

## *RSC Adv*

### *Supplementary Information*

**A  $\pi$ -extended luminogen with colorimetric and off/on fluorescent multi-channel detection for  $\text{Cu}^{2+}$  in high selectivity and sensitivity via nonarylamine-based organic mixed-valence**

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## 1 Optical Spectra

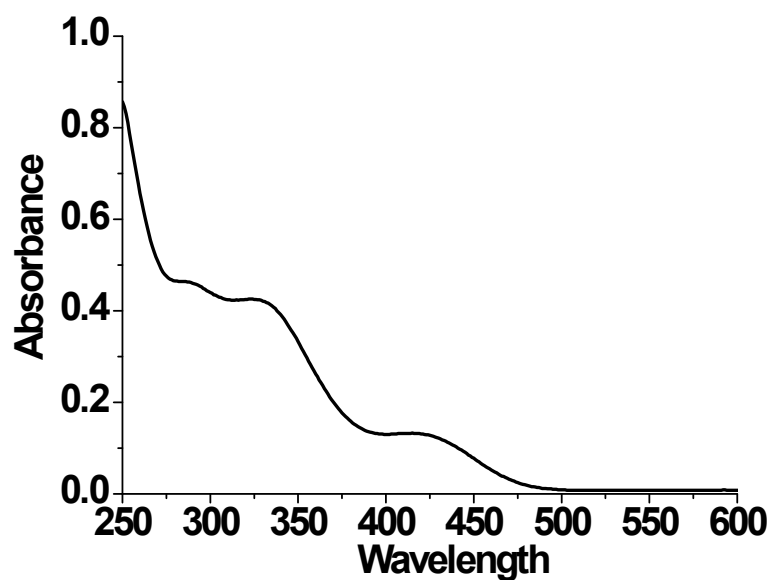


Figure. S1 UV-vis spectra of ITP-TPE ( $2 \times 10^{-5}$  M) in CH<sub>3</sub>CN solution.

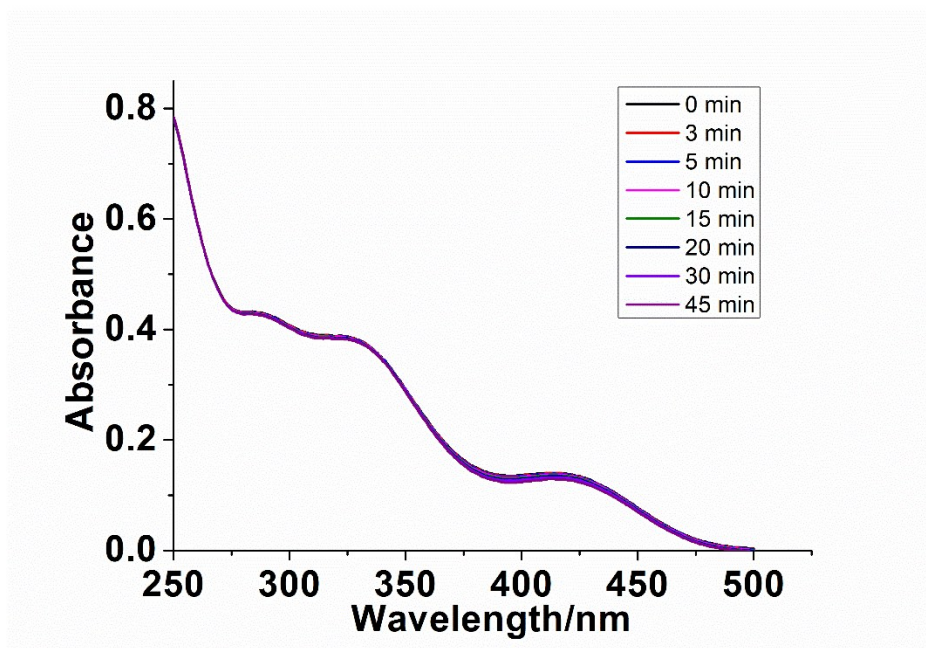
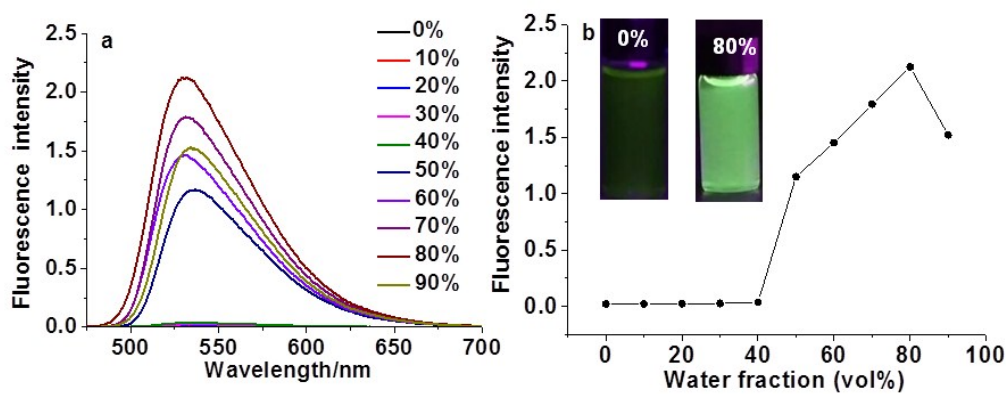
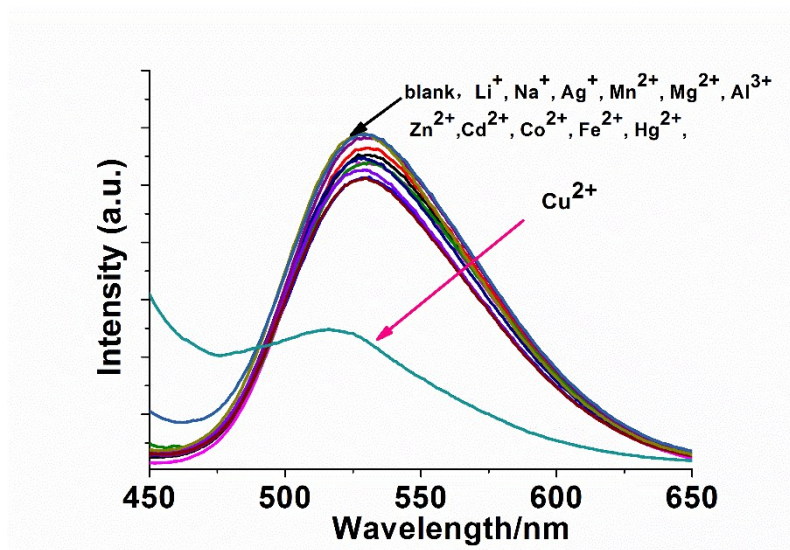


Figure. S2 UV-vis spectra of ITP-TPE ( $2 \times 10^{-5}$  M) in CH<sub>3</sub>CN solution at different irradiation time.



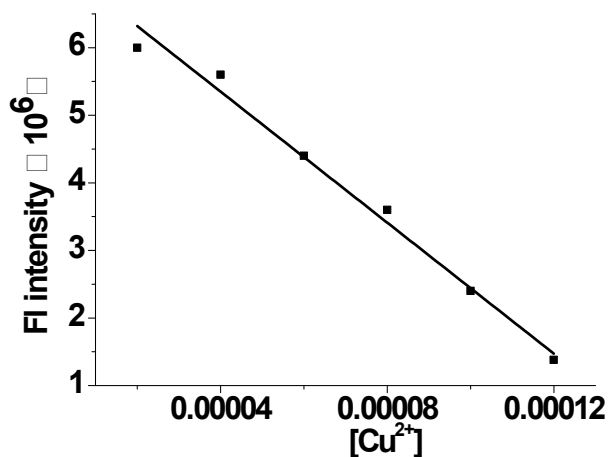
**Figure.S3** Fluorescence spectra of ITP-TPE (a) in  $\text{CH}_3\text{CN}$ -water mixtures ( $1.0 \times 10^{-5}$  M, with varied volumetric fractions of water; (b) the fluorescence intensity change spectra of ITP-TPE at different content of water.



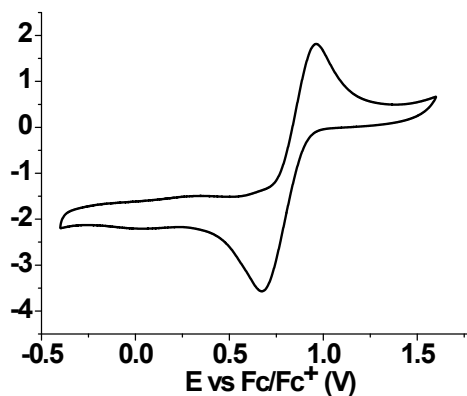
**Figure.S4** Back titration fluorescence spectra of ITP-TPE ( $2 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}$ -water (9:1) solution upon addition of 1 equiv. of various metal ions.

### Detection Limit Calculation for This Method <sup>S1</sup>:

Through fluorometric titrations, the detection limit for  $\text{Cu}^{2+}$  was determined. According to the definition, detection limit =  $3S_{\text{bi}}/k$ , where  $S_{\text{bi}}$  is standard deviation of 6 blank measurements and  $k$  is the slope obtained from the calibration curve. In this method, the standard deviation  $S_{\text{bi}}$  of 671 and the slope from the graph  $k$  of 48478 are calculated. Therefore, the detection limit =  $4 \times 10^{-7}$  M ( $R = 0.98$ ) can be obtained.



**Figure. S5** Linear relationship between fluorescence intensity of ITP-TPE ( $2 \times 10^{-5}$  M in  $\text{CH}_3\text{CN}$ ) at 402 nm and the concentration of  $\text{Cu}^{2+}$  ( $0.1 - 2 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}$ .



**Figure. S6** Cyclic voltammograms of  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  measured in  $\text{CH}_3\text{CN}$  (0.1 mol/L  $n\text{-Bu}_4\text{NPF}_6$ ) at a scan rate of 100 mV/s.

## 2 $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra for New Compounds

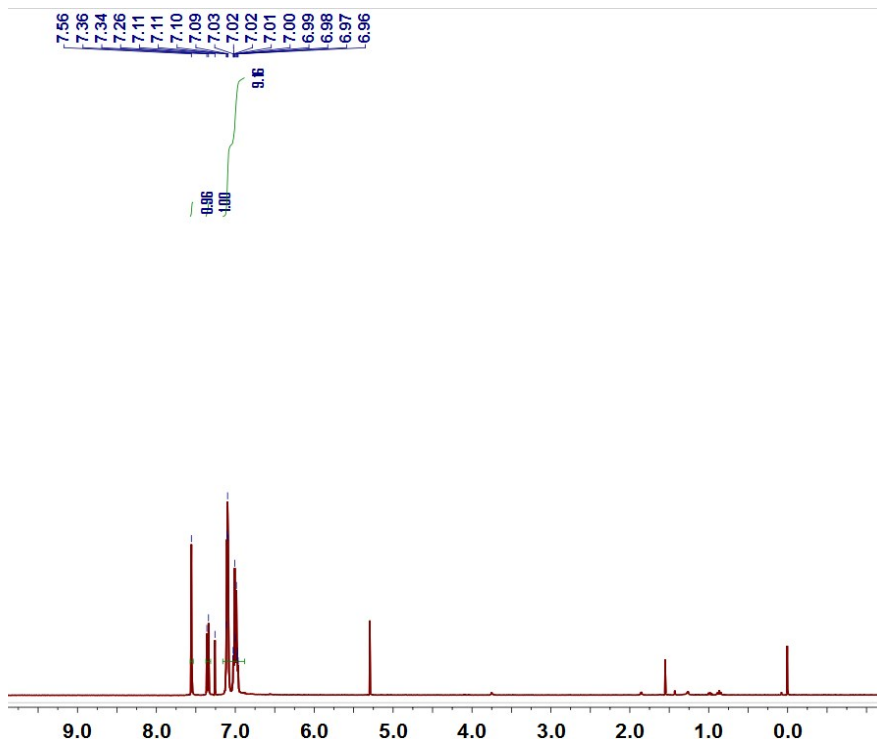


Figure. S7.  $^1\text{H}$  NMR spectra of compound 2 (400MHz,  $\text{CDCl}_3$ , ppm)

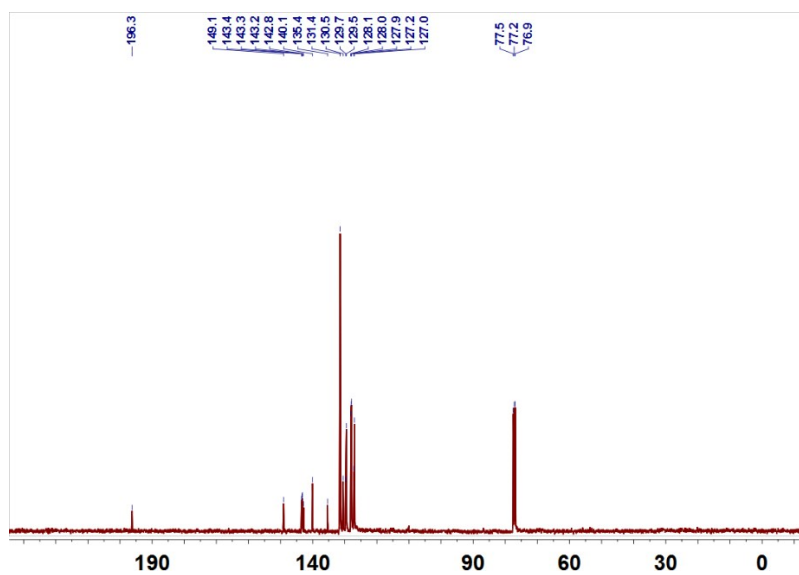
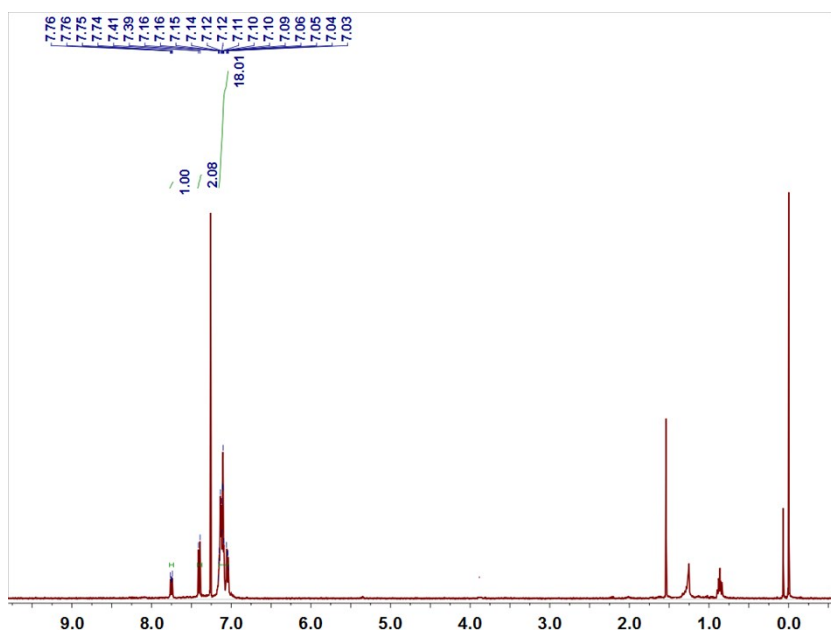
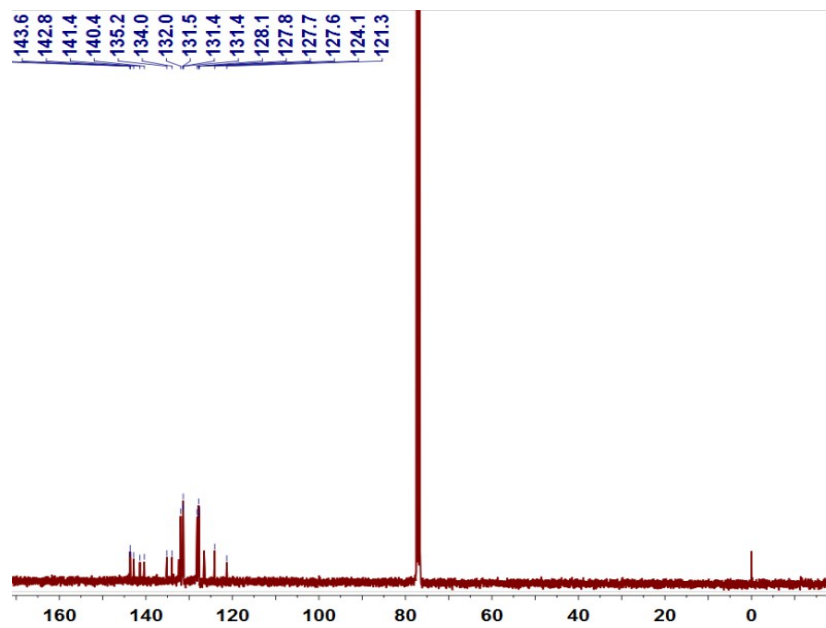


Figure. S8.  $^{13}\text{C}$  NMR spectra of compound 2 (100MHz,  $\text{CDCl}_3$ , ppm)



**Figure. S9**  $^1\text{H}$  NMR spectra of compound ITP-TPE (400MHz,  $\text{CDCl}_3$ , ppm)



**Figure. S10**  $^{13}\text{C}$  NMR spectra of compound ITP-TPE (100MHz,  $\text{CDCl}_3$ , ppm)

## Mass Spectrum SmartFormula Report

<b>Analysis Info</b>		Acquisition Date	6/18/2015 3:22:19 PM
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Method	tune-posAPCI-300-1200_1411111.m	Instrument / Ser#	micrOTOF-Q II 10324
Sample Name	trz1		
Comment			

<b>Acquisition Parameter</b>					
Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	1200 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source

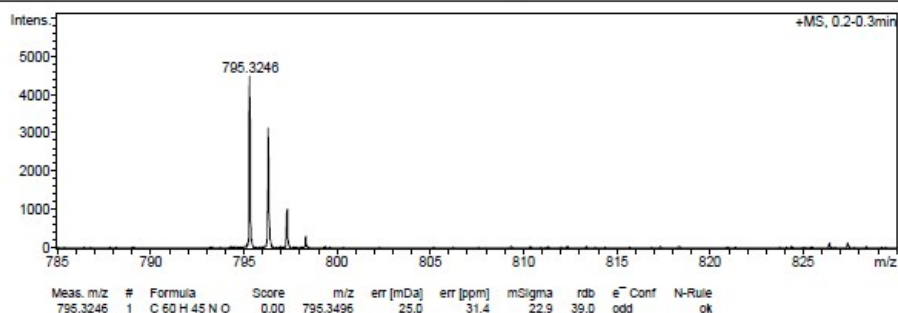


Figure S11. NMRS of 2

## Mass Spectrum SmartFormula Report

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Sample Name	trz3		
Comment			

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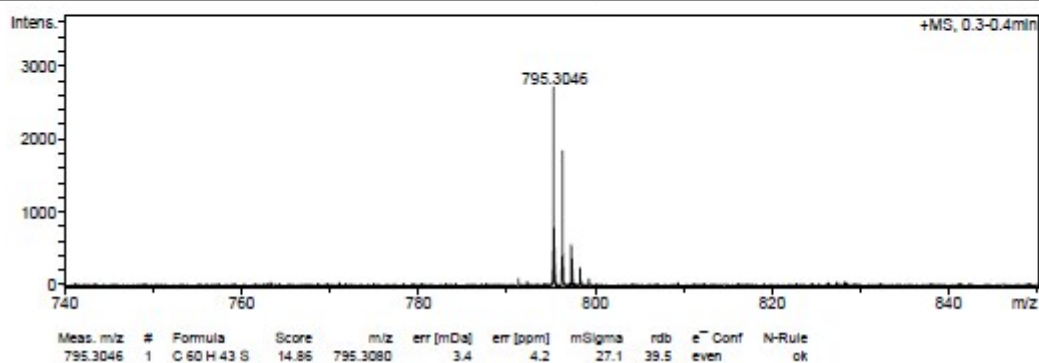


Figure S12. NMRS of ITP-TPE

### 3 References

S1 (a) V. Thomsen, D. Schatzlein, and D. Mercurio, *Spectroscopy*, 2003, **18**, 112; (b) F. Zheng, F. Zeng, C. Yu, X. Hou and S. Wu, *Chem. Eur.J.*, 2013, **19**, 936; (c) A. Roy, D. Kand, T. Saha, P. Talukdar, *Chem. Commun.*, 2014, **50**, 5510.