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A fluorescent chemosensor for Zn(II). Exciplex formation in solution and the solid state[†]

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The macrocyclic phenanthrolinophane 2,9-[2,5,8-triaza-5-(N-anthracene-9-methylamino)ethyl]-[9]-1,10phenanthrolinophane (L) bearing a pendant arm containing a coordinating amine and an anthracene group forms stable complexes with Zn(II), Cd(II) and Hg(II) in solution. Stability constants of these complexes were determined in 0.10 mol dm^{-3} NMe₄Cl H₂O–MeCN (1:1, v/v) solution at 298.1 ± 0.1 K by means of potentiometric (pH metric) titration. The fluorescence emission properties of these complexes were studied in this solvent. For the Zn(II) complex, steady-state and time-resolved fluorescence studies were performed in ethanol solution and in the solid state. In solution, intramolecular π -stacking interaction between phenanthroline and anthracene in the ground state and exciplex emission in the excited state were observed. From the temperature dependence of the photostationary ratio ($I_{\text{Exc}}/I_{\text{M}}$), the activation energy for the exciplex formation (E_a) and the binding energy of the exciplex ($-\Delta H$) were determined. The crystal structure of the $[ZnLBr](ClO_4)$ ·H₂O compound was resolved, showing that in the solid state both intra- and inter-molecular π -stacking interactions are present. Such interactions were also evidenced by UV-vis absorption and emission spectra in the solid state. The absorption spectrum of a thin film of the solid complex is red-shifted compared with the solution spectra, whereas its emission spectrum reveals the unique featureless exciplex band, blue shifted compared with the solution. In conjunction with X-ray data the solid-state data was interpreted as being due to a new exciplex where no π -stacking (full overlap of the π -electron cloud of the two chromophores – anthracene and phenanthroline) is observed. L is a fluorescent chemosensor able to signal Zn(II) in presence of Cd(II) and Hg(II), since the last two metal ions do not give rise either to the formation of π -stacking complexes or to exciplex emission in solution.

The search for new molecules able to perform complex movements has been an elected field for chemical research in the past two decades.¹ Light has been the principal driving force for the consideration of such supramolecular dynamics.² However, the idea of a supramolecular machine as being an entity where individual molecules are parts of a whole structure, working as cooperating functional units, involves more steps and procedures than just light absorption. Donor and acceptor units can be linked and be sensitive to light, protons or electrons thus performing the role of active/inactive devices. In recent years, molecules containing polyamine chains linking aromatic fluorophores have proved useful as fluorescent chemosensors for protons, cations and/or anions.³⁻⁹

The pursuit for new structures able to respond efficiently to external stimuli has been considered by our groups in recent publications.^{10–17} A chemical complex consisting in the binding of Zn(II) to L and showing to behave as an elementary molecular machine driven by pH and by light was briefly described in a previous communication.¹¹ Structurally this new complex results from the presence of two chromophores (phenanthroline and anthracene) connected by a polyamine structure (and chain) where Zn(II) is included. This new complex was shown to display the peculiar emission from a new species, attributed to exciplex emission resulting from the movement of the anthracene moiety to get into contact with the phenanthroline chromophore.¹¹

The aim of the present work was to extend the study to solid conditions and to obtain thermodynamic parameters in solution in



order to fully equate the movement leading to exciplex formation. To this purpose, the photophysical behaviour of the complex was investigated in the solid state both in a KBr matrix and in a thin film. The energetics of exciplex formation (activation energy E_a and binding energy of the exciplex, ΔH) were obtained in ethanol where a significant range of temperatures is allowed.

In order to investigate the possible use of this ligand as a selective chemosensor, the solution study was extended to Cd(II) and Hg(II) metal ions.

Results and discussion

Crystal structure of [ZnLBr](ClO₄)·H₂O

The crystal structure of $[ZnLBr](ClO_4)$ ·H₂O consists of $[ZnLBr]^+$ complex cations, perchlorate anions and water molecules. Fig. 1 shows an ORTEP drawing of the $[ZnLBr]^+$ cation with atom labelling and Table 1 lists bond lengths and angles for the metal coordination environment.

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Fig. 1 ORTEP drawing of the [ZnLBr]⁺ complex cation.

In [ZnLBr]⁺ the zinc ion is heptacoordinated by all nitrogen atoms of the ligand and by a bromide anion. The metal coordination geometry can be best described as a distorted pentagonal bipyramid. The N1, N2, N3, N4 and N5 nitrogens of the macrocyclic ring define the basal plane (max deviation from the plane 0.40 Å for N4), while the N6 amine group of the pendant arm and the Br1 anion occupy the apical positions. The zinc atom lies 0.092(1) Å above the basal plane, shifted toward N6. The N6–Zn and Br1–Zn bonds form angles of 3.46 and 1.66°, respectively, with the normal to the basal plane.

The Zn–N bonds, ranging between 2.200 and 2.357 Å, are somewhat longer than those generally found in Zn(II) polyamine complexes.

It is of interest to compare the present structure with that of the zinc complex with the ligand 2,5,8-triaza[9]-10,23-phenanthrolinophane (L1),¹⁸ consisting of the macrocyclic framework of L, the pendant arm with the anthracene group being replaced by a hydrogen atom. In contrast with the present structure in which the macrocyclic ring is almost coplanar (Fig. 1), in $[ZnL1(H_2O)]^{2+}$ the ligand is folded along the axis linking the two benzylic nitrogens, forming an angle of 93.0° between the plane defined by the phenanthroline unit and that defined by the amine groups of the aliphatic chain. Most likely, coordination of the pendant arm prevents the folding of the macrocyclic ring in the L complex.

However, the most interesting finding is the almost perpendicular disposition of the two aromatic moieties in [ZnLBr]⁺. Actually, the phenanthroline plane and the anthracene unit form a dihedral angle of 83.6°, with a distance between C25 and C26 anthracene carbons and the centroid of the central ring of phenanthroline of 3.88 and 3.92 Å, respectively, accounting for edge-to-face stacking interaction between the two aromatic rings.¹⁹

Besides this CH··· π stacking interaction, inspection of the crystal packing (Fig. 2) reveals the presence of intermolecular CH··· π interactions between the centroid of a lateral ring of anthracene (Ct1) and CH groups (C2, C3, C11) of two phenanthroline units belonging to two different complexes (Ct1···C2, 3.63 Å; Ct1···C3, 3.48 Å; Ct1···C11, 3.75 Å). Further intermolecular CH··· π interactions are found between the centroid of the central ring of anthracene (Ct2) and a CH group (C2) of a phenanthroline (Ct2···C2, 3.33 Å). The shorter intermolecular π -stacking distances reveal that the interaction between phenanthroline and anthracene units of different complex cations is stronger than that between the two aromatic rings within the same complex cation.

Ligand protonation in H₂O-CH₃CN (50:50, v/v)

The stepwise protonation constants of L are reported in Table 2. In the pH range investigated $(2.5 \le \text{pH} \le 10.5)$ L behaves as a tri-

Table 1Selected bond lengths (Å) and angles (°) for the Zn(II) coordination environment in $[ZnLBr](CIO_4)$ ·H2O

Zn1–N1 Zn1–N2 Zn1–N3 Zn1–N4	2.226(5) 2.200(5) 2.293(6) 2.308(6)	Zn1–N5 Zn1–N6 Zn1–Br1	2.357(6) 2.228(6) 2.7781(15)
N2–Zn1–N1 N2–Zn1–N6 N1–Zn1–N6 N2–Zn1–N3 N6–Zn1–N3 N2–Zn1–N4 N1–Zn1–N4 N6–Zn1–N4 N3–Zn1–N4 N2–Zn1–N4	73.2(2) 92.8(2) 88.5(2) 71.2(2) 143.2(2) 102.2(2) 144.8(2) 140.3(2) 80.3(2) 76.5(2) 141.0(2)	N1–Zn1–N5 N6–Zn1–N5 N3–Zn1–N5 N4–Zn1–N5 N2–Zn1–Br1 N1–Zn1–Br1 N6–Zn1–Br1 N3–Zn1–Br1 N4–Zn1–Br1 N5–Zn1–Br1	69.6(2) 97.5(2) 141.2(2) 74.2(2) 90.28(15) 89.92(16) 175.99(14) 81.24(17) 98.62(17) 78.54(18)

Table 2 Protonation and metal ion complexation constants obtained in 0.10 mol dm⁻³ NMe₄Cl H_2O –MeCN (1:1, v/v) solution at 298.1 ± 0.1 K

Reaction	logK	
$\begin{array}{l} L + H^+ = LH^+ \\ LH^+ + H^+ = LH_2{}^{2+} \\ LH_2{}^{2+} + H^+ = LH_3{}^{3+} \\ Zn{}^{2+} + L = [ZnL]{}^{2+} \\ [ZnL]{}^{2+} + H^+ = [ZnLH_2]{}^{4+} \\ [ZnLH_3]{}^{3+} + H^+ = [ZnLH_2]{}^{4+} \\ [ZnL]{}^{2+} + OH^- = [ZnLOH]{}^{+} \\ [ZnLOH]{}^{+} + OH^- = [ZnLOH]{}^{+} \\ [ZnLOH]{}^{+} + L = [CdL]{}^{2+} \\ [CdL]{}^{2+} + H^+ = [CdLH]{}^{3+} \end{array}$	$\begin{array}{c} 9.0(1)^a\\ 8.3(1)\\ 6.1(2)\\ 14.0(1)\\ 5.8(1)\\ 4.6(1)\\ 6.1(1)\\ 4.3(1)\\ 15.2(1)\\ 5.8(1)\end{array}$	
$\begin{array}{l} Hg^{2+} + L = [HgL]^{2+} \\ [HgL]^{2+} + H^{+} = [HgLH]^{3+} \end{array}$	$14.4(1)^b$ $4.2(1)^b$	

^{*a*} Values in parentheses are standard deviation in the last significant figure ^{*b*} Conditional stability constants (see Experimental section).



Fig. 2 Crystal packing of [ZnLBr](ClO₄)·H₂O.

protic base. In order to ascertain which amine groups are involved in the proton transfer processes, protonation of L was followed by means of ¹H NMR measurements in D₂O–CD₃CN (50:50, v/v) at different pH values. The spectrum of the ligand at pH 11, where the free amine is prevalent in solution displays two sets of signals, six in the aliphatic region and eight in the aromatic one, in accord with an overall C_{2v} time-averaged symmetry. This symmetry is preserved throughout all the pH range investigated. As shown by the downfield shifts of the resonances of protons H8, H9, H12 and H13, adjacent to the amine groups N1 and N3 (Fig. 3), taking place upon ligand protonation, all three protonation stages involve the three benzylic nitrogens N3, N3' and N1, in agreement with the greater basicity of secondary amines with respect to tertiary ones in water.



Fig. 3 (a) pH Dependence of the ¹H signals of L. The H10 signal has been omitted for clarity. It does not significantly shift in the pH range investigated. (b) Distribution diagram of the protonated species of L.

On the other hand, Fig. 3 shows that the formation of the $[H_3L]^{3+}$ species gives rise to marked downfield shifts of the signals of the aromatic protons of phenanthroline, and to a lesser extent, of those of anthracene. While the slight shift of the anthracene resonances can be ascribed to a charge effect due to protonation of the adjacent N1 nitrogen, the larger downfield displacements of the phenanthroline signals suggest a direct participation of phenanthroline nitrogens in ligand protonation, most likely *via* hydrogen bonding to the aliphatic ammonium groups.

Metal complexation in H₂O-CH₃CN (50:50, v/v)

The binding ability of L towards Zn(II), Cd(II) and Hg(II) were investigated by performing the speciation of the relevant complex systems and determining the stability constants of the formed species by means of potentiometric titrations in 0.10 mol dm⁻³ NMe₄Cl H₂O–MeCN (1:1, v/v) solution at 298.1 ± 0.1 K. A list of the complex species with the relevant stability constants are reported in Table 2. Zn(II) gives rise to the formation of many complex species with L. From acidic to alkaline solutions the species [ZnH₂L]⁴⁺, [ZnHL]³⁺, [ZnLOH]⁺, and [ZnL(OH)₂] are consecutively

formed. As can be seen from Table 2, the equilibrium constants for protonation of [ZnL]²⁺, to form the mono- and di-protonated species, are significantly high, if compared with the protonation constants (Table 2) of the metal-free ligand, suggesting that in [ZnL]²⁺ a couple of nitrogen atoms are only weakly coordinated, or not coordinated at all, to the metal ion. As a matter of fact, in the crystal structure of the [ZnLBr]+ complex cations some Zn-N bonds are rather long and complex solvation may cause further weakening, or breaking, of these bonds. Hence, it is not surprising that facile protonation of the complex may occur in solution. In addition the presence of weakly coordinated, or not coordinated, amine groups rationalises the formation of hydroxylated complexes in alkaline solution. On the contrary, the larger Cd(II) and Hg(II) cations, which are not able to form hydroxylate complexes and show a lower tendency to bear protonation, seems to give a better fit of the macrocyclic ligand cavity, with stronger metal-to-ligand interactions.

Metal coordination was also followed by means of ¹H NMR measurements carried out in D₂O-CD₃CN (50:50, v/v) solutions. By adding 0.1 eq. of $M(ClO_4)_2$ (M = Zn(II), Cd(II) or Hg(II)) to a solution of L, a different set of signals appears in the 1H NMR spectra, together with the resonances of the ligand alone, evidencing the formation in solution of a metal complex slowly exchanging on the NMR time scale with the free ligand. On addition of further M(II), the signals of this species are enhanced, while the resonances of L show a clear decrease in intensity. When the L: M(II) 1:1 molar ratio is reached, the ¹H NMR L subspectrum disappears and the recorded ¹H NMR spectrum can be reasonably due to a unique mononuclear M(II) complex. Addition of further M(II) does not alter the ¹H spectrum. As shown in Fig. 4 for Zn(II) and Cd(II), metal coordination leads to significant changes in both the aromatic and the aliphatic regions of the spectrum of L. The signals of protons of the cyclic framework are generally downfield shifted in both Zn(II) and Cd(II) complexes, as generally found in metal complexes with polyamine ligands. The most interesting finding is the very large downfield shift of the signals of aromatic protons upon Zn(II) complexation. Minor shifts, instead, are observed in case of the Cd(II) complex. The Hg(II) complex shows spectral features similar to the Cd(II) one.



Fig. 4 $\,$ $^1\!H$ NMR spectra of L (a) and its Zn(II) (b) and Cd(II) (c) complexes.

Although Zn(II) coordination to the nitrogen donors could simply explain the downfield shifts observed for the phenanthroline protons, the marked changes in the anthracene subspectrum is difficult to interpret on the basis of the effects of Zn(II) coordination and would suggest a π -stacking interaction between the two aromatic units. This prompted us to carry out ¹H NMR pH-metric titrations on solutions containing M(II) and L in 1 : 1 molar ratio. Fig. 5 reports the pH dependence of selected ¹H NMR signals of L in the presence of Zn(II) ([L] = [Zn(II)] = 1 × 10⁻³ M), compared with the species distribution diagram determined on the basis of the potentiometric results. The most interesting finding is the significant downfield shift of the signals of the ethylenic chain H9 and H10 of the anthracene pendant observed upon deprotonation of [ZnLH₂]⁴⁺

to give the monoprotonated [ZnLH]³⁺ species in the pH range 3-6. This strongly suggests that the formation of [ZnLH]³⁺ implies metal coordination by the amine group of the pendant. Simultaneously, a remarkable upfield shift is observed for the methylenic protons H8 and for the aromatic ones H1, H2 and H3. Minor shifts are also observed for the resonances of the remaining anthracene and phenanthroline protons. This indicates the formation of intramolecular π -stacking interactions²⁰ between the two aromatic moieties of the ligand in the [ZnLH]³⁺ complex, most probably occurring in the face-to-face mode, in contrast to the edge-to-face mode found in the solid state. Probably packing effects, including the important intramolecular π -stacking observed in the solid complex, are critical in determining the intramolecular π -stacking interaction mode. As shown in Fig. 5, the chemical shifts do not show significant variation in the pH range 6–10.5, where the $[ZnL]^{2+}$ and $[ZnL(OH)]^{-1}$ species are formed. Very interestingly, the binding of the second hydroxide anion leads to detachment of the NH group from the metal, as shown by the upfield shift experienced by the H9 and H10 signals above pH 10.5. The downfield shift displayed by the signals of the anthracene protons H1, H2 and H3 and by H8 indicates that the π -stacking interaction is lost upon detachment of the N1 amine group from the Zn(II) ion.



Fig. 5 (a) pH Dependence of selected ¹H NMR signals of L in the presence of Zn(II). (b) Distribution diagram for the system Zn(II)/L ([L] = $[Zn(II)] = 1 \times 10^{-3}$ M).

The pH-controlled coordination of the amine group of the pendant arm is also observed in the Cd(II) and Hg(II) complexes. In these cases, however, only the monoprotonated $[MLH]^{3+}$ and the $[ML]^{2+}$ complexes are detected in solution. According to Fig. 6, for the Cd(II) complexes, coordination of the amine group N1 occurs upon deprotonation of the $[CdLH]^{3+}$ complex to give the $[CdL]^{2+}$ one in the pH range 4–7, as supported by the downfield shifts of the H9 and H10 signals in this pH range. Differently from Zn(II), binding of N1 to the metal is accompanied by negligible shifts of the signals of the protons of the two aromatic units. This suggests that in the $[CdL]^{2+}$ complex the two aromatic moieties do not interact, or they weakly interact *via* π -stacking. The Hg(II) complexes display an almost equivalent behaviour; coordination of the amine N1 of the pendant arm in the $[HgL]^{2+}$ complex does not give any π -stacking interaction between the phenanthroline and the anthracene units.



Fig. 6 pH Dependence of selected ¹H NMR signals of L in the presence of Cd(II) and distribution diagram for the system Cd(II)/L ([L] = [Cd(II)] = 1×10^{-3} M).

Fluorescence emission in H₂O-CH₃CN (50:50, v/v)

We anticipated in a previous communication¹¹ that the fluorescence emission from L solutions is strictly dependent upon the protonation state of the compound. A total quenching of the emission is observed for the species L, HL⁺ and H₂L²⁺, while H₃L³⁺ exhibits an intense emission. Such quenching effect can be explained by an electron transfer process from unprotonated amine groups in benzylic position to the excited anthracene. Indeed, as shown by the NMR study, in H₃L³⁺ all three amine groups in benzylic positions are protonated and the species is emissive.

Like protonation, also coordination of Zn(II) to the amine groups precludes the electron transfer quenching effect. Accordingly, the quenching effect occurs only at pH values that permit the existence of nitrogen atoms which are neither attached to the metal nor protonated. This occurs for all Zn(II) complexes except $[ZnH_2L]^{4+}$ which exhibits an intense emission with a maximum at 418 nm (excitation at 352 nm). The most interesting feature of this system, however, is an exciplex emission occurring, at about 550 nm (excitation at 352 nm), for all complex species with the exception of $[ZnL(OH)_2]$, revealed by the formation of a non-structured and red-shifted emission band (Fig. 7) ascribed to an intramolecular π -stacking complex in the excited state, involving phenanthroline and anthracene. As described above, the π -stacking complex is already formed in the ground state for the species $[ZnHL]^{3+}$, $[ZnL]^{2+}$ and $[ZnL(OH)]^+$, but not in the case of [ZnH₂L]⁴⁺ and [ZnL(OH)₂]. As a consequence, in the case of $[ZnH_2L]^{4+}$, the π -stacking complex is exclusively formed during the excited state lifetime. The π -stacking complex in the ground state and the exciplex emission from the excited state, are driven by the coordination of the nitrogen atom of the pendant arm to the metal, since this coordination forces the phenanthroline and the anthracene moieties to stay close to each other. Such an arrangement is maintained upon coordination of a single OH- ion to the metal, probably because the binding occurs at the opposite side of the pendant arm, while the exciplex emission, as well as the π -stacking complex, disappear at more basic pH values, in agreement with the detachment of the amine nitrogen of the pendant arm caused by coordination of the second OH- ion.

In contrast to the Zn(II) behaviour, no exciplex emission is observed with the Cd(II) and Hg(II) complexes of L. As found for the Zn(II) complex, quenching of the strong emission at 418 nm is also observed upon formation of $[CdL]^{2+}$ and $[HgL]^{2+}$, but the π -stacking complex is not formed by these two compounds, neither in the ground state, as shown above by the NMR study, nor in the excited state. Most likely, the larger Cd(II) and Hg(II) cations are



Fig. 7 Fluorescence emission spectra ($\lambda_{exc} = 352 \text{ nm}$) of the Zn(II) complexes with L at different pH values (1.69, 3.73, 4.4, 4.87, 5.1, 5.57, 6.05, 6.55, 10.37). Inset: fluorimetric titration of the same system: (•) emission at 418 nm, (\circ) exciplex emission at 600 nm. Species distribution curves in the inset represent mol fractions.

large enough to prevent the two heteroaromatic moieties to come in contact even when the nitrogen atom of the arm is coordinated to the metal. Hence, the exciplex emission might be used for selective signalling of Zn(II) in the presence of Cd(II) and Hg(II).

Unlike the Zn(II) complex, behaving as an elementary molecular machine driven by pH and by light, the Cd(II) and Hg(II) complexes can perform only controlled molecular movements driven by pH.

Fluorescence emission and fluorescence temperature dependence in ethanol

The fluorescence emission spectra of compounds L and $[ZnL]^{2+}$ in ethanol are presented in Fig. 8, together with the exciplex band obtained by subtracting the emission spectra of L from that of the complex. The emission spectra of $[ZnL]^{2+}$ and L show the characteristic structured band of anthracene, with maximum intensity at 412 nm. In the case of $[ZnL]^{2+}$, again an additional structureless broad band (exciplex band), appears at longer wavelength values (with maximum at *ca*. 525 nm). A significant increase in the total intensity of this band is observed when compared to the behaviour found in H₂O–CH₃CN (50:50, v/v).



Fig. 8 Fluorescence emission spectra of compound $[ZnL]^{2+}$ and L in ethanol at 293 K. The exciplex band results from the subtraction of the emission spectra of L from that of $[ZnL]^{2+}$.

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Independently of the temperature in the range 288–353 K, the metal-free ligand does not show the exciplex emission band, as previously observed in H_2O – CH_3CN (50:50, v/v) at room temperature, revealing that without metal coordination the two aromatic moieties do not interact with each other.

The steady-state temperature dependence of L, shown in Fig. 9, reveals a decrease of the fluorescence emission intensity with increasing temperature. This is a well-known phenomenon occurring with aromatic-like molecules, which translates the gradual predominance of the radiationless processes relative to the radiative processes.



Fig. 9 Fluorescence emission spectra of L in ethanol, as a function of temperature. Shown, as inset, is the linear dependence of the fluorescence intensity with temperature.

However, this is not the case occurring with $[ZnL]^{2+}$, where the appearance of the new exciplex band gives rise to two different behaviours, depending on the temperature range studied.

The variation of the ratio of the exciplex to monomer bands (I_{Exc}/I_M) with temperature can be described within the framework of the classic Birks kinetic scheme²¹ (see ESI†). The Stevens–Ban plots of $\ln(I_{Exc}/I_M)$ vs. the reciprocal of the absolute temperature for $[ZnL]^{2+}$ are presented in Fig. 10. The exciplex-to-monomer intensity ratio (I_{Exc}/I_M) reaches its maximum at about 268 K. From the low-temperature regime (LTL) and high temperature regime (HTL) it is possible to extract respectively the activation energy for the exciplex formation, $E_a = 12.3$ kJ mol⁻¹ and the enthalpy of exciplex formation ($\Delta H = -7.9$ kJ mol⁻¹).¹⁷ As expected, the enthalpy for exciplex formation is negative thus showing that the process is thermodynamically favorable.

Of relevance in Fig. 10 is the fact that the difference between the $\ln(I_{Exc}/I_M)$ at the crossover temperature and that obtained by extrapolation of the linearizations obtained in the HTL and LTL is $\Delta = 0.35$, which is about half ($\Delta = \ln 2 = 0.69$) of the expected value considering the classical Birks' kinetic scheme, where no groundstate excimers or exciplex exist. This difference usually implies that some degree of exciplex is already present in the ground-state as was previously established to occur in H₂O–CD₃CN (50:50, v/v).¹¹

Moreover the fluorescence quantum yield for L and $[ZnL]^{2+}$ were determined in ethanol solution at room temperature. The fluorescence quantum yield of L ($\phi_M = 0.031$) was obtained by using naphthalene ($\phi_F = 0.27$) as a standard, while the fluorescence quantum efficiency for the exciplex (ϕ_F^E) occurring with $[ZnL]^{2+}$, was



Fig. 10 Arrhenius plot for $[ZnL]^{2+}$ in ethanol showing the two temperature regimes and the crossover temperature.

determined by using L as a standard; the total fluorescence quantum yield was $\phi^{T}_{F} = 0.012$. With the use of eqn. (1)

$$\phi_{\rm F}^{\rm E} = \frac{\phi_{\rm Exc}^{\rm Ap}}{1 - \frac{\phi_{\rm M}^{\rm Ap}}{\phi_{\rm M}}} \tag{1}$$

where ϕ_{Exc}^{Ap} and ϕ_{M}^{Ap} are the integrated areas under the exciplex and monomer bands with $\phi_{F}^{T} = \phi_{Exc}^{Ap} + \phi_{M}^{Ap}$, the value for ϕ_{F}^{E} was determined to be 0.0064.

Solid state behaviour

Fig. 11 shows the fluorescence and fluorescence excitation spectra recorded for a thin film of the solid complex and for an ethanol solution of the complex. Comparison between the two media (solid and liquid) reveals that the fluorescence excitation spectrum of the solid (film) is red-shifted (*ca.* 5 nm) with respect to the absorption spectra obtained in solution. However, the fluorescence emission spectrum of the solid is now blue-shifted by about 46 nm. These observations are compatible with the X-ray data of the complex (Figs. 1 and 2), *i.e.*, in the solid state a new exciplex-like conformation, with relative perpendicular orientations of the phenanthroline and anthracene moieties, is observed.



Fig. 11 Thin film and solution fluorescence and fluorescence excitation spectra of [ZnL]²⁺ obtained at 293 K.

Conclusions

The ligand L forms very stable metal complexes in solution thanks to its polyamine macrocyclic moiety behaving as primary coordination site. Coordination of the additional amine group located in the pendant arm to the metal ion can be controlled by competitive reaction with H⁺ (protonation), hence by modulating the solution pH. Binding of metal ions such as Zn(II), Cd(II), and Hg(II) determines a total quenching of the intense fluorescence emission from the anthracene fluorophore, centred at 418 nm, signalling the binding process. In the case of Zn(II), but not with Cd(II) and Hg(II), complex formation gives rise, upon excitation, to an exciplex emission, at about 550 nm, due to the intramolecular association via π -stacking of phenanthroline and anthracene groups in the excited state. According to such exciplex emission, L behaves as a selective fluorescent chemosensor for Zn(II) over Cd(II) and Hg(II). A similar π -stacking association occurs also in the ground state, as shown by means of ¹H NMR study, for all Zn(II) complex species except for $[ZnH_2L]^{4+}$ and $[ZnL(OH)_2]$. The formation of the $[ZnL(OH)_2]$ species occurring at alkaline pH disrupts the π -stacking complex, both in the ground state and in the excited state, switching off the exciplex emission. On the other hand, [ZnH₂L]⁴⁺, in contrast with the ground state behaviour, gives rise to a π -stacking complex and exciplex emission in the excited state. Hence, around pH 4, where this species is formed, the movement of the pendant arm leading to the formation of the π -stacking complex is controlled by light irradiation. In terms of intramolecular movement of the pendent functionality, complexes of L with Zn(II), Cd(II), and Hg(II) behave as elementary molecular machines driven by pH, and by light in the case of [ZnH₂L]4+

Exciplex formation, which is a thermodynamically favourable process in solution, occurs also in the solid state, although different π -stacking modes of interaction, namely face-to-face in solution and edge-to-face in the solid, are probably operative.

Experimental

Materials

The synthetical procedure to obtain L (2,9-[2,5,8-triaza-5-(*N*-an-thracene-9-methyl-amino)ethyl]-[9]-1,10-phenanthrolinophane trihydrobromide) is depicted in Scheme 1. 2,9-bis(bromomethyl)-1,10-phenanthroline (1)²² and tris[2-(*N*-tosylaminoethyl)]amine (2)²³ were prepared as previously described. Anthracene-9-carbaldehyde (5) was purchased from Aldrich.



2,9-[2,5,8-Triaza-2,8-ditosyl-5-(*N*-tosylaminoethyl)]-[9]-1,10-phenanthrolinophane (3)

A solution of 1 (4 g, 3.6 mmol) in dry CH₃CN (250 cm³) was added over a period of 6 h to a refluxing and vigorously stirred suspension of **2** (5.3 g, 8.7 mmol) and K₂CO₃ (25 g, 0.18 mol) in CH₃CN (400 cm³). After the addition was completed, the solution was refluxed for an additional 2 h. The resulting suspension was filtered out and the solution was vacuum evaporated to give a crude solid. The product was purified by column chromatography on neutral alumina using CH₂Cl₂–acetone (10:1) as eluting solvent, affording product **3** as a white solid. Yield: 2.7 g (37%). Elemental analysis: calc. (%) for C₄₁H₄₄N₆S₃O₆: C 60.57, H 5.45, N 10.34; found: C 60.4, H 5.4, N 10.2. ¹H NMR (300 MHz, CDCl₃): δ 1.39 (s, 6H), 2.31 (s, 3H), 2.5 (t, 4H), 2.71 (t, 2H), 3.14 (t, 4H), 3.59 (t, 2H), 4.81 (s, 4H), 7.43 (d, 6H), 7.76 (d, 2H), 7.89 (m, 8H), 8.33 (d, 2H); ¹³C NMR (300 MHz, CDCl₃): δ 21.91, 29.69, 41.35, 47.87, 53.46, 53.73, 54.96, 123.98, 126.84, 127.46, 128.34, 130.26, 137.05, 137.61, 143.89, 145.45, 156.69.

2,9-(2,5,8-Triaza-5-aminoethyl)-[9]-1,10-phenanthrolinophane trihydrobromide (4·3HBr)

Compound **3** (2.7 g, 3.3 mmol) and phenol (25 g, 0.266 mol) were dissolved in 33% HBr/CH₃COOH (200 cm³). The reaction mixture was kept under stirring at 90 °C for 22 h until a precipitate was formed. The solid was filtered out and washed several times with CH₂Cl₂. The trihydrobromide salt was recrystallized from a EtOH–water 2 : 1 mixture. Yield 0.56 g (28%). Elemental analysis: calc. (%) for C₂₀H₂₆N₆·3HBr: C 40.49; H, 4.92, N 14.17; found: C 40.52, H 5.1, N 14.34. ¹H NMR (300 MHz, D₂O, pH = 5): δ 2.46 (t, 2H), 2.74 (t, 2H), 2.87 (t, 4H), 3.22 (t, 4H), 4.48 (s, 4H), 7.50 (d, 2H), 7.62 (s, 2H), 8.18 (d, 2H); ¹³C NMR (300 MHz, D₂O, pH = 5): δ 34.03, 45.95, 46.15, 50.56, 51.18, 122.68, 127.17, 129.08, 139.09, 143.14, 150.36; MS: *m/z* = 351 [M + H⁺].

2,9-[2,5,8-Triaza-5-(*N*-anthracene-9-methylamino)ethyl]-[9]-1,10-phenanthrolinophane trihydrobromide (L·3HBr)

Compound 4 (0.35 g, 1 mmol) and anthracene-9-carbaldehyde (5) (0.2 g, 0.97 mmol) were dissolved in ethanol (50 cm³) and allowed to react for 48 h at room temperature. Then NaBH₄ (0.5 g, 13 mmol) was added and the resulting solution warmed at 50 °C for 4 h. The solvent was vacuum evaporated; the residue was then dissolved in water (50 cm³) and extracted with CH₂Cl₂ for at least four times (150 cm³). After drying over Na_2SO_4 , the solvent was evaporated under reduced pressure; the solid residue was washed several times with cyclohexane and then dissolved in ethanol. Dropwise addition of concentrated HBr yields L·3HBr as a solid compound, which was filtered off, washed with ethanol and dried in vacuum. Yield 0.55 g (73%). Elemental analysis: calc. (%) for C₃₅H₃₉N₆Br₃Br: C 53.66, H 5.02, N 10.73; found: C 53.72, H 5.15, N 10.87. ¹H NMR (300 MHz, CDCl₃): δ 3.16 (m, 12H), 4.19 (s, 4H), 4.49 (s, 2H), 7.30 (m, 6H), 7.72 (s, 2H), 7.79 (d, 2H), 8.00 (s, 1H), 8.05 (d, 2H), 8.14 (d, 2H); ¹³C NMR (300 MHz, D₂O–CD₃CN): δ 46.80, 50.02, 54.38, 58.16, 60.21, 120.54, 120.95, 123.83, 125.24, 126.05, 127.10, 127.60, 128.73, 128.94, 136.98, 148.21; MS: *m*/*z* = 541 [M + H⁺].

[ZnLBr](ClO₄)·H₂O

Crystals of $[ZnLBr](ClO_4) \cdot H_2O$ used for X-ray analysis were obtained by slow evaporation at room temperature of a water–MeCN (1:1, v/v) solution containing $Zn(ClO_4)_2$ and L·3HBr at pH 7.

$Crystallographic data \ collection \ and \ refinement \ of \ the \ crystal structure \ of \ [ZnLBr](ClO_4) \cdot H_2O$

Crystal data: C₃₅H₃₈BrClN₆O₅, M = 803.44, monoclinic, space group $P2_1$, a = 11.540(5), b = 12.480(5), c = 12.160(5) Å, $\beta = 106.600(5)^\circ$, Z = 2, U = 1678.3(12) Å³, T = 298 K, $\mu = 3.582$ mm⁻¹, F(000) = 824. *Data collection*: P4 X-ray Bruker X-ray diffractometer, $\lambda = 1.5418$ Å (Cu-K α), graphite monochromated. 3722 Reflections collected, 3211 unique. The structure was solved by direct methods using the SIR97 program.²⁴ Anisotropic thermal parameters were used for all the non-hydrogen atoms. Hydrogen atoms, except those of the water molecules, were included in calculated positions and their coordinates and thermal factors refined accordingly to the linked atoms. Refinement were performed using full-matrix least-squares methods with the SHELXL-97 program.²⁵ Final agreement factors were $R_1 = 0.0487$ ($I > 2\sigma(I)$), $wR_2 = 0.1498$ (all data).

CCDC reference number 220491.

See http://www.rsc.org/suppdata/dt/b4/b403743j/ for crystallographic data in CIF or other electronic format.

Potentiometric measurements

All pH-metric measurements $(pH = -log[H^+])$ employed for the determination of ligand protonation and metal complex stability constants were carried out in 0.10 mol dm-3 NMe₄Cl H₂O-MeCN (1:1, v/v) solution at 298.1 \pm 0.1 K by means of conventional titration experiments under inert atmosphere. The choice of this solvent mixture was dictated by the low solubility of the ligand in pure water. The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO2-free NaOH solutions and determining the equivalent point by Gran's method²⁶ which allows one to determine the standard potential E° and the ionic product of water ($pK_{w} = 14.99(1)$). At least three measurements (about 100 data points for each) were performed for each system in the pH range 2.5-10.5. In all experiments the ligand concentration [L] was about 1×10^{-3} mol dm⁻³. In the complexation experiments the metal ion concentration was [M(II)] = 0.8[L]. The computer program HYPERQUAD²⁷ was used to calculate the equilibrium constants from emf data. In the case of Hg(II), under the experimental conditions employed, the formation of metal-chloride complexes is expected to occur. The formation of such complexes was not taken into account in calculations; hence, the stability constants of Hg(II) complexes reported in Table 2 must be referred to the specific composition of the medium employed (0.10 mol dm⁻³ NMe₄Cl H₂O-MeCN (1:1, v/v)).

NMR measurements

300.07 MHz ¹H and 75.46 MHz ¹³C NMR spectra in D₂O–CD₃CN solutions at different pH values were recorded at 298.1 K in a Varian Unity 300 MHz spectrometer. Peak positions are reported relative to TMS. ¹H–¹H and ¹H–¹³C 2D correlation experiments were performed to assign the signals. Small amounts of 0.01 mol dm⁻³ NaOD or DCl solutions were added to a solution of L in the absence or in the presence of metal (1:1 molar ratio) to adjust the pH.

Spectroscopic measurements

The solvents used were of spectroscopic or equivalent grade. Ethanol was previously dried over CaO and then distilled. Water was twice distilled and passed through a Millipore apparatus. All aqueous solutions were prepared in 0.1 mol dm⁻³ NaCl. The measured pH values were obtained with a Crison micropH 2000 and adjustments of H⁺ concentration was made with diluted HCl and NaOH solutions. [ZnLBr](ClO₄)·H₂O was used for both solution and solid-state studies.

Absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Jovin-Yvon Spex Fluorog 3–2.2. spectrometers, respectively. The fluorescence quantum yield of compound L was determined using anthracene ($\phi_F = 0.27$) as standard. The fluorescence quantum yield of compound [ZnL]²⁺ was measured using compound 1 ($\phi_F = 0.031$) as standard.

Thin films of the Zn(II) complex were obtained with a Desk-Top Precision Spin Coating System, Model P6700 Series from Speedline Technologies. The solid-state thin film of the complex was obtained by deposition of a few drops of an ethanol solution of [ZnLBr](ClO₄)·H₂O in a quartz lamella followed by spin coating at 430–635 mmHg and in Ar saturated atmosphere (2 psi).

The $I_{\text{Exc}}/I_{\text{M}}$ ratio was obtained from the decomposed area under the monomer and exciplex bands. The general procedure to obtain those values consisted in matching the emission spectra of L in ethanol with the monomer band of ZnL. The resulting differential spectrum is the exciplex emission band. In this procedure the *x*-*x*'scale must be in energetic units.

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