

Supplementary Data

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

Hai-Tao Feng,^a Song Song,^a Yi-Chang Chen,^a Chang-Hong Shen,^b and Yan-Song Zheng^{a*}

^aSchool of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China; ^bSchool of Chemistry and Materials Science, South Central University for Nationalities, Wuhan 430074, China.

Measurements:

¹H NMR and ¹³C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in CDCl₃. 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 H₂O/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 nonlinearly curve fitting according to the following formula (Eq. 6), which was derived in a similar way to literature.¹

The reaction formula could be expressed as equation 1.



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

$$K = \frac{[\mathbf{3}\text{Cu}_2]}{[\mathbf{3}][\text{Cu}]^2} = \frac{[\mathbf{3}\text{Cu}_2]}{([\mathbf{3}]_0 - [\mathbf{3}\text{Cu}_2])([\text{Cu}]_0 - 2[\mathbf{3}\text{Cu}_2])^2} \quad (\text{Eq. 2})$$

Among the above equation,

[**3**Cu₂] 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.

$$([\text{Cu}]_0 - 2[\text{3Cu}_2])^2 = \frac{[\text{3Cu}_2]}{K([\text{3}]_0 - [\text{3Cu}_2])} \quad (\text{Eq. 3})$$

$$[\text{Cu}]_0 = 2[\text{3Cu}_2] \pm \sqrt{\frac{[\text{3Cu}_2]}{K([\text{3}]_0 - [\text{3Cu}_2])}} \quad (\text{Eq. 4})$$

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.

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

ΔA denotes the absorbance difference of **3** at 595 nm without and with addition of copper ion.
 ε denotes the molar extinction coefficient of 1:2 complex of **3** with copper ion.

$$[\text{Cu}]_0 = \frac{2\Delta A}{\varepsilon} \pm \sqrt{\frac{\frac{\Delta A}{\varepsilon}}{K([\text{3}]_0 - \frac{\Delta A}{\varepsilon})}} \quad (\text{Eq. 6})$$

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

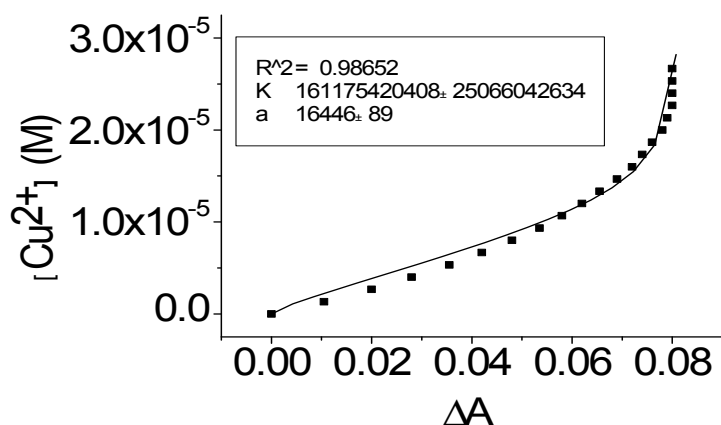


Fig. S1. Change of absorbance difference with concentration of copper ion. The solid curve is the result from fitting.

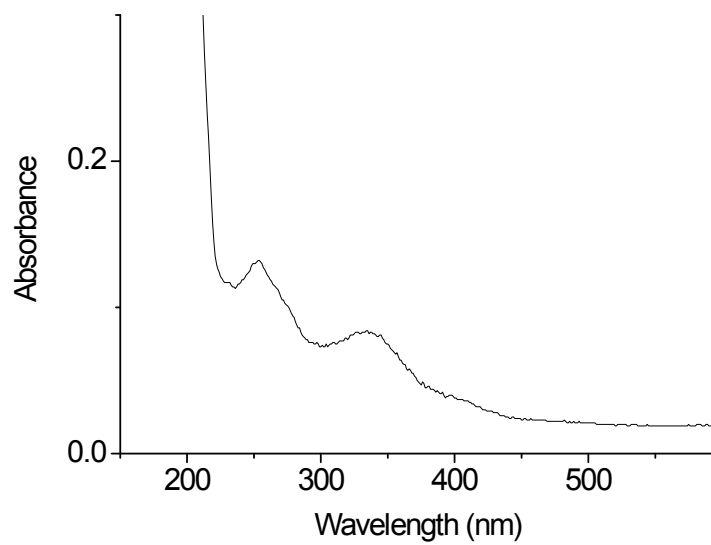


Fig. S2. UV-Vis spectrum of a suspension of **3** in H₂O/THF 9:1 ([**3**] = 1.0×10⁻⁶ M).

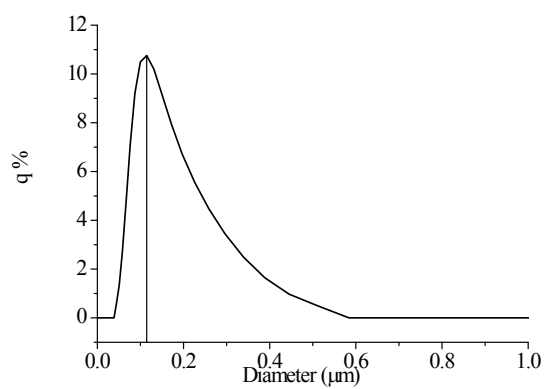
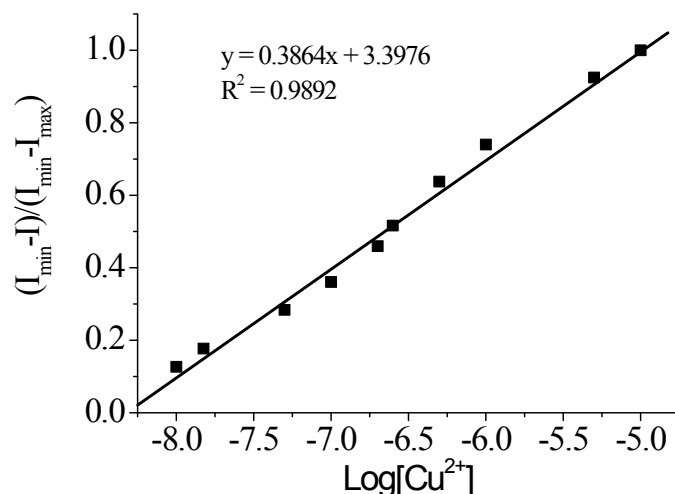


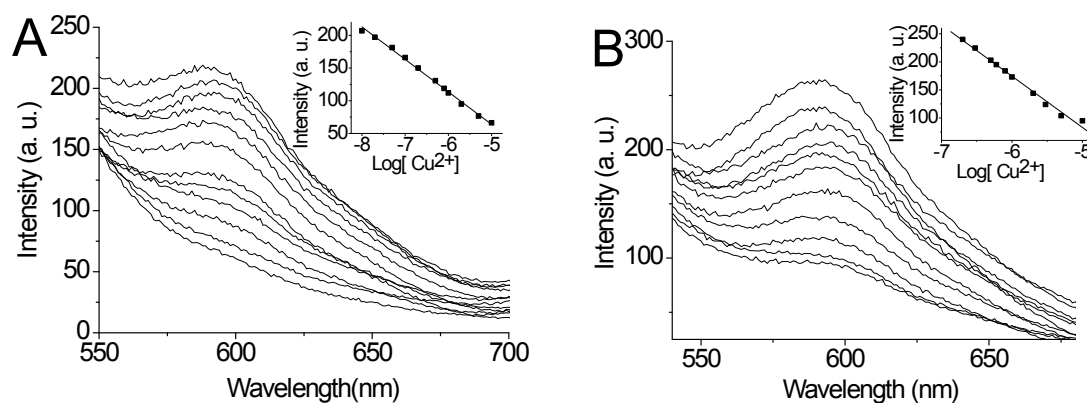
Fig. S3. Dynamic light scattering (DLS) diagram of a suspension of **3** in H₂O/THF 9:1 ([**3**] = 1.0×10⁻⁵ M).



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).

1. L. Yuan, W.Y. Lin, *Chem. Eur. J.* 2011, 17, 689 – 696.
2. M. Shortreed, R. Kopelman, M. Kuhn, B. Hoyland, *Anal. Chem.* 1996, 68, 1414-1418.
3. W. Lin, L. Yuan, L. Long, C. Guo, J. Feng, *Adv. Funct. Mater.* 2008, 18, 2366-2372.

Fig. S4. Plot of normalized fluorescence intensity of **3** as a function of $\log [\text{Cu}^{2+}]$ in $\text{H}_2\text{O}/\text{THF}$ (9:1) ($\lambda_{\text{ex}} = 365$ nm). ($\text{Log} [\text{Cu}^{2+}] = -8.941$).



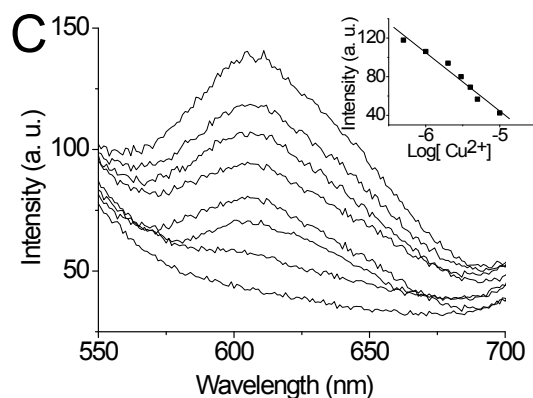


Fig. S5. Fluorescence spectrum change of **3** with concentrations of copper ions in river (A), lake (B) and tap (C) H₂O/THF 9:1. For river water, [Cu²⁺] = 0, 0.010, 0.020, 0.050, 0.10, 0.20, 0.50, 0.80, 1.0, 2.0, 5.0, 10.0/10⁻⁶ M; For lake water, [Cu²⁺] = 0, 0.20, 0.30, 0.50, 0.60, 0.80, 1.0, 2.0, 3.0, 5.0, 10/10⁻⁶ M; For tap water, [Cu²⁺] = 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.

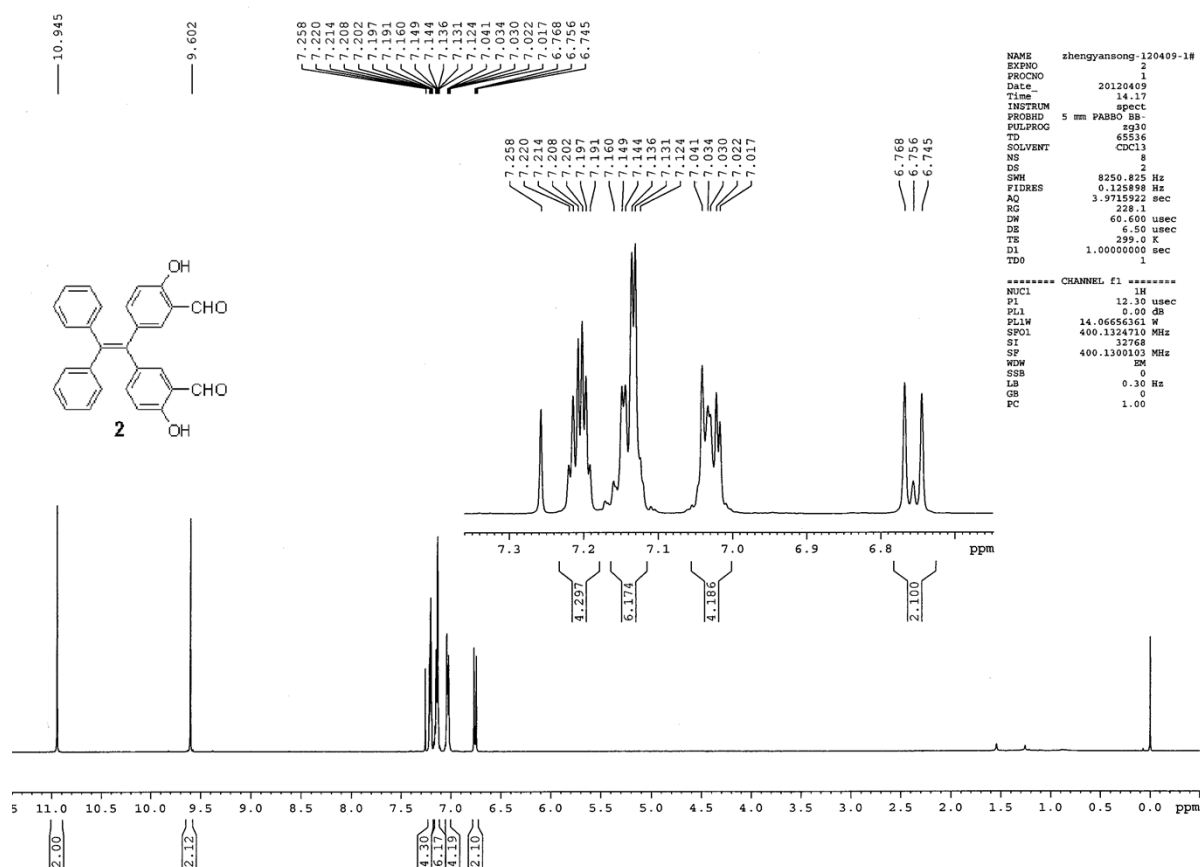


Fig. S6. ¹H NMR spectrum of compound **2** in CDCl₃.

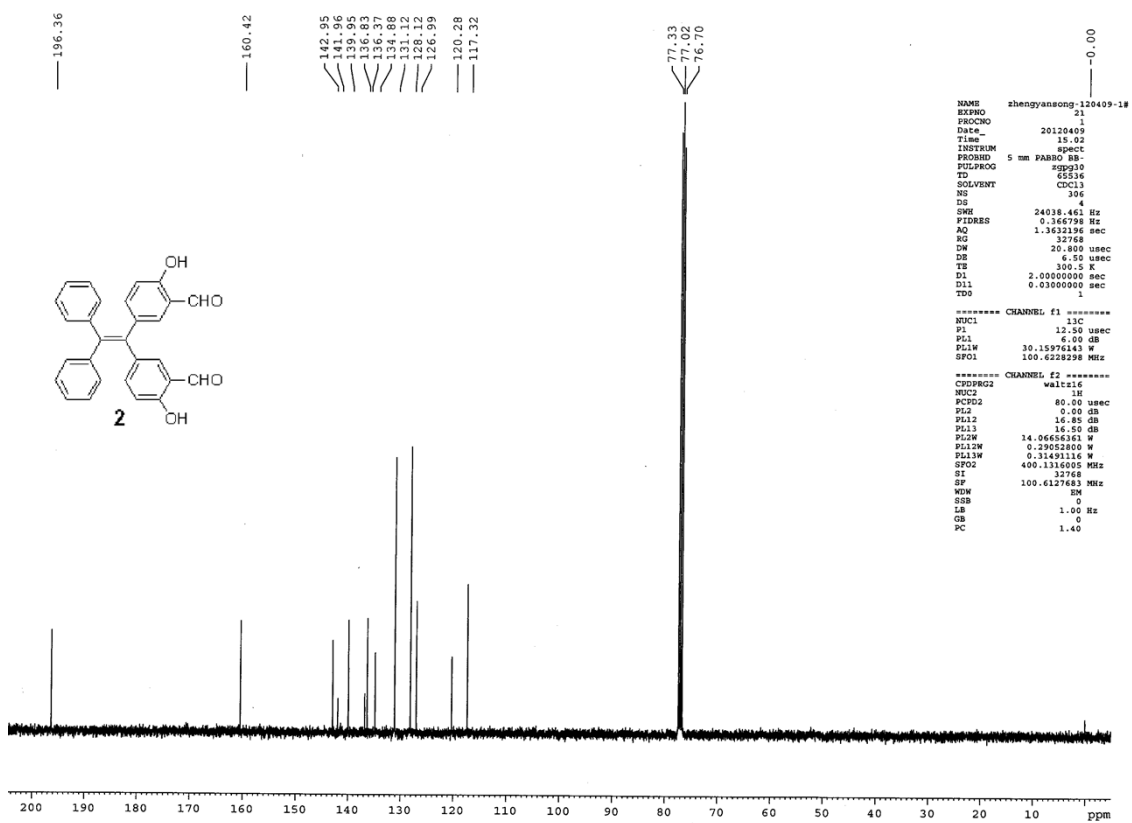


Fig. S7. ¹³C NMR spectrum of compound 2 in CDCl₃

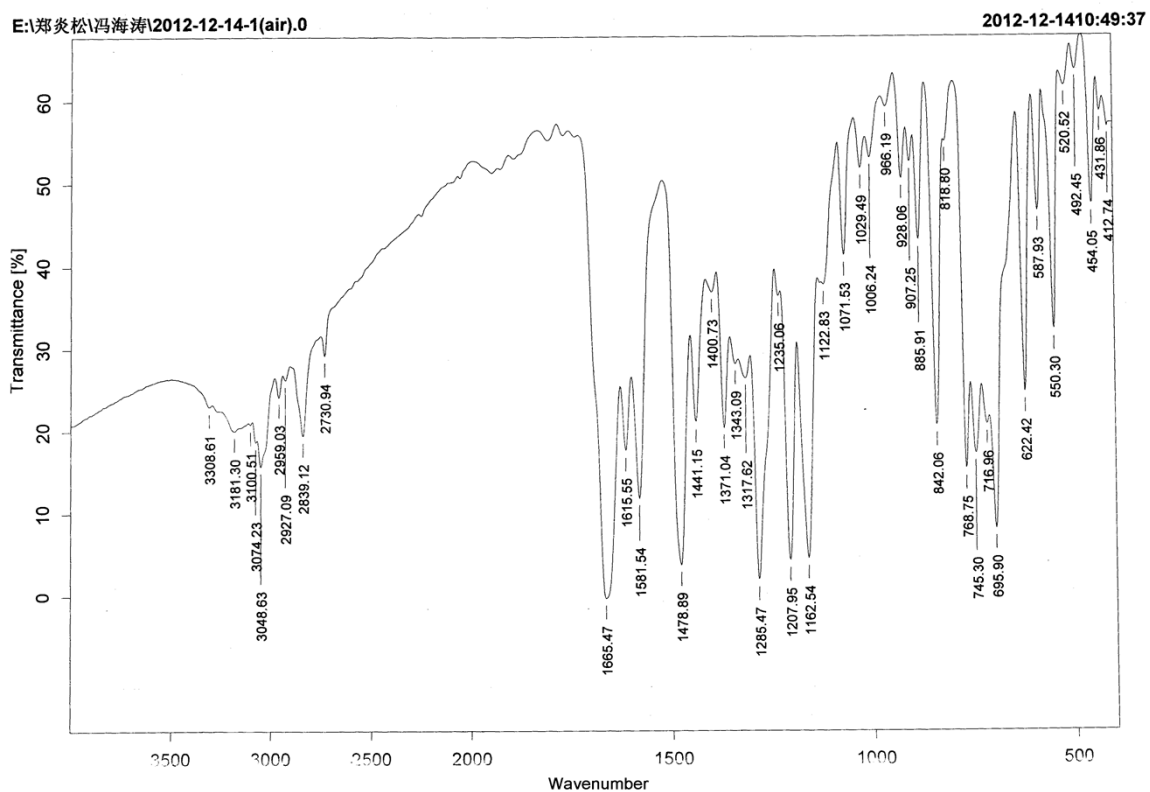
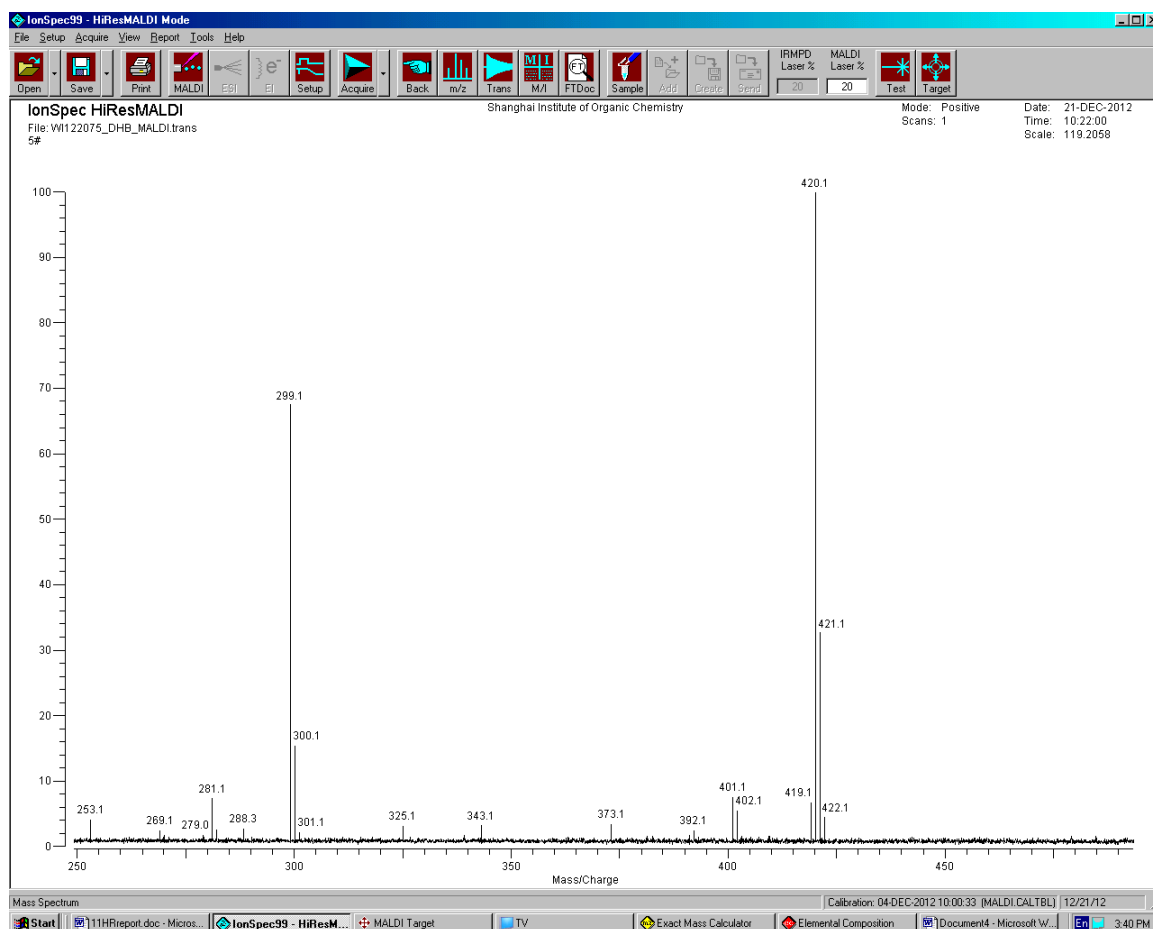


Fig. S8. IR spectrum of compound 2.



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Chinese Academic of Sciences

High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI12 2076

Sample Serial Number: 5#

Operator : HuaQin Date: 2012/12/21

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 420.1356 ± 0.002

Charge = +1

Possible Elements:

Element	Exact Mass	Min	Max
C	12.000000	0	100
H	1.007825	0	100
O	15.994915	0	100

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer

Minimum DBE = 0

Search Results:

Number of Hits = 1

m/z	Delta m/z	DBE	Formula
420.13561	-0.00001	19.0	C ₂₈ H ₂₀ O ₄ ⁺¹

Fig. S9. HRMS spectrum of compound 2

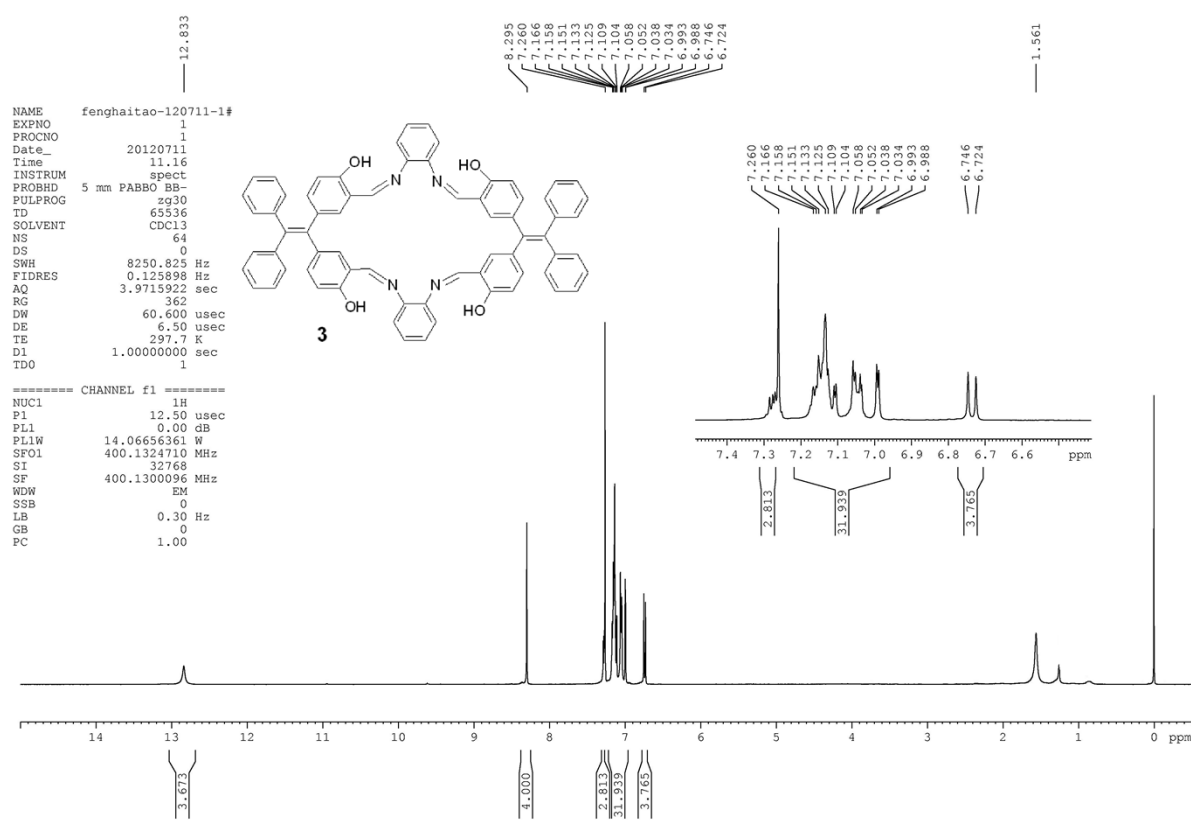


Fig. S10. ¹H NMR spectrum of compound 3 in CDCl₃.

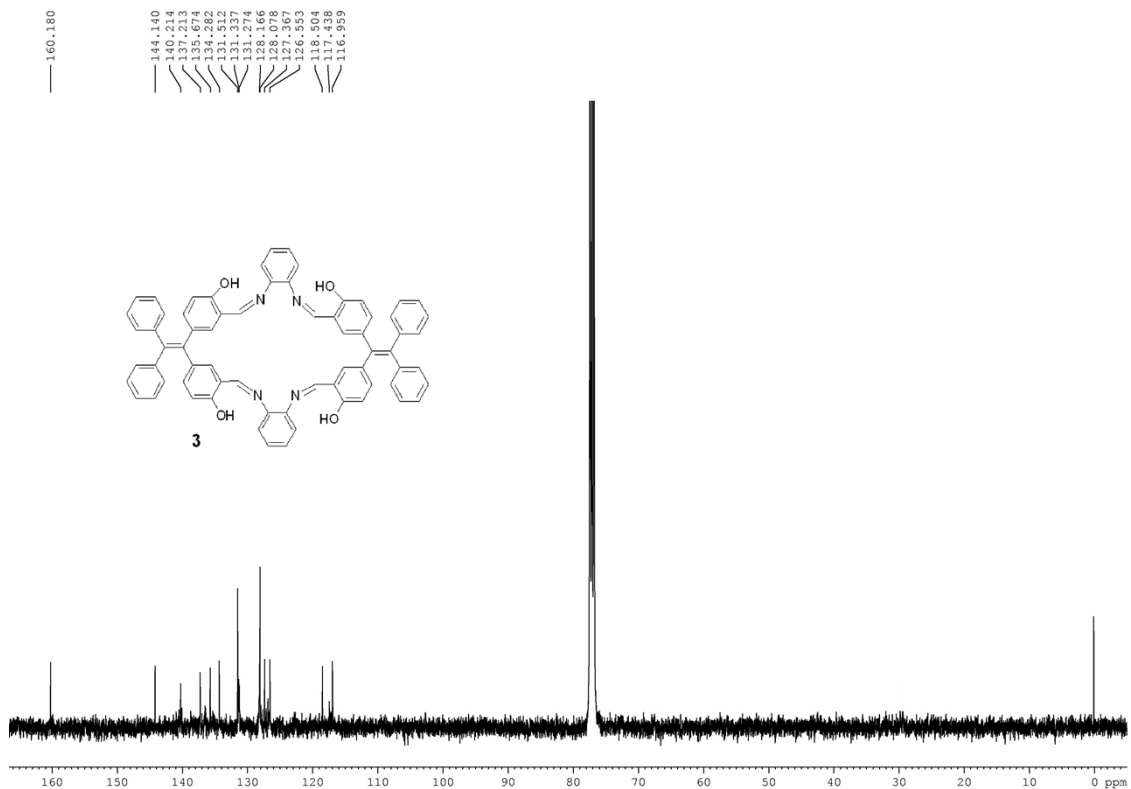


Fig. S11. ¹³C NMR spectrum of compound 3

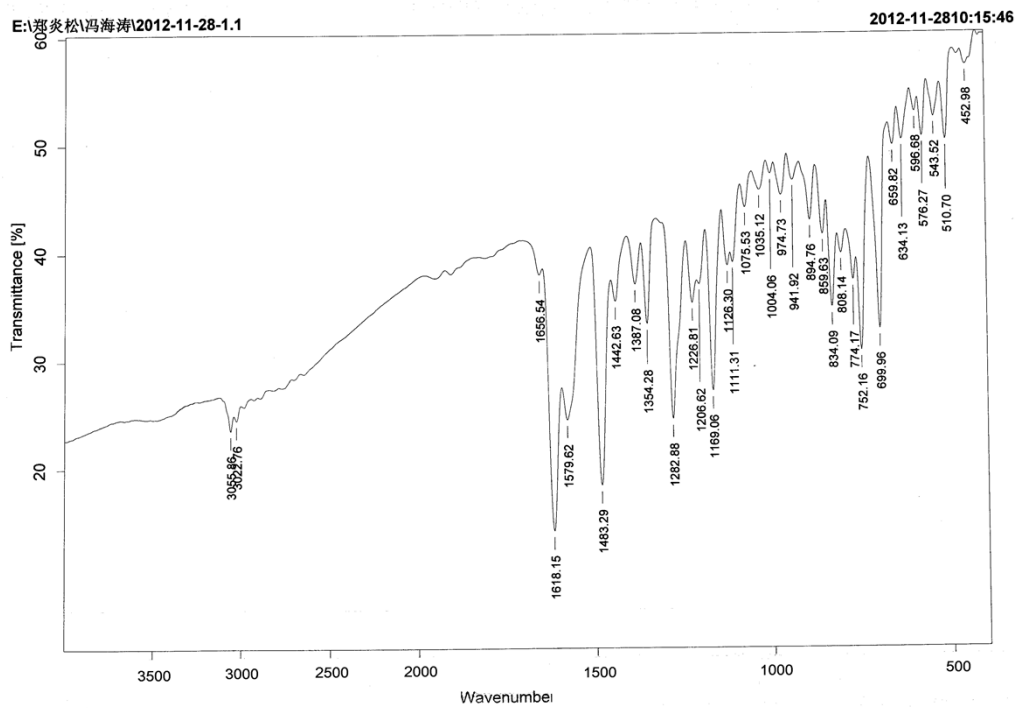
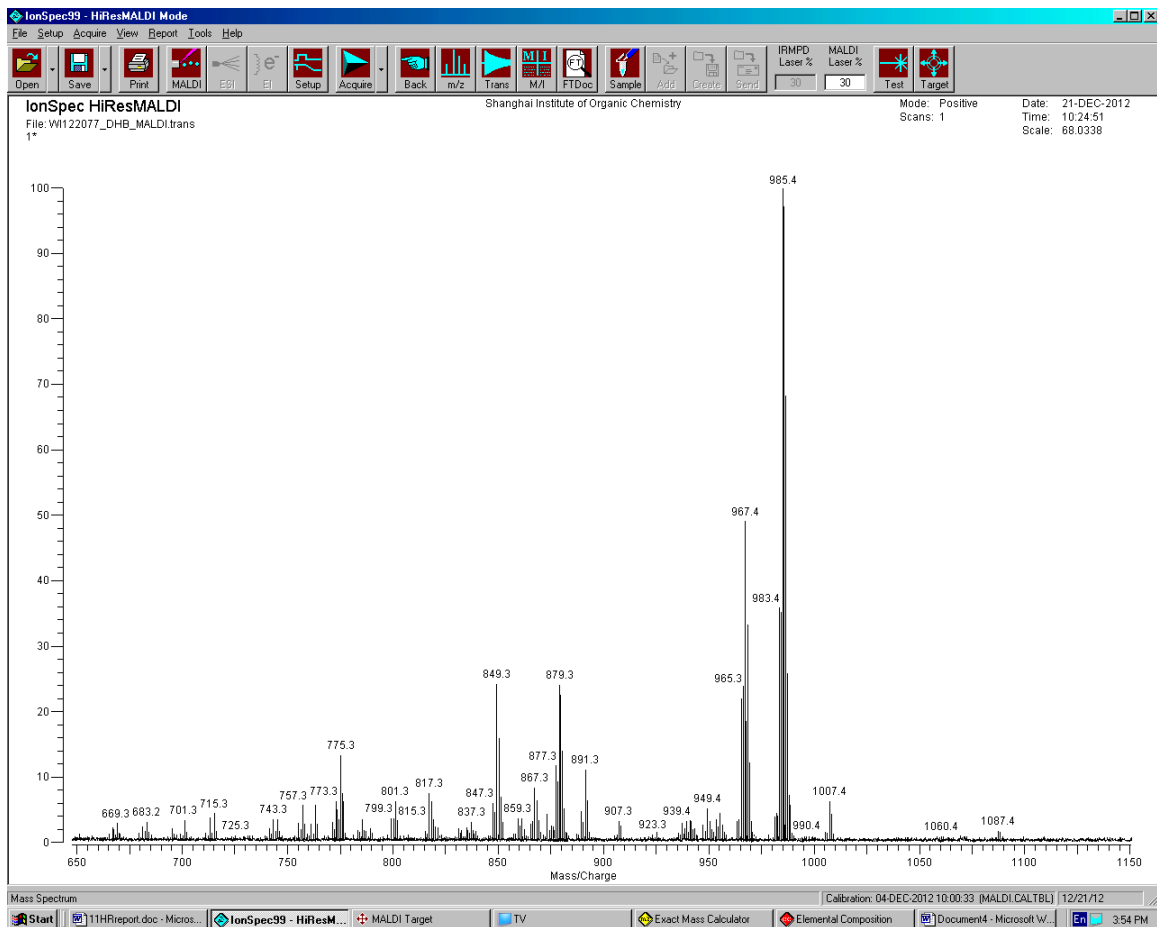


Fig. S12. IR spectrum of compound 3.



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High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI12 2078

Sample Serial Number: 1*

Operator : HuaQin Date: 2012/12/21

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 985.3773 ± 0.004

Charge = +1

Possible Elements:

Element	Exact Mass	Min	Max
C	12.000000	0	100
H	1.007825	0	100
N	14.003074	0	5
O	15.994915	0	5

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer

Minimum DBE = 0

Search Results:

Number of Hits = 4

<u>m/z</u>	<u>Delta m/z</u>	<u>DBE</u>	<u>Formula</u>
985.37751	-0.00021	51.0	C ₇₁ H ₄₇ N ₅ O ⁺¹
985.37618	0.00112	46.0	C ₇₀ H ₅₁ NO ₅ ⁺¹
985.37885	-0.00155	50.5	C ₇₃ H ₄₉ N ₂ O ₂ ⁺¹
985.37483	0.00247	46.5	C ₆₈ H ₄₉ N ₄ O ₄ ⁺¹

Fig. S13. HRMS spectrum of compound 3.