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## ARTICLE

# Specific Cu(II) detection using a novel tricarbazolyl-tristriazolotriazine based on photoinduced charge transfer

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Tricarbazolyl-tristriazolotriazine, a novel Cu(II)-sensing and selective fluorescent sensor, was designed and synthesised on the basis of the mechanism of photoinduced charge transfer. The synthesised compound exhibits highly sensitive and significant fluorescence decline response towards Cu<sup>2+</sup> over other metal ions, with a detection limit of 0.2 μM in THF-H<sub>2</sub>O (9:1, v/v) at neutral pH. Its optical, thermal, electrochemical and morphological properties were studied. The results demonstrate that the compound has high relative fluorescence quantum yield ( $\Phi_f = 0.99$ ) in xylene solution, excellent thermal stability ( $T_d = 325^\circ\text{C}$ ,  $T_g = 99.9^\circ\text{C}$ ), wide energy gap ( $E_g = 4.09$  eV), desirable triplet energy ( $E_T = 2.98$  eV) and the highest occupied molecular orbital energy ( $-5.67$  eV). Morphological investigation showed that the compound easily forms ribbon-like microstructures.

## Introduction

Copper is important in various applications, particularly in biological and environmental fields. Cu is an essential element in the ecosystem, and is the third most abundant transition element in our bodies and in many living organisms<sup>1-4</sup>. Although the divalent copper cation [Cu(II)] participates in a series of biological processes, at certain high concentrations it is a toxic and harmful heavy metal element to humans and some organisms. Elevated concentrations of Cu in the human body are connected with neurodegenerative diseases, such as Menkes syndrome and Wilson's diseases. High Cu concentration also causes infant liver damage<sup>5-9</sup>. Moreover, Cu is a common contaminant in agriculture and other industries. It can be incorporated in the environment, drinking water and food chain<sup>10</sup>. Therefore, an efficient and selective method to detect Cu ions is important for environmental protection and human health.

High-sensitivity detection of copper ions in various samples has been performed using several traditional methods, including voltammetry<sup>11</sup>, inductively coupled plasma mass spectroscopy (ICP-MS)<sup>12</sup>, ICP-atomic emission spectrometry<sup>13</sup> and atomic absorption spectrometry<sup>14</sup>. However, these detection methods require complicated pretreatment procedures and sophisticated instrumentations, making them unsuitable for on-line or in-field monitoring<sup>15</sup>. In the past decade, design and development of fluorescent chemosensors with high selectivity and sensitivity targeting Cu ions have been given significant attention because

they allow nondestructive, low-cost and prompt detection of metal cations, as well as easy-to-realise in situ and real-time detection by a simple fluorescence enhancement or quenching response<sup>5, 8, 16-20</sup>.

Thus far, numerous luminescent organic compounds in probe development for selective detection of Cu ions have been developed<sup>21-23</sup>. However, some of them weaken or are even quenched at high concentrations. The effective ranges of their practical application are limited<sup>24</sup>. Developing fluorescent probes with high fluorescence quantum yield, strong fluorescent emission, large extinction coefficient and insensitivity to solvents for Cu detection remains a challenge. Given their excellent photophysical properties, internal charge transfer (ICT) compounds are being given significant interest in cation sensing. Moreover, their inherently large Stokes shift addresses the problem of self-reabsorption and makes them important candidates for probe applications<sup>25-27</sup>. The mechanism of ICT compounds interacting with a cation is called photoinduced charge transfer (PCT), which has been extensively used to explain sensing mechanism<sup>28-31</sup>. Heterocycle tris[1,2,4]triazolo[1,3,5]triazine reportedly exhibits good organic solvent compatibility and strong fluorescence in a solution<sup>32</sup>. Nevertheless, carbazole derivatives are highly efficient blue fluorescence materials that are widely used in Organic Light-Emitting Diodes (OLEDs)<sup>33-35</sup>. According to these inspirations, a combination of tris[1,2,4]triazolo[1,3,5]triazine and carbazole may be advantageous for application as fluorescent probe for the

detection of Cu(II). To the best of our knowledge, the application of triazolotriazine derivative in discotic liquid crystals has been studied; however, it has never been reported as a fluorescent probe.

In this paper, based on PCT sense mechanism, a novel disc-like fluorescent chemosensor, namely tricarbazolyl-triazolotriazine (compound 5), containing the electron-donating carbazole moieties and the electron-accepting tris[1,2,4]triazolo[1,3,5]triazine (TTT) core, was successfully designed and synthesised. As non-planar conformation products, the disc-like compounds avoid  $\pi$ - $\pi$  molecular stacking leading to fluorescence quenching at elevated concentration. In addition, we determined the thermal, electrochemical and morphological properties of these compounds, revealing that compound 5 has a potential extensive application.

## Experimental

### Materials

All the reagents were obtained from commercial sources and used without further purification. The organic solvents were of analytical grade quality and all were dried by traditional methods. In general, all the intermediates and final compounds were purified by column chromatography on silica gel (200-300 mesh), and crystallization from analytical grade solvents. Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254).

### Characterization

$^1\text{H}$  NMR spectra was obtained with a Varian inova-400-MHz instrument using tetramethylsilane (TMS) as the internal standard.  $^{13}\text{C}$  NMR spectra was recorded on a Varian inova-100-MHz spectrometer. Glass transition temperature was determined by DSC measurements carried out utilizing Netzsch Gerätebau GmbH R.O. Thermal stability was determined by thermogravimetric analyzer (TGA, Netzsch STA449F3) over a temperature range of 25-1000°C at a heating rate of 10°C min<sup>-1</sup> under a nitrogen atmosphere. EI/MS spectra was obtained on an Agilent 1100 LC-MS. ESI/HRMS was obtained on a micrOTOF-Q II mass spectrometer (BrukerDaltonik, Germany).

MALDI-TOF-MS data were obtained on a Bruker BIFLEX III TOF mass spectrometer. A MAPADA UV-3200PCS spectrophotometer was used to record absorption spectra. Fluorescence spectra was recorded on a Hitachi F-2500 and relative quantum yield was obtained according to published method<sup>36</sup> using 2-phenyl-5-(4-bi-phenyl)-1,3,4-oxadiazole (PBD) as standard ( $\Phi_F = 0.83$ )<sup>37</sup>. The electrochemical measurement was carried out with a ChenHua 660D potentiostat. Cyclic voltammograms was recorded at scan rates of 50, 100, 200 and 500 mV s<sup>-1</sup> from a solution of compound 5 (10<sup>-3</sup> mol dm<sup>-3</sup>) in dry dichloromethane solution containing 0.1 mol dm<sup>-3</sup> tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), using a gastight single-compartment three-electrode cell

equipped with carbon working, platinum wire auxiliary, and Ag/AgCl pseudo-reference electrodes<sup>32</sup>.

### Synthesis

**SYNTHESIS OF 9-BUTYL-9H-CARBAZOLE<sup>38</sup> (1):** To a 250 mL flask containing carbazole (16.7 g, 100 mmol), NaOH (6.0 g, 150 mmol), hexadecyltrimethyl ammonium bromide (0.15 g) and acetone (100 mL). The mixture was stirred at 60°C for 2 h. After cooling to room temperature, 1-bromobutane (100 mmol) was added dropwise to a stirred mixture solution. After the addition the mixture was refluxed with stirring for 24 h. Then acetone was evaporated as far as possible. The residue mixture was poured into a large number of ice water, and vigorous stirred. The white precipitates collected by filtration were recrystallized from absolute ethanol to give white acicular crystal (yield 92%): m.p. 57.5-57.7°C.

**SYNTHESIS OF 3-BROMO-9-BUTYL-9H-CARBAZOLE<sup>39</sup> (2):** 3.47 g (19.51 mmol) of N-bromosuccinimide (NBS) dissolved in dimethylformamide (DMF, 27 mL) was added dropwise at room temperature to a stirred DMF (20 mL) solution of 4.167 g (18.58 mmol) 9-butyl-9H-carbazole, after the addition the mixture was stirred overnight. The reaction was quenched by addition of ice water. The solids formed were extracted with ethyl acetate (3×50 mL), the combined ethereal extracted was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness to leave a colorless residue, further purification by silica gel column chromatography [petroleum ether (PE):ethyl acetate (EA) = 50:1, v/v] to give a white solid (yield 90%): m.p. 48.1-48.2°C.

**SYNTHESIS OF 3-CYANO-9-BUTYL-9H-CARBAZOLE<sup>40</sup> (3):** A mixture of the 3-bromo-9-butyl-9H-carbazole (2.4 g, 8 mmol) and dried copper cyanide (1.0 g, 12 mmol) in dried N-methyl-2-pyrrolidone (NMP) 1 mL, the solution was stirred and heated at 140°C under nitrogen atmosphere overnight. Then 2 N HCl (25 mL) and CH<sub>2</sub>Cl<sub>2</sub> were poured into the reaction mixture. The mixture was filtered, and then the solution was extracted and washed with an aqueous saturated solution of NaCl. The organic layer is dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, the solvents were evaporated furnishing the crude product which was purified by column chromatography on silica-gel (PE:EA = 20:1, v/v) to give a white solid (yield 75%): m.p. 65.0-65.2°C.

**SYNTHESIS OF 5-(9-BUTYL-9H-CARBAZOLYL)TETRAZOLE<sup>41</sup> (4):** A suspension of 1 g (4.03 mmol) of 3-cyano-9-butyl-9H-carbazole, 1.0156 g (16.12 mmol) of sodium azide, and 0.08624 g (16.12 mmol) of ammonium chloride in 3 ml of DMF were stirred at 160°C under nitrogen atmosphere overnight. After cooling, the solvent was concentrated in a rotary evaporator and the reaction mixture was poured into 25 mL of ice/water and acidified with hydrochloric acid. The white precipitate was isolated by filtration, washed with ice water to give the crude product. Purification was by column chromatography on silica-gel (CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH = 50:1, v/v) to give the pure product as a pale solid (yield 60%): m.p. 240.1-240.2°C.

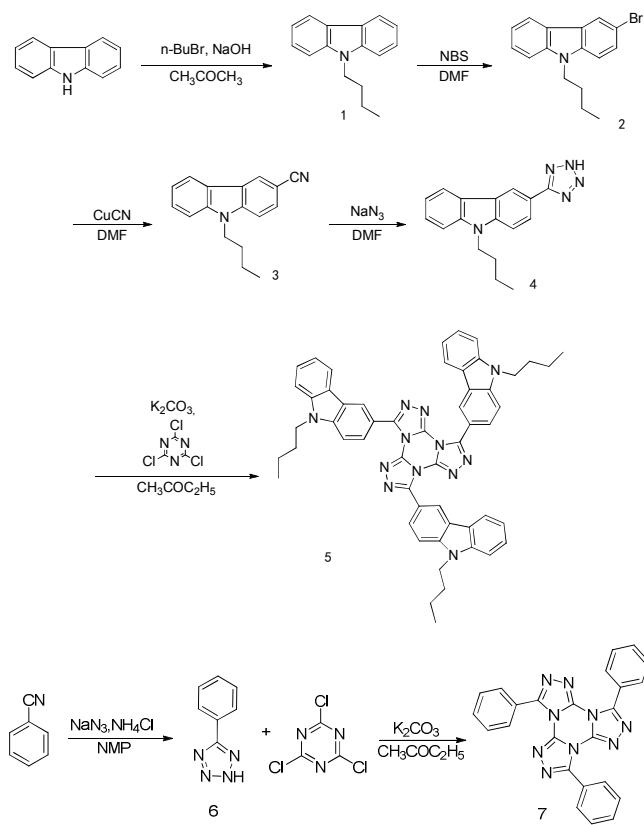
**SYNTHESIS OF TRIS-(3-(9-BUTYL-9H-CARBAZOLYL)TRIS[1,2,4]TRIAZOLO[1,3,5]TRIAZINES<sup>32, 42</sup> (5):**

A mixture of corresponding tetrazole (9 mmol), cyanuric chloride (3 mmol), and anhydrous potassium carbonate (36 mmol) in butanone (80 mL) was heated at temperature of reflux under nitrogen atmosphere and vigorous stirring for 20 h. The still hot reaction mixture was filtered off washing with dichloromethane. The solvents were evaporated furnishing the crude product which was purified by column chromatography on silica-gel (eluant dichloromethane) to give the pure product as a white solid (yield 37%). <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400MHz): δ (ppm) 8.99(m, 3H), 8.33(dd, J<sub>2</sub> = 8.61 Hz, J<sub>1</sub> = 1.72 Hz, 3H), 8.19(d, J = 7.59 Hz, 3H), 7.59(d, J = 8.55 Hz, 3H), 7.51(m, 6H), 7.29(m, 3H), 4.34(t, J = 7.16 Hz, 6H), 1.92(m, 6H), 1.46(m, 6H), 0.98(t, J = 7.38 Hz, 9H). LC-MS (EI) m/z 864.4 [M]<sup>+</sup>. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm) 13.9, 20.6, 31.1, 43.1, 108.6, 109.0, 120.9, 122.8, 123.1, 126.3, 127.6, 140.7, 141.0, 142.2, 152.0.

**SYNTHESIS OF 5-PHENYL-2H-TETRAZOLE<sup>41</sup> (6):** This prepared and after treated in the same manner as with compound 4 to obtain white solid (yield 60%): m.p. 188.1-188.7°C.

**SYNTHESIS OF 3,7,11-TRIPHENYLTRIS([1,2,4]TRIAZOLO[1,3,5]TRIAZINE<sup>32, 42</sup> (7):**

Compound 7 was obtained from cyanuric chloride and 6. The crude product was purified by column chromatography on silica-gel (PE:DCM:EA = 5:2:1) to give the pure product as a white powder (yield 50%): m.p. 298.7-299.0°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ (ppm) 8.13 (dd, J<sub>2</sub> = 7.60 Hz, J<sub>1</sub> = 0.8 Hz, 6H), 7.62 (m, 9H). MALDI-TOF MS: m/z 430.2 [M+H]<sup>+</sup>.



**Scheme 1** Synthesis and structure of compound 5 and 7

## Results and discussion

The synthetic routes for compounds 5 and 7 are shown in Scheme 1. Compounds 1 to 4 and 6 were prepared according to previous procedures.<sup>32, 38-42</sup> All of the compounds were characterised by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained. The final product gives [M+Na]<sup>+</sup> peaks at m/z 887.4025 (calculated for C<sub>54</sub>H<sub>48</sub>N<sub>12</sub>Na<sup>+</sup> = 887.4017) in the HRMS spectra for compound 5 (Fig. S2, ESI).

Combination of typical electron-donating carbazole and electron-accepting TTT groups offers ready ICT process in compound 5. Given that photophysical characterisations of the donor- $\pi$ -acceptor (D- $\pi$ -A) conjugated molecules in solutions are strongly dependent on the solvent polarity<sup>43</sup>, we first tested the absorption and emission properties of target compounds in varying solvents. As shown in Fig. 1a, the UV-vis absorption spectra of compound 5 in various organic solvents exhibit two characteristic absorption bands. A strong absorption peak is observed at approximately 295 nm to 305 nm, which is attributed to the  $\pi$ - $\pi^*$  transitions in the heteroaromatic portion of the molecule caused by the high molar absorption coefficient ( $\epsilon = 0.83 \times 10^4$  to  $1.92 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). A weak shoulder near 327 nm to 332 nm is assigned to the donor-acceptor charge transfer (CT) between the carbazole groups and TTT core. In general, the UV-vis absorption spectra from  $\pi$ - $\pi^*$  transitions exhibit redshifting with the increase in solvent polarity. However, the absorption maxima of compound 5 shows an obvious bathochromic shift from 295 nm in acetonitrile to 305 nm in benzene. This phenomenon may be due to the  $\pi$ - $\pi^*$  interactions between the TTT core with the benzene ring, leading to the redshifting of the maximum absorption wavelength. In addition, the intensity ratio of shoulder absorption to main absorption decreases significantly in the polar solvents, such as dimethylformamide and acetonitrile, which is ascribed to hydrogen-bonding interactions between the solute and the solvent. The hydrogen-bonding interactions increase the energy gap between ground and excited states, which cause bathochromic shift of shoulder absorption. By contrast, the increasing energy gap reduces the chance of electronic transition, thereby causing significant decrease in shoulder absorption peak.

In terms of emission behavior (Fig. 1b), compound 5 shows intense blue fluorescence in different organic solvents with maximum emission wavelengths at approximately 400 nm. The relative photoluminescence quantum yield (PLQY) is up to 0.99 in xylene solution, according to a published method<sup>36</sup> that uses PBD as standard ( $\Phi_F = 0.83$ )<sup>37</sup>. Such high relative PLQY is ascribed to carbazole conjugated with TTT, which extends the degree of conjugation. The emission peak undergoes negligible shifts upon varying solvent polarity, indicating that the solvent polarity has almost no effect on the excitation state of compound 5. In addition, the fluorescence spectra of compound 5 remain unchanged when the excitation wavelength at 300 and 320 nm are chosen, respectively, which are due to the existence of the energy transfer between  $\pi$ - $\pi^*$  transitions in the heteroaromatic portion of the molecule and the ICT transitions. The triplet energy ( $E_T$ ) of compound 5 is calculated



to be 2.98 eV by low-energy phosphorescence emissions in frozen solution ( $\text{CHCl}_3$ , 77 K)<sup>44</sup>.

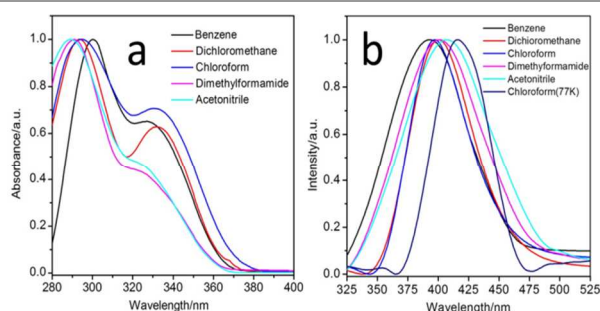


Fig. 1. Normalised (a) absorption and (b) emission spectra of compound 5 in various organic solvents and phosphorescence spectra in chloroform at 77 K.

ICT compounds have been used as fluorescent probes. Therefore, the recognition profiles of compound 5 towards various metal cations (Fig. 5a), such as  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$ , were primarily investigated by fluorescence spectroscopy in THF- $\text{H}_2\text{O}$  (v:v = 9:1). The stock solution of compound 5 was prepared at 100  $\mu\text{M}$  THF. The test solution of compound 5 (10  $\mu\text{M}$ ) in 2 mL aqueous tetrahydrofuran solution was prepared by placing 0.2 mL of compound 5 stock solution and 0.2 mL of the aqueous sample solution in 1.6 mL THF. The mixture solution was mixed and kept at room temperature for 10 min before the spectra were recorded. As shown in Fig. 2a, when 20 equiv. of  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  were added to a THF solution of compound 5 (10  $\mu\text{M}$ ), these metal cations showed very weak effect on the fluorescence intensity of compound 5 (blank bar). By contrast, when 20 equiv. of  $\text{Cu}^{2+}$  was added to a THF solution of compound 5 (10  $\mu\text{M}$ ), a significant fluorescence decline was found. Moreover, we tested the competition experiments to verify the practical applicability of compound 5 for  $\text{Cu}^{2+}$  detection. The same concentrations of interfering metal ions and  $\text{Cu}^{2+}$  (0.2 mM) were added to a THF solution of compound 5, and the detection results showed almost unchanged fluorescence intensity to  $\text{Cu}^{2+}$  before and after the addition of other competing metal ions [Fig. 2a (black bar)]. This result indicates that the designed probe has a significant potential for selective response, which can be used in various applications.

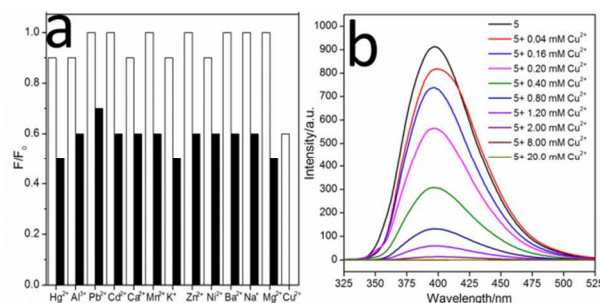


Fig. 2. (a) Fluorescence response of compound 5 (10  $\mu\text{M}$ ) in THF- $\text{H}_2\text{O}$  (9:1, v/v) in the presence of 20 equiv. of other metal ions (blank bar) and to the mixture of 20 equiv. of other metal ions with 2.0 mM (black bar); (b) fluorescence spectra of

compound 5 with varying  $\text{Cu}^{2+}$  concentrations (from 0.04 to 20 mM);  $\lambda_{\text{ex}} = 287$  nm.

To determine the fluorescent response range of compound 5 towards  $\text{Cu}^{2+}$ , fluorescence emission spectral variation of compound 5 (10  $\mu\text{M}$ ) in THF- $\text{H}_2\text{O}$  (9:1, v/v) was monitored with different  $\text{Cu}^{2+}$  concentrations from 0.04 mM to 20 mM. As shown in Fig. 2b, the fluorescence intensity of compound 5 decreased with increase in  $\text{Cu}^{2+}$  concentrations, and significant fluorescence quenching was observed when the concentration of  $\text{Cu}^{2+}$  reached 2.00 mM. Similarly, a sensitivity test experiment employing a series of  $\text{Cu}^{2+}$  concentrations was performed. The results are shown in Fig. 3. The fluorescent response of compound 5 towards the  $\text{Cu}^{2+}$  ions covered a dynamic range from 0.2  $\mu\text{M}$  to 2 mM (Fig. 3, inset), with a detection limit of 0.2  $\mu\text{M}$  for  $\text{Cu}^{2+}$ . Meanwhile, compound 5 exhibited a cyan fluorescence upon excitation with the use of a UV lamp at 254 nm, and its intensities decreased with the increase in  $\text{Cu}^{2+}$  concentration and could be observed by the naked eye (Fig. 3, photographs), making it feasible for instrument-free  $\text{Cu}^{2+}$  detection. This result provides solid support to the specific detection of  $\text{Cu}(\text{II})$  by fluorescent methodology.

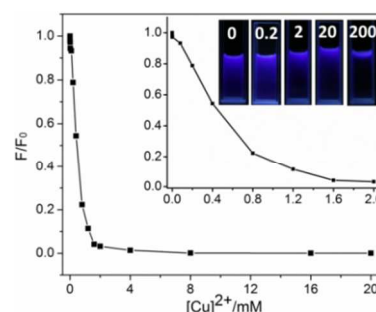


Fig. 3. Calibration plot of relative  $F/F_0$  of compound 5 against different  $\text{Cu}^{2+}$  concentrations.  $F_0$  and  $F$  stand for the fluorescent intensities in the absence and presence of  $\text{Cu}^{2+}$ . (inside) Images of compound 5 solution (10  $\mu\text{M}$ ) upon the addition of 0, 0.2, 2, 20 and 200  $\mu\text{M}$   $\text{Cu}^{2+}$ .

For the D- $\pi$ -A conjugated molecules, they undergo ICT from the donor to the acceptor upon excitation by light. Two possible binding modes for fluorescent PCT cation sensors exist. If a cation interacting with a group acted as an electron donor within the fluorophore, then a blueshift of the absorption spectrum is observed together with a decrease in the extinction coefficient. Given the resulting conjugation reduction, the ground state is more stabilised by the cation than the excited state. By contrast, if the acceptor group interacts with a cation, then the electron-withdrawing character of this group is enhanced. The ground state is then more strongly unstable because of the cation than the excited state. The absorption spectrum is thus redshifted and the molar absorption coefficient is increased.<sup>28</sup> To verify the  $\text{Cu}^{2+}$  sensing mechanism of compound 5, the UV-Vis absorption spectra of compound 5 was first recorded. Fig. 4a shows that the molar absorption coefficient increased with the increase in  $\text{Cu}^{2+}$  concentrations. The results preliminary suggest that  $\text{Cu}^{2+}$  interacts with the

acceptor group. To investigate the mechanism further, another triazolotriazine without pendant carbazolyl (compound 7) was designed and synthesised. The UV–Vis absorption and fluorescence emission spectra of compound 7 were determined in the presence of different  $\text{Cu}^{2+}$  concentrations. As shown in Fig. 4b, the absorption wavelength of compound 7 significantly redshifted and the molar absorption coefficient increased in the presence of  $\text{Cu}^{2+}$ . Compared with compound 7, the maximum absorption wavelength of compound 5 showed no obvious redshift due to the distances and weak interaction between fluorophores of compound 5 and  $\text{Cu}^{2+}$ .<sup>45</sup> Thus, the absorption wavelength of compound 5 was almost unchanged in the presence of  $\text{Cu}^{2+}$ . Meanwhile, the emission spectra (Fig. S3) of compound 7 indicated that its fluorescence intensity decreased with the increase in  $\text{Cu}^{2+}$  concentrations. In addition, obvious fluorescence quenching was observed when the concentration of  $\text{Cu}^{2+}$  reached 1.2 mM. These data suggest that  $\text{Cu}^{2+}$  interacts with the electron-accepting TTT groups of compound 5, thereby causing a change in the fluorescence intensity of compound 5. In addition,  $\text{Cu}^{2+}$  is a paramagnetic ion with an unfilled d orbital that could lead to strong fluorescence quenching of nearby fluorophores via electron or energy transfer.<sup>46–48</sup> Meanwhile, we compared the trend of fluorescence intensity of compounds 5 and 7 with different  $\text{Cu}^{2+}$  concentrations; their decreased tendency of fluorescence intensity were similar (Fig. S4). However, the detection range of compound 5 was a little wider than that of compound 7. This difference further confirms the farther distances and the weaker interaction between fluorophores and  $\text{Cu}^{2+}$ .

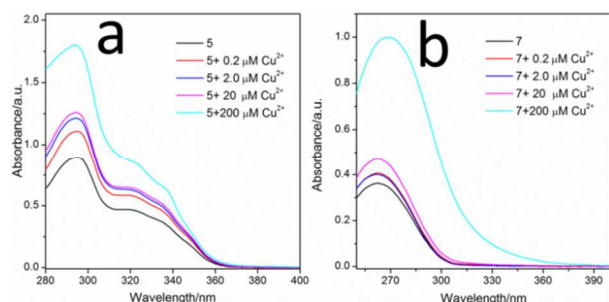


Fig. 4. Absorption spectra of compounds 5 (a) and 7 (b) (10  $\mu\text{M}$ ) upon addition of 0, 0.2, 2.0, 20 and 200  $\mu\text{M}$   $\text{Cu}^{2+}$  in THF– $\text{H}_2\text{O}$  (9:1, v/v).

Carbazole-based compounds are used in OLEDs because of their intense blue luminescence. We determined the thermal, electrochemical and morphological properties of compound 5 (ESI). The results demonstrate that compound 5 has excellent thermal stability ( $T_d = 325^\circ\text{C}$ ,  $T_g = 99.9^\circ\text{C}$ ) and a wide energy gap ( $E_g = 4.09$  eV). It also showed the highest occupied molecular orbital energy ( $-5.67$  eV). The morphology of compound 5 shows that its molecule easily formed ribbon-like microstructures. These results indicate that compound 5 has extensive potential applications.

## Conclusions

A new molecule was synthesised with the use of electron-donor carbazole unit and electron-acceptor TTT building blocks. The compound was used for cation detection for the first time based on PCT. The compound exhibits significant fluorescence decline response towards  $\text{Cu}^{2+}$  in THF– $\text{H}_2\text{O}$  solution with high sensitivity and selectivity. The test showed a wide dynamic range from 0.2  $\mu\text{M}$  to 2 mM, with a detection limit of 0.2  $\mu\text{M}$ . The compound also exhibits excellent selectivity in the presence of other common cations, such as  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{K}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ , which could meet the selective requirements for practical applications. Moreover, the synthesised compound possesses wide energy gap ( $E_g = 4.09$  eV), excellent quantum efficiency ( $\Phi_F = 0.99$ ), high triplet energy ( $E_T = 2.98$  eV), good thermal stability ( $T_d = 325^\circ\text{C}$ ) and glass-transition temperature of approximately  $100^\circ\text{C}$ . These superior performances suggest that the molecule can be used in various applications.

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## Notes and references

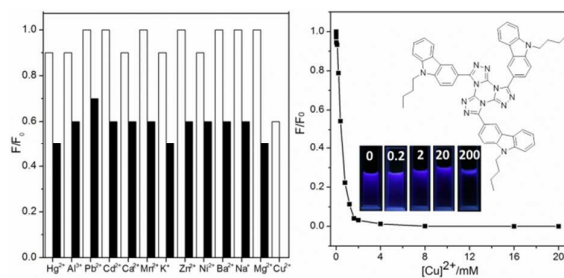
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Electronic Supplementary Information (ESI) available: Experimental details for  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EI-MS and HRMS of compound 5 and  $^1\text{H}$  NMR and LRMS of compound 7. Fluorescence spectra of compound 7 with varying concentrations of  $\text{Cu}^{2+}$ . Calibration plots of relative  $F/F_0$  of the compound 5 and 7 against different concentrate of  $\text{Cu}^{2+}$ . TGA and DSC thermograms of compound 5 recorded under nitrogen atmosphere at the heating rate of  $10^\circ\text{C min}^{-1}$ . Representative cyclic voltammogram of compound 5 measured. SEM microphotographs of compound 5. See DOI: 10.1039/b000000x/

1. M. C. Linder and M. Hazegeh Azam, *Am. J. Clin. Nutr.*, 1996, **63**, 797S–811S.
2. C. Vulpe, B. Levinson, S. Whitney, S. Packman and J. Gitschier, *Nat. Genet.*, 1993, **3**, 7–13.
3. D. R. Brown and H. Kozlowski, *Dalton. T.*, 2004, 1907–1917.
4. S. Zhang, J. M. Yan, A. J. Qin, J. Z. Sun and B. Z. Tang, *Chin. Chem. Lett.*, 2013, **24**, 668–672.
5. C. Yu, J. Zhang, R. Wang and L. Chen, *Org. Biomol. Chem.*, 2010, **8**, 5277–5279.
6. X. Ma, J. Liu, Y. Du, G. Wei and D. Wei, *Sci. China. Chem.*, 2011, **55**, 626–631.
7. W. Chouyok, Y. Shin, J. Davidson, W. D. Samuels, N. H. LaFemina, R. D. Rutledge, G. E. Fryxell, T. Sangvanich and W. Yantasee, *Environ. Sci. Technol.*, 2010, **44**, 6390–6395.
8. M. Z. Tian, M. M. Hu, J. L. Fan, X. J. Peng, J. Y. Wang, S. G. Sun and R. Zhang, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 2916–2919.

9. Y. Zhao, X. B. Zhang, Z. X. Han, L. Qiao, C. Y. Li, L. X. Jian, G. L. Shen and R. Q. Yu, *Anal. Chem.*, 2009, **81**, 7022-7030.
10. C. Zong, K. Ai, G. Zhang, H. Li and L. Lu, *Anal. Chem.*, 2011, **83**, 3126-3132.
11. A. A. Ensafi, T. Khayamian, A. Benvidi and E. Mirmomtaz, *Anal. Chim. Acta.*, 2006, **561**, 225-232.
12. E. Hywel Evans, *Analyst.*, 1998, **123**, 699-703.
13. Y. Liu, P. Liang and L. Guo, *Talanta*, 2005, **68**, 25-30.
14. A. Gonzales, M. Firmino, C. Nomura, F. Rocha, P. Oliveira and I. Gaubeur, *Anal. Chim. Acta.*, 2009, **636**, 198-204.
15. T. T. Wei, J. Zhang, G. J. Mao, X. B. Zhang, Z. J. Ran, W. Tan and R. Yu, *Anal. Methods*, 2013, **5**, 3909-3914.
16. H. F. Higginbotham, R. P. Cox, S. Sandanayake, B. A. Graystone, S. J. Langford and T. D. M. Bell, *Chem. Commun.*, 2013, **49**, 5061-5063.
17. Z. Lv, J. Liu, Y. Zhou, Z. Guan, S. Yang, C. Li and A. Chen, *Chem. Commun.*, 2013, **49**, 5465-5467.
18. H. Yu, L. Jin, Y. Dai, H. Li and Y. Xiao, *New J. Chem.*, 2013, **37**, 1688-1691.
19. Y. Zhang, G. Zhuang, M. Ouyang, B. Hu, Q. Song, J. Sun, C. Zhang, C. Gu, Y. Xu and Y. Ma, *Dyes Pigments*, 2013, **98**, 486-492.
20. M. Khorasani-Motlagh, M. Noroozifar, S. Niroomand and A. Moodi, *J. Lumin.*, 2013, **143**, 56-62.
21. A. Barbieri, G. Accorsi and N. Armaroli, *Chem. Commun.*, 2008, 2185-2193.
22. N. C. Lim, J. V. Schuster, M. C. Porto, M. A. Tanudra, L. Yao, H. C. Freake and C. Bruckner, *Inorg. Chem.*, 2005, **44**, 2018-2030.
23. G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Edit.*, 2008, **47**, 1184-1201.
24. G. Yang, S. Li, S. Wang, R. Hu, J. Feng, Y. Li and Y. Qian, *Pure Appl. Chem.*, 2013, **85**, 1465-1478.
25. M. S. T. Gon alves, *Chem. Rev.*, 2008, **109**, 190-212.
26. Y. Zhou, Z. Xu and J. Yoon, *Chem. Soc. Rev.*, 2011, **40**, 2222-2235.
27. Z. Xu, Y. Xiao, X. Qian, J. Cui and D. Cui, *Org. Lett.*, 2005, **7**, 889-892.
28. B. Valeur and I. Leray, *Coordin. Chem. Rev.*, 2000, **205**, 3-40.
29. M. G. B.H. Bakker, N. Hoebe, H.J. van Ramesdonk, J.W. Verhoeven, M.H.V. Werts, J.W. Hofstraat, *Coordin. Chem. Rev.*, 2000, **208**, 3-16.
30. A. P. De Silva, H. N. Gunaratne, T. Gunnlaugsson, A. J. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515-1566.
31. R. M. M. a. F. Sancenon, *Chem. Rev.*, 2003, **103**, 4419-4476.
32. R. Cristiano, H. Gallardo, A. J. Bortoluzzi, I. H. Bechtold, C. E. M. Campos and R. L. Longo, *Chem. Commun.*, 2008, 5134-5136.
33. K. Justin Thomas, J. T. Lin, Y.-T. Tao and C. W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404-9411.
34. J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 575-581.
35. N. Agarwal, P. K. Nayak, F. Ali, M. P. Patankar, K. L. Narasimhan and N. Periasamy, *Synthetic. Met.*, 2011, **161**, 466-473.
36. E. W. Rodrigo Cristiano, Ivan H. Bechtold, Adailton J. Bortoluzzi and Hugo Gallardo, *Tetrahedron*, 2007, **63**, 2851-2858.
37. R. M. P. V. N. Salimgareeva, V. A. Ponomareva, N. S. Sannikova, S. V. Kolesov, and G. V. Leplyanin, *Russ. J. Appl. Chem.*, 2003, **76**, 1655-1658.
38. Y. Wang, H. Zhao, P. Zhang, Z. Liu and B. Dai, *Journal of Shihezi University (Natural Science)*, 2013, **31**, 99-102.
39. F. M. C. Maria B. Ponce, Sergio M. Bonesi and Rosa Erra Balsells, *Helv. Chim. Acta*, 2006, **89**, 1123-1138.
40. M. V. K.R.Justin Thomas, Jiann T.Lin, Yu Tai Tao, Chang Hao Chuen, *Adv. Funct. Mater.*, 2004, **14**, 387-392.
41. H. Gallardo, R. Magnago and A. J. Bortoluzzi, *Liq. Cryst.*, 2001, **28**, 1343-1352.
42. R. Huisgen, H. J. Sturm and M. Seidel, *Chem. Ber.*, 1961, **94**, 1555-1562.
43. Y. Gong, Y. Tan, J. Liu, P. Lu, C. Feng, W. Z. Yuan, Y. Lu, J. Z. Sun, G. He and Y. Zhang, *Chem. Commun.*, 2013, **49**, 4009-4011.
44. L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong and J. Kido, *Adv. Mater.*, 2011, **23**, 926-952.
45. L. Jia, Y. Zhang, X. Guo and X. Qian, *Tetrahedron Lett.*, 2004, **45**, 3969-3973.
46. A. W. Varnes, R. B. Dodson and E. Wehry, *J. Am. Chem. Soc.*, 1972, **94**, 946-950.
47. Y. Li and C. M. Yang, *Chem. Commun.*, 2003, 2884-2885.
48. S. Khatua, S. H. Choi, J. Lee, J. O. Huh, Y. Do and D. G. Churchill, *Inorg. Chem.*, 2009, **48**, 1799-1801.



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