[1,2,3]Triazolo[1,5-*a*]pyridine derivatives as molecular chemosensors for zinc(II), nitrite and cyanide anions†

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Three recently prepared tridentate ligands TPF, TPS and TPT, based on the triazolopyridine–pyridine nucleus possessing fluorescent properties, have been tested as chemosensors for metal ions. A particular response is obtained in the case of $ZnTPT^{+2}$. The Zn^{2+} TPT 1 : 1 complex has proved to be an efficient chemosensor for anions especially nitrite and cyanide.

Introduction

As an essential component of many proteins, zinc plays an important role in hydrolytic enzymes and has structural functions in transcription factors and related proteins.[1] In addition to bound Zn^{2+}, there are other amounts of relatively free Zn^{2+} located in the brain and nervous system which are believed to play key roles in neurotransmission and neurodegeneration.[2] Alterations in zinc homeostasis are claimed to be implicated in diseases such as Alzheimer's.[1,3] Therefore, the detection of trace concentrations of Zn^{2+} is a research goal of great current interest.[4] In this sense, fluorescent methods offer the possibility of lowering the detection limit and require simple equipment available in many research laboratories.

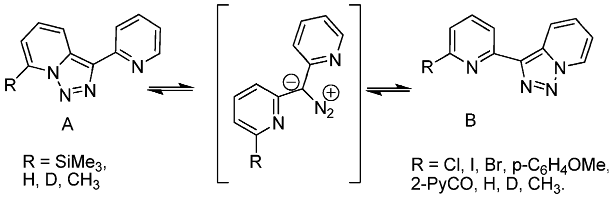
In recent years we have been developing different [1,2,3]triazolo[1,5-*a*]pyridine compounds and we have studied their synthesis,[5] coordination capacity,[6] and fluorescence behavior.[7–8] In this respect, we have recently reported on a triazolopyridine-based molecule which reveals very important changes in its optical properties upon coordination to Zn^{2+}.[8]

Additionally, we proved that coordination of anionic species to the preformed Zn^{2+} complex generated photo-induced charge transfer processes (PCT) that could be advantageously used for the detection of the bound anions.[8] In order to improve this behavior by reaching lower detection limits we now report on the luminescence properties of three potentially tridentate triazolopyridine molecules.[9–12] Triazolopyridine–pyridine rearrangements offer an interesting strategy for preparing tridentate ligands (Scheme 1). Ring–chain–ring isomerization between **A** and **B** derivatives depends on the electronic properties of the R substituent.[13] Compounds **B** have structures that permit their tridentate coordination provided that the R substituents have an additional donor atom.

Therefore, to prepare the new ligands we undertook the strategy depicted in Scheme 2. The first step consisted of direct regioselective lithiation of 3-pyrid-2′-yl-[1,2,3]triazolo[1,5-*a*]-pyridine **1** at position C-7.[14] The chiral alcohol **2** (TPF) was prepared by adding (−)-fenchone to lithiated **1**.[9] The sulfoxide **4** (TPS) was obtained by Pd catalyzed[10,11] reaction using iodo derivative **3**, obtained by quenching the lithio derivative with iodine.[13] Synthesis of ligand **6** (TPT) was possible by quenching with ethyl picolinate giving **5**, followed by reaction with tosylhydrazine in NaOH (Scheme 2).[12]

Results and discussion

TPF, TPS and TPT are soluble in organic solvents like EtOH, MeOH, CH_2Cl_2 and are highly fluorescent. The fusion of a triazole (electron-donating group) and a pyridine moiety (electron acceptor) provides extremely interesting fluorescence properties to these three ligands. The close spectral characteristics and quantum yields of the three compounds can be attributed to the fact that the fluorophoric behavior is marked by the triazolopyridine–pyridine system. The fluorescence of 98 : 2 v/v ethanol–water solutions of TPS and TPT keeps constant with time. The TPF fluorescence decreases



Scheme 1 The triazolopyridines–pyridine ring rearrangement.

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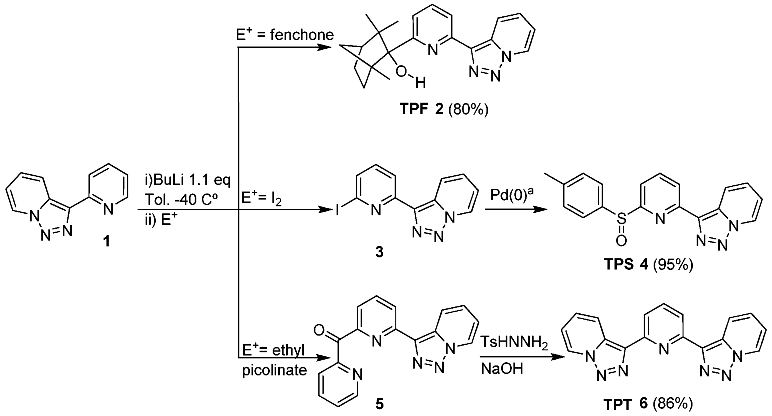
† Electronic supplementary information (ESI) available: UV-Vis spectra (Fig. S1 and S2), fluorescence spectra/data (Fig. S3–S23, S26), LOD (Fig. S24 and S25), X-ray refinement details and packing (Fig. S27), ^{1}H-NMR spectra comparison (Fig. S28). CCDC 736124. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906992e



Scheme 2 Procedure for the synthesis of triazolopyridine derivatives TPF, TPS and TPT. (a) *tert*-butyl-3-(*p*-tolylsulfinyl)propanoate (1 eq.), Pd_2dba_3 (0.05 eq.), Xantphos (0.1 eq.), KOH (10 eq.), toluene–water (1 : 1), 3 h, reflux.

significantly, which can be associated with the occurrence of some precipitation.

Zn^{2+}–L complexes were prepared by the reaction of zinc(II) chloride etherate with each one of the three ligands. FAB or ESI-MS supported, in all cases, the formation of 1 : 1 $[Zn(L)]^+$–Cl aggregates. However, in the system Zn^{2+}–TPT, ESI-MS also shows the presence of a complex of $[Zn(TPT)_2Cl]^+$ stoichiometry. As a matter of fact, it was possible to get suitable crystals for X-ray diffraction of the complex $[Zn(TPT)_2](ClO_4)_2\cdot 1/2CH_3CN$ (**7**) by slow evaporation of CH_3CN solutions of TPT and $Zn(ClO_4)_2$. The asymmetric unit of **7** consists of two almost equivalent $[Zn(TPT)_2]^{2+}$ cations, ClO_4^- counter-anions and one CH_3CN molecule. The cationic complexes (Fig. 1) display distorted octahedral geometry with meridional arrangement of the bis(triazolopyridino)pyridine moieties, which behave as tridentate ligands through the nitrogen donor atom of the central pyridine ring and the nitrogens placed at the 2-positions of the triazole rings. The bond distances of the metal ion with the pyridine nitrogens (average distance 2.13 Å) are slightly shorter than those with the triazolo nitrogens (average distance 2.20 Å). The ligand is slightly domed with a mean angle between the triazolopyridine units of *ca.* 10° (see Fig. 1). The crystal packing shows π–π-stacking interactions between the cationic units which give rise to a sort of pillar-like chains (see Fig. S26 in the ESI†).

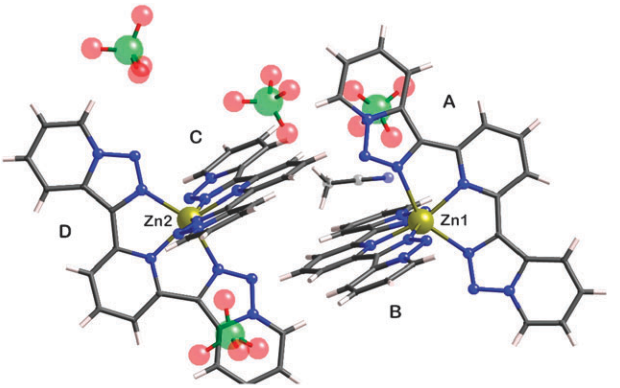


Fig. 1 X-Ray structure of $Zn(TPT)_2\cdot(ClO_4)_2\cdot 1/2CH_3CN$, (**7**) asymmetric unit (red oxygen, blue nitrogen, green chlorine, gray carbon and white hydrogen atoms).

Table 1 Fluorescent properties of compounds TPS and TPT and their corresponding complexes with Zn^{2+}

	TPS	$ZnTPS^{2+}$	TPT	$ZnTPT^{2+}$
Quantum yield[a] (%)	2	2	2	23
λ_{absb}/nm	340	340	359	359
λ_{emsb}/nm	384 401[b]	384 403[b]	412	404

[a] 10^{-5} solution of the corresponding ligand were used. [b] Most intense signal.

The spectroscopic characteristics of the Zn^{2+} complexes were analyzed in 98 : 2 v/v ethanol–water solution of $Zn(ClO_4)_2$ and the ligands TPS and TPT (see Table 1). The system Zn^{2+}–TPF was not analyzed due to the above mentioned precipitation of this compound.

Although addition of Zn^{2+} to TPS produced very slight changes in the fluorescence intensity and quantum yield values, addition of Zn^{2+} to TPT solutions leads to very significant chelation enhancements of fluorescence (CHEF) (Fig. 2 and Table 1). The intensity and quantum yield increase after addition of one equivalent of Zn^{2+} to TPT very significantly (Table 1, Fig. 3). The fluorescence increase is accompanied by a small (8 nm) hypsochromic effect. These fluorescence properties can be explained by a PCT mechanism.[15] The shift in the position of the band is smaller than those we have previously reported for the triazolopyridine molecule in previous works.[8] While in that system, coordination of Zn^{2+} occurs at the electron-donating pyridine fragments, in the present systems Zn^{2+} coordination involves both the electron-accepting pyridine fragment and the electron-donating triazolopyridine ring compensating the effect.

The less significant changes observed for TPS can probably be due to the high electron withdrawing properties of the sulfoxide.

The fluorescence behavior of TPS and TPT was also checked in the presence of the divalent transition metal ions Co^{2+}, Ni^{2+} and Cu^{2+} and of the post-transition ones Zn^{2+}, Cd^{2+} and Pb^{2+} (Fig. 3). As observed for Zn^{2+}, the fluorescence changes are, in general, larger for TPT than for TPS. Although not so large as in the case of Zn^{2+}, significant CHEF effects are also produced in the system Cd^{2+}–TPT.[16] Quenching

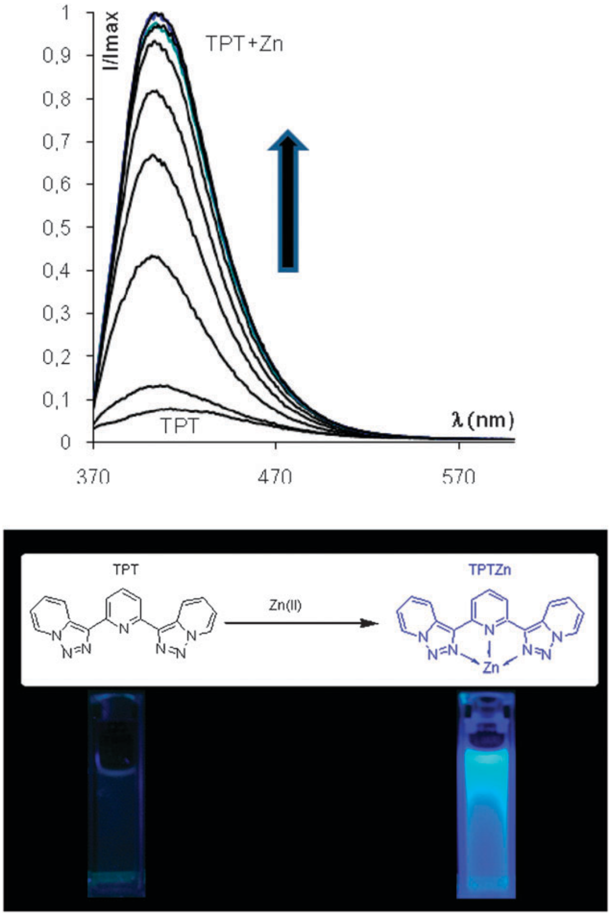


Fig. 2 Fluorescence spectra of TPT (8×10^{-5} M) in ethanol–water 98 : 2, and changes produced upon Zn(II) addition.

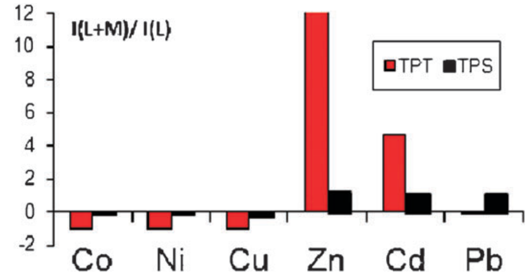


Fig. 3 Fluorescent responses upon addition of equimolar amounts M^{2+} solutions of TPT and TPS. Quenching effects are represented with negative intensity.

phenomena were observed with Cu^{2+}, Ni^{2+} and Co^{2+}. However, even large excesses of Na^+, K^+, Ca^{2+} and Mg^{2+}, which are most biologically relevant potentially competing mobile ions, do not perturb the fluorescence of TPT. At this pH, the extent of formation of the complexes of these metal ions is very limited and therefore the changes in fluorescence are not significant.

$Zn(TPT)^{2+}$ 1 : 1 complex has a coordinatively unsaturated coordination sphere. Three positions are occupied by ancillary ligands, likely solvent molecules, that can be readily replaced by anionic ligands. Such substitutions should affect the emissive properties of the system and can thereby be used to detect anionic species.[17] We have checked the interaction of solutions containing Zn^{2+} and TPT in 1 : 1 molar ratio for which the 1 : 1 complex is the predominant species in solution, with different monovalent anions (F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, NO_2^-, NO_3^-) by adding solutions of tetrabutylammonium salts of all anions (except $NaNO_2$) to $Zn(TPT)^{2+}$ solutions. In all cases, quenching of the emission was produced.

The analysis of the fluorescence spectra with the program SPECFIT[18] has allowed determination of the stability constants shown in Table 2 for the formation of mixed $Zn(TPT)^{2+}$–anion complexes. Only complexes of 1 : 1 stoichiometry were inferred from the analysis of the data.

The constants shown for the halide anions reveal the stability sequence $F^- > Cl^- \approx Br^- < I^-$. The CN^- binding constant is one order of magnitude lower than SCN^- while NO_2^- anions interact much more strongly than NO_3^- with $Zn(TPT)^{2+}$.

However, as is often observed, the magnitudes of the binding constants do not correlate exactly with the extension of the quenching phenomena.[19] Particularly, in spite of having a lower binding constant, CN^- anions exert a much more marked quenching than SCN^- anions. It is also interesting to remark the neat thermodynamic and sensing discrimination that our system produces between NO_2^- and NO_3^- (Fig. 4). The π-acceptor character of these two ligands CN^- and NO_2^- may be contributing to these quenching effects. Taking into account the sensitivity of the equipment and a plot of the fluorescence intensity variation with respect to the concentration of the substrate detection limits for NO_2^- of 3.2 ppb and below 1 ppb for CN^- were calculated (see ESI†).[20]

Conclusions

In conclusion we have reported the fluorescence properties of the triazolopyridine–pyridine TPT system. These systems act as fluorophores and coordinating molecules; revealing TPT as a suitable chemosensor for Zn(II); and the complex $Zn(TPT)^{2+}$ as a sensor for anions especially cyanide and nitrite. Encouraged by our preliminary results, we are currently investigating the recognition of amino acids and the development of new structures with similar fluorescent characteristics.

Experimental

Synthesis of ligands TPF, TPS and TPT

A detailed description has been given in ref. 11, 10 and 12, respectively.

Anhydrous sample preparation for the ESI-MS and NMR analysis

The general procedure for the preparation of solid Zn^{2+} complexes for MS analysis was in all cases as follows: to a solution of the corresponding ligand (0.14 mmol) in dichloromethane (20 mL), a solution of $ZnCl_2$ in ether (0.15 mL, 1 M) was added. The yellow-white solution formed was then stirred (30 min) at room temperature. Evaporation of the solvent gave

Table 2 Logarithms of the binding constants[18] (log *K*) for the formation of Zn(TPT) (anion) complexes in ethanol–water (98 : 2 v/v)

	F^-	Cl^-	Br^-	I^-	CN^-	SCN^-	NO_2^-	NO_3^-
log *K*	4.85 ± 0.05	4.08 ± 0.04	4.23 ± 0.02	4.58 ± 0.02	3.87 ± 0.09	4.88 ± 0.04	5.07 ± 0.03	3.50 ± 0.02

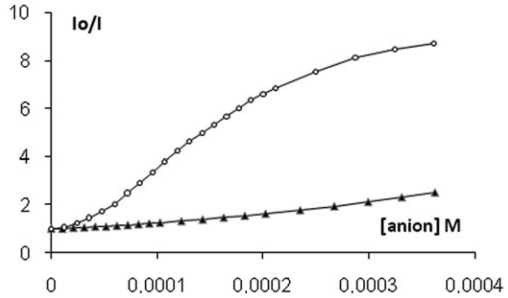


Fig. 4 Plot of I_0/I of $Zn(TPT)^{2+}$ (8×10^{-5} M) in 98 : 2 v/v $EtOH–H_2O$ upon successive additions of nitrite (up) and nitrate (down) (λ_{exc} = 359 nm).

yellow-white solids that were washed with hot ethyl acetate and characterized by ESI-MS.

ESI-MS $[ZnTPSCl]^+$ 432 (100), 433 (28), 434 (95), 435 (34), 436 (59), 436 (18), 440 (5).

ESI-MS $[ZnTPTCl]^+$ 412 (100), 413 (22), 414 (89), 415 (89), 415 (38), 416 (60), 417 (19), 418 (18), 419 (6).

ESI-MS $[Zn(TPT)_2Cl]^+$ 725 (100), 726 (40), 727 (89), 728 (45), 729 (65), 730 (25), 731 (19), 732 (7) 1.

At rt $ZnCl_2$ in ether (0.1 mL, 1 M) was added to a solution of TPT (0.1 mmol) in $CDCl_3–D_3COD$ (1 mL 80 : 20 v/v was added providing $[ZnTPTCl_2]$.[21] ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 8.61$ (d, $J = 6.9$ Hz, 2H, ^{7}H), 8.09 (d, $J = 8.9$ Hz, 2H, ^{6}H), 7.91 (t, $J = 8.1$ Hz, 1H, $^{4\prime}$H), 7.79 (d, $J = 8.1$ Hz, 2H, $^{3\prime}$H), 7.35 (dd, $J = 8.9$ and 6.7 Hz, 2H, ^{5}H), 6.97 (dd, $J = 6.9$ and 6.7 Hz, 2H, ^{6}H).

Spectrophotometric and spectrofluorimetric titrations

The solvents used were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus. UV-Vis absorption spectra were recorded on an Agilent 8453 spectroscopy system. The emission spectra were recorded with a PTI MO-5020 spectrofluorimeter in the 300–500 nm range. Quantum yield was determined with a Hamamatsu-PHA equipment.

The absorbance of the excitation wavelength was maintained lower than 0.15. 10^{-5} M solutions of ligands were prepared using 98/2 ethanol–water v/v as a solvent. M^{2+} solutions were prepared solving the corresponding perchlorate in 98/2 ethanol–water v/v 10^{-3} mol dm^{-3} concentration. Working solutions were obtained mixing 2 mL of the solution of ligands with the corresponding amounts of the solutions of the metals. 10^{-3} mol dm^{-3} aqueous solutions of the anions were prepared from $NaNO_2$, or the corresponding tetrabutylammonium analytical grade salts 10^{-3} mol dm^{-3}.

X-Ray crystallography

X-Ray data for compound $Zn(TPT)_2 \cdot (ClO_4)_2 \cdot 1/2CH_3CN$ (7). Pale yellow lath grown by slow evaporation of CH_3CN, 0.24 × 0.06 × 0.04 mm size, monoclinic, *Pc*, $a = 12.045(2)$, $b = 26.990(5)$, $c = 11.652(2)$ Å, $\beta = 103.01(3)°$, $V = 3690.7(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.640$ g cm^{-3}, $\theta_{max} = 27.10$, MoKα ($\lambda = 0.71073$ Å), ω-scan, diffractometer Nonius KappaCCD, $T = 150(2)$ K, 26 633 reflections collected of which 14 522 were independent ($R_{int} = 0.068$), multi-scan absorption correction ($T_{min}/T_{max} = 0.836/0.969$), direct primary solution and refinement on F^2 (SHELXS-97 and SHELXL-97[22]), 1129 refined parameters, residual electron density tentatively refined as a disordered CH_3CN molecule, disordered atoms refined isotropically, hydrogen atoms refined as riding, enantiomeric twin with components 0.405(12) and 0.595(12),[23] possible higher symmetry ($P21/c$ space group) has been closely examined (see ESI†), $R_1[I > 2\sigma(I)] = 0.0529$, wR_2(all data) = 0.1229.

Acknowledgements

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