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PAPER

A turn-on fluorescent chemosensor for selective responses of copper(II) ion pairs †

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A fluorescent chemosensor was designed and synthesized by incorporating the imidazolium and 1,8-naphthalimide dye moieties into the preorganized tripodal receptor. The novel sensor displays high selectivity for $Cu(ClO_4)_2$ and $Cu(NO_{3)2}$ over a wide range of tested metal ions, anions, and Cu^{2+} salts ion pairs. Upon adding $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ to the solution of probe, the fluorescence emission is dramatically turned on concomitant with a blue shift in emission energy, due to the anion-induced conformational change and coordination effect. Further binding model studies by ^1H nuclear magnetic resonance spectroscopy and mass spectroscopy demonstrated that the receptor formed a 1:1 host–guest complexation with $Cu(ClO_4)_2$ or $Cu(NO_3)_2$.

1. Introduction

Design of receptor for ion-pairs is an area of intense research activity, because they are potentially attractive for use in such areas as salt solublization, ion extraction, and through-membrane transport.[1] Especially, much attention has been drawn to design different binding models depending on the size of the ions. Recently, synthetic strategies for constructing functional ion-pair receptors with various structures and novel binding properties have been well established.[2] Substantial developments have been made in the creation of ideal-type models that can be used for sensing more special ion-pairs with selective signal responses.[3] In this case, the major challenge goes beyond achieving a suitable size- or guest-selective dynamic ion-pair binding and includes detecting and amplifying guest-bonding events to produce a measurable output. Thus, a proper communication system that is able to transduce the recognition information into an easy-to-measure signal must be included in the overall molecular design.

Most ion-pair receptors studied thus far have been designed to bind the alkaline-earth metal cations and use nuclear magnetic resonance (NMR) technology as an output signal.[4] Development of receptors for transition metals with visual functional fluorescent output has been a formidable challenge yet to be achieved.[5] As a continuation of our research work on the tripodal receptors,[6] we herein report a new strategy to prepare artificial chemosensors that have the potential to distinguish Cu^{2+} ion pairs by combining three piperazine-based aminonaphthalimide groups onto a podands-shape molecule linked by three imidazolium moieties (Scheme 1, **TIPA1**). Each amino-naphthalimide group acts as both chromophore and fluorophore, since aminonaphthalimide is a promising signaling subunits emitting in the green (λ~540-550 nm) with high quantum yields (Φ_f).[7] Imidazolium cations were commended as the anions receiving moieties, while three piperazines served as multi-site coordination for the transition metals especially for the heavy and transition metal (HTM) cations.[8] The three necessary factors were introduced as trigger sites to achieve efficient ion-pair interactions and a consequently good signal response.[9] Since "push-pull" nature of the internal charge transfer (ICT) excited state of **TIPA1** (caused by the electron-donating amine and the electron-withdrawing imidazole) may perturb the electronic distribution on the tripod backbone of the ligand, such host-guest interactions can affect the charge transfer associated with the aminonaphthalimide units and lead to significant changes in the optical properties.[10] Indeed, among various metal salts ion-pairs, the chemosensor **TIPA1** in acetonitrile solution, displayed highly selective responses upon the addition of $Cu(ClO_4)_2$ and $Cu(NO_3)_2$, which induced a 22 nm blue-shifted fluorescence emission from 518 nm to 496 nm, together with a significant colour change from yellow green to bright blue. However, this new chemosensor have no responses to the Cu^{2+} cations and the ClO_4^- as well as the NO_3^- anions when exposed these species in the presence of other counterions. Further binding model studies indicated that **TIPA1** formed a 1:1 host-guest complexation with $Cu(ClO_4)_2$ or $Cu(NO_3)_2$. To the best of our knowledge, **TIPA1** was the first ion-pair receptor afforded an interesting fluorescent output for the heavy and transition metal.

2. Experimental

2.1 General experimental

All reagents were of AR grade and used without further purification unless otherwise noted. All solvents were dried using standard procedure prior to use.

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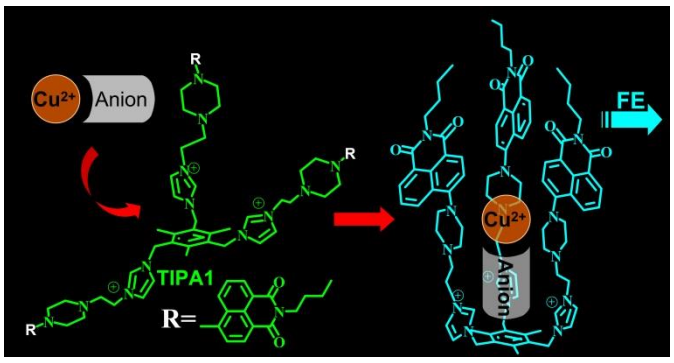


Scheme 1. Structure of tripodal imidazolium cation-based aminonaphthalimide receptor **TIPA1** and the proposed binding model of **TIPA1** toward $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ in CH_3CN solution. FE is the fluorescence enhancement.

^1H NMR and ^{13}C NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in DMSO-d^6 or $CDCl_3$, TMS as internal standard). Mass spectrometric data were obtained on HP1100LC/MSD and LCQ-Tofmass spectrometers. Fluorescence emission spectra were obtained using EDINBURGH FS920 luminescence spectrometer. For all fluorescent measurements, both excitation and emission slit widths were 1 nm. Optical absorption spectra were measured on a TU-1900 Uv/Vis spectrophotometer at room temperature.

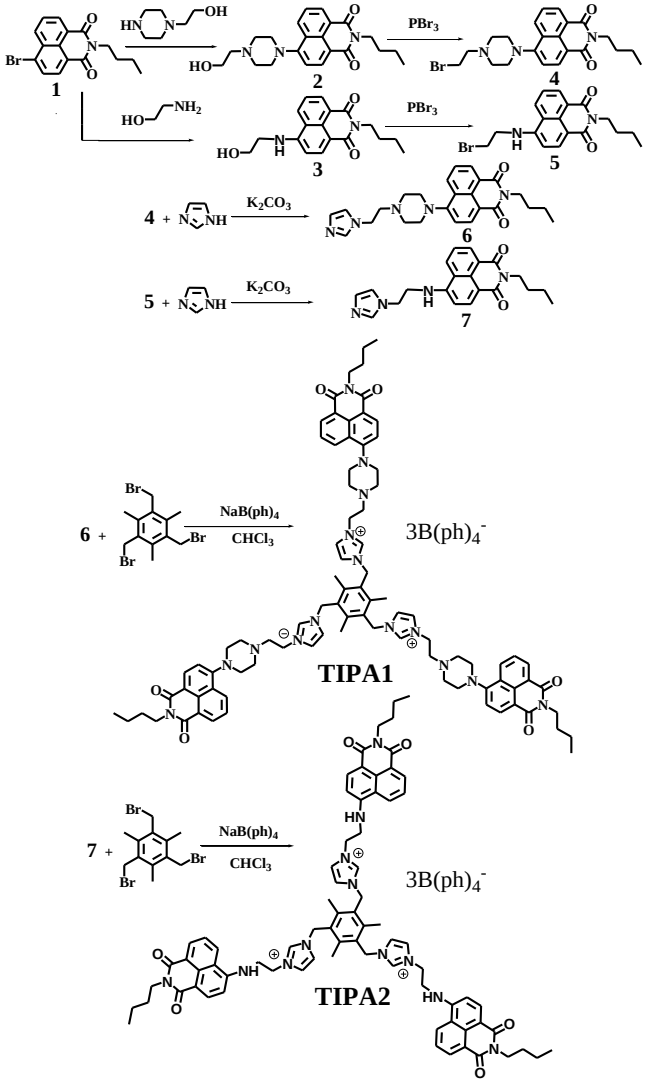
2.2 General procedures for spectroscopy

Stock solutions (2×10^{-2} M) of the CH_3CN perchlorate salts of K^+, Na^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Ag^+, Pb^{2+} and Hg^{2+} were prepared and diluted to the appropriate concentration. Stock solution of **TIPA1** and **TIPA2** (1 mM) were also prepared in distilled CH_3CN solution. Test solutions were prepared by placing 40 uL of host stock solution into a quartz cell of 1 cm optical path length including 2 mL distilled CH_3CN solution, and then adding an appropriate aliquot of each metals stock by using a micro-syringe. The fluorescence quantum yield was determined using optically matching solutions of Rhodamine-6G (Φ_f = 0.94 in ethanol) as the standard at an excitation wavelength of 500 nm. Excitation and emission slit widths were modified to adjust the luminescent intensity in a suitable range. All the spectroscopic measurements were performed at least in triplicate and averaged.

All NMR spectra were measured on a VARIAN INOVA-400 spectrometer at 298 K. A solution (1 mM) of recepter **TIPA1** in DMSO-d_6 was titrated with sufficit quantum of $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $NaClO_4$ and $Na(NO_3)_2$ by using a micro-syringe. The chemical shift changes of the proton of imidazolium and 1, 8-naphthalimides units were monitored.

2.3 Synthesis and characterization

The synthetic scheme for the preparation of the **TIPA1** and **TIPA2** are shown in Scheme 2. 1, 3, 5-Tris(bromomethyl)-2, 4, 6-trimethylbenzene was synthesized according to the literature method.[11] **1**, **3** and **5** were synthesized according the literature methord.[12]



Scheme 2. Synthetic procedure of **TIPA1** and **TIPA2**

Compound 2. A mixture of **1** (6.64 g, 20 mmol) and 1-(2-Hydroxyethyl)piperazine (7.77 g, 60 mmol) was heated to reflux in 2-methoxylethanol (80 mL) under nitrogen atmosphere for 48 h. After removal of 2-methoxylethanol, the residues was purified by silica gel column chromatography using dichloromethane/hexane (10:1) as eluent to afford **2** as a yellow solid (82%). Anal calc. for $C_{22}H_{27}N_3O_3$: C 69.27, H 7.13, N 11.02, O 12.58%. Found: C 69.12, H 7.28, N 11.08, O 12.52%; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.58 (d, $1H_{Ar}$, J = 7.6Hz), 8.52 (d, $1H_{Ar}$, J = 8Hz), 8.39 (d, $1H_{Ar}$, J = 9.6Hz), 7.69 (t, $1H_{Ar}$, J = 15.6Hz), 7.23 (d, $1H_{Ar}$, J = 8Hz), 4.17 (t, $2H_{CH2}$, J = 15.2Hz), 3.74 (m, $2H_{CH2}$), 3.34 (m, $4H_{piperdine}$), 2.90 (m, $4H_{piperdine}$), 2.76 (m, $4H_{CH2}$), 1.85 (s, $1H_{OH}$), 1.71 (m, $2H_{CH2}$), 1.45 (m, $2H_{CH2}$), 0.97 (t, $3H_{CH3}$, J = 14.8Hz); API-ES m/z: 382.3 $[M+H]^+$, 404.2 $[M+Na]^+$.

Compound 4. 4 was synthesized in the same method as that of **5**. Anal calc. for $C_{22}H_{26}BrN_3O_2$: C 59.46, H 5.90, Br 17.98, N 9.46, O 7.20%. Found: C 59.45, H 5.91, Br 17.92, N 9.50, O 7.22%; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.59 (d, $1H_{Ar}$, J = 7.2Hz), 8.52 (d, $1H_{Ar}$, J = 8Hz), 8.39 (d, $1H_{Ar}$, J = 8.4Hz), 7.69 (t, $1H_{Ar}$, J = 15.6Hz), 7.23 (d, $1H_{Ar}$, J = 8Hz), 4.17 (m, $2H_{CH2}$), 3.53 (m, $2H_{CH2}$), 3.32 (m,

$4H_{piperdine}$), 2.97 (m, $2H_{CH2}$), 2.89 (m, $4H_{piperdine}$), 1.71 (m, $2H_{CH2}$), 1.43 (m, $2H_{CH2}$), 0.97 (t, $3H_{CH3}$, J = 14.8Hz).

Compound 6. Imidazole (0.12 g, 1.77 mmol) was added to anhydrous potassium carbonate (K_2CO_3) (0.06 g, 0.2 mmol) and anhydrous THF (10 mL). The mixture was stirred at room temperature for 10 min prior to the addition of **4** (0.37 g, 0.83 mmol). The mixture was then stirred under reflux for 24 h. After filtration, the THF was removed under vacuum to leave a yellow solid which was dissolved in dichloromethane (DCM) (20 mL) and washed with water (3×25 mL). The organic layer was then extracted using hydrochloric acid (HCl) (2 M, 3×15 mL) followed by water (2×25 mL). The combined acid layer was neutralised with solid saturated sodium bicarbonate ($NaHCO_3$) and then extracted into DCM (2×20 mL). The combined DCM layer was washed with water (3×25 mL), dried over anhydrous magnesium sulfate ($MgSO_4$) and filtered. Removal of DCM under vacuum gave a yellow solid, which was purified by silica gel column chromatography using CH_2Cl_2/CH_3OH (50:1) as eluent to afford compound **6** as a yellow solid (0.05 g, 12%). Anal calc. for $C_{25}H_{29}N_5O_2$: C 69.58, H 6.77, N 16.23, O 7.24%. Found: C 69.55, H 6.80, N 16.22, O 7.25%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, $1H_{Ar}$, J = 8Hz), 8.52 (d, $1H_{Ar}$, J = 8Hz), 8.38 (d, $1H_{Ar}$, J = 8Hz), 7.75 (s, $1H_{imidazole}$), 7.69 (t, $1H_{Ar}$, J = 16Hz), 7.22 (d, $1H_{Ar}$, J = 8Hz), 7.11 (s, $1H_{imidazole}$), 7.05 (s, $1H_{imidazole}$), 4.17 (m, $4H_{CH2}$), 3.29 (m, $4H_{piperdine}$), 2.87 (m, $2H_{CH2}$), 2.81 (m, $4H_{piperdine}$), 1.71 (m, $2H_{CH2}$), 1.44 (m, $2H_{CH2}$), 0.97 (t, $3H_{CH3}$, J = 14.8Hz). API-ES m/z: 432.3 $[M+H]^+$, 863.5 $[2M+H]^+$。

Compound 7. 7 was synthesized in the same method as that of **6** (16 %), yellow powder. Anal calc. for $C_{21}H_{22}N_4O_2$: C 69.59, H 6.12, N 15.46, O 8.83%. Found: C 69.55, H 6.16, N 15.44, O 8.85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58 (d, $1H_{Ar}$, J = 7.2Hz), 8.48 (d, $1H_{Ar}$, J = 8Hz), 8.07 (d, $1H_{Ar}$, J = 8Hz), 7.62 (s, $1H_{imidazole}$), 7.60 (t, $1H_{Ar}$, J = 14.8Hz), 7.11 (s, $1H_{imidazole}$), 6.95 (s, $1H_{imidazole}$), 6.75 (d, $1H_{Ar}$, J = 8Hz), 5.72 (m, $1H_{NH}$), 4.37 (m, $2H_{CH2}$), 3.16 (m, $2H_{CH2}$), 3.87 (m, $2H_{CH2}$), 1.71 (m, $2H_{CH2}$), 1.44 (m, $2H_{CH2}$), 0.97 (t, $3H_{CH3}$, J = 14.8Hz). API-ES m/z: 363.3 $[M+H]^+$, 725.3 $[2M+H]^+$.

Compound TIPA1. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (0.133 g, 0.33 mmol) and **6** (0.431 g, 1.01 mmol) were dissolved in $CHCl_3$ (20 mL) and stirred at reflux for 15 h. During this time, a white precipitate formed. The product was filtered off and washed with $CHCl_3$ to give the desired tribromo anions product as a yellow powder. A solution of the mixture of $NaB(C_6H_5)_4$ (0.88 g, 2.6 mmol) and product of $3Br^-$ (0.42 g, 0.25 mmol) was stirred at room temperature in CH_3OH (30 mL) for 1 hr. The yellow precipitated formed was filtered, washed with methanol and diethyl ether, and dried in vacuo. Yield: 0.66 g, yellow powder. Anal calc. for $C_{159}H_{162}B_3N_{15}O_6$: C 79.19, H 6.77, B 1.34, N 8.71, O 3.98%. Found: C 79.16, H 6.80, B 1.36, N 8.68, O 3.99%; ^{1}H NMR (400 MHz, DMSO-d^6) δ: 9.19 (s, $1H_{imidazole}$), 8.41 (d, $1H_{Ar}$, J = 8Hz), 8.30 (m, $2H_{Ar}$), 7.80 (s, $1H_{imidazole}$), 7.73 (t, $1H_{Ar}$, J = 14Hz), 7.70 (s, $1H_{imidazole}$), 7.07 (d, $1H_{Ar}$), 5.59 (s, $2H_{CH2}$), 4.35 (s, $2H_{CH2}$), 3.98 (s, $2H_{CH2}$), 3.01 (m, $4H_{piperdine}$), 2.77 (s, $2H_{CH2}$), 2.70(m, $4H_{piperdine}$), 2.33 (s, $3H_{CH3}$), 1.56 (m, $2H_{CH2}$), 1.31 (m, $2H_{CH2}$), 0.91 (t, $3H_{CH3}$, J = 14.8Hz); ^{13}C NMR (400 MHz, DMSO-d^6) δ: 164.12, 163.58, 163.33, 163.09, 162.83, 162.60, 155.16, 141.15, 135.90, 135.51, 131.99, 130.59, 130.14, 129.33, 128.90, 126.03, 125.28, 122.96, 122.46, 122.17, 122.48, 115.62, 114.68, 52.52, 52.22, 47.71, 29.65, 19.77, 16.35, 13.68; LCQ-Tof MS: 484.71 $[M]^{3+}$.

Compound TIPA2. TIPA2 was synthesized in the same method as that of **TIPA1** as a yellow powder. Anal calc. for $C_{147}H_{141}B_3N_{12}O_6$: C 80.10, H 6.45, B 1.47, N 7.63, O 4.36%. Found: C 80.12, H 6.47, B 1.45, N 7.64, O 4.37%; ^{1}H NMR (400 MHz, DMSO-d^6) δ: 9.21 (s, $1H_{imidazole}$), 8.41 (d, $1H_{Ar}$, J = 8Hz), 8.27 (d, $1H_{Ar}$, J = 6Hz), 7.99 (d, $1H_{Ar}$, J = 8Hz), 7.85 (s, $1H_{imidazole}$), 7.67 (s, $1H_{imidazole}$), 7.60 (s, $1H_{NH}$), 7.50 (t, $1H_{Ar}$, J = 16Hz), 6.65 (d, $1H_{Ar}$, J = 8Hz), 5.41 (s, $2H_{CH2}$), 4.53 (s, $2H_{CH2}$), 3.94 (m, $2H_{CH2}$), 3.84 (m, $2H_{CH2}$), 2.13 (s, $3H_{CH3}$), 1.55 (m, $2H_{CH2}$), 1.33 (m, $2H_{CH2}$), 0.91 (t, $3H_{CH3}$, J = 14.8Hz); ^{13}C NMR (100 MHz, DMSO-d^6) δ: 164.55, 164.06, 163.57, 163.08, 150.19, 141.63, 136.41, 135.99, 134.52, 134.07, 129.40, 127.89, 127.80, 127.16, 125.77, 125.74, 122.77, 122.19, 121.97, 120.50, 109.16, 104.50, 48.50, 42.98, 30.24, 20.29, 16.61, 14.20; LCQ-Tof MS: 415.2864 $[M]^{3+}$, 663.40 $[M+DMSO]^{2+}$, 782.56 $[M+B(ph)_4]^{2+}$.

3. Results and discussion

The syntheses of **TIPA1** and **TIPA2** were shown in scheme. 2, which can be readily prepared by the reaction of piperazine-based aminonaphthalimide derivative **6** with 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene in $CHCl_3$, and followed by an anion exchange reaction with $NaB(C_6H_5)_4$. All compounds were characterized by EA, NMR and MS.

Free receptor **TIPA1** exhibited a strong green emission with max at 518 nm, assignable to the 1,8-naphthalimide (Φ_f = 0.08) upon excitation at 390 nm.[13] The addition of $Cu(ClO_4)_2$ resulted in a blue-shifted emission from 518 nm to 496 nm, accommodated by a significant colour change from yellow green to bright blue(Fig. 1), and fluorescence enhancement until a plateau was reached (Φ_f = 0.23). Under the same conditions, no marked fluorescence enhancement of **TIPA1** (20 μM) was observed in the presence of other tested metal salts of ClO_4^- (Zn^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Ag^+, Cd^{2+}, Pb^{2+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Na^+, K^+). Furthermore, the competition experiments revealed that **TIPA1** retained the excellent $Cu(ClO_4)_2$ specificity in the presence of a variety of other metal salts of ClO_4^- found in environmental and biological settings. This means that the luminescence enhancement induced by $Cu(ClO_4)_2$ was little affected by these metal ions (Fig. 2). These results suggest that **TIAP1** could respond to $Cu(ClO_4)_2$ with high selectivity by a fluorescence output manner.

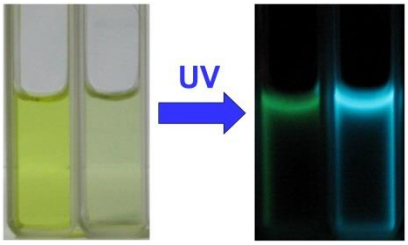


Fig. 1 Change in color and fluoresence of **TIPA1** (20 μM) upon addition of concentration of $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ in CH_3CN. Excitation was provided at 365 nm.

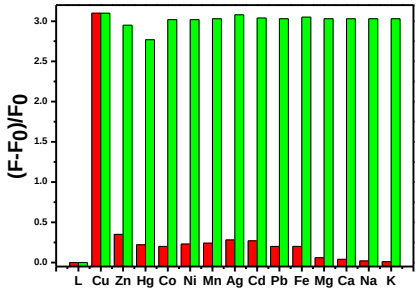


Fig. 2 Fluorescence responses of **TIPA1** (20 μM) to various metal salts of ClO_4^- in CH_3CN solutions. The red bars represent the emission intensities of **TIPA1** in the presence of 15 eq of cations (0.3 mM) of interest, respectively. The green bars represent the emission intensities that occur upon the subsequent addition of 15 eq of Cu^{2+} (0.3 mM) to the above mentioned solutions, respectively. Excitation was provided at 390 nm, and the emission intensities were recorded at 496 nm.

The fluorescence titration was carried out by gradual addition of various concentrations of Cu^{2+} perchlorate (Fig. 3) in CH_3CN with an excitation wavelength at 390 nm. As shown in Fig. 3 (inset), upon addition of lower than 10 equiv of Cu^{2+} (0.2 mM), 518 nm emission increases slowly. However, addition of the later of 7 equiv of Cu^{2+} (0.2 mM) leads to a drastic increase in the shorter wavelength emission, along with a continuous blue-shift of the emission band. The emission color continuously changes from yellow green to bright blue with increasing $Cu(ClO_4)_2$ amount. The process of $Cu(ClO_4)_2$ binding in **TIPA1** includes two distinct phases. It seemed that the first phase of the slight fluorescence enhancement was due to an anion-induced conformational change after the imidazolium units binding with perchlorate, while the second phase of the drastic fluorescence enhancement was due to a coordination effect after the piperazine units binding with Cu^{2+}. The nature of fluorescence blue-shift was caused by the ICT and the enhancement was ascribed the photoinduced electron transfer (PET) mechanisms. Accordingly, a combination of PET and ICT mechanisms are responsible for the two obvious changes.[14] This visible emission allows **TIPA1** to be readily distinguished by the naked eye, and sensor **TIPA1** thus combines the sensitivity of fluorescence with the convenience and aesthetic appeal of a colorimetric assay (Fig. 1).

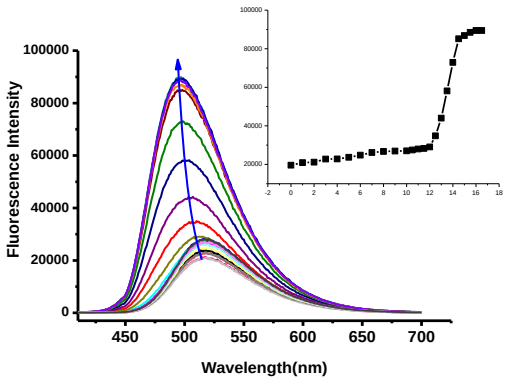


Fig. 3 Fluorescence titration of **TIPA1** (20 μM) with $Cu(ClO_4)_2$ in CH_3CN. [Cu^{2+}]: 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, 15.5, 16.0, 16.5 equiv. λ_{ex}= 390 nm. Inset: plot of I_f vs.[Cu^{2+}].

TIPA1 exhibited a 1,8-naphthalimide characteristic absorption band at 395 nm (log ε =5.53) in acetontrile solution.[15] The addition of $Cu(ClO_4)_2$ cause a significant spectra variation. Addition of 16 equiv of $Cu(ClO_4)_2$ (0.32 mM) produced a 18 nm blue shift of the absorption maximum (Fig. S1, ESI†) corresponding that of emission spectrum which has the same titration profile.

We then proceeded to investigate the effect of the anions. $CuCl_2$, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, and $Cu(OAc)_2$ are four common polluted Cu^{2+} salts which are also soluble of acetonitrile. Interestingly, only the $Cu(NO_3)_2$ has the fully same photophysical spectrum response as that of $Cu(ClO_4)_2$ (Fig. S2, ESI†). While not any enhancement of the fluorescence of **TIPA1** (20 μM) are observed in the presence of $CuCl_2$, $Cu(OAc)_2$ and anions salts of $NaClO_4$, $Na(NO_3)_2$ (0.32 mM) (Fig. S3 and S4, ESI†). These results suggest that **TIPA1** could only response ion-pairs of $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ with high selectivity by a fluorescent output manner.

To investigate the ion-pairs binding model of receptor **TIPA1**, **TIPA2** was designed and synthesized in multi-steps (Scheme 2). The piperazidine groups were replaced by secondary amine groups which lose the character of coordination site only. Indeed, upon addition of the $Cu(ClO_4)_2$ or $Cu(NO_3)_2$, a CH_3CN solution of **TIPA2** gave rise to negligible changes in the fluorescent spectra (Fig. S5, ESI†). From this vantage point, it should be noted that the piperazidine portions play an important role in binding Cu^{2+} cation by a possible multi-site coordination complexation mode, leading to the observed fluorescent enhancement and blue-shift of the 1,8-naphthalimide band, like that reported by Qian et.al.[16, 8c, 8d] This binding model is also supported by ESI-MS, which will be discussed later. ^1H NMR spectra of the receptor **TIPA1** (1 mM) upon addition of $Cu(ClO_4)_2$ (sufficit quantum) exhibited a significant downfield shift (ca. 0.17 ppm) of the $(C\text{-}H)^+$ proton H_1 on the imidazolium ring, and chemical shift of the H_2 (0.02 ppm), H_3 (0.09 ppm) comparing to the free **TIPA1** in the same experimental conditions, suggesting the formation of $(C\text{-}H)^{+\cdots}O$ charged hydrogen bonds between the imidazolium of **TIPA1** and perchlorate groups.[17] Most of flexible di- or tripods complexes contains rigid planar fluorescent groups may occur excimer effect after the addition of guest, our experiments did not support the possibility for the formation of corresponding excimer.[18] The small but significant shifts of the signals corresponding to the aromatic protons within the 1,8-naphthalimide (ca. 0.03 ppm), demonstrated the drastic charge transfer (ICT and PET) caused by the strong binding process of ion-pairs and **TIPA1**, as showen in Fig. 4. Similar results obtained when $Cu(NO_3)_2$ instead of $Cu(ClO_4)_2$ (Fig. S6, ESI†).

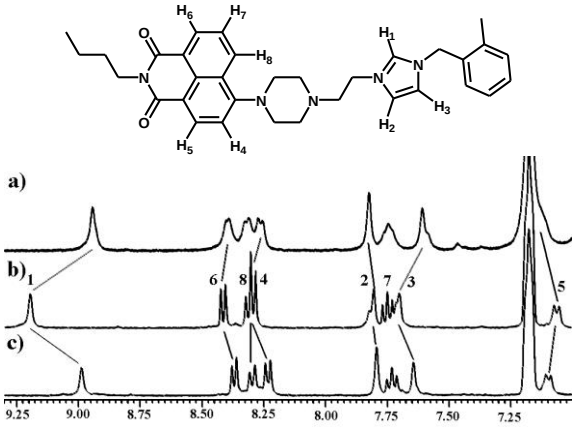


Fig. 4 Partial ^{1}H NMR spectra for (a) **TIPA1**+$Cu(ClO_4)_2$ (sufficit quantum), (b) pure **TIPA1** and (c) **TIPA1**+$NaClO_4$ (sufficit quantum) in DMSO-d^6, respectively.

The ion-pair binding model was further supported by the ESI-MS spectra. In the case of a CH_3CN solution of **TIPA1** in the presence of a sufficit amount of $Cu(ClO_4)_2$ (Fig. 5), an exact comparison of the most interesting experimental peak (which is observed at m/z 857.36 and 907.36) with the simulation results obtained on the basis of natural isotopic abundances reveals that this two divalently charged species can be reasonable assigned to [(**TIPA1**-H)+$2ClO_4$+Cu]$^{2+}$ and [(**TIPA1**-3H)+$3ClO_4$+Cu]$^{2+}$, thus providing not only a direct evidence of a 1:1 stoichiometric host-guest complexation but also a anions exchange process. The peak at m/z 776.44, on the other hand, can be safely assigned to the species [**TIPA1**+ClO_4]$^{2+}$. Upon addition of $Cu(NO_3)_2$ (Fig. S7, ESI†), instead of $Cu(ClO_4)_2$, the only peak at m/z 757.96 was observed and could be attributed to the [(**TIPA1**-3H)+Cu]$^{2+}$ species. This peak providing a further evidence of a 1:1 stoichiometric host-guest complexation. While not any changes of the MS spectra are observed in the presence of $CuCl_2$ or $Cu(OAc)_2$. These results suggest that the binding model may be that imidazolium cations of **TIPA1** were introduced as the anions receiving moieties, while three piperazines served as multi-site coordination for the heavy and transition metal Cu^{2+} cations. The two necessary factors were introduced as trigger sites to achieve efficient ion-pair interactions and a consequently good signal response.

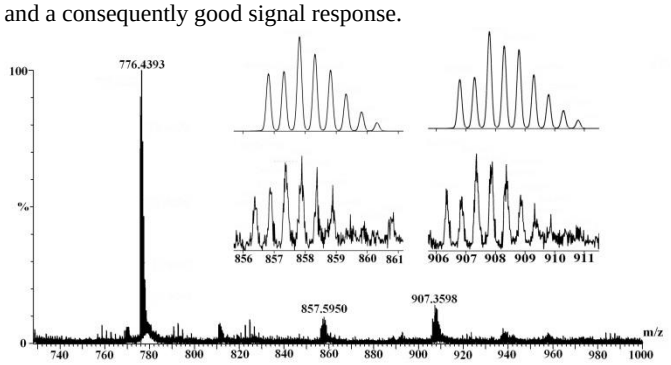


Fig. 5 ESI-MS of **TIPA1** in the presence of $Cu(ClO_4)_2$ in CH_3CN solution. The inset shows the measured and the simulated isotopic patterns at 857.8950 and 907.3598 Dalton, respectively.

4. Conclusion

We have designed and synthesized a new naphthalimide-based fluorescent probe **TIPA1** for Cu^{2+} ion-pair sensing which introduces imidazolium cations as the anions receiving moieties. **TIPA1** exhibites a selective "turn-on" and "blue-shift" fluorescent property for $Cu(ClO_4)_2$ and $Cu(NO_3)_2$ over a wide range of tested metal ions, anion, and Cu^{2+} salts ion pairs. Upon adding $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ to the solution of probe, the fluorescence emission is dramatically turned on concomitant with a 22 nm blue shift in emission energy, due to the anion-induced conformational change and coordination effect. The fluorescence blue-shift was caused by the ICT and the enhancement was ascribed the PET mechanisms. MS, NMR, and spectroscopic titration studies indicated that **TIPA1** formed a 1:1 host-guest complexation with $Cu(ClO_4)_2$ or $Cu(NO_3)_2$. To the best of our knowledge, **TIPA1** was the first ion-pair receptor for selective responses of heavy and transition metal by an interesting fluorescent output manner.

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