Conformational switching fluorescent chemodosimeter for the selective detection of silver(I) ions†

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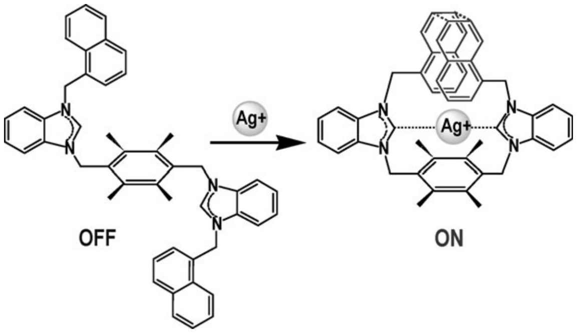
A new selectively fluorescent chemodosimeter exhibiting a conformational switching "off–on" signalling process for Ag(I) was achieved by incorporating imidazolium units and naphthyl lumophores into a two-arm dipodand.

The development of sensitive and selective fluorescent sensor molecules is a fundamental goal in fluorimetric metal ion analysis.[1] In particular, chemosensors targeting heavy and transition metal (HTM) cations are very important due to the environmental and biological relevance of such metal ions.[2] So far, the fluorescence sensing of HTM ions, such as Hg(II), Pb(II), Cu(II) and Ag(I), has been particularly challenging, since these ions generally act as fluorescence quenchers,[3] which is disadvantageous for high signal outputs upon complexation and hampers the temporal separation of spectrally-similar complexes by time-resolved fluorimetry. Many investigations have been conducted to prepare fluorescent chemosensors for Hg(II)[4,5] and Cu(II)[6] in organic and aqueous solutions; however, few reports have explored Ag(I)[7] due to the fact that its moderate coordination ability makes its discrimination from chemically similar heavy ions quite difficult.

N-Heterocyclic carbenes, the most stable carbene derivatives, are some of the few ligands that exhibit a higher coordination ability for Ag(I) over almost all other HTM ions stabilized in the environment and biological systems.[8] Accordingly, we expect that a highly selective fluorescent sensor for the detection of Ag(I) should be achieved by incorporating naphthalene fluorophores and benzoimidazolium binding sites into a dipodand molecule (Scheme 1). The receptor falls well into the fluorophore–spacer–receptor model category, and could act as a conformational switching fluorescent sensor involving excimer formation.[9,10] In the free receptor **H_2L**, the electrostatic interactions between the benzoimidazolium groups lead to a dipodal receptor stabilized in a *trans*-conformation, in which the two naphthyl lumophores are separated from each other and no excimer fluorescence is observed ("off" state). In the presence of Ag(I), the coordination bonds between the metal ion and the carbene moieties (deprotonated benzoimidazolium) induce the dipodand receptor into displaying a *cis*-conformation, with both arms orientated in the same direction, bringing the naphthalene lumophores into close proximity and leading to excimer fluorescence ("on" state).[11,12]

Compound **$H_2L·2Br$** was synthesized by reacting 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene and 1-(1-naphthyl-methyl)-1-benzoimidazole in $CHCl_3$. A single-crystal structure analysis confirmed the presence of the *trans*-conformation dipodal receptor, with the two arms positioned on opposite sides, thus causing the **H_2L** moiety to lie at an inversion centre (Fig. 1).† Each bromide anion connects to a C-2 hydrogen atom of a benzoimidazolium group and a methanol solvent molecule of crystallization, with C···Br and O···Br distances of 3.602(8) and 3.296(7) Å, respectively, as well as C–H···Br and O–H···Br angles both being of 146°. Such a C···Br distance agrees well with those found in related benzoimidazolium-containing compounds.[13]

$H_2L·2Br$ exhibited a weak fluorescence at about 355 nm in an acetonitrile/dichloromethane (1 : 1) solution (Fig. 2), which was assigned to the characteristic emission of the naphthyl groups. Upon the addition of Ag(I) ions, the luminescence of the compound increased concomitantly. The fluorescence enhancement, with the fluorescent wavelength being fixed, is explained by the fact that the coordination of Ag(I) deprotonates the benzoimidazolium moieties, precluding the PET quenching pathway from the excited naphthalene ring to the benzoimidazolium moiety.[14] Besides the fluorescence enhancement caused by PET process blocking, the most interesting feature of this system is the formation of a non-structured and red-shifted emission band at 425 nm,



Scheme 1

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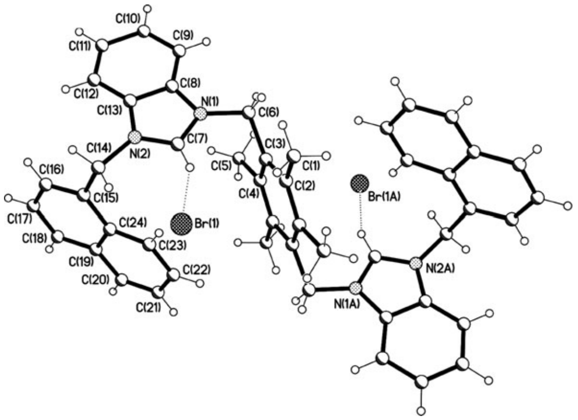

Fig. 1 The structure of $\mathbf{H_2L{\cdot}2Br}$. The methanol solvent molecule is omitted for clarity. Symmetry code A: $-x$, $1 - y$, $2 - z$.

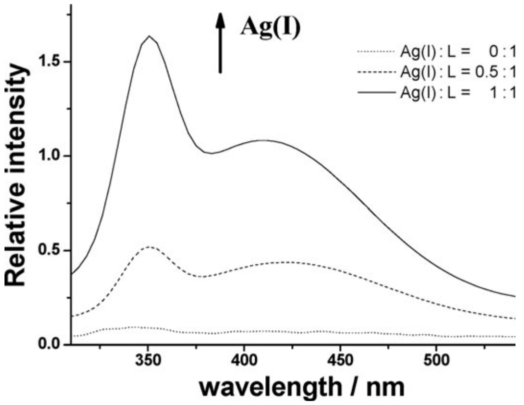

Fig. 2 Fluorescence emission spectra of $\mathbf{H_2L{\cdot}2Br}$ (excitation at 295 nm) upon titration with a solution of $AgNO_3$ in acetonitrile. The concentration of $\mathbf{H_2L{\cdot}2Br}$ is 40 μM.

which could possibly be assigned to the emission of an excimer in the presence of Ag(I) ions in the solution. During the titration, the luminescence intensities of both bands responded to the concentration of Ag(I) in a linear fashion up to 1 equivalent of added Ag(I); further addition of Ag(I) caused the precipitation of AgBr from the solution. While the titration behaviour suggests the formation of a 1 : 1 Ag(I) : **L** coordination species, the association constant was too large to be calculated. In fact, even the presence of bromide anion did not influence the signalling response, indicating that the association constant is larger than 10^{13} M^{-1} (the decomposition constant of AgBr in aqueous solution).

Meanwhile, no UV-vis spectral changes were observed during the titration of Ag(I) into a solution of the receptor, confirming the PET process. Furthermore, the fluorescence intensity around 425 nm was observed to increase markedly over time (Fig. 3). Depending upon the origin of the naphthyl dimer, there are two kinds of excimer: a *dynamic* excimer and a *static* excimer. The excitation spectrum of $\mathbf{H_2L{\cdot}2Br}$ in the presence of Ag(I) ions monitored at 425 nm was shifted by about 10 nm in comparison to that recorded at 355 nm, suggesting the formation of the naphthyl static excimer.[15] The high association constant and linear response to Ag(I) suggests that $\mathbf{H_2L{\cdot}2Br}$ should act as a fluorescent chemodosimeter for Ag(I) detection.

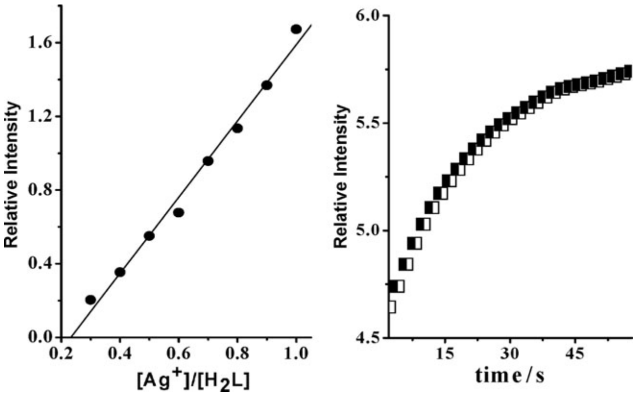

Fig. 3 Left: The linear relationship between the luminescence intensity *vs.* the concentration of Ag(I) added. Right: The time-dependent fluorescence intensity at 425 nm of $\mathbf{H_2L{\cdot}2Br}$ (0.4 mM) in the presence of Ag(I) (0.4 mM).

Fluorescence spectra of $\mathbf{H_2L{\cdot}2Br}$ recorded in the presence of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Ba(II), Cd(II) and Hg(II) metal ions did not alter the shape or intensity of the fluorescence spectrum (Fig. 4). Subsequently, the fluorescence response of $\mathbf{H_2L{\cdot}2Br}$ was found to show a unique selectivity for Ag(I), responding in an "off–on" manner. Reasonably, this should be contributed-to by the unique coordination properties of the *N*-heterocyclic carbene towards Ag(I), occurring by the silver-induced deprotonation of the benzoimidazolium groups, resulting in a high selectivity towards Ag(I).[8]

As a validation of above verdict, the binding properties of receptor $\mathbf{H_2L{\cdot}2Br}$ was investigated by ^{1}H NMR spectroscopy (Fig. 5). The presence of Ag(I) caused the disappearance of the proton signal of the hydrogens attached to the electron-deficient C-2 carbon atoms in the benzoimidazolium groups, suggesting their deprotonation and the existence of carbenes, which might be the donors for the coordination to Ag(I). The large upfield shift of almost all the signals in the ^{1}H NMR spectrum confirmed the deprotonation of the cationic species.

The ESI-MS of the titration solution exhibited two strong peaks at *m*/*z* 675.4 and 781.3 (Fig. 6), which were assigned to

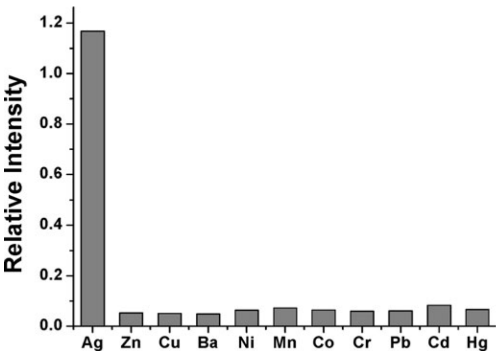

Fig. 4 The fluorescence response of $\mathbf{H_2L{\cdot}2Br}$ to various cations in acetonitrile/dichloromethane (1 : 1). The bars represent the emission of $\mathbf{H_2L{\cdot}2Br}$ in the presence of 1 equivalent of each respective cation.

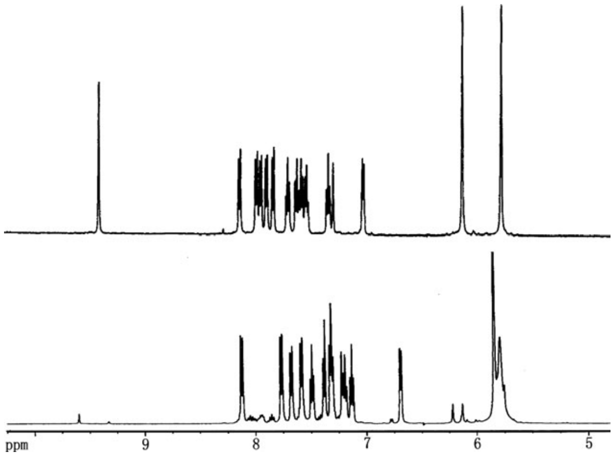

Fig. 5 Top: ^{1}H NMR spectrum of $\mathbf{H_2L{\cdot}2Br}$. Bottom: ^{1}H NMR spectrum of $\mathbf{H_2L{\cdot}2Br}$ in the presence of 1 equivalent of Ag(I) in $CDCl_3$ (1.0×10^{-3} M).

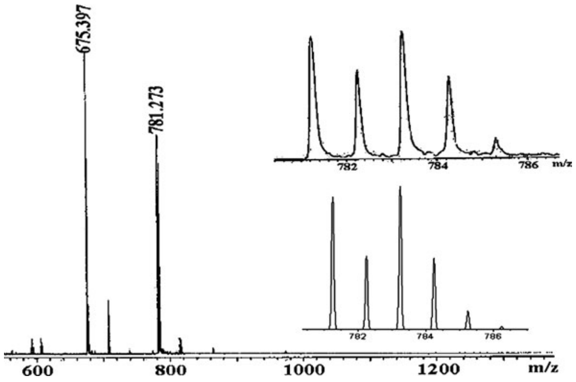

Fig. 6 The ESI-MS of $\mathbf{H_2L{\cdot}2Br}$ with Ag(I) in water. Insets: The top insert picture is the high resolution spectrum close to *m*/*z* 781 and the bottom inset is the simulation pattern of the $[\mathbf{AgL}]^+$ species.

the species $\mathbf{HL}^+$ and $[\mathbf{AgL}]^+$, respectively, confirming the formation of a 1 : 1 Ag(I)–**L** complexed species. The stability of the +1 charged species indicates that the $\mathbf{H_2L}$ chemosensor has lost its benzoimidazolium protons and is coordinated to the Ag(I).

In summary, we have designed and synthesized a fluorescent chemodosimeter with selectivity for Ag(I) based upon the ion's known reactivity toward benzoimidazolium derivatives. The compound $\mathbf{H_2L}$ responds to Ag(I) through a combined signalling by both PET and excimer formation mechanisms. We believe that this method may find application in a variety of settings that require rapid and accurate Ag(I) ion analysis.

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Experimental section

Synthesis

$\mathbf{H_2L{\cdot}2Br}$: 1-(1-Naphthylmethyl)-1-benzoimidazole (0.517 g, 2 mmol) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (0.331 g, 1 mmol) were dissolved in $CHCl_3$ (40 mL) and stirred at reflux for 10 h; during this time, a white precipitate formed. The product was filtered off and washed with $CHCl_3$ and Et_2O to give the desired product as a white powder (0.80 g, 94%). Compound $\mathbf{H_2L{\cdot}2Br}$: Anal. calc. for $C_{48}H_{44}N_4Br_2{\cdot}3.5H_2O$: C, 64.0; H, 5.7; N, 6.2. Found: C, 63.9; H, 5.6; N, 6.2%. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 9.88 (s, 2H, benzimidazole), 8.25 (d, 2H, J = 8.0, ArH), 8.20 (d, 2H, J = 8.0, ArH), 8.01 (d, 2H, J = 8.0, ArH), 7.96 (d, 2H, J = 8.0, ArH), 7.84 (d, 2H, J = 8.0, ArH), 7.75 (t, 2H, J = 7.2, ArH), 7.65 (t, 2H, J = 7.6, ArH), 7.60 (t, 2H, J = 7.2, ArH), 7.57 (t, 2H, J = 7.6, ArH), 7.48 (t, 2H, J = 7.6, ArH), 7.38 (d, 2H, J = 7.2, ArH), 6.39 (s, 4H, CH_2), 5.91 (s, 4H, CH_2) and 2.31 (s, 12H, CH_3). ESI-MS: *m*/*z* = 338.1 $[H_2L]^{2+}$ and 755.

General spectroscopic methods

The fluorescent titrations of $\mathbf{H_2L{\cdot}2Br}$ were carried out in acetonitrile/dichloromethane (1 : 1) solutions. Stock solutions (0.4 mM) of the nitrate salts of Ag(I), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Ba(II), Cd(II) and Hg(II)$^+$ were prepared in acetonitrile. The emission response in each case was recorded 2 min after the addition of Ag(I) ions.

X-Ray crystallography

Crystallographic data was collected on a Bruker APEX CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ (λ = 0.71073 Å) radiation using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by full matrix least-squares methods using SHELXTL version 5.1. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on their parent non-hydrogen atoms.

Crystal data for $\mathbf{H_2L{\cdot}2Br{\cdot}2CH_3OH}$: $C_{50}H_{52}Br_2N_4O_2$, M_r = 900.78, monoclinic, space group $P2_1/c$, a = 10.8056(9), b = 12.5425(11), c = 16.8485(14) Å, β = 96.964(2)°, V = 2266.6(3) Å^3, Z = 2, ρ_{calc} = 1.320 Mg m^{-3}, T = 293(2) K, μ = 1.831 mm^{-1}, S = 1.012, R_1 = 0.0681 for 1365 reflections with $I > 2\sigma(I)$, wR_2 = 0.1409 for all 3978 unique reflections.†

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