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

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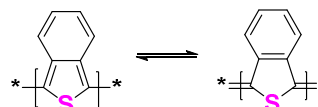
A luminogen (ITP-TPE) comprising isothianaphthene-bridged tetraphenylethene units was concisely synthesized. Its unique extended π -conjugated structure allows for colorimetric and off/on fluorescent detection for Cu^{2+} in extremely high selectivity and sensitivity, by the formation of nonarylamine-based organic mixed-valence state.

Introduction

Owing to the industry environmental monitoring and biological importance of Cu^{2+} ,¹ a lot of researches have been mainly focused on design and synthesis of functional chromophores to monitor the Cu^{2+} change. In this aspect, organic luminogens have become a very effective sensor due to their high sensitivity, selectivity and quick response, in particular, their versatile molecular structures associated with the rich functionalities. Among them, the colorimetric sensors offer a low-cost and portable detection through the “naked-eye” observation. And the emission-based chemosensors enable providing very rich spectra information via various fluorimetric techniques (e.g. choice of excitation and emission wavelengths), and thus accessible for the detection in a complicated system. Currently, there are two contemporary approaches to detection of Cu^{2+} contents by using chemosensors through metal coordination or arylamine-based organic mixed-valence state. Compared with the former method that has been extensively studied,² the latter one is relatively few and not arousing the attention until very recently. Generally, arylamine with relative lower oxidation potential, its radicals can be generated by electrochemical oxidation or by chemical oxidants such as metal ions.³ This mechanism offers a simple way to design functional chromophores to examine Cu^{2+} . Such as tris(4-anisyl)amine,⁴ arylaminofluorene derivatives,⁵ thiazolothiazole-based derivatives,⁶ *N,N*-dimethyl-amino phenylenedi-amine (DMPD),⁷ naphthalenediimides,⁸ indoline- benzothiadiazle derivatives,⁹

and their corresponding arylaminium cation radicals, which were readily produced by Cu^{2+} in CH_3CN . However, there are still rare reports about nonarylamine-based organic mixed-valence luminogens for probing Cu^{2+} .

Isothianaphthene is widely used as a key building block in organic functional materials applicable for various optoelectronic devices, such as organic field transistors (OFETs), organic solar cells (OPVs), and organic light-emitting devices (OLEDs),¹⁰ because it has promising electronic properties, associated with its ready conversion between aromatic and quinoid resonance structures (Scheme 1).¹¹



Scheme 1. A conversion between aromatic and quinoid structures for isothianaphthene.

Because of their excellent AIE effect, tetraphenylethene (TPE) and its derivatives have drawn a great deal of interest in a broad range from small molecule luminogens to functional materials¹². However, in most cases, TPE typically as a key functional group offers strong fluorescent emitting in aggregate state.¹³ While, using TPE for achieving π -extended conjugation system seems not to be fully explored so far, owing to its less rigidity with respect to its four freely rotatable bulk phenyl groups. With these in our mind, our effort is to integrate isothianaphthene and tetraphenylethene units for building up an extended π -conjugated system. In this work, we report the synthesis of a novel luminogen comprising one isothianaphthene core and two tetraphenylethene (TPE) units in the lateral sides, for achieving isothianaphthene instead of triphenylamine as the reactive platform for generating nonarylamine radical cations by Cu^{2+} and two

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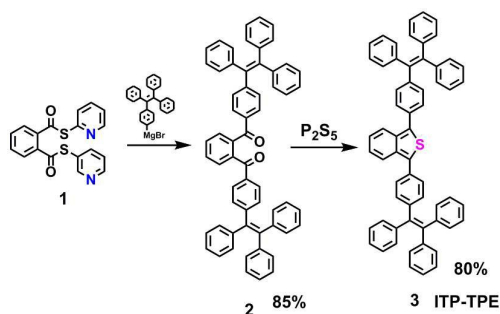
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tetraphenylethene ligands facilitate the stability of corresponding radical cations via extending spin density and changing charge distribution. Its π -extended conjugation was verified by the two successive reversible redox processes in cyclic voltammetry. And combined with its rich photophysical properties, its unique colorimetric and off/on fluorometric sensing Cu^{2+} through the formation of the relatively stable radical cation has also been revealed.

Results and discussion

Synthetic procedures

The synthetic approach to the target luminogen (ITP-TPE) was illustrated in **Scheme 2**. First, the key intermediate 1,2-di(S-(pyridine-2-yl)benzenedithioate) (**1**) was easily accessed according to our previous report.¹⁴ Afterwards, 4-(1,2,2-triphenylvinyl) phenyl magnesium bromide was added into the suspension of **1** in THF at 0 °C and stirred overnight, affording **2** in a yield of 85%. Finally, upon the treatment of **2** with Lawesson reagent,¹⁵ ITP-TPE was achieved in 80% yield. All new compounds were fully characterized by ^1H , ^{13}C NMR spectroscopy, and high resolution mass spectroscopy, verifying the chemical identity of the new compounds.



Scheme 2. Synthetic route towards ITP-TPE.

The optical properties of ITP-TPE was investigated by UV-vis and fluorescence spectroscopies. UV-vis spectra of ITP-TPE (2×10^{-5} M) revealed two main absorption bands at 327 nm and 420 nm in the high energy regions, respectively, assignable to the π - π^* transition of the aromatic skeleton (**Fig S1**) and it exhibits well photostability (**Figure.S2**). Typically, the tetraphenylethene-based luminogens undergo serious fluorescence emission quenching due to the non-radiative transition from the free rotation of tetraphenylethene unit in the non-aggregation state. Interestingly, in our case, the fluorescence spectra of ITP-TPE showed visible green fluorescence in CH_3CN (**Fig S3**) and the fluorescence quantum yield up to 1.8%. Such a phenomenon is probably attributed to the promising isothianaphthene unit as a bridge favourable for π -electron delocalization over the whole molecular skeleton, which somehow might weaken the free rotation of the phenyl groups in tetraphenylethene units, and thus decrease the corresponding nonradiative decay. As expect, the as-prepared luminogen in a H_2O - CH_3CN mixture with the water fraction above 50% shows a remarkably enhanced fluorescence

intensity due to the classical AIE effect (**Fig. S2**). When the water content reaches to a maximum value at 80% (v/v), the fluorescence quantum yield increases to ($\Phi_f = 10.45\%$).

Electrochemical properties

Moreover, the electrochemical behaviour of ITP-TPE was studied by cyclic voltammetry (CV) measurement (**Fig.1**). Two consecutive one-electron reversible oxidation processes can be observed for this molecule. Accordingly, the two oxidation potentials of the waves were calculated to $E_{\text{ox1}} = 0.45$ V and $E_{\text{ox2}} = 0.85$ V, with respect to the formation of the stable radical cation and dication, respectively. Such two successive oxidation processes also manifest that such kind of luminogen possesses an extended π -conjugated system over the whole molecular skeleton.

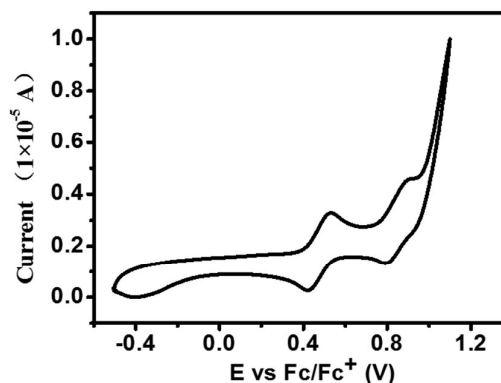


Fig.1 Cyclic voltammograms of ITP-TPE (1×10^{-3} M) measured in CH_2Cl_2 (0.1 mol/L $n\text{-Bu}_4\text{NPF}_6$) at a scan rate of 100 mV/s.

Cu^{2+} detection

These unique photophysical properties and electrochemical behaviours of ITP-TPE, encouraged us to further explore its application in the examination of metal ions because of their important roles in environmental protection, and biological metabolism.

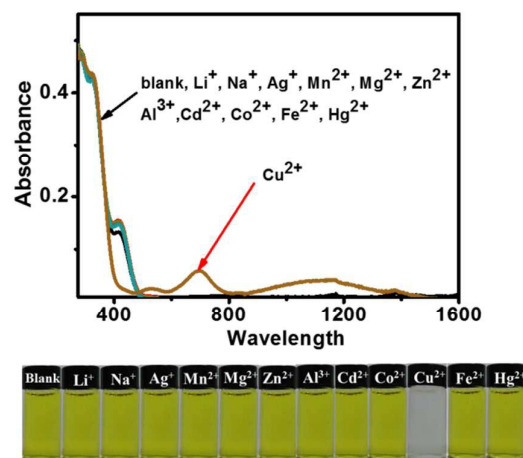


Fig. 2 Upon the addition of various metal ions (1 equiv), UV-vis-NIR spectra of ITP-TPE (2×10^{-5} M) in CH_3CN solution (Top), and colorimetric changes of ITP-TPE (2×10^{-4} M) (Bottom). Wavelength unit: nm.

The sensing of ITP-TPE to metal ions was evaluated by adding 1.0 equiv of various Li^+ , Na^+ , Al^{3+} , Ag^+ , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} in CH_3CN , and monitored by UV-vis spectroscopy. As shown in Fig. 2, two new absorption peaks at 692 nm and 1097 nm appeared after the addition of Cu^{2+} (1.0 equiv). The NIR absorption band may be attributed to the generation of corresponding radical cations. Accordingly, a significant change of the solution colour from yellow to colourless (10^{-3} M in violet) was observed within 5 seconds by naked eye. On the contrary, by compared with the blank sample, there is no obvious change of either the absorption profiles or the solution colour in the presence of the other metal ions, indicative of the highly selective colorimetric detection for Cu^{2+} .

Fluorescence response behaviours of ITP-TPE were also investigated by the addition of various metal ions in CH_3CN (Fig. 3). 1 equiv Cu^{2+} enables resulting in approximately complete fluorescence emission quenching as shown by fluorescence spectroscopy and the image under UV light. Whereas, the addition of the other ions, could not remarkably affect the green fluorescence emission relative to a blank sample. Reasonably, the quenching effect could be attributed to the formation of radical cation with respect to the mixed-valence state of ITP-TPE upon Cu^{2+} oxidation. Regard to the aforementioned AIE effect of this luminogen, a back titration was further conducted. To a solution of ITP-TPE (2×10^{-4} M) containing different metal ion (1 equiv) was added water in a ratio of $\text{H}_2\text{O}:\text{CH}_3\text{CN}=9:1$. Interestingly, a strong fluorescence emission immediately turned on in the case of the Cu^{2+} containing sample. It is worthy to note that the released pale green emission is significantly different from that of the blank sample (Figure.S4). As a contrast, the other metal ion-containing samples could not offered any obvious difference in both colour and intensity of the fluorescence emission with respect to a blank sample. This unexpected phenomenon might be related to the formation of some new teraphenylethene derived AIE-active species under Cu^{2+} oxidation followed by a water treatment. Such unique optical response of ITP-TPE to a synergetic stimuli performance might also allow us to develop anti-counterfeiting technique with increased security.^{12b}

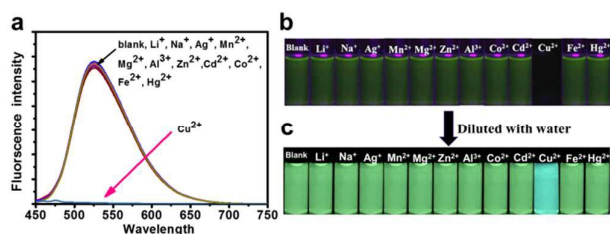


Fig. 3 Fluorescence spectra of ITP-TPE (2×10^{-5} M) in CH_3CN solution upon addition of 1 equiv. of various metal ions (a). Fluorescence images of ITP-TPE (2×10^{-4} M) upon the addition of various metal ions (1 equiv.). Wavelength unit: nm. (b). Fluorescence images of metal ion-containing ITP-TPE samples (2×10^{-5} M) in a mixture solution with water: $\text{CH}_3\text{CN} = 9:1$ under 365 nm (c).

To gain a better understanding of the impact of Cu^{2+} on the optical properties of ITP-TPE. The UV-vis-NIR absorption spectra of ITP-TPE titrated with Cu^{2+} in CH_3CN are shown in Fig. 4. With the addition of Cu^{2+} , the absorption peak at 420 nm gradually decreased, and two new bands with the progressively enhanced intensities at 692 and 1097 nm respectively, can be observed, which may be characteristic of the cation radicals. Moreover, the addition of Cu^{2+} made the fluorescence intensity consecutively declined, and nearly quenched at 1.0 equiv amount due to the formation of the ITP-TPE radical cations, suggesting the extremely high sensitivity of the as-made luminogen for Cu^{2+} . Accordingly, a detection limit of 4×10^{-7} M was calculated, which is the lowest value for the organic mixed-valence type of Cu^{2+} sensors (Fig.S5).⁸

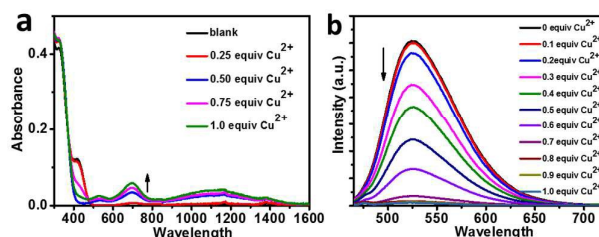


Fig. 4 UV-vis-NIR absorption spectra (a) and fluorescence spectra (b) of ITP-TPE (2×10^{-5} M) in CH_3CN with the addition of Cu^{2+} . Wavelength unit: nm.

These phenomena can be essentially elucidated by the combination of the aforementioned electrochemical measurement of ITP-TPE and the redox properties of Cu^{2+} . Given that the oxidation potential of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ in CH_3CN is 0.80 V vs Fc/Fc^+ (Fig.S6) higher than the first oxidation potentials of ITP-TPE ($E_{\text{ox1}} = 0.45$ V) and lower than that of second oxidation potential ($E_{\text{ox2}} = 0.85$ V), the free energy change was calculated from the Rehm-Weller equation $\Delta G_0 = E_{\text{ox}} - E_{\text{red}} - e^2/d\epsilon$, where E_{ox} is the oxidation potential of the electron donor (ITP-TPE in this case), E_{red} is the redox potential of the electron acceptor (Cu^{2+} in this case), d is the center-to-center distance between the ITP-TPE and Cu^{2+} in the collision, and ϵ is the dielectric constant of CH_3CN (≈ 37).¹⁰ In polar solvents like CH_3CN , the Coulombic term is neglected. Their free energy change (ΔG_{ET}) in the exergonic thermal electron transfer from ITP-TPE to Cu^{2+} is -0.35 (ΔG_{ET1}) and $+0.05$ eV (ΔG_{ET2}), respectively, which is sufficiently high to readily oxidize ITP-TPE to form the corresponding monocation radical (ITP-TPE $^+$), but not a dication radical (ITP-TPE $^{2+}$).

The formation of cation radical (ITP-TPE $^+$) and the oxidation state of Cu^{2+} during the oxidation processes were further supported by electron spin resonance (ESR) spectroscopy (Fig.5). The addition of 1 equiv of Cu^{2+} to a solution of ITP-TPE in CH_3CN , a ESR signal centered at $g = 2.0022$ appears, which can be attributed to the formation of the mono-radical cation of ITP-TPE, in concomitance with a reduction of Cu^{2+} to Cu^+ . Such a result is consistent with the above photophysical and electrochemical analyses.

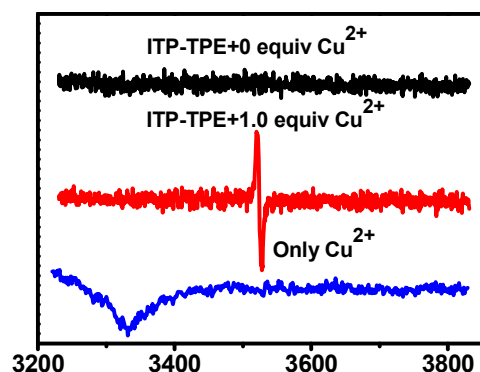
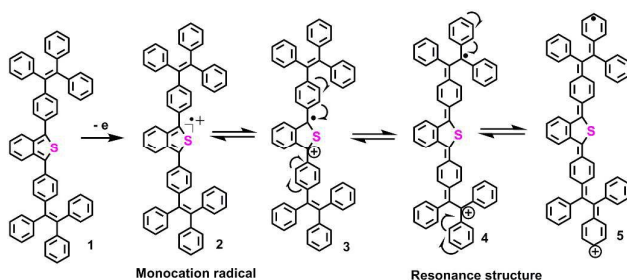


Fig. 5 ESR spectra of ITP-TPE (1×10^{-3} M) in CH_3CN solution with different equivalents of Cu^{2+} .

All these results seem to coincide with such a possible mechanism (**Scheme 3**): At first, ITP-TPE was converted to a monocation radical in a single electron oxidation process by Cu^{2+} . This open-shell species (**2**) can be stabilized through the formation of a series of resonance structures, associated with the quinoid structures favourable to maximally delocalize the electron over the molecular skeleton. On the other hand, the open-shell resonance structures seem to lack of stability, and subjected to form the other kinds of new compounds, which might directly lead to the unusual optical properties, such as water-stimuli fluorescence response in the aforementioned back titration.



Scheme 3. Plausible mechanism for the formation of the organic mixed-valence states of ITP-TPE by Cu^{2+} oxidation.

Conclusions

In conclusion, we have efficiently synthesized a new luminogen consisting of an isothianaphthene core and two tetraphenylethene units in the lateral sides, which features π -extended conjugated structure, very rich photophysical properties, AIE activity and electrochemical behaviour with the two successive one-electron reversible oxidation processes. This kind of luminogen enable undergoing colorimetric and off/on fluorimetric multi-channel detection for Cu^{2+} in very high selectivity, and sensitivity with the lowest detection limit up to 4×10^{-7} M, representing a new type of non-arylamine chemosensors. This new approach also might be able to use for developing highly safety anti-counterfeiting technique associated with synergetic stimuli response, or building up the other functional materials.

Experimental

Synthesis

All solvents and reagents employed were purchased from Sigma-Aldrich and Adamas-beta. CHCl_3 , CH_3CN were distilled from calcium hydride. THF were distilled from Na. And all performances were carried out using standard Schlenk technique.

Instruments

^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Mercury Plus 400 (400 MHz for proton, 100 MHz for carbon) spectrometer with tetramethylsilane as the internal reference using CDCl_3 as solvent in all cases. Mass spectrometry was measured with an Ultra Performance Liquid Chromatography & Quadrupole-Time-of-Flight Mass Spectrometer. UV-vis spectra were recorded on a HITACHI U-4100 Spectrophotometer. Fluorescent spectra were obtained with a FluoroMax-4 spectrophotometer. Electron paramagnetic resonance spectra were recorded on Bruker BioSpin Corp., Germany. Cyclic voltammetry (CV) was performed on a Chenhua 650D electrochemical analyzer in anhydrous CH_2Cl_2 containing recrystallized tetra-*n*-butyl-ammoniumhexafluoro phosphate (TBAPF_6 , 0.1 M) as supporting electrolyte at 298K. A conventional three electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with a polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to Ag/AgCl reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of nitrogen.

Synthetic procedures

Synthesis of 1, 2-[4-(1, 2, 2-triphenylvinyl)] diphenyl methanone (**2**)

A solution of 4-bromo-(1, 2, 2-triphenylvinyl)diphenyl (1742 mg, 4.25 mmol) in THF (10 mL) was slowly added to a mixture of iodine activated magnesium (122.0 mg, 5.1 mmol) in THF (5 mL) to form the Grignard reagent in 4 h. Afterwards, the cold Grignard reagent was slowly added to a solution of **1** (600.0 mg, 1.70 mmol) in dry THF (50 mL) at 0°C , and stirred overnight. Then, the reaction was quenched with 10% HCl (50 mL) and extracted with CH_2Cl_2 (50 mL \times 3). The combined organic fractions were washed with 1.0 M NaHCO_3 and water, and dried over MgSO_4 . The solution was filtered out, and then the solvent was removed under reduced pressure. The resulting residue was further purified by column chromatography using CH_2Cl_2 /petroleum (2:1) as eluent, to afford the product **2** as a yellow solid (1150.0 mg, 80%). ^1H NMR (400 MHz, CDCl_3): δ = 7.56 (d, 4H, J = 8.0Hz), 7.09 (m, 18H), 7.00 (m, 16H). ^{13}C NMR (100 MHz, CDCl_3): 196.3, 149.1, 143.4, 143.3, 143.2, 142.8, 140.1, 135.4, 131.4, 130.5, 129.7, 129.5, 128.1, 128.0, 127.9, 127.2, 127.0. HRMS. ($\text{C}_{60}\text{H}_{42}\text{O}_2$, ESI^+): calculated for $[\text{M}+\text{H}]^+$ 795.3258, Found: 795.3246.

Synthesis of 1, 3-[4-(1, 2, 2-triphenylvinyl)]isothianaphthene (ITP-TPE)

In a Schlenk flask, a solution of **2** (794 mg, 1.0 mmol) in dry toluene (15 mL), Lawesson's reagent (808 mg, 2.0 mmol) was added in one

portion, then the mixture was heated to 110 °C and stirred overnight. The reactant was poured into brine and extracted by dichloromethane for (50 mL × 3). The organic phase was dried over MgSO₄ and the solvent was evaporated in vacuum. The product ITP-TPE was purified by chromatography (CH₂Cl₂/hexane=1/1) on silica gel as yellow solid (635 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (dd, 2H, J = 8.0 Hz, J = 4.0 Hz), 7.39 (d, 4H, J = 8.0 Hz), 7.10 (m, 36H). ¹³C NMR (100 MHz, CDCl₃): δ = 143.7, 143.6, 143.6, 142.8, 141.4, 140.4, 135.2, 134.0, 132.0, 131.5, 131.4, 131.4, 128.1, 127.8, 122.7, 127.6, 124.1, 121.3. HRMS. (C₆₀H₄₃S, ESI⁺): calculated for [M+H]⁺ 795.3080, Found: 795.3046.

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Graphical Abstract

