:1 so that the concentration of the probe 3 was approximately invariable. The absorption spectra were measured as soon as the metal ion was added. Association constant K was calculated by nonlinear curve fitting according to the following formula (Eq. 6), which was derived in a similar way to literature.  

$$\text{The reaction formula could be expressed as equation 1.}$$

$$3 + 2\text{Cu} \rightarrow 3\text{Cu}^2$$  \hspace{1cm} (Eq. 1)

Therefore, the association constant K could be written as equation 2.

$$K = \frac{[3\text{Cu}^2]}{[3][\text{Cu}]^2} = \frac{[3\text{Cu}^2]}{([3]_0 - [3\text{Cu}^2])([\text{Cu}]_0 - 2[3\text{Cu}^2])^2}$$  \hspace{1cm} (Eq. 2)

Among the above equation,

[3Cu$_2$] denotes the molar concentration of 1:2 complex of 3 with copper ion at equilibrium;

[3] denotes the molar concentration of 3 at equilibrium;

[Cu] denotes the molar concentration of copper ion at equilibrium;

[3]$_0$ denotes the total molar concentration of 3;

[Cu]$_0$ denotes the total molar concentration of copper ion.

Equation 4 can be obtained from the equation 2 by simply mathematic derivation.
Due to being a new absorption at 595 nm and almost no change of the absorption maximum wavelength during titration, it could be considered that this absorption is mainly ascribed to the 1:2 complex of 3 with copper ion. Therefore, equation 6 can be derived according to the absorbance change at 595 nm by equation 5.

\[
[3\text{Cu}_2] = \frac{\Delta A}{\varepsilon}
\]  
(Eq. 5)

\(\Delta A\) denotes the absorbance difference of 3 at 595 nm without and with addition of copper ion. 
\(\varepsilon\) denotes the molar extinction coefficient of 1:2 complex of 3 with copper ion.

\[
[Cu]_0 = 2[3\text{Cu}_2] + \sqrt{\frac{[3\text{Cu}_2]}{K([3]_0 - [3\text{Cu}_2])}}
\]  
(Eq. 6)

In order to calculate the association constant \(K\) by Origin software without further deriving equation 6, here \([Cu]_0\) was directly acted as dependent variable and the absorbance difference \(\Delta A\) as independent one to carry out the nonlinearly curve fitting (Fig. S1).

![Graph](image)

**Fig. S1.** Change of absorbance difference with concentration of copper ion. The solid curve is the result from fitting.

Fig. S2. UV-Vis spectrum of a suspension of 3 in H$_2$O/THF 9:1 ([3] = 1.0×10$^{-6}$ M).

Fig. S3. Dynamic light scattering (DLS) diagram of a suspension of 3 in H$_2$O/THF 9:1 ([3] = 1.0×10$^{-5}$ M).
Calculation of detection limit: The detection limit was determined from the fluorescence titration data based on a reported method [1-3]. According to the result of titration experiment, the fluorescent intensity data at 595 nm were normalized between the minimum intensity and the maximum intensity. A linear regression curve was then fitted to these normalized fluorescent intensity data, and the point at which this line crossed the axis was considered as the detection limit (1.1 × 10⁻⁹ M).


Fig. S4. Plot of normalized fluorescence intensity of 3 as a function of log [Cu²⁺] in H₂O/THF (9:1) (λₑₓ = 365 nm). (Log [Cu²⁺] = -8.941).
**Fig. S5.** Fluorescence spectrum change of 3 with concentrations of copper ions in river (A), lake (B) and tap (C) H$_2$O/THF 9:1. For river water, [Cu$^{2+}$] = 0, 0.010, 0.020, 0.050, 0.10, 0.20, 0.50, 1.0, 2.0, 5.0, 10.0/10$^{-6}$ M; For lake water, [Cu$^{2+}$] = 0, 0.20, 0.30, 0.50, 0.60, 0.80, 1.0, 2.0, 3.0, 5.0, 10/10$^{-6}$ M; For tap water, [Cu$^{2+}$] = 0, 0.50, 1.0, 2.0, 3.0, 4.0, 5.0, 10/10$^{-6}$ M; [3] = 2.0 × 10$^{-6}$ M. Insets: curve of fluorescence intensity vs logarithm of Cu (II) concentration.

**Fig. S6.** $^1$H NMR spectrum of compound 2 in CDCl$_3$. 
Fig. S7. $^{13}$C NMR spectrum of compound 2 in CDCl$_3$.

Fig. S8. IR spectrum of compound 2.
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Fig. S9. HRMS spectrum of compound 2

Fig. S10. $^1$H NMR spectrum of compound 3 in CDCl$_3$. 
Fig. S11. $^{13}$C NMR spectrum of compound 3

Fig. S12. IR spectrum of compound 3.
Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences

High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS
Card Serial Number: W112 2078
Sample Serial Number: 1*
Operator: HuaQin Date: 2012/12/21
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**Fig. S13.** HRMS spectrum of compound 3.