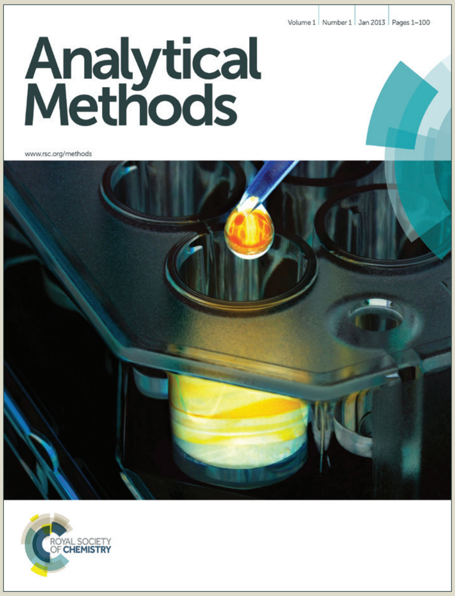
Analytical Methods

Accepted Manuscript



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A novel colorimetric sensor based on diarylethene derivative for selective detection of Cu(II)

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Abstract: A new diarylethene derivative with excellent photochromism and remarkable fatigue resistance in solution was synthesized. The interaction between its closed-ring diarylethene and Cu^{2+} caused a notable change in its absorption spectrum with an significant color change from purple to red. However, this as-synthesized diarylethene derivative did not have any obvious change with other metal ions. The 1 : 1 binding stoichiometry between Cu^{2+} and derivative was obtained using the Job's plot and ESI-MS analysis. The binding constant of $(1.29 \pm 0.17) \times 10^4$ M^{-1} for diarylethene-Cu^{2+} complex was calculated from the Benesei-Hildebrand plot. The detection limit for the analysis of Cu^{2+} ions was found to be 1.62×10^{-6} mol L^{-1}.

1. Introduction

Recently, there has been a growing demand for highly selective chemical sensors to detect metal ions in environmental and biological samples.[1] Although copper is an essential trace element and plays a critical role in many environmental, biological, and chemical systems,[2] Cu^{2+}-polluted surroundings can cause neurodegenerative diseases, such as Alzheimer's and Wilson's diseases, probably because it is involved in the production of reactive oxygen species in human body.[3] Therefore, a reliable and convenient method to determine Cu^{2+} in environmental and biological samples is required.[4]

Except of atomic absorption spectrometry,[5] fluorescence techniques,[6] and electrochemical methods,[7] colorimetric methods to detect toxic ions, including Cu^{2+}, have attracted considerable attention recently due to its excellent sensitivity, low cost, convenience, and most importantly 'naked-eye' detection.[8] Among the reported photoresponsive materials, diarylethenes are the most promising with excellent thermal stability, remarkable fatigue resistance and rapid response,[9] because many ions can induce diarylethenes to undergo multi-state transformations.[10] However, only a few colorimetric sensors based on diarylethenes for Cu^{2+} have been reported.[11]

It is well-known that di-2-picolylamine has a high affinity to transition metal cations and has been used widely in the design and synthesis of many sensors.[12] Additionally, hydroxyl group could also affect the absorption spectrum by deprotonation or coordination with metal ions.[13] Therefore, the constructed colorimetric sensor based on diarylethene with di-2-picolylamine unit and hydroxyl group may have excellent selectivity for transition and post-transition metal cations, such as Zn^{2+}, Cd^{2+}, Cu^{2+}, et al. More importantly, a large shift in absorption spectrum could also be expected due to the significant enhancement of the intramolecular charge transfer (ICT) from the donating part (phenolic hydroxyl group) to the electronic withdrawing part (diarylethene), thus significant color change can be observed by the naked eyes.

In this study, a novel diarylethene with a di-2-picolylamine unit and a hydroxyl group has been designed and synthesized for the first time. Its closed-ring isomers sensitivity and selectivity for Cu^{2+} ions were systematically investigated, in which Cu^{2+} ions caused significant changes in the absorption spectra and visible color change from the purple to red. The photochromic process of the diarylethene was shown in Scheme 1.

< Scheme 1>

2. Experimental

2.1 General methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as solvent and tetramethylsilane as an internal standard. IR spectra were carried out on a Bruker Vertex-70 spectrometer. Mass spectra were measured on a Bruker AmaZon SL Ion Trap Mass spectrometer. Elemental analysis was carried out on a PE CHN 2400 analyzer. UV-vis absorption spectra were measured on an Agilent 8453 UV-vis spectrometer. Photo-irradiation was carried out with an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 visible lamp. Lights of appropriate wavelengths were isolated by different light filters. All solvents used were of spectrograde and purified by distillation prior to use. All other reagents were obtained from J&K Scientific Ltd. without further purification.

2.2 Synthesis

Diarylethene **1o** was synthesized as presented in Scheme 2. 3-Bromo-2-methyl-5-(4-methoxyl-phenyl) thiophene (**2**) was synthesized through Suzuki coupling reaction,[14] 1-Fluorine-2-(2,5-dimethyl-3-thienyl) perfluorocyclopentene (**3**) was synthesized from

(2,5-dimethyl-3-bromine) thiophene.[15] Lithiation of **2** in THF at 198 K was followed by the addition of **3** to generate compound **4**, which was then treated with BBr_3 in dichloromethane at 198 K to produce diarylethene **5** (yield: 91%).[10h] MS (ESI, *m/z*): $[M^+]$ calcd. of $C_{22}H_{16}F_6OS_2$, 474.1; found, 473.2 $[M\text{-}H]^+$.

A mixture of di-2-picolylamine (0.24 g, 1.20 mmol) and paraformaldehyde (0.06 g) was refluxed in ethanol (10 mL) and became a clear yellow solution. The solution was refluxed for 48 h after compound **5** (0.28 g, 0.60 mmol) was added. The solvent was removed with rotary evaporation, and the residue was purified by column chromatography on silica gel with the eluent petroleum ether/ethyl acetate (2:1 v/v). The solvent was removed with rotary evaporation to give a yellow solid **1o** (yield: 76%). Mp. = 336-337 K; Anal. calcd for $C_{35}H_{29}F_6N_3OS_2$ (%): C, 61.30; H, 4.26; N, 6.13, found: C, 61.28; H, 4.28; N, 6.15; ^1H NMR (400 MHz, $CDCl_3$, TMS), δ (ppm): 1.78 (s, 3H), 1.80 (s, 3H), 2.35 (s, 3H), 3.75 (s, 2H), 3.84 (s, 4H), 6.66 (s, 1H), 6.85 (d, 1H, $J = 8.0$ Hz), 7.03 (s, 1H), 7.12 (t, 2H, $J = 6.0$ Hz), 7.16 (s, 1H), 7.27 (d, 3H, $J = 7.2$ Hz), 7.57 (t, 2H, $J = 7.2$ Hz), 8.51 (d, 2H, $J = 4.0$ Hz), 11.42 (s, 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ (ppm): 14.6, 14.8, 15.1, 56.8, 59.0, 117.2, 120.8, 122.3, 123.2, 123.5, 124.5, 124.7, 124.9, 125.8, 126.6, 127.6, 127.8, 136.8, 137.6, 139.8, 142.3, 148.9, 157.8, 158.2; IR (ν, cm^{-1}): 761, 823, 894, 983, 1051, 1115, 1191, 1271, 1337, 1373, 1436, 1479, 1596, 2823, 2922, 3427; MS(ESI, *m/z*): $[M^+]$ calcd. of $C_{35}H_{29}F_6N_3OS_2$, 685.2; found, 686.1 $[M+H]^+$.

<Scheme 2>

2.3 UV-vis experiments

The diarylethene solution (2.0×10^{-5} mol L^{-1}) was prepared in CH_3CN. Metal nitrates were used as ion sources in this study, except of $HgCl_2$, $MnCl_2$, $BaCl_2$. All the metal salts were dissolved in distilled water (0.1 mol L^{-1}). The volume of the diarylethene solution used in the UV-vis measurements was 3.0 mL. The effects of Cu^{2+} ions on the diarylethene with a concentration of 2.0×10^{-5} mol L^{-1} in CH_3CN could be easily observed by the naked eye.

2.4 Mass spectra experiments

The diarylethene solution (2.0×10^{-4} mol L^{-1}) was prepared in methanol (2.0 mL). After irradiation with 297 nm light to the closed-ring state, 12 μL of the Cu^{2+} solution (0.1 mol L^{-1}) were transferred to the solution. The mixture was shaken up for a few seconds, mass spectra were taken at room temperature.

2.5 Determination of cyclization/cycloreversion quantum yields

The cyclization and cycloreversion quantum yields were determined using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as reference with values of 0.59 and 0.013, respectively.[16] The absorbance of the sample and the reference at the irradiation wavelength (297 nm) were adjusted to be the same for the cyclization quantum yield measurement. The reaction rate of the sample and the reference were measured in the same conditions and compared. For the cyclization quantum yield measurement, absorbance (A) at the absorption maximum of the closed-ring isomer was plotted against time. For the cycloreversion quantum yield measurement, -log A at the absorption of the irradiated wavelength was plotted against time. The measurement was carried out three times, and the value was determined by averaging.

3. Results and Discussion

3.1 Photochromic properties of 1o

Diarylethene **1o** showed favorable photochromism and could be switched between the colorless open-ring isomers (**1o**) and the colored closed-ring isomers (**1c**) through alternating irradiation with UV light and visible light. In acetonitrile, the absorption spectral and color changes of **1o** were shown in Fig. 1a. The absorption maximum of **1o** was observed at 299 nm ($\varepsilon = 2.60 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$) due to $\pi \rightarrow \pi^*$ transition.[17] Upon irradiation with 297 nm light, the colorless solution of **1o** turned purple and a new visible absorption band centered at 558 nm ($\varepsilon = 1.20 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$) emerged due to the formation of closed-ring isomer **1c**. Reversely, the purple solution of **1c** could be completely bleached upon irradiation with visible light ($\lambda > 500$ nm) and the original absorption spectrum was recovered quantitatively. With 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as the reference compound,[16] the ring cyclization and cycloreversion quantum yields were determined to be 0.15 and 0.053, respectively. The fatigue resistance of **1** was tested in acetonitrile through alternative irradiation with UV and visible light in air at room temperature. As showed in Fig. 1b, the coloration and decoloration cycles of **1** could be repeated for 50 times with only 6.8 % degradation.

<Fig. 1>

3.2 Optical response of 1c to metal ions

The recognition between **1c** and different metal cations were investigated with UV-vis spectroscopy in acetonitrile solution. From the absorption spectrum of **1c** in acetonitrile, it could be found that an intensive absorption band appeared in visible region peaked at 558 nm. Variation of absorption spectra of **1c** upon addition of 5.0 equiv. of different metal cations, including Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{3+}, Cr^{3+} and Al^{3+}, was shown in Fig. 2. Generally, di-2-picolylamine has been extensively used as a Zn^{2+} ligand for its high affinity and excellent selectivity.[18] Interestingly, there was a slight increase and red shift in the absorption spectra of **1c** with the titration of Zn^{2+} as other metal ions, such as Cd^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+},

Mn^{2+}, Ca^{2+}, Mg^{2+}, etc. Small decrease at 558 nm was observed in the presence of Al^{3+} and Cr^{3+}. Upon the addition of Fe^{3+}, the absorption maximum had a slight increase and a minimal blue shift. The maximum absorption peak had an obvious blue shift from 558 to 504 nm upon the addition of Cu^{2+} to **1c**, which was accompanied by a color change from purple to red. These results indicated that the capture of Cu^{2+} by the receptor di-2-picolylamine could result in a decrease of the electron-donating ability of the phenolic hydroxyl group, thus resulting in a decrease in intramolecular charge transfer (ICT) efficiency.[12e,18a] Upon irradiation with visible light (λ > 500 nm), the red solution of **1c-Cu**$^{2+}$ did not change again. The red solution could remained stable for ten days at room temperature in the dark.

<Fig. 2>

3.3 UV-vis properties of 1c and 1o with Cu^{2+} ions

In order to study the interaction of **1c** and Cu^{2+}, an ultraviolet absorbance titration experiment was carried out. The UV-vis absorbance titration study revealed a steady rise of absorbance at 504 nm on increasing the concentration of copper ions from 4.0×10^{-6} to 6.0×10^{-5} mol L^{-1}. Consistent with the UV-Vis spectral change, the color of **1c** solution changed from purple to red in the presence of Cu^{2+} ions (Fig. 3a). These results indicated that **1c** could serve as a potential candidate for a "naked eyes" sensor of Cu^{2+} with excellent selectivity. The color change could be due to the formation of the complex of Cu^{2+} and **1c**. Even with the addition of ethylene diamine tetraacetic acid disodium salt (Na_2EDTA) aqueous solution, the red solution of **1c** and Cu^{2+} did not change again (Fig. 3a insert), suggesting the sensing process of **1c** in response to Cu^{2+} ions was irreversible. From the absorbance titration data, according to the methodology presented in reference,[19] the limit of detection (LOD) of 1.62×10^{-6} mol L^{-1} was estimated from the calibration curve (Fig. 3b) and then compared with some recently reported Cu^{2+} sensors (Table 1). The significant changes in the spectra could be used to estimate the stoichiometry and association constant of the metal complex through spectrophotometric titration.

<Fig. 3>

<Table 1>

Job's plot analysis of **1c** and Cu^{2+} was carried out according to the methodology presented in reference.[24] the Job's plot analysis of **1c** and Cu^{2+} has been carried out by UV-vis titration in acetonitrile as shown in Fig. 4 with the maximum mole fraction of 50% in accordance with the proposed binding stoichiometry of 1 : 1. With UV-vis titration results, the association constant (K_a) of **1c** with Cu^{2+} could be calculated from the Benesi-Hildebrand equation,[25] and the relationship between $A_0/(A-A_0)$ and $1/[Cu^{2+}]$ was linear with a good linear constant (R = 0.998) (Fig. 5). Based on the 1 : 1 stoichiometry and UV-vis titration data, Ka turned out to be $(1.29 \pm 0.17) \times 10^4$ L mol^{-1}, which was within the previously reported values (10^4-10^5) for Cu^{2+}-binding chemosensors.[26]

<Fig. 4>

<Fig. 5>

As **1c**, the interaction between **1o** and Cu^{2+} was also investigated through ultraviolet absorbance titration. Upon the addition of Cu^{2+}, there was not clear color changes of **1o** solution. As shown in Fig. 6, the absorption maximum at 299 nm of **1o** was decreased with a new absorption maximum at 360 nm, which could be ascribed to the MLCT transition and ($\pi \rightarrow \pi^*$), with some mixing of metal-perturbed intraligand (IL) ($\pi \rightarrow \pi^*$) transition.[9b,27] These results indicated that **1o** also had significant binding affinity to Cu^{2+}.

<Fig. 6>

3.4 Mechanism of 1c with Cu^{2+} ions

In order to confirm the coordination between **1c** and Cu^{2+}, NMR, mass spectrometry (MS) and infrared (IR) spectra were also used to further study the binding affinity of **1c** to Cu^{2+}. ^1H NMR experiments were carried out in DMSO-d_6. But the ^1H NMR spectrum of **1c-Cu^{2+}** does not provide useful information due to the paramagnetic character of Cu^{2+}.[12e] An intensive peak at m/z 748.0 assigned to $[\mathbf{1c}+\mathbf{Cu}]^+$ was observed (calcd 748.1) (Fig. 7a), which provided strong evidence for the formation of 1 : 1 complex between **1c** and Cu^{2+} in the electron-spray ionization (ESI) measurements. In IR spectroscopy, two new bands at 422 and 488 cm^{-1} and a new band at 655 cm^{-1} of **1c-Cu^{2+}** corresponding to the characteristic vibration of Cu-N and Cu-O, respectively.[28] The band at 3427 cm^{-1} corresponding to the vibration of O-H was disappeared upon addition of Cu^{2+} ions (Fig. 7b). These results also confirmed the formation of complex **1c-Cu^{2+}**. Based on the IR spectra and ESI-mass spectrometry, the structure of a 1 : 1 complex from **1c** and Cu^{2+} could be determined. In this complex, Cu^{2+} may coordinate with nitrogen atoms of two pyridine groups, oxygen atom of hydroxyl group and nitrogen atom of the tertiary amine. The proposed interaction mode between **1c** and Cu^{2+} was given in Fig. 8.

< Fig. 7>

< Fig. 8>

3.5 Selective response of 1c to Cu^{2+}

The selectivity of **1c** to Cu^{2+} was investigated. Variation of absorption of **1c** at 504 nm upon the addition of 5.0 equivalents of other metal cations, including Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Cr^{3+} and Al^{3+}, were shown in Fig. 9a. The absorption at 504 nm showed no significant change upon the addition of the metal ions above mentioned. Only a slight increase at

504 nm was observed in the presence of Ba^{2+} and Fe^{3+} as showed in Fig. 9b. However, the color of **1c** changed to red with the addition of Cu^{2+}, which might be due to the special binding affinity between Cu^{2+} and the di-2-picolylamine moiety in diarylethene system.[10b] The effect of competitive metal ions was studied by adding Cu^{2+} to **1c** solution in the presence of the above mentioned metal ions (Fig. 9c). The miscellaneous competitive cations did not lead to any significant absorption in the visible region. Moreover, in the presence of 5.0 equiv. of other competitive cations, the Cu^{2+} still resulted in the similar absorption change. These results indicated that the selectivity of **1c** for Cu^{2+} over other competitive cations is remarkably high, and that **1c** could serve as a potential candidate for colorimetric sensor of Cu^{2+}.

<Fig. 9>

4. Conclusion

In summary, a new photochromic diarylethene derivative with a di-2-picolylamine unit and a hydroxyl group was designed and synthesized firstly. This diarylethene derivative exhibited excellent photochromism with remarkable fatigue resistance. Furthermore, the closed-ring isomer of the diarylethene exhibited excellent sensitivity and selectivity to Cu^{2+} over other metal cations. A significant color change from purple to red could be observed directly with naked eyes, suggesting the possibility to make a diarylethene-based colorimetric sensor for detection of Cu^{2+}. This study showed a simple and convenient method to detect Cu^{2+} based on a diarylethene derivative.

Acknowledgements

The authors are grateful for the financial support from the National Natural Science Foundation of China (21362013, 51373072), the Science Fund of Natural Science Foundation of Jiangxi

Province (20132BAB203005), and the Project of the Science Funds of Jiangxi Education Office (KJLD12035, GJJ12587).

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Graphical Abstract

A novel colorimetric sensor based on diarylethene derivative for selective detection of Cu(II)

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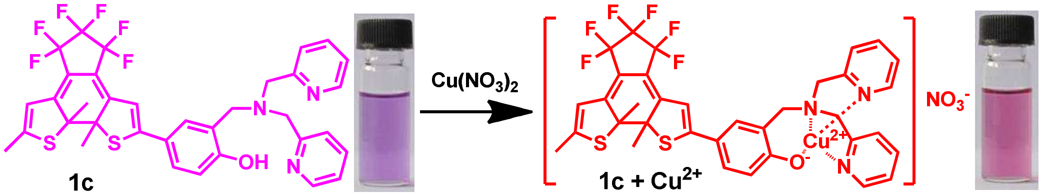


A novel photochromic diarylethene derivative with a di-2-picolylamine unit and a hydroxyl group was designed and synthesized firstly. Its closed-ring isomers selective interaction with Cu^{2+} ions was investigated systematically. The results indicated that the diarylethene derivative could be used as a colorimetric sensor for the selective recognition of Cu^{2+} ions.

Table 1 Comparative study of analytical performance of **1c** with other reported sensors

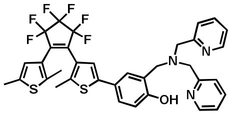
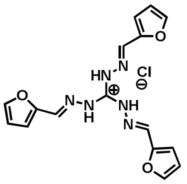
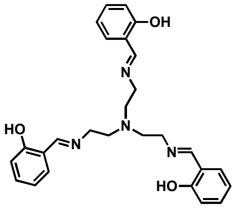
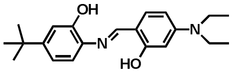
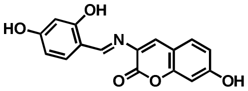
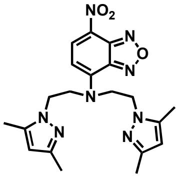
No.	Sensors	Association constant (Ka) (L mol^{-1})	LOD (mol L^{-1})	Approaches	Ref.
1		$(1.29 \pm 0.17) \times 10^4$	1.62×10^{-6}	Colorimetry	This work
2		1.1×10^5	2.7×10^{-6}	Colorimetry	20
3		5.0118×10^4	1.5×10^{-6}	Colorimetry	21
4		1.5×10^4	1.15×10^{-6}	Emission	19
5		NA	1.04×10^{-4}	Emission	22
6		2.62×10^4	NA	Emission	23

Figure captions

Scheme 1. Photochromism of diarylethene **1o**.

Scheme 2. Synthetic route of diarylethene **1o**.

Fig. 1. (a) Absorption and color changes of **1o** (2.0×10^{-5} mol L^{-1}, in CH_3CN) upon irradiation with UV-vis light; (b) Fatigue resistance of **1** in acetonitrile in air at room temperature.

Fig. 2. Absorption changes of **1c** (2.0×10^{-5} mol L^{-1}, in CH_3CN) upon addition of 5.0 equiv. of different metal cations.

Fig. 3. Absorption (a) and color (b) changes of **1c** (2.0×10^{-5} mol L^{-1}, in CH_3CN) upon addition with Cu^{2+} ions.

Fig. 4. Job's plot analysis of **1c** and Cu^{2+} in CH_3CN. The total molar concentration of **1c** and Cu^{2+} is 2.0×10^{-5} mol L^{-1}.

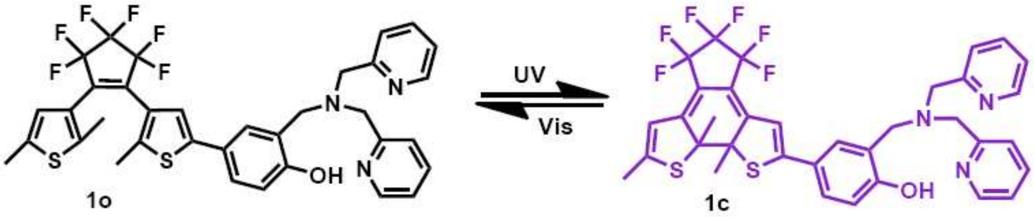
Fig. 5. Hildebrand-Benesi plot based on the 1 : 1 for **1c** with $K_a = (1.29 \pm 0.17) \times 10^4$ L mol^{-1}.

Fig. 6. Absorption changes of **1o** (2.0×10^{-5} mol L^{-1}, in CH_3CN) upon addition with Cu^{2+} ions.

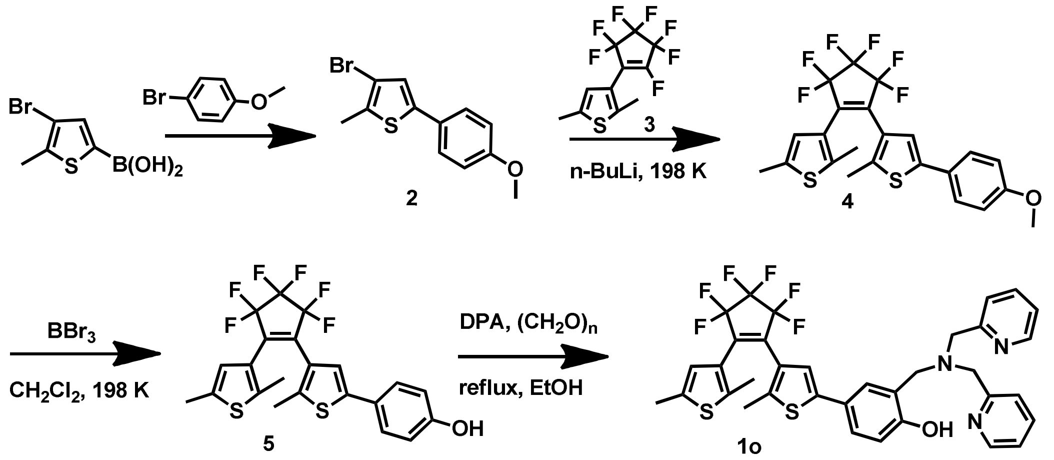
Fig. 7. (a) Mass spectra of **[1c+Cu]**$^+$; (b) IR spectra of **1c** and **1c-Cu^{2+}**.

Fig. 8. Proposed complexation mechanism of **1c** with Cu^{2+}.

Fig. 9. The $(A-A_0)/A_0$ ratio of **1c** at 504 nm (a) and its color changes (b) in CH_3CN in the presence of 5.0 equiv. of respective metal ions; (c) The A/A_0 ratio of **1c** at 504 nm in the presence of various ions (5.0 equiv.) and additional Cu^{2+} ions (3.0 equiv.) in CH_3CN.



Scheme 1


Br
B(OH)$_2$
Br
O
2
3
n-BuLi, 198 K
4
BBr$_3$
CH$_2$Cl$_2$, 198 K
5
OH
DPA, (CH$_2$O)$_n$
reflux, EtOH
1o
N
F
S

Scheme 2

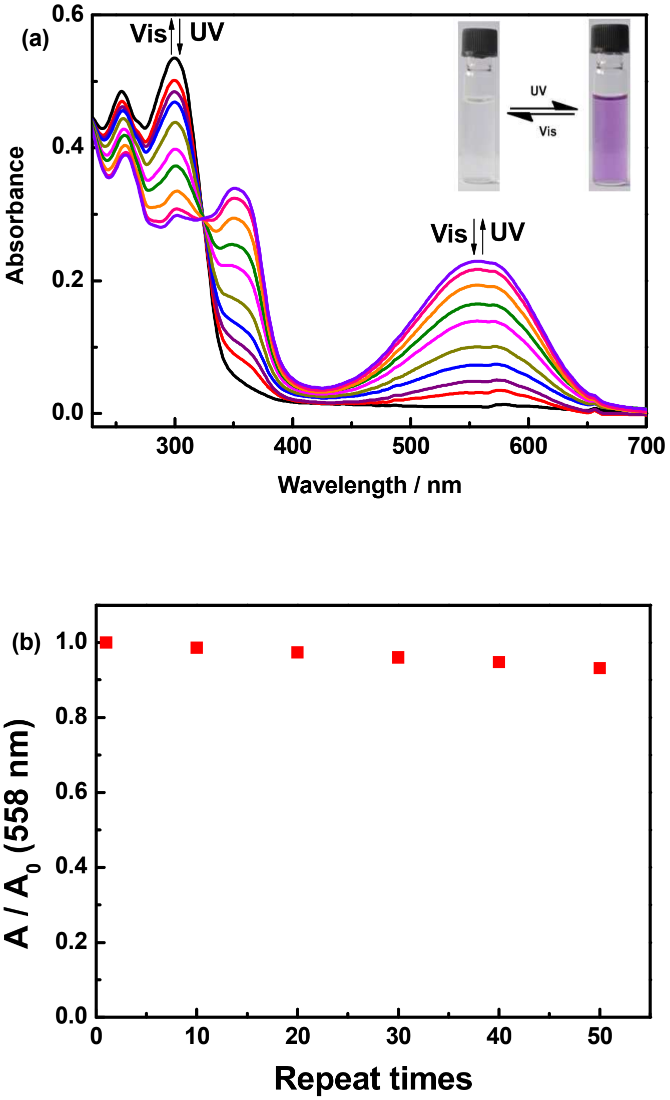

(a)
Vis
UV
UV
Vis
Vis
UV
0.6
0.4
0.2
0.0
Absorbance
300
400
500
600
700
Wavelength / nm
(b)
1.0
0.8
0.6
0.4
0.2
0.0
A / A$_0$ (558 nm)
0
10
20
30
40
50
Repeat times

Fig. 1

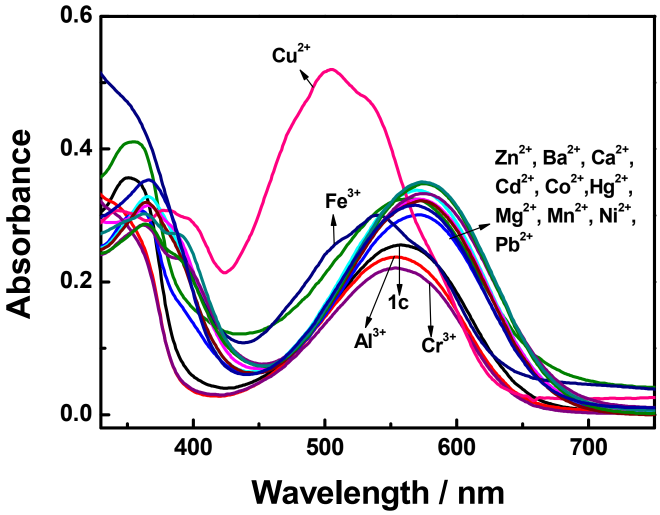

Cu2+
Fe3+
Zn2+, Ba2+, Ca2+,
Cd2+, Co2+,Hg2+,
Mg2+, Mn2+, Ni2+,
Pb2+
1c
Al3+
Cr3+
Absorbance
0.0
0.2
0.4
0.6
400
500
600
700
Wavelength / nm

Fig. 2

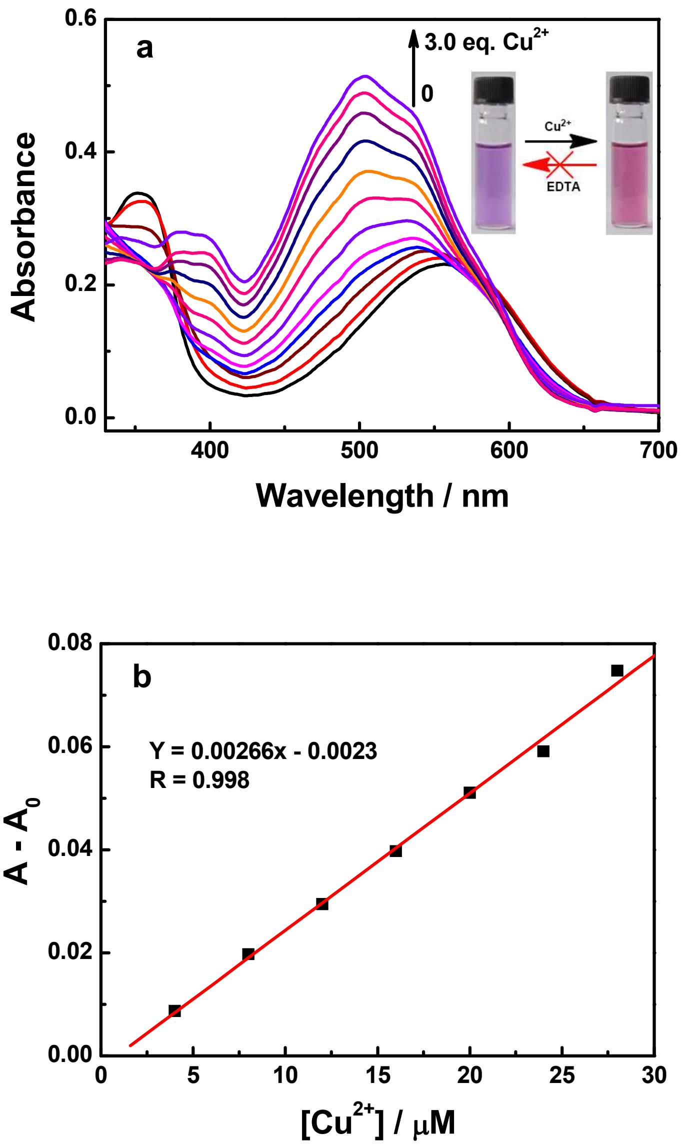

a
0.6
0.4
0.2
0.0
Absorbance
400
500
600
700
Wavelength / nm
3.0 eq. Cu^{2+}
0
Cu^{2+}
EDTA
b
0.08
0.06
0.04
0.02
0.00
$A - A_0$
Y = 0.00266x - 0.0023
R = 0.998
0
5
10
15
20
25
30
$[Cu^{2+}]$ / μM

Fig. 3

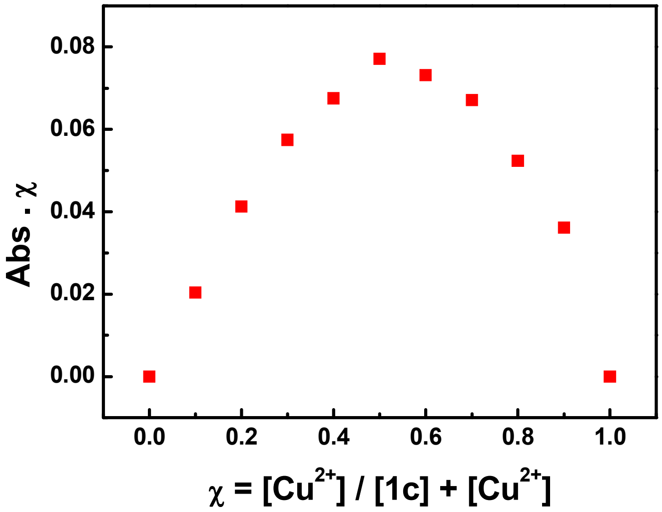


Fig. 4

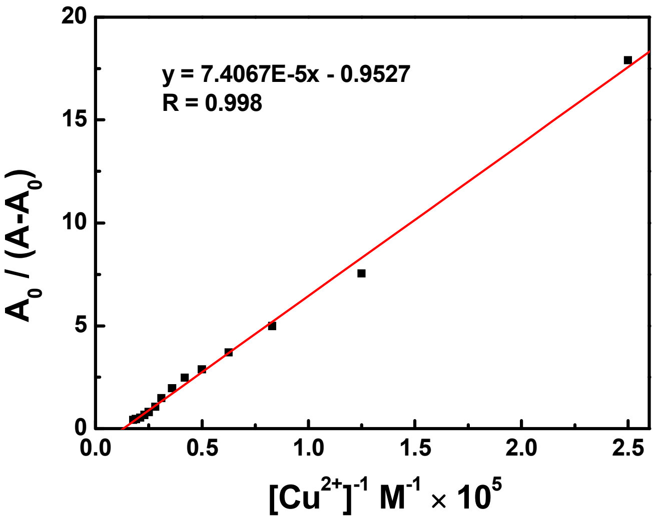

y = 7.4067E-5x - 0.9527
R = 0.998
A0 / (A-A0)
0
5
10
15
20
0.0
0.5
1.0
1.5
2.0
2.5
[Cu2+]-1 M-1 × 105

Fig. 5

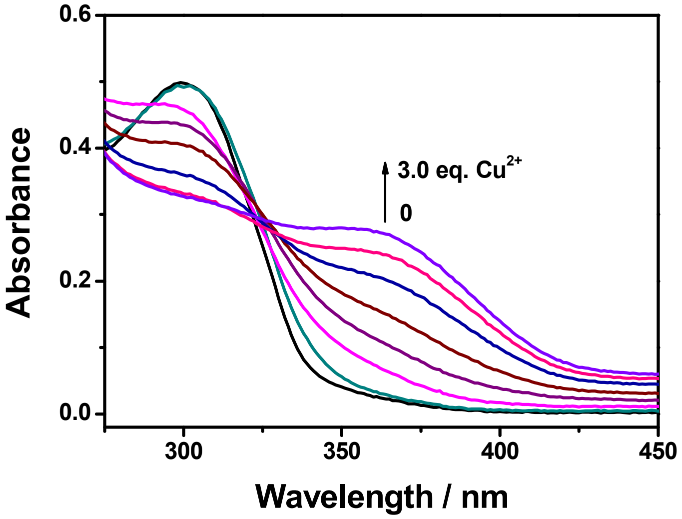

Absorbance
0.6
0.4
0.2
0.0
300
350
400
450
Wavelength / nm
3.0 eq. Cu2+
0

Fig. 6

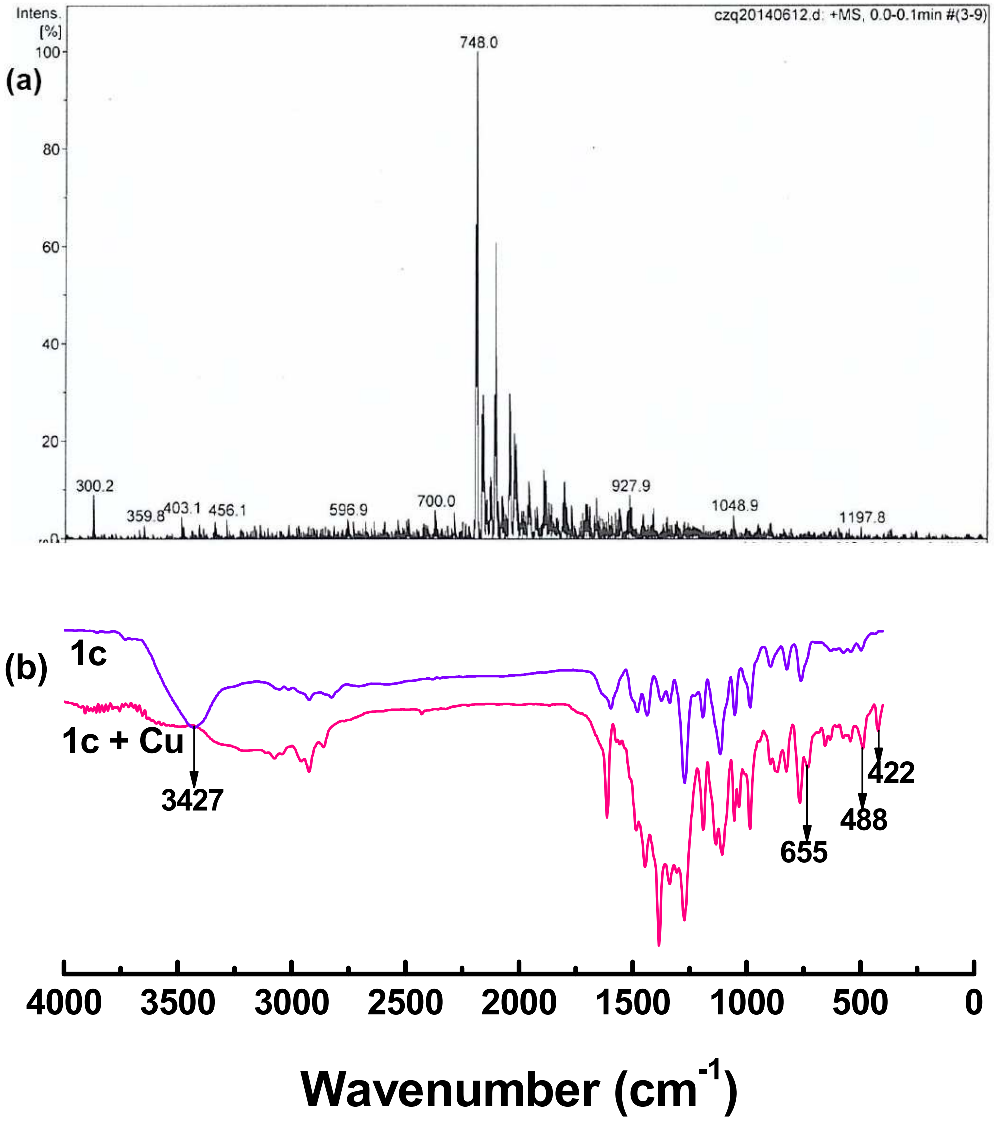

(a)
Intens. [%]
100
80
60
40
20
0
czq20140612.d: +MS, 0.0-0.1min #(3-9)
748.0
300.2
359.8
403.1
456.1
596.9
700.0
927.9
1048.9
1197.8
(b)
1c
1c + Cu
3427
655
488
422
4000
3500
3000
2500
2000
1500
1000
500
0
Wavenumber (cm-1)

Fig. 7

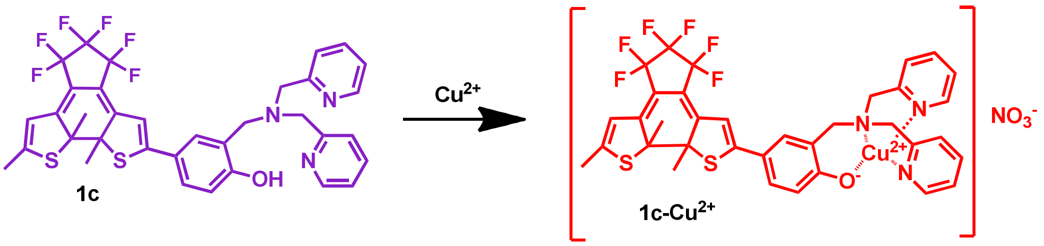


Fig. 8

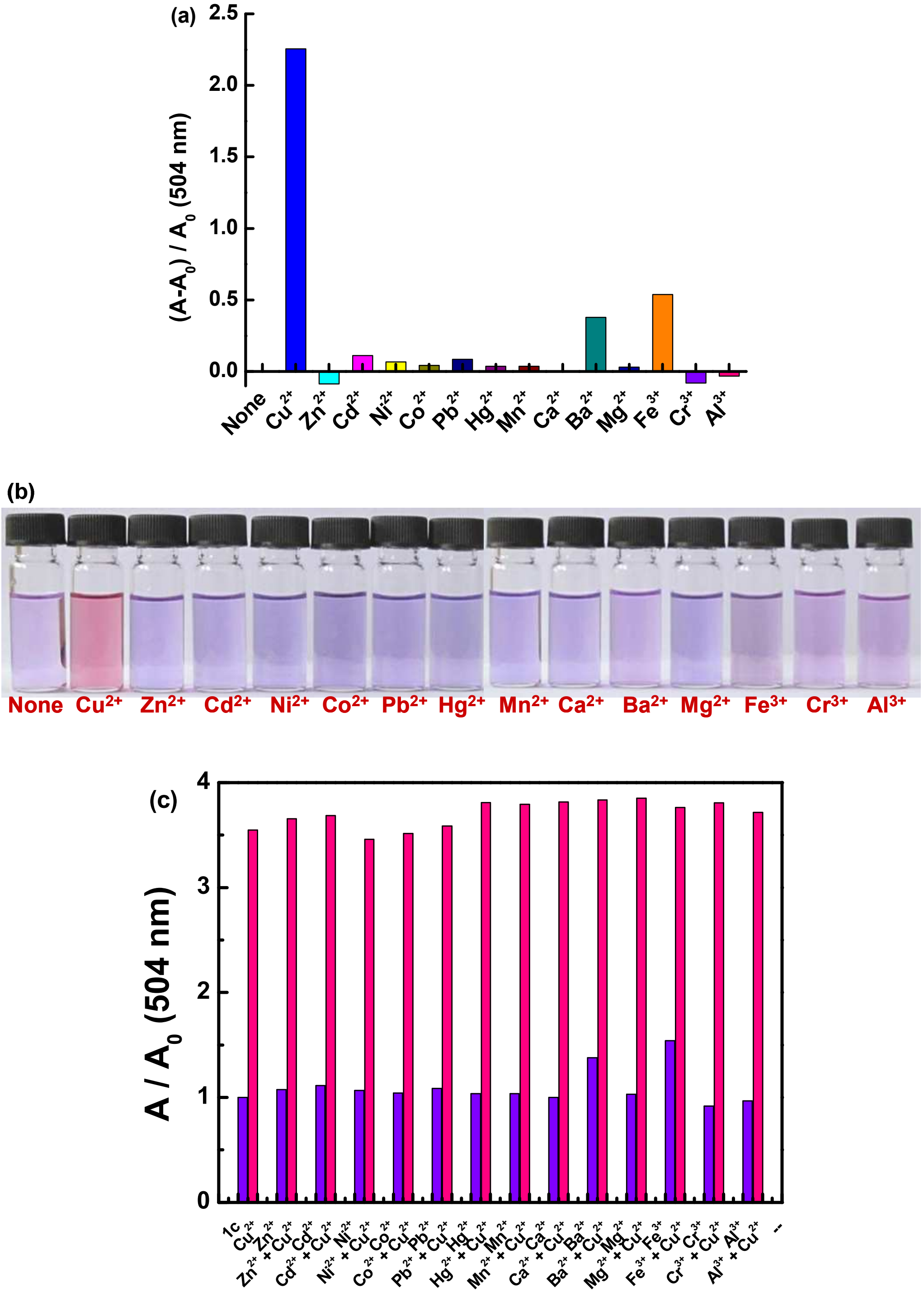

(a)
(A-A$_0$) / A$_0$ (504 nm)
2.5
2.0
1.5
1.0
0.5
0.0
None
Cu^{2+}
Zn^{2+}
Cd^{2+}
Ni^{2+}
Co^{2+}
Pb^{2+}
Hg^{2+}
Mn^{2+}
Ca^{2+}
Ba^{2+}
Mg^{2+}
Fe^{3+}
Cr^{3+}
Al^{3+}
(b)
None Cu^{2+} Zn^{2+} Cd^{2+} Ni^{2+} Co^{2+} Pb^{2+} Hg^{2+} Mn^{2+} Ca^{2+} Ba^{2+} Mg^{2+} Fe^{3+} Cr^{3+} Al^{3+}
(c)
A / A$_0$ (504 nm)
4
3
2
1
0
1c
Cu^{2+}
Zn^{2+}
Zn^{2+} + Cu^{2+}
Cd^{2+}
Cd^{2+} + Cu^{2+}
Ni^{2+}
Ni^{2+} + Cu^{2+}
Co^{2+}
Co^{2+} + Cu^{2+}
Pb^{2+}
Pb^{2+} + Cu^{2+}
Hg^{2+}
Hg^{2+} + Cu^{2+}
Mn^{2+}
Mn^{2+} + Cu^{2+}
Ca^{2+}
Ca^{2+} + Cu^{2+}
Ba^{2+}
Ba^{2+} + Cu^{2+}
Mg^{2+}
Mg^{2+} + Cu^{2+}
Fe^{3+}
Fe^{3+} + Cu^{2+}
Cr^{3+}
Cr^{3+} + Cu^{2+}
Al^{3+}
Al^{3+} + Cu^{2+}
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Fig. 9