Triazole-Imidazole (TA-IM) as Ultrafast Fluorescent Probes for the Selective Silver Detection

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Triazole-Imidazole (TA-IM) as Ultrafast Fluorescent Probes for Selective Ag^+ Detection

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The 1,2,3-triazole-imidazole derivatives (TA-IM) were prepared as fluorescent probes for silver ions detection. The design principle is the incorporation of an intramolecular H-bond between the imidazole and triazole moiety that enables a co-planar conformation to achieve fluorescence emission in UV-blue range. Screening of different metal ions revealed excellent binding affinity of this new class of compounds toward silver ions in aqueous solution. The novel probe provided ultrafast detection (< 30 s) even for a very low concentration of silver ions (at nM range) with good linear correlation, making it a practical sensor for detection of silver ions.

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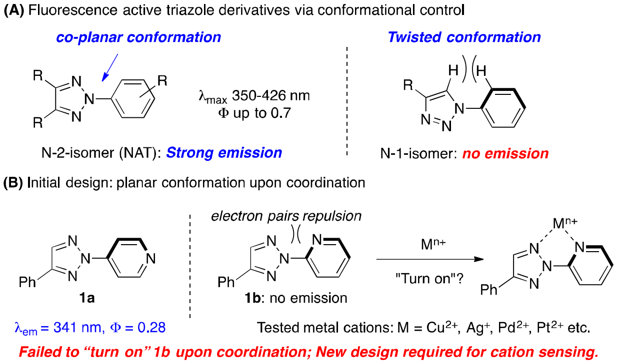
Fluorescence active molecules are of great importance in chemical,[1] biological[2] and medicinal research.[3] New class of small organic molecules with good fluorescence emission could offer opportunity for interesting applications.[4] Over the past decade, our group has been working on the development of functional 1,2,3-triazole (TA) as ligands for metal coordination.[5] A series of triazole ligands have been identified to promote metal-catalyzed reactions.[6] Upon synthesis of triazole derivatives,[7] we found that N-2 aryl triazole (NAT) showed strong emission in UV-blue range (λ_{max} between 380 nm and 430 nm). In contrast, the N-1 isomer exhibited almost no emission (Φ< 0.02). According to our structural analysis, strong fluorescence emission can be attributed to the co-planar conformation between triazole ring and N-2 aryl groups (**Scheme 1A**).[8]

Based on these unique features,[9] we wondered whether 1,2,3-triazole can be developed as novel fluorescence probe for metal cation detection upon coordination. Herein, we report imidazole substituted 1,2,3-triazole (TA-IM) as a new class of fluorescent active compounds with excellent selectivity toward Ag^+ (over 20 other tested cations) in aqueous media. This new fluorescent probe also gave high sensitivity with linear concentration-emission correlation. Moreover, compared with other reported Ag^+ detecting methods, TA-IM demonstrated ultrafast response time less than 30 seconds upon coordination. All these features make TA-IM a new practical sensor for Ag^+ detection.



Scheme 1. Design of triazole-based fluorescent probes

Our interest in developing triazole derivatives as metal cation sensor was originated from its conformational analysis of N-2-aryl triazole (NAT) fluorophore. As shown in **Scheme 1B**, we have previously demonstrated that 4-pyridyl triazole **1a** showed good fluorescence emission (Φ = 0.28), while the 2-pyridyl isomer **1b** was fluorescence-inactive (no emission). X-ray crystal structure of **1b** revealed the twisted conformation between the two aromatic rings, likely due to repulsion between the lone pair electrons of nitrogen.[8] Based on this analysis, we postulated that metal coordination between the two nitrogen atoms in **1b** could force the two aromatic rings to adopt a co-planar conformation and, therefore, may "turn on" the fluorescence emission upon coordination. To confirm this idea, we performed the coordination experiments of **1b** (TA-Py) with various metal cations (Cu^{2+}, Ag^+, Pd^{2+}, Pt^{2+}, Ni^{2+} etc.). Unfortunately, no fluorescence emission change was observed

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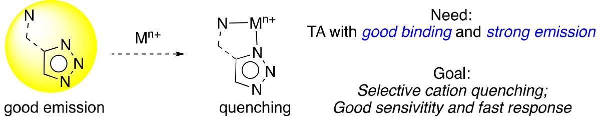
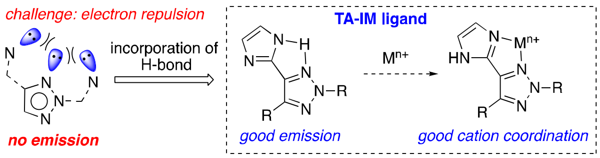
†Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data, NMR spectra and X-ray data for **5a**(CCDC 1835133), **5b**(CCDC 1835134), **5d**(CCDC 1835139), **5i**(CCDC 1835140) and **5k** (CCDC 1835141). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

in all cases (see detail in SI, **Figure S1**). In spite of the possible co-planar conformation upon chelation, the results suggested that NAT exciting state was nevertheless quenched due to potential electron and/or energy transfer upon cation binding.[10] As a result, the initial turn-on sensor hypothesis did not work, and we turned to design the turn-off sensor with similar framework.

(A) Revised sensing strategy: application of new fluorescence active ligand



(B) Ligand design: Conformation control via H-bond to avoid electron repulsion

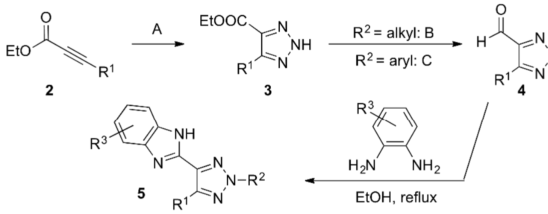


Scheme 2. Revised sensing strategy with TA-IM ligand

With the assumption that fluorescence quenching occurs upon metal coordination for TA-Py ligand **1b**, we sought out to develop new triazole ligands with both good fluorescence emission and metal binding ability to achieve metal sensing (**Scheme 2A**).[11] As discussed above, no fluorescence emission was observed for TA-Py ligand due to the nitrogen lone pair electron repulsion (**Scheme 2B**). To address this problem while keeping the bi-dentate binding nature, we proposed a new ligand system as triazole-imidazole (TA-IM). The key of our design is the incorporation of intramolecular H-bond to avoid lone pair electron repulsion so to enhance the formation of co-planar conformation for effective fluorescence emission while maintains the bi-dentate nitrogen binding mode. As shown in **Figure 1A**, a group of TA-IM compounds was successfully prepared. The structures of these TA-IM are summarized in **Figure 1B**.

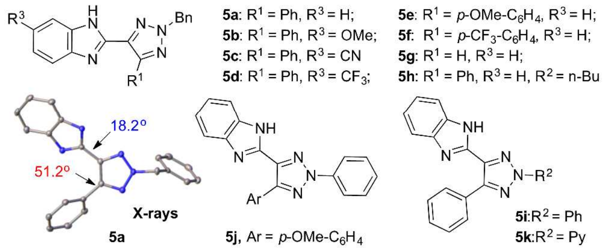
Figure 1. General synthetic route for TA-IM ligands

(A) General synthesis of TA-IM



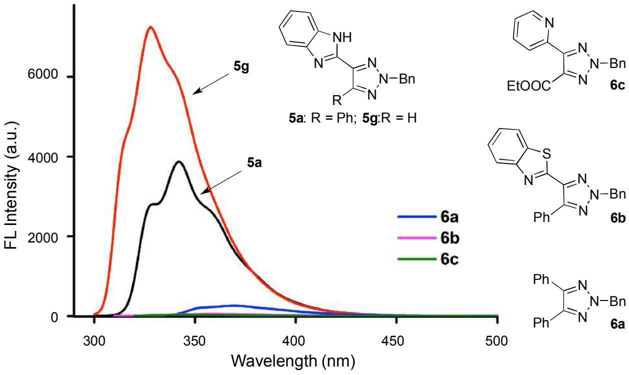
A) NaN$_3$, DMSO, 60 °C. B) K$_2$CO$_3$, R^{2}Br; LiAlH$_4$, THF; PCC, CH$_2$Cl$_2$.
C) LiAlH$_4$, THF; I$_2$, TBSCl, DMF; ArI, CuI, Proline; TBAF, THF; PCC, CH$_2$Cl$_2$.

(B) Structures of TA-IM compounds prepared



X-ray crystal structures of TA-IM were successfully obtained with several TA-IM compounds (**5a**, **5b**, **5d**, **5i** and **5k**), which verified the proposed N-2 isomer conformation. Moreover, as highlighted in **Figure 1B**, compared with C-5 phenyl ring, the C-4 imidazole ring had a much smaller dihedral angle (18.2°) with triazole ring, which suggested the formation of intramolecular H-bond. With the TA-IM successfully prepared and N-2-isomer identified, we evaluated their fluorescence emission to verify our initial design that intramolecular H-bond plays a crucial role in providing conformational control for effective fluorescence emission. The emission spectra of several representative TA-derivatives including TA-IM are shown in **Figure 2**

Figure 2. Fluorescence emission of some TA-IM ligands[a]



[a] Fluorescence emission of compound **5a**-**6c**. Concentration: 20 μmol/L in EtOH.

As expected, TA-IM **5a** and **5g** displayed strong fluorescence emission with quantum yields (Φ_{PL}) of 0.77 and 0.98 respectively. The stronger emission obtained with **5g** over **5a** is likely due to the reduced steric hindrance of C-5-H in **5g** over C-5-Ph in **5a.** It suggested that **5g** favored the co-planar

Table 2. Optical data of TA-IM ligands[a]

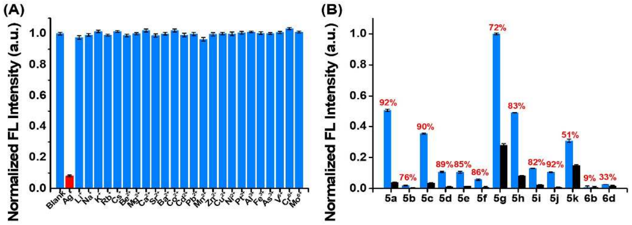
Ligand	Excitation λmax (nm)	Emission λmax (nm)	Stokes shift (nm)	ΦPL (%)	Intensity (a. u.)
5a	290	342	52	77	3837
5b	310	364	54	64	2318
5c	309	346	37	45	3154
5d	293	329	36	41	2062
5e	290	352	62	64	1836
5f	293	349	56	86	2935
5g	296	328	32	98	7246
5h	292	341	49	72	3576
5i	291	368	77	93	2780
5j	309	378	69	66	2532
5k	309	380	71	54	1717
6a	317	370	53	-	258
6b	-	-	-	-	47
6c	-	-	-	-	31

[a] Fluorescence emission of compound **5a**-**6c**. Concentration: 20 μmol/L in EtOH.

conformation. Switching imidazole to phenyl (**6a**), thiazole (**6b**) and pyridine (**6c**) almost shut down the fluorescence emission completely, which highlighted the crucial role of intramolecular H-bond in achieving the fluorescence-active TA-ligand. Importantly, fluorescence intensity of **5a** in solution remained the same even after ten months (**Figure S6**), suggesting the excellent stability of the new TA-IM fluorophore. Detailed excitation and emission information of all TA-IM substrates **5** are summarized in **Table 1**.

To As shown in **Table 1**, all tested TA-IM **5** exhibited strong UV-blue fluorescence emission with λ_{max} between 330 nm and 380 nm. Electron donating group on imidazole (**5b**) caused emission red-shift while electron withdrawing group resulted in slightly blue-shift (**5d**). No significant electronic effect was observed on the phenyl substitution (**5e** vs **5f**). Large red-shift was obtained with conjugated N-2 aryl substrates (**5i**, **5j** and **5k**), similar to the previously reported N-2-aryl triazoles (NAT) system. Compared with NAT, TA-IM possessed similar UV-blue emission and comparable fluorescence intensity/efficiency, suggesting similar planar intramolecular charge transfer (PICT) mechanism as proposed. With the fluorescence-active ligand available, we tested whether metal cation coordination may influence TA-IM fluorescence emission.

Figure 3. A) The high selectivity of the TA-IM for detection of Ag^+. (B) Sensitivity of all TA-IM (**5a**-**5k**) in response to silver cation.[a, b]



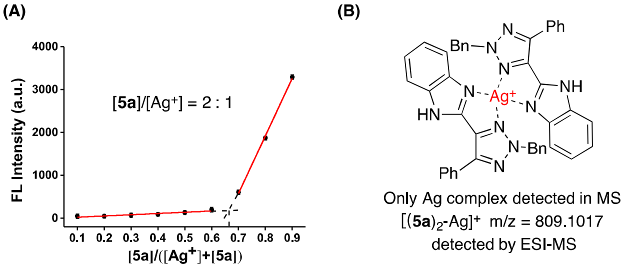
[a] Concentration: **5a**-**5k**, 2 μmol/L; metal ions, 2 μmol/L; EtOH: Hepes, v:v=1:99.

[b] The blue bar is the normalized FL intensity of **5a**-**6d**; the blank bar is the FL intensity of **5a**-**6d** after treating with Ag^+; the red number is quenching ratio of FL.

As shown in **Figure 3A**, treating a solution of **5a** with various metal cations (24 cations tested) showed almost no fluorescence change except for Ag^+ cation. Notably, this highly selective Ag^+ induced fluorescence quenching is very efficient (92%) under mild conditions (room temperature). Impressively, this Ag^+ sensing was very robust, showing almost no influence by other cations and anions (no significant change while combining Ag^+ with more than 30 cations and anions, see details in **Figure S7, S8**). This result is interesting and suggests that TA-IM can be developed as a potential fluorescent sensor toward Ag^+ detection. Since silver and silver ion-containing materials have been increasingly used in the industry[12]. A large amount of non-biodegradable silver ion from industrial wastes has been discharged into the environment.[13] This could cause a severe harm to the environment[14] and human health.[15] Hence, establishment of an efficient and reliable sensor for the Ag^+ detection is great demand.

To identify the best TA-IM in Ag^+ sensing, comparisons of quenching efficiency among all prepared TA-IMs (**5a**-**5k**) were performed. Compound **5a** was identified as the optimal ligand with the highest sensitivity (92%) in response to Ag^+ binding (**Figure 3B**). To explore Ag^+/TA-IM coordination, standard titration was performed (Job' method, **Figure 4A**). A 2:1 ligand/cation ratio was revealed. ESI-MS further confirmed the formation of $[L_2Ag]^+$ complex with the detection of m/z at 809.10 as the major complex peaks (**Figure 4B,** see detailed MS spectra in **Figure S9**).

Figure 4. (A) Job's plot: total concentration of 5a [a]and Ag^+ was 10 μmol/L. (B) ESI-MS of $[(5a)_2\text{-}Ag]^+$ ion.

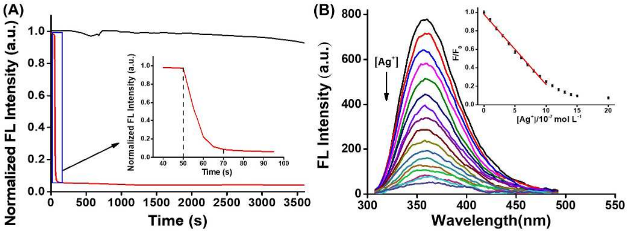


[a] EtOH: Hepes, v:v = 1:99.

Based on Benesi-Hildebrand equation, the binding association constant K_a was determined as 1.01×10^7 M^{-2}, suggesting a strong coordination between ligand and Ag^+ (**Figure S10**). The fluorescence lifetime of **5a** was monitored (**Figure S11**), giving no changes in the absence and presence of Ag^+. This result suggested that the observed silver cation sensing was attributed to static quenching as proposed.[16]

One important feature for any cation fluorescence probe is the response time. As shown in **Figure 5A**, solution fluorescence intensity decreased immediately upon treating with silver cation and reached an equilibrium within 20 seconds. To the best of our knowledge, this sensing response rate is faster than any previously reported Ag^+ fluorescent probes.[17] Moreover, FL emission intensity of **5a** solution remained the stable even after 120 min irradiation treatment with xenon lamp (**Figure S12**). Detections within pH range from 4.0 to 9.0 were performed with no clear drop of sensitivity and stability (**Figure S13**). All these features (ultrafast response time, excellent stability and wide pH operating range in aqueous medium) warrant TA-IM a promising fluorescent sensor for Ag^+ detection.

Figure 5. (A) Time dependent titration of **5a** (2 μmol/L) with Ag^+ (2 μmol/L); (B) Linear correlation of $[Ag]^+$ and FL emission.[a]



[a] EtOH: Hepes, v:v=1:99.

Finally, to establish the quantitative detection curve, titration of Ag^+ with TA-IM ligand was performed (**Figure 5B**). Under the concentration from 1.0×10^{-7} to 1.0×10^{-6} mol/L, a good linear correlation between fluorescent intensity and Ag$^+$ concentration was obtained with $R^{2.}$ = 0.9948. The detection limit (LOD) was calculated to be 9.4 nmol/L (based on S/N = 3, n = 20). To the best of our knowledge, this is much lower than previously reported fluorescent probes (see detailed comparison of TA-IM with reported Ag$^+$ sensors in SI, **Table S5**).

Conclusions

In summary, we have successfully developed triazole-imidazole ligands as highly selective fluorescent probes for detection of silver ions. The introduction of intramolecular H-bond allows TA-IM to exhibit strong emission in both organic and aqueous solutions. This sensor can be used in aqueous media with ultrafast response time (< 30 s), which highlighted the practical advantages of this new cation probe and importance of these triazole-based fluorescence compounds in chemical and material research.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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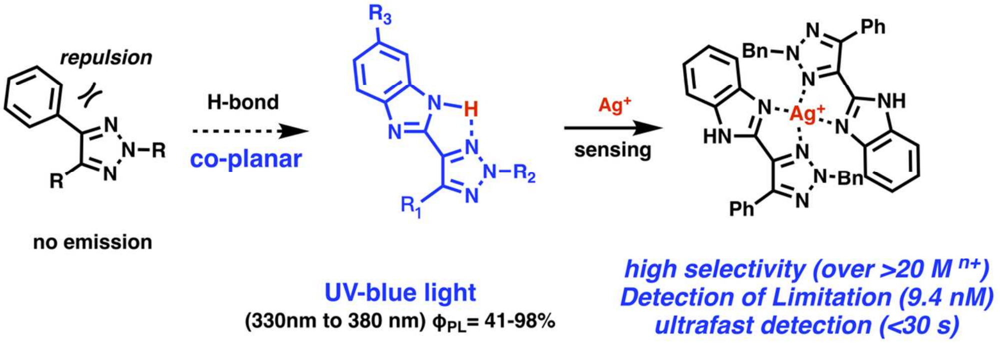

UV-blue light

(330nm to 380 nm) ϕ_{PL}= 41-98%

high selectivity (over >20 M $^{n+}$)

Detection of Limitation (9.4 nM)

ultrafast detection (<30 s)

57x20mm (600 x 600 DPI)