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# A new tridentate fluorescent-colorimetric chemosensor for copper(II) ion

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## ABSTRACT

A new tri-imidazolium salt, tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy) ethyl)-1H-imidazole-3'-ium-1'-yl)phenyl)amine hexafluorophosphate was prepared and characterized. Particularly, the recognition performance of the tri-imidazolium salt for cations was investigated through fluorescence and ultraviolet titrations, MS, IR spectra and <sup>1</sup>H NMR titrations. The results indicated that the tri-imidazolium salt can distinguish effectively copper(II) ion from other cations by the changes of spectroscopy and colour (from yellow to orange under sunlight). Furthermore, the tri-imidazolium salt was also used in detecting Cu<sup>2+</sup> through employing smartphone with the computed detection limit down to 0.51  $\mu$ M.

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## 1. Introduction

Copper is a fundamental trace element in human body [1]. Excessive or lack of copper in the human body will lead to a series of severe diseases, such as haematological manifestations, liver damage, gastrointestinal disturbances, neurodegenerative diseases, Wilson's, Parkinson's and Alzheimer's disease [2–13]. In addition, the excessive copper(II) ion of nature will destroy the ecosystem [14]. Therefore, the accurate detection of  $Cu^{2+}$  is very important to human and environment. Among the detection of  $Cu^{2+}$ , the fluorescent method is one of significant tools. Particularly, fluorescent chemosensors with colour change have attracted great attention of researchers owing to their speediness and convenience for providing qualitative information of analyte without any expensive and sophisticated instrument [15,16]. Though lots of chemosensors for  $Cu^{2+}$  have been reported [17–29], the design and synthesis of new practical chemosensors are still desirable.

Herein, a new tri-imidazolium salt tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy)ethyl)-1H-imidazole-3'-ium-1'-yl)phenyl)amine hexafluorophosphate (**1**) was designed and synthesized. The recognition performance of **1** for cations was

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https://doi.org/10.1016/j.tet.2019.130675 0040-4020/© 2019 Elsevier Ltd. All rights reserved. investigated through fluorescence and ultraviolet titrations, MS, IR spectra and <sup>1</sup>H NMR titrations.

## 2. Results and discussion

## 2.1. Preparation and characterization of tri-imidazolium salt 1

Triphenylamine was treated with bromine to give tris(4bromophenyl)amine, which further reacted with imidazole to get tris(4-(1H-imidazole-1-yl)phenyl)amine. Finally, tris(4-(1H-imidazole-1-yl)phenyl)amine was treated with 1-(2-bromoethoxy)-8hydroxy-9,10-anthraquinone to generate tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy)ethyl)-1H-imidazole-3'-ium-1'-yl)phenyl)amine bromide, followed using NH<sub>4</sub>PF<sub>6</sub> to perform anion exchange in MeOH to afford tris(4-(3-(2-((8hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy)ethyl)-1Himidazole-3'-ium-1'-yl)phenyl)amine hexafluorophosphate (1) (Scheme 1). Compound 1 had good stability in the air, and it was soluble in CH<sub>2</sub>Cl<sub>2</sub>, THF and DMSO, but nearly insoluble in petroleum ether, ethyl acetate, diethyl ether and water. From the <sup>1</sup>H NMR spectra of 1 (Fig. S12), the signal of phenolic hydroxyl (ArOH) and the signal of imidazolium proton (NCHN) were observed at  $\delta = 12.44$  ppm and 10.11 ppm, which are analogous to the signals of known 1-hydroxy-9,10-anthraquinone [30-32] and imidazolium salts [33-40].



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Scheme 1. Preparation of compound 1.

## 2.2. Detection of Cu(II) employing 1 as a chemosensor

Several cations (Na<sup>+</sup>, Li<sup>+</sup>, NH<sup>+</sup><sub>4</sub>, Ag<sup>+</sup>, K<sup>+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup> and Hg<sup>2+</sup>, using nitrate salts of them) were selected as guests to research the cation detection capability of **1** via fluorescence and UV spectroscopy.

As displayed in Fig. 1(a), the emission peak of 1 at ca. 577 nm was

ascribed to the emission of anthraquinone ( $\lambda_{ex} = 415$  nm, slit: 10 nm/10 nm, an equilibration time of 10 min). When 2.0 equivalent of Na<sup>+</sup>, Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ag<sup>+</sup>, K<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup> and Hg<sup>2+</sup> were added to the solutions of **1**, no obvious variations of fluorescent spectra and color were observed. However, the fluorescence intensity decreased drastically when the same amount of Cu<sup>2+</sup> was added, and the color of solution altered from yellow to orange under sunlight within 1 min



free 1  $\text{Li}^+$  Na<sup>+</sup> K<sup>+</sup> NH<sub>4</sub><sup>+</sup> Ag<sup>+</sup> Ni<sup>2+</sup> Ca<sup>2+</sup> Co<sup>2+</sup> Cu<sup>2+</sup> Fe<sup>2+</sup> Fe<sup>3+</sup> Mn<sup>2+</sup> Cr<sup>3+</sup> Cd<sup>2+</sup> Zn<sup>2+</sup> Mg<sup>2+</sup> Al<sup>3+</sup> Pb<sup>2+</sup> Hg<sup>2+</sup>

**(b)** 

**Fig. 1.** (a) The fluorescent spectra of 1 ( $5 \times 10^{-6}$  M) and adding 2.0 equivalent of different cations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Cu<sup>2+</sup>, Cu<sup>2+</sup>, Cra<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup> and Al<sup>3+</sup>, using nitrate salts of them) in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v = 1:49) at 25 °C ( $\lambda_{ex}$  = 415 nm, slit: 10 nm/10 nm,  $\lambda_{em}$  = 577 nm). (b) Visual colour variations of **1** with various cations.

(Fig. 1(b)). The change of this fluorescent intensity should be ascribed to the switched-on of the photoinduced electron transfer (PET) process from the imidazole to anthraquinone [41–44]. Additionally, the absorption peak of **1** ( $\varepsilon = 2.3 \times 10^4 \text{ mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ) at 415 nm did not exhibit any remarkable response to the addition of these cations except Cu<sup>2+</sup> (Fig. S1). These results showed that **1** was able to effectively distinguish Cu<sup>2+</sup> from other cations.

After that, the fluorescence titration experiments were conducted (Fig. 2). With the increasing  $C_{Cu}^{2+}$ , the fluorescent intensities of **1** at *ca*. 577 nm reduced little by little. When the ratio of  $C_{Cu}^{2+}/C_1$ ( $C_{Cu}^{2+}$  and **C**<sub>1</sub> being the concentrations of  $Cu^{2+}$  and **1**) was no more than 2:1, the fluorescence intensity quickly decreased with increasing  $C_{Cu}^{2+}$ . When the ratio was between 2:1 and 5:1, the decreasing tendency of the fluorescence intensity slowed down. Upon exceeding 5:1 of the ratio, higher  $C_{Cu}^{2+}$  did not lead to further emission decrease (the inset of Fig. 2). The reducing behavior of the fluorescent intensity of **1** with the increasing  $C_{Cu}^{2+}$  was discovered to abide by a traditional Stern-Volmer equation (Eq. (1)) [45,46].

$$F_0 / F = 1 + K_{SV} C_{Cu}^{2+}$$
 (1)

in which  $F_0$  represented the fluorescent intensity of free **1**, and *F* represented the fluorescent intensity of **1** with the addition of  $C_{cu}^{2+}$ . The  $K_{SV}$  defined the quenching efficiency of Cu<sup>2+</sup> to **1**.

The equation revealed that the value of  $F_0/F$  increased along with the increasing  $C_{cu}^2$ . The  $C_{cu}^{2+}$  from 0 to  $1 \times 10^{-5}$  M displayed a good linear relationship (R = 0.998) to the value of  $F_0/F$ , and the  $K_{SV}$  for  $1 \cdot Cu^{2+}$  was calculated as  $1 \times 10^5 \text{ M}^{-1}$  by using equation (1) (Fig. S2). Also, the limit of detection (LOD) was determined to be 0.049 µM according to the changes in fluorescence titrations (Fig. S3) [47], and this value was similar to the minimum that of reports [1,14,48,49] (the limits of detection for literatures were from 0.023 µM to 2.16 µM).

In addition, the UV titration experiments and Job's plot analysis were also carried out. The absorption peak of **1** at 373–485 nm reduced little by little with the enhancing  $C_{Cu}^{2+}$  (Fig. 3). In the inset of Fig. 3, the  $\chi\Delta A$  value approached the maximum value while molar fraction ( $\chi$ ) of **1** was equal to 0.5 [50], which displayed a stoichiometry of 1:1 for **1** · Cu<sup>2+</sup>. Through the standard Benesi-Hildebrand method, the value of *K* (stability constant) for **1** · Cu<sup>2+</sup> was



**Fig. 2.** The fluorescent titration spectra of **1** ( $5 \times 10^{-6}$  M) with various  $C_{cu}^{+}$  in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v = 1:49) at 25 °C ( $\lambda_{ex}$  = 415 nm, slit: 10 nm/10 nm,  $\lambda_{em}$  = 577 nm).  $C_{cu}^{+}$  for curves 1–23 are 0, 0.3, 0.6, 0.9, 1.5, 2, 2.5, 3, 3.5, 4.0, 4.5, 5, 6, 7, 8, 9, 12, 15, 18, 21, 25, 30, 35 × 10<sup>-6</sup> M. Inset: the fluorescence of **1** as a function of  $C_{cu}^{+}/C_1$  at 577 nm.



**Fig. 3.** The ultraviolet spectra of 1  $(1 \times 10^{-5} \text{ M})$  in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v = 1:49) at room temperature. The concentrations of Cu<sup>2+</sup> for curves 1–19 are 0, 0.04, 0.07, 0.11, 0.25, 0.43, 0.50, 0.57, 0.63, 0.85, 0.9, 1, 1.2, 1.4, 1.6, 2, 2.5, 3,  $4 \times 10^{-5}$  M. Inset: the Job's plot of  $1 \cdot Cu^{2+}$  complex at 415 nm in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v = 1:49).

computed as  $2.8 \times 10^5 \text{ M}^{-1}$  (R = 0.997) [51,52] (Eq. (2), Fig. S4), and it was analogous to the value of  $K_{SV}$  (1 × 10<sup>5</sup> M<sup>-1</sup>) obtained by fluorescent method.

$$A_0 / (A_0 - A) = [\varepsilon_r / (\varepsilon_r - \varepsilon_c)](1 / KC_{Cu}^{2+} + 1$$
(2)

where the absorption of free **1** was  $A_0$ , and the discrepancy of absorption between free **1** and  $\mathbf{1} \cdot \mathbf{Cu}^{2+}$  was ( $A_0$ -A). The molar extinction coefficients of free **1** and  $\mathbf{1} \cdot \mathbf{Cu}^{2+}$  were  $\varepsilon_r$  and  $\varepsilon_c$ , respectively. The ratio of intercept/slope was the stability constant *K* [53].

To measure the special selective capacity for  $Cu^{2+}$ , the competition experiments were carried out (Fig. S5). Firstly, 2.0 equivalent of several cations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup> and Hg<sup>2+</sup>) was added to solution of **1**, and then the same amount of Cu<sup>2+</sup> was added ( $5 \times 10^{-6}$  moL/L). But no remarkable interference was aroused by adding several cations, and the result displayed **1** had good selectivity for Cu<sup>2+</sup> [54].

The anti-jamming capability to counteranions of **1** has also been tested via using Cu(OAc)<sub>2</sub>, CuSO<sub>4</sub>, CuCO<sub>3</sub> and CuCl<sub>2</sub>. After adding 2.0 equiv. of Cu(OAc)<sub>2</sub>, CuSO<sub>4</sub>, CuCO<sub>3</sub> and CuCl<sub>2</sub> to the solutions of **1** ( $5 \times 10^{-6}$  moL/L), the decrease of fluorescence intensity and quick colour change (from yellow to orange under sunlight) were observed, which were similar to the case of only addition of Cu(NO<sub>3</sub>)<sub>2</sub>. This test indicated that the recognition of **1** for Cu<sup>2+</sup> had high capacity of resisting disturbance to the anions (Fig. S6). Also, we carried out reversible binding tests. From Fig. S7, the fluorescent intensities of **1** at *ca*. 577 nm enhanced with adding EDTA, because EDTA can capture Cu<sup>2+</sup> from  $1 \cdot Cu^{2+}$  to release free **1**. After adding Cu<sup>2+</sup> again,  $1 \cdot Cu^{2+}$  was regenerated and the fluorescent intensities reduced again. This result showed that compound **1** exhibited good regeneration ability.

## 2.3. Interactions of **1** with $Cu^{2+}$

The nitrogen atom of triphenylamine in compound **1** is sp<sup>3</sup> hybridization based on literatures [55–57], therefore, compound **1** should be a trigonal pyramidal molecular geometry as shown in Scheme 2. According to the characteristics of **1**,  $Cu^{2+} \cdots N$ ,  $Cu^{2+} \cdots O$  and  $Cu^{2+} \cdots \pi$  interactions are the most likely binding mode. To get

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Scheme 2. The interactions of Cu<sup>2+</sup> with 1.

relative information about the binding pattern for  $Cu^{2+}$  and **1**, <sup>1</sup>H NMR titration tests were conducted in DMSO- $d_6$  (Fig. 4). As depicted in Fig. 4, when  $C_{Cu}^{2+}$  changed from 0 to 1 equivalent, the signals of Ha-Hg on anthraquinone moved little by little to upfield, whereas other proton signals of **1** did not had remarkable shift. Thus,  $Cu^{2+}\cdots N$  interactions (N being from triphenylamine) can be removed, otherwise, the proton signals on benzene rings of triphenylamine should have obvious shift. In IR spectra (Fig. S9), because of the carbonyl signal (O=C) having no remarkable change,  $Cu^{2+}\cdots O=C$  interactions should also be excluded. Besides,  $Cu^{2+}\cdots HO$  interactions were not likely binding mode, and the reason was if there existed  $Cu^{2+}\cdots HO$  interactions, the proton signals on OH not only had remarkable shift but also widen due to the paramagnetism effect of  $Cu^{2+}$ . But experimental results displayed that only upfield shift for proton signals on OH was



**Fig. 4.** The partial <sup>1</sup>H NMR spectra. (i) Free 1; (ii) 0.25 equivalent of  $Cu^{2+}$  and 1; (iii) 0.5 equivalent of  $Cu^{2+}$  and 1; (iv) 0.75 equivalent of  $Cu^{2+}$  and 1; (v) 1 equivalent of  $Cu^{2+}$  and 1; (vi) 1.5 equivalent of  $Cu^{2+}$  and 1.

observed, and no widen signals was observed [58–60]. Therefore,  $Cu^{2+}\cdots\pi$  interactions ( $\pi$  being from anthraquinone) was most possible acting force between  $Cu^{2+}$  and **1**, and this was corresponding above-mentioned the experimental results that the signals of Ha-Hg on anthraquinone had remarkable changes.  $Cu^{2+}\cdots\pi$ interactions are also reasonable from the consideration of electron cloud density, because anthraquinone has larger electron cloud density in all  $\pi$  systems of **1**, and it is easier to combine with the positive charge of copper(II) ion.  $Cu^{2+}\cdots\pi$  interactions are not uncommon, and they have been reported in some literatures [61-63]. Furthermore, through comparison of Fig. 4(v) and Fig. 4(vi), the signals of Ha-Hg stayed the same upon adding more Cu<sup>2+</sup>, which displayed the formation of 1:1 complexation between **1** and  $Cu^{2+}$ . Additionally, the ESI-MS and cold ESI-MS of  $1 \cdot Cu^{2+}$ (Fig. S8 (a) and (b)) were measured with gas temperature at 300 °C and 220 °C. Fig. S8(a) at 300 °C displayed weak peaks in the range of m/z = 475-480. But the peak of  $[1-3(PF_6^-) + Cu(NO_3)_2]^{3+}/3$   $(m/z)^{3+}/3$ 477.1354) can be observed after Fig. S8(a) being enlarged as shown in inset of Fig. S8(a). In Fig. S8(b) at 220 °C, a distinct peak of  $[1-3(PF_6) + Cu(NO_3)_2]^{3+}/3$  (*m*/*z* 477.1354) was observed. This further determined that a 1:1 complexation between **1** and Cu<sup>2+</sup> was generated. These results agreed with the survey of Job's plot experiment (Inset of Fig. 3). In IR spectra (Fig. S9), the absorption peaks of phenolic hydroxyl group shifted from 3392 cm<sup>-1</sup> in free **1** to  $3431 \text{ cm}^{-1}$  in **1** · Cu<sup>2+</sup>, C–O bending vibration peaks shifted from 1063 cm<sup>-1</sup> in free **1** to 1080 cm<sup>-1</sup> in **1** · Cu<sup>2+</sup>.

Through the comprehensive analyses of above results,  $Cu^{2+}$  was held by three anthraquinones through  $Cu^{2+}\cdots\pi$  interactions. It was unfortunate that we failed to get the single crystal of  $1 \cdot Cu^{2+}$ .

## 2.4. Integration of 1 through RGB colour value

A smartphone APP of free downloads (RGB Colour Value; Red, Green and Blue) was applied to detect the various analytes [64-66], which can provide a method for the spot quantitative inspection of Cu<sup>2+</sup>.

Herein, we integrated **1** with a APP of smartphone (RGB Colour Value) to record the values of RGB when the yellow colour of free **1** changed to orange with increasing  $C_{Cu}^{2+}$ . The whole-number value for each of the three colours (red, green and blue) from 0 to 255 represented the standard RGB scale. The variation in standard RGB values (the number [0,0,0] was absolute black, whereas [255,255,255] was true white) were recorded through applying the back camera (using iPhone 6, we downloaded online the APP). The RGB values of vials including **1** solution ( $5 \times 10^{-6}$  M) with different  $C_{Cu}^{2+}$  (0, 2, 4, 8, 12, 16, 20, 24, 28, 32,  $36 \times 10^{-6}$  M) were obtained by scanning these vials via the APP. In Fig. 5, the  $C_{Cu}^{2+}$  from 0 to

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Fig. 5. The RGB colour values were caught through smartphone APP for confirming  $C_{Cu}^{2+}$  in solvent.

 $36 \times 10^{-6}$  M displayed a good linear relationship (R = 0.98) to the value of R/G. According to the calibration curve (R<sup>2</sup> = 0.98), the linear equation (3) was obtained as

$$Y = 0.02505X + 1.05329 \tag{3}$$

in which Y was R/G ratio and X was the  $C_{Cu}^{2+}.$  Furthermore, the limit of detection was calculated to be 0.51  $\mu M.$ 

## 3. Experimental section

## 3.1. General procedures

1-(2-Bromoethoxy)-8-hydroxy-9,10-anthraquinone was prepared according to the method reported in literature [30,31]. The solvents and chemicals for experiment were analytical grade by purchasing commercially. A RF-5301PC fluorescence spectrophotometer (Shimadzu) was used for the report of the fluorescence spectra at room temperature (the emission and excitation slits were 10/10 nm). UV–vis absorption spectra were recorded using JASCO-V570 spectrometer at room temperature. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected using a Varian spectrometer. Perkin-Elmer 2400C Elemental Analyzer was applied in the test of elemental analyses and the samples were prepared after crystallization. Infrared spectra were reported applying a PerkinElmer spectrophotometer. The Accurate-Mass Q-TOF LC/MS (Agilent) was applied for recording ESI-MS spectra. A Boetius Block apparatus was applied for measuring melting points.

## 3.2. Preparation of tris(4-bromophenyl)amine

A chloroform solution (30 mL) of triphenylamine (5.50 g, 22.4 mmol) was stirred for 10 min at 0 °C and then the bromine (13.46 g, 84.2 mmol) was dropped slowly. The ethanol (100 mL) was added when the solution color of the reaction turned green. The mixture was continually stirred for 24 h at 40 °C, and a large amount of solid was formed. After filtration, the crude product was washed with cold ethanol (20 mL) to obtain a white powder of tris(4-bromophenyl)amine. Yield: 5.95 g (55%). Mp: 140–142 °C. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>Br<sub>3</sub>N: C, 44.85; H, 2.5; N, 2.9%. Found: C, 44.6; H, 2.3; N, 3.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  6.93 (d, *J* = 8.8 Hz, 6H, Ar*H*).

## 3.3. Preparation of tris[4-(1H-imidazole-1-yl)phenyl]amine

A DMF (50 mL) suspension of K<sub>2</sub>CO<sub>3</sub> (1.27 g, 9.2 mmol), tris(4bromophenyl)amine (610 mg, 1.3 mmol), imidazole (920 mg, 13.5 mmol) and CuI (210 mg, 1.1 mmol) was stirred for 36 h at 130 °C. After filtration, the mother solution was kept in ice bath for 0.5 h, and a white precipitate was formed. The precipitate was separated by filtration. Then this solid was dissolved in ethanol (100 mL), and the insoluble matter was removed through filtering. The ethanol was removed by rotary evaporator to afford a white powder of tris(4-(1H-imidazole-1-yl)phenyl)amine. Yield: 0.45 g (80%). Mp: 243–245 °C. Anal. Calcd for C<sub>27</sub>H<sub>21</sub>N<sub>7</sub>: C, 73.1; H, 4.7; N, 22.1%. Found: C, 73.05; H, 4.6; N, 22.35%. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.11 (s, 3H, ArH), 7.20 (d, J = 8.8 Hz, 6H, ArH), 7.62 (d, J = 8.8 Hz, 6H, ArH), 7.69 (s, 3H, ArH), 8.20 (s, 3H, ArH).

## 3.4. Preparation of tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'dihydroanthracen-1-yl)oxy)ethyl)-1H-imidazole-3'-ium-1'-yl) phenyl)amine hexafluorophosphate (**1**)

A DMF (100 mL) solution of tris(4-(1H-imidazole-1-vl)phenvl) amine (150 mg, 0.3 mmol) and 1-(2-bromoethoxy)-8-hydroxy-9,10-anthraquinone (350 mg, 1.0 mmol) was stirred for 48 h at 120 °C. A yellow solid was precipitated after cooling to room temperature. By filtration and washing with a small part of CH<sub>3</sub>CN, a yellow powder of tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy)ethyl)-1H-imidazole-3'-ium-1'-yl)phenyl) amine bromide was obtained. And then this yellow powder was dissolved in methanol (15 mL), following the methanol solution (15 mL) of NH<sub>4</sub>PF<sub>6</sub> (130 mg, 0.9 mmol) was added with stirring for 24 h at ambient temperature to form a yellow precipitate. A yellow powder of tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy)ethyl)-1H-imidazole-3'-ium-1'-yl)phenyl)amine hexafluorophosphate (1) was gained by filtration. Yield: 0.35 g (71%). M.p: 259–260 °C. HRMS (EI): m/z [(1 - 3PF<sub>6</sub>)<sup>3+</sup>/ 3] = 415.0414. Anal. Calcd for C<sub>75</sub>H<sub>54</sub>N<sub>7</sub>O<sub>12</sub>F<sub>18</sub>P<sub>3</sub>: C, 53.6; H, 3.2; N, 5.8%. Found: C, 53.7; H, 3.4; N, 6.0%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  4.68 (t, J = 2.2 Hz, 6H, CH<sub>2</sub>), 4.84 (t, J = 2.2 Hz, 6H, CH<sub>2</sub>), 7.25 (d, *J* = 8.4 Hz, 3H, Ar*H*), 7.43 (d, *J* = 8.8 Hz, 6H, Ar*H*), 7.53 (d, *J* = 7.6 Hz, 3H, ArH), 7.62 (t, J = 8.0 Hz, 3H, ArH), 7.72 (d, J = 8.8 Hz, 3H, ArH), 7.87 (t, J = 3.8 Hz, 9H, ArH), 7.96 (t, J = 4.0 Hz, 3H, ArH), 8.22 (s, 3H, ArH), 8.37 (s, 3H, ArH), 10.11 (s, 3H, imiH), 12.40 (s, 3H, ArOH). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 48.7 (CH<sub>2</sub>), 67.0 (CH<sub>2</sub>), 116.6 (ArC), 118.4 (ArC), 120.0 (ArC), 120.2 (ArC), 120.9 (ArC), 123.2 (ArC), 124.3

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(ArC), 125.2 (ArC), 126.4 (ArC), 129.7 (ArC), 130.3 (ArC), 132.3 (ArC), 134.9 (ArC), 136.5 (ArC), 147.2 (ArC), 158.6 (ArC), 161.2 (ArC), 181.7 (CO), 188.1 (CO). IR (KBr, cm<sup>-1</sup>): 3392s, 2938w, 2861w, 2403w, 2389w, 1653 m, 1574 m, 1435w, 1359w, 1289w, 1063vs, 1009 m, 937s. 761w. 741w. 517s.

## 3.5. Fluorescent experiment

The stock solutions  $(1 \times 10^{-4} \text{ M for } \mathbf{1} \text{ or } 1 \times 10^{-3} \text{ M for guests})$ were prepared through dissolving **1** or the guests in DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v = 1:49). In the screening experiments of cations, placed the stock solutions (0.5 mL for 1 and 0.1 mL for guests) into a 10 mL volumetric flask, which were diluted to 10 mL with DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v=1:49) to prepare test solutions  $(5 \times 10^{-6} \text{ M for } 1 \text{ and } 1)$  $10 \times 10^{-6}$  M for guests). In fluorescence titrations, placed the stock solutions (0.5 mL for 1 and 0-0.35 mL for guests) into a 10 mL volumetric flask, which were diluted to 10 mL with DMSO/CH<sub>2</sub>Cl<sub>2</sub> (v:v=1:49) to prepare test solutions  $(5 \times 10^{-6} \text{ M for } 1 \text{ and } 1)$  $0-35 \times 10^{-6}$  M for guests). After adding Cu<sup>2+</sup>, an equilibration time of 10 min was allowed before the fluorescence spectra were recorded, and the colour change was from yellow to orange under sunlight within 1 min. A Shimadzu RF-5301PC fluorescence spectrophotometer was applied for reporting fluorescence spectra in the range of 485–710 nm, and the excitation wavelength was 415 nm (slit: 10 nm/10 nm).

#### 3.6. UV titrations

In UV titrations, we prepared the stock solutions using similar to the methods of fluorescent titrations. The  $C_{1}$  and  $C_{Cu}^{2+}$  were  $1\times 10^{-5}$  moL/L and 0–4  $\times 10^{-5}$  moL/L. A JASCO-V570 spectrometer was used for recording absorption spectra in the range of 373–485 nm at room temperature.

## 3.7. Job's plot

We prepared also the stock solutions using similar to the methods of fluorescent tests. The total concentration maintained  $10\times 10^{-6}\,M$  in the test solutions, and the molar ratios of  $C_{Cu}^{2+}/C_1$ changed from 0:1 to 1:0. The absorption spectra were recorded on according to the methods of UV titrations.

## 4. Conclusions

In sum, a new compound tris(4-(3-(2-((8-hydroxy-9,10-dioxo-9',10'-dihydroanthracen-1-yl)oxy)ethyl)-1H-imidazole-3'-ium-1'yl)phenyl)amine hexafluorophosphate (1) was prepared and characterized. The cation recognition performance of 1 was explored through fluorescent and ultraviolet titrations, MS, <sup>1</sup>H NMR titrations and IR spectra. These results displayed that 1 was of good selectivity for  $Cu^{2+}$ . After **1** was mixed with  $Cu^{2+}$ , a distinct and quick colour change from yellow to orange under sunlight within 1 min was observed for naked eyes accompanying with obvious fluorescent reducing. Even if the limit of detection was down to 0.049  $\mu$ M, the detection of **1** to Cu<sup>2+</sup> was still sensitive. Furthermore, this chemosensor can be also used in the detecting  $Cu^{2+}$ through applying smartphone with the computed detection limit down to  $0.51 \,\mu$ M. Therefore, compound **1** may have latent uses for detection of  $Cu^{2+}$ .

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.130675.

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