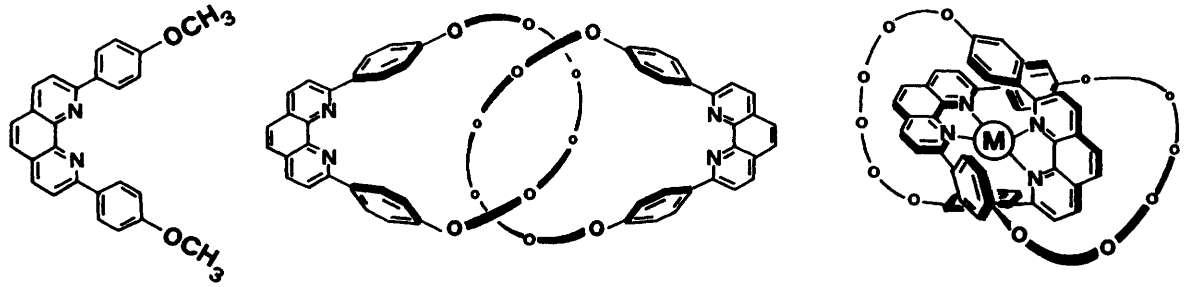
Absorption and Emission Properties of a 2-Catenand, its Protonated Forms, and its Complexes with Li^+, Cu^+, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+} and Cd^{2+}: Tuning of the Luminescence over the Whole Visible Spectral Region

Nicola Armaroli,[a] Luisa De Cola,[a] Vincenzo Balzani,*[a] Jean-Pierre Sauvage,[b] Christiane O. Dietrich-Buchecker,[b] Jean-Marc Kern[b] and Abdelhakim Bailal[b]
[a] *Dipartimento di Chimica 'G. Ciamician', Università di Bologna, I-40126 Bologna, Italy*
[b] *Laboratoire de Chimie Organo-Minerale, UA 422 au CNRS, Institut de Chimie, F-67000, Strasbourg, France*

The absorption spectra (at 298 K), luminescence spectra and lifetimes (at 77 and 298 K) and luminescence quantum yields (at 298 K) of a catenand, its mono- and diprotonated forms, and its complexes with Li^+, Cu^+, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+} and Cd^{2+} in CH_2Cl_2 solutions are obtained. The catenand (L) consists of two interlocked 30-membered rings, each one containing a 2,9-diphenyl-1,10-phenanthroline-type co-ordinating moiety. Upon addition of trifluoroacetic acid to CH_2Cl_2 solutions of L, significant changes in the absorption and luminescence properties are observed, that are fully reversed on addition of base. Comparison with the behaviour of a reference compound, 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline suggests that the catenand protonation does not occur at each phenanthroline-type moiety, but involves co-ordination of both moieties around one or two protons (in HL^+ or H_2L^{2+} respectively). The free catenand shows $^1(\pi\pi^*)$ fluorescence (λ_{max} = 400 nm, τ = 2.0 ns, Φ = 0.42) at 298 K, and both $^1(\pi\pi^*)$ fluorescence (λ_{max} = 382 nm, τ = 2.2 ns) and $^3(\pi\pi^*)$ phosphorescence (λ_{max} = 524 nm, τ = 0.79 s) in a rigid matrix at 77 K. The metal complexes of L are forced to have a tetrahedral-type co-ordination geometry because of the entwined arrangement of the two phenanthroline ligands. The only exception is for the Pd^{2+} complex in which orthometallation is observed to avoid a tetrahedral co-ordination. The complexes with Li^+, Cd^{2+} and Zn^{2+} exhibit ligand-centred (l.c.) fluorescence and phosphorescence, this being considerably more perturbed from that of L for the divalent ions. The complexes of Co^{2+} and Ni^{2+} are not luminescent, as expected because of the presence of low energy metal-centred levels which offer a pathway to a fast radiationless decay of the l.c. levels. The copper(I) complex exhibits an emission band in the red spectral region (298 K: λ_{max} = 730 nm, τ = 175 ns, Φ = 0.0011; 77 K: λ_{max} = 690 nm, τ = 1.1 μs), that can be assigned to the lowest energy triplet metal-to-ligand charge transfer (m.l.c.t.) excited state. For the silver(I) complex no emission can be observed at room temperature, whereas in a rigid matrix at 77 K a very intense, long-lived band is present at about 498 nm (τ = 0.012 s) that can be assigned to the lowest ^{3}l.c. level. The palladium(II) complex, in which the first co-ordination sphere of the metal ion is constituted by C^--phenyl and two phenanthroline nitrogens of a diphenylphenanthroline unit and a nitrogen of the other diphenylphenanthroline unit, displays an emission band at 555 nm (τ = 3.0×10^{-4} s) at 77 K that can be assigned to a perturbed ^{3}m.l.c.t. level. The emission maxima of L, HL^+ and H_2L^{2+} and its six luminescent metal complexes cover the range 378–730 nm, showing that it is possible to tune the luminescence of the L derivatives over the whole visible spectral region.

There is currently a growing interest in the chemistry of systems made up of molecular components (supramolecular chemistry).[1–6] One of the reasons for this interest is the design of supramolecular species capable of performing useful light induced functions.[7] A rapidly developing area of supramolecular chemistry is that concerning *catenanes* which are species composed of interlocked rings.[8–12] Catenanes which contain co-ordinating units constitute a new class of ligands (*catenands*) which exhibit special properties.[8,9] The catenand (L) shown in Fig. 1 is made of two interlocked 30-membered rings, each one



dap L ML

Fig. 1 Schematic structure formulae of 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline [dap (2,9-dianisyl-1,10-phenanthroline)], the catenand (L), and a metal catenate (ML). In L and ML the oxygen atoms are linked through $-(CH_2)_2-$ groups containing a 2,9-diphenyl-1,10-phenanthroline type co-ordinating unit.[13] Previous investigations have shown that L can be protonated[14] and can give rise to complexes with metal ions (*catenates*).[15] It should be pointed out that co-ordination to the nitrogens of two entwined phenanthroline units (Fig. 1) can only give rise to metal complexes with a tetrahedral-type arrangement regardless of the nature of the metal ion. In addition, the metal centre is efficiently shielded by the supramolecular structure towards interactions with solvent and/or other species. In particular, co-ordination of additional (fifth or sixth) ligands is sterically prevented. The co-ordinated L can also be regarded as a 'cluster' of aromatic (phenanthroline and phenyl) rings gathered in a small volume around the metal. Their interaction could be significant and therefore co-ordinated L could display properties different from those of the isolated chelate sub-units. This characteristic of complex of L may lead to novel photophysical and photochemical properties and may thus contribute to the design of new photochemical molecular devices.[7]

In a recent paper[16] we have investigated the effects of protonation on the absorption and luminescence properties of 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline [dap (2,9-dianisyl-1,10-phenanthroline)], which can be considered as the acyclic analogue of L, and of its parent compounds 2,9-diphenyl-1,10-phenanthroline (dpp) and 1,10-phenanthroline (phen). We report now the results of a detailed investigation on (*i*) the effect of protonation on the absorption and luminescence properties of L, and (*ii*) the absorption and luminescence properties of the catenates of Li^+, Cu^+, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+} and Cd^{2+} with L.

Experimental

The preparation of L[13] and of its metal complexes[15] has been previously reported. Trifluoroacetic acid was a Merck product. All the experiments were performed in Merck pro analysi dichloromethane, which was found to contain less acidic impurities than Uvasol dichloromethane. The organic base 1,5-diazabicyclo[4.3.0]non-5-ene (dbn) was obtained from Aldrich. The absorption spectra were recorded with a Perkin-Elmer λ6 spectrophotometer using cells of 1 cm path length. Corrected luminescence spectra and phosphorescence lifetimes were obtained with a Perkin-Elmer LS 50 spectrofluorimeter, and corrected excitation spectra at room temperature were obtained with a Perkin-Elmer LS5 spectrofluorimeter. Luminescence quantum yields were measured with a Perkin-Elmer 650-40 spectrofluorimeter by using the method described by Demas and Crosby[17] {standards used: anthracene in cyclohexane, $\Phi = 0.34$;[18] quinine sulfate in 0.1 mol dm^{-3} H_2SO_4, $\Phi = 0.52$;[19] $[Ru(bipy)_3]Cl_2$ (bipy = 2,2'-bipyridine) in water, $\Phi = 0.028$;[20] $[Os(bipy)_3]^{2+}$ in MeCN, $\Phi = 0.005$[21]}. An Edinburgh single photon counting apparatus was used to obtain luminescence lifetimes. Single-exponential decays were observed in all cases, except for solutions at the highest acid concentration which contained two luminescent species (see below). The changes in the luminescence intensity on addition of acid were measured exciting the solution at the lowest energy isosbestic point.

Results

Catenand L *and its Protonated Forms*.—Addition of dbn base to CH_2Cl_2 solutions of L did not cause any spectral change. By contrast, the addition of trifluoroacetic acid caused remarkable changes in the absorption spectra and in the luminescence properties. As shown in Fig. 2 the initial spectral changes occurred with maintenance of isosbestic points at 252, 266, 304 and 368 nm. When the concentration of added acid was increased from 1.0 × 10^{-5} to 5.0 × 10^{-3} mol dm^{-3}, no further spectral change was observed. The species present in the solution under such conditions is the previously investigated[14] monoprotonated species HL^+. Upon addition of much larger amounts of acid, new spectral changes were observed (Fig. 3) with isosbestic points at 282, 313 and 338 nm. This indicates that a second protonation process takes place at higher acid concentrations. For acid concentration higher than 3.0 × 10^{-2} mol dm^{-3} no further spectral change was observed. Addition of an excess of dbn base to the acid solution gave back the initial spectrum of L.

The changes in the absorption spectra were accompanied

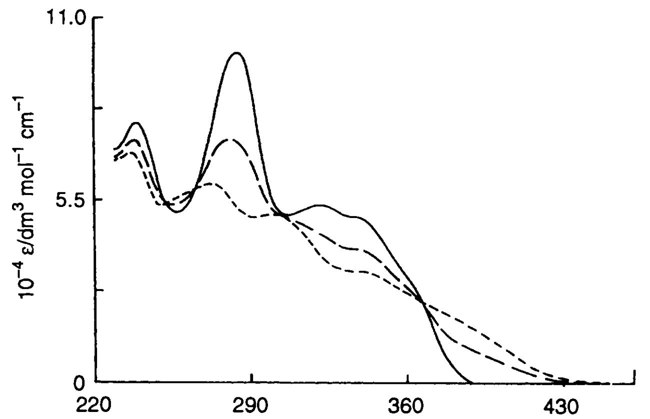


Fig. 2 Absorption spectra of a 1.0 × 10^{-5} mol dm^{-3} solution of L in CH_2Cl_2 containing the following concentrations of CF_3CO_2H: 0 (—), 1.0 × 10^{-5} (— — —) and ≈ 5.0 × 10^{-5} to ≈ 7.0 × 10^{-3} mol dm^{-3} (- - -)

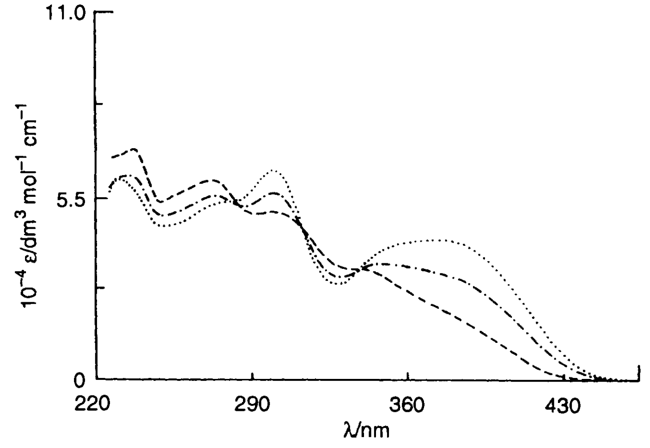


Fig. 3 Absorption spectra of a 1.0 × 10^{-5} mol dm^{-3} solution of L in CH_2Cl_2 containing the following concentrations of CF_3CO_2H: ≈ 5.0 × 10^{-5} to ≈7.0 × 10^{-3} (- - -), 1.0 × 10^{-2} (· - ·) and 3.0 × 10^{-2} mol dm^{-3} (·····)

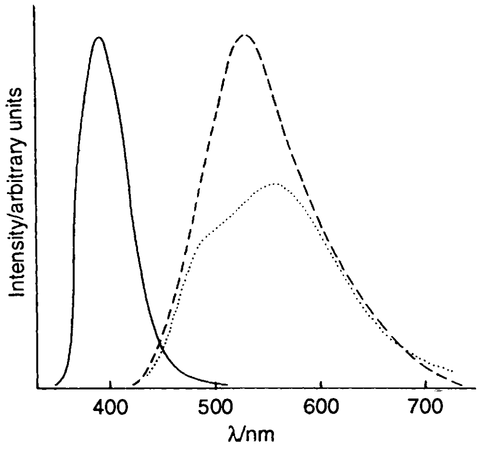


Fig. 4 Luminescence spectra of L in CH_2Cl_2 solution at 298 K containing the following concentrations of CF_3CO_2H: 0 (—), 5.0 × 10^{-5} (- - -) and 3.0 × 10^{-2} mol dm^{-3} (·····)

Table 1 Luminescence data in deaerated CH_2Cl_2 solution

	T = 298 K			77 K			
	λ/nm[a]	τ/ns	Φ	λ/nm[a]	τ/ns	λ/nm[a]	τ/s
dap[b]	396	2.2	0.29	376	3.1	508	1.0
$Hdap^+$[b]	578	14.0	0.062	488	20.0	525	0.90
L	400	2.0	0.42	382	2.2	524	0.79
HL^+	555	11.0	0.022	460	13.0	515	0.87
H_2L^{2+}[c]	590	4.5	0.015	485	6.4	515	0.74
$[LiL]^+$	400	2.5	0.35	378	2.5	532	2.1
$[CuL]^+$	730	175[d]	0.0011	—	—	685	1.1×10^{-6}
$[AgL]^+$[e]	—	—	—	—	—	498[f]	0.012
$[CoL]^{2+}$[e]	—	—	—	—	—	—	—
$[NiL]^{2+}$[e]	—	—	—	—	—	—	—
$[ZnL]^{2+}$	463	2.0	0.082	433	5.0	495	0.78
$[PdL]^{2+}$	—	—	—	—	—	555	3.0×10^{-4}
$[CdL]^{2+}$[e]	443	< 1	0.015	420	7.5	498	0.35

[a] Corrected values of the maximum of the emission band. [b] Ref. 16. [c] At least two luminescent species are present, see text; the reported fluorescence lifetime is the shortest one. [d] τ = 120 ns in air-equilibrated solution. [e] The previously reported[15] preliminary results were wrong (see text). [f] Very strong band.

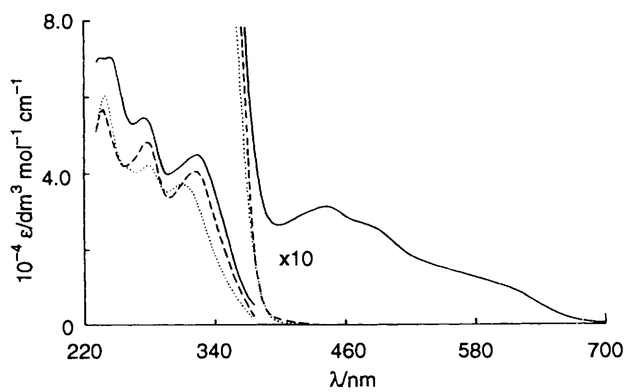


Fig. 5 Absorption spectra of the catenates of Li^+ (– – –), Cu^+ (—) and Ag^+ (·····). Concentrations: UV region 1.0×10^{-5}; visible region 1.0×10^{-4} mol dm^{-3}.

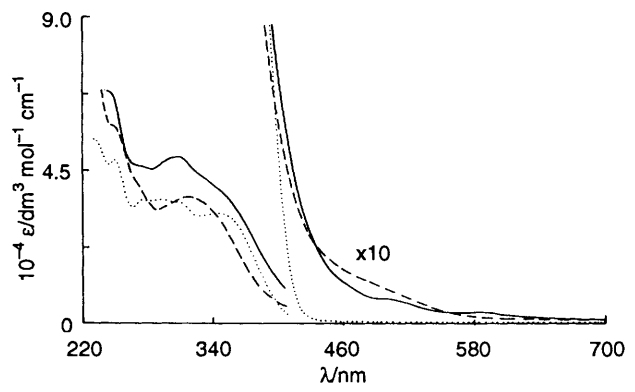


Fig. 6 Absorption spectra of the catenates of Co^{2+} (—), Ni^{2+} (– – –) and Zn^{2+} (·····). Concentrations: UV region 1.0×10^{-5}, visible region 1.0×10^{-4} mol dm^{-3}.

by changes in the luminescence properties (Table 1, Fig. 4). The fluorescence spectrum of the monoprotonated species (CF_3CO_2H concentration between 3.0×10^{-5} and 1.0×10^{-4} mol dm^{-3}) is considerably red-shifted compared to that of L, the fluorescence lifetime is longer, and the fluorescence quantum yield is smaller. On further addition of acid, the changes in the absorption spectra (Fig. 3) are again accompanied by changes in the luminescence properties (Table 1, Fig. 4). The final fluorescence spectrum is less intense, considerably broader, and shows a shoulder on the UV side. The fluorescence decay is non-exponential and can be fitted with two lifetime values, 4.5 and 12 ns.

The corrected excitation spectra of L and HL^+ at room temperature were found to match the corresponding absorption spectra.

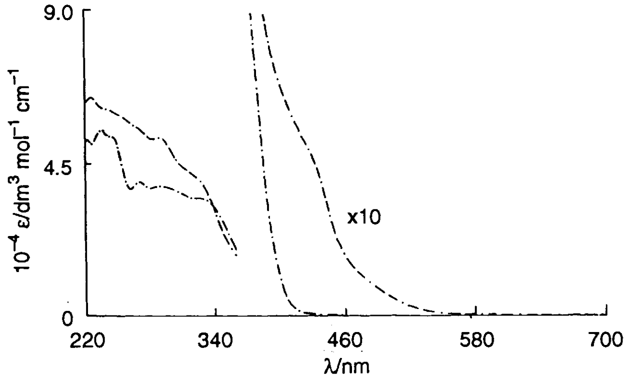


Fig. 7 Absorption spectra of the catenates of Pd^{2+} (· – – ·) and Cd^{2+} (· – ·). Concentrations: UV region 1.0×10^{-5}, visible region 1.0×10^{-4} mol dm^{-3}.

Catenates.—The absorption spectra of the metal catenates (Figs. 5–7) in the UV spectral region are substantially different from the spectrum of L (Fig. 2). The spectra of the monovalent ions (Li^+, Cu^+, Ag^+) are similar to one another, but rather different from the spectra of the complexes of the divalent ions (Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}). The spectrum of the palladium(II) complex, which has a peculiar type of co-ordination,[15b] is substantially different from the spectra of the complexes of the other divalent cations. The luminescence behaviour (Table 1, Figs. 8 and 9) of the catenates depends on the nature of the metal ion. The lithium complex shows a spectrum quite similar to that of the free ligand (Fig. 4). The copper(I) complex shows a low energy, broad and weak luminescence band, with a lifetime in the μs time scale. The silver(I) and palladium(II) complexes do not emit at room temperature. At 77 K they exhibit a phosphorescence band, that in the case of the silver(I) catenate is at least ten times more intense than the corresponding band of the other species. The complexes of Co^{2+} and Ni^{2+} are not emissive under any conditions. The behaviour of the complexes of Zn^{2+} and Cd^{2+} is similar to that of L and $[LiL]^+$ but at room

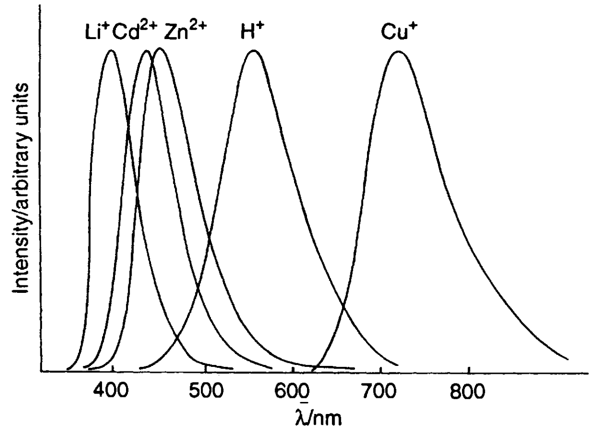


Fig. 8 Luminescence spectra of metal catenates in CH_2Cl_2 solution at 298 K

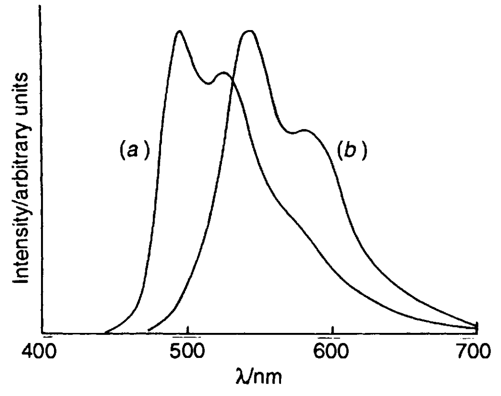


Fig. 9 Luminescence spectra of $[AgL]^+$ (*a*) and $[PdL]^{2+}$ (*b*) in CH_2Cl_2 at 77 K

temperature the emission bands are considerably weaker and red shifted.

The corrected excitation spectra of $[LiL]^+$, $[CdL]^{2+}$, $[ZnL]^{2+}$ and $[CuL]^+$ at room temperature were found to match the corresponding absorption spectra.

Discussion

Cantenand L *and its Protonated Forms.* The monoprotonated HL^+ species was previously isolated as a ClO_4^- salt.[14] An X-ray crystal structure investigation showed that its structure is that of a *proton catenate*, that is the two macrocycles are interlocked and the two dpp fragments are entwined. The proton is localized on a nitrogen, and it is involved in hydrogen-bond interactions with the other three nitrogens. In solution, the proton undergoes fast exchange (NMR time scale) on the four nitrogen atoms. NMR studies indicated that also the diprotonated form, H_2L^{2+}, exhibits an entwined geometry.[14] The results obtained in the present investigation are fully consistent with those findings.

The unprotonated forms of L and dap (which is the acyclic analogue of L, Fig. 1) exhibit quite similar absorption and luminescence properties, as expected from the presence in L of two dap-type non-interacting units. Upon addition of trifluoroacetic acid to dap[16] or L in CH_2Cl_2 solutions, significant spectral changes are observed. The amount of acid needed to reach a plateau in the ΔA *vs.* acid concentration plots is much smaller for L than for dap, in agreement with the previously observed[14] stronger basicity of L. Furthermore, as one can see from Fig. 10, HL^+ and $Hdap^+$ display very different absorption spectra, and the luminescence properties of the two species are also different (Table 1). This indicates that the first protonation of L does not consist in the simple, independent protonation of one or both of its dap-type chromophoric units, but rather in the formation of a proton catenate (Fig. 11). The absorption spectrum of HL^+ (Fig. 10) bears a noticeable similarity with the absorption spectrum of the catenates of monovalent cations (Fig. 5), which is consistent with a proton catenate structure for HL^+. It should be stressed that HL^+ contains one proton for two phen sites (4 nitrogen atoms, Fig. 11), whereas $Hdap^+$ has one proton for only one phen site. The protonated catenand HL^+ has a surprisingly broad stability range considering its acid-base stoichiometry.

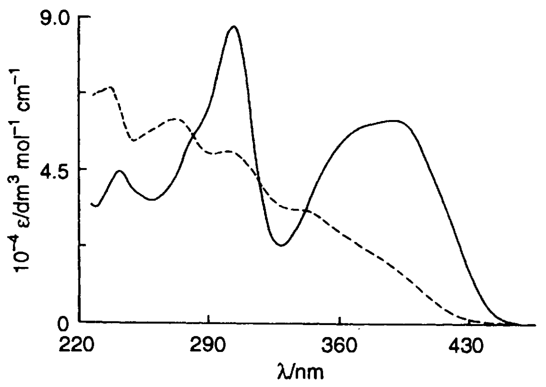


Fig. 10 Absorption spectra of $Hdap^+$ (—) and HL^+ (- - -). Concentration: 1.0×10^{-5} mol dm^{-3}

In the case of dap, after formation of the monoprotonated species further addition of acid does not cause any change in the absorption spectrum or in the luminescence properties.[16] This means that, under the experimental conditions used, $Hdap^+$ does not undergo further protonation. For L, however, after formation of HL^+ there is only a defined acidity region where the absorption spectrum and the luminescence properties remain constant. Further addition of acid causes new spectral changes (with maintenance of new isosbestic points, Fig. 3) and new variations in the photophysical properties. The luminescence intensity decreases, and at the highest CF_3CO_2H concentration used the emission spectrum is very broad (Fig. 4). There is evidence that the shoulder at about 460 nm is due to a small amount of impurity.* NMR investigations,[14] showed that CF_3CO_2H is not acidic enough to fully displace the equilibrium toward the diprotonated H_2L^{2+} form. According to the NMR results, H_2L^{2+} maintains an entwined topography, which is remarkable owing to the high concentration of positive charge. By contrast, $Hdap^+$ does not show any sign of self-association and entwining. Our results are again consistent with these conclusions. If the second protonation occurred by disentangling the two dap fragments of L (Fig. 11), one would have obtained two dap-type protonated sites (about 12 Å apart), and H_2L^{2+} would have then exhibited the luminescence properties of $Hdap^+$. This, however, does not seem to be the case since further protonation of HL^+ shortens the luminescence lifetime and decreases the luminescence quantum yield, in contrast with what is expected to occur for conversion of the HL^+ proton catenate into a doubly protonated H_2L^{2+} species which contains two non-interacting $Hdap^+$-type moieties (Table 1). On the other hand, the absorption spectrum at the highest acid concentration is similar to that exhibited by a 2:3 mixture of HL^+ and $Hdap^+$. This suggests that the entwined-type structure of H_2L^{2+} is somewhat loose compared to that of HL^+, as is perhaps required by the need to host a

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* We have found that dap and L in CH_2Cl_2 solution give rise to a photoproduct (most likely, a *N*-alkylated type species) which displays a luminescence band with a maximum at about 460 nm. Such a photoproduct can be obtained with high yield under UV irradiation, and it is slowly formed also under laboratory light.

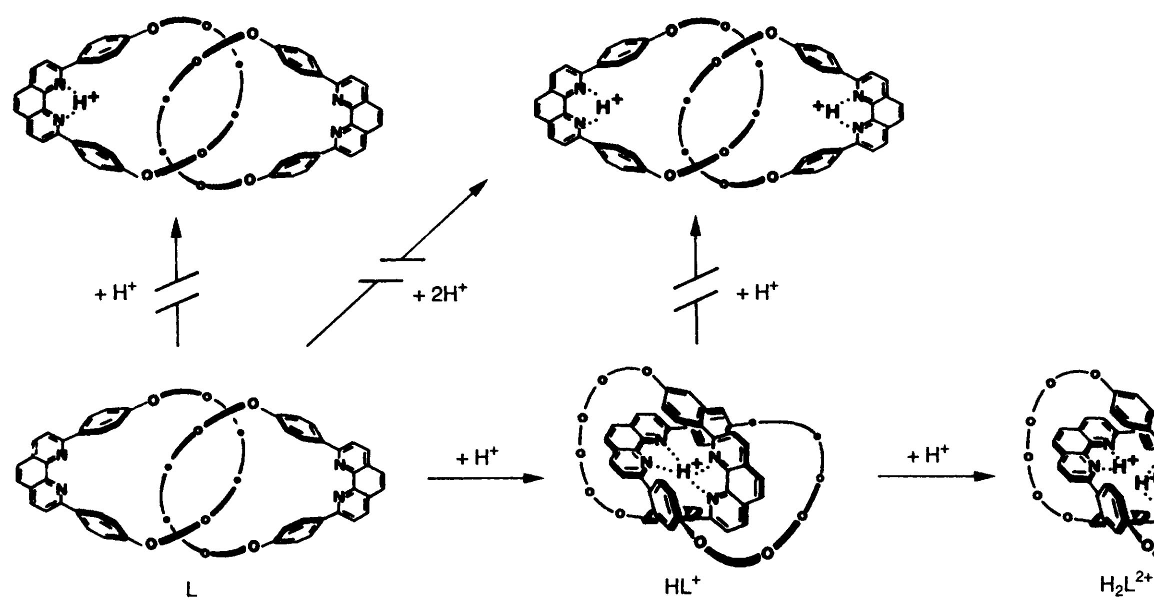

Fig. 11 Schematic representation of the structures of HL^+ and H_2L^{2+}. For more details, see text

water molecule or a counter ion in the tetrahedral cavity formed by the phenanthroline nitrogens, in order to reduce electrostatic repulsion.

Catenates.—The spectroscopic properties of transition-metal complexes are usually discussed with the assumption that the ground state as well as the excited and redox states involved can be described in a sufficiently approximate way by localized molecular-orbital configurations.[22] With such an assumption, the various spectroscopic transitions are classified as metal-centred (m.c.), ligand-centred (l.c.), or charge-transfer [either metal-to-ligand (m.l.c.t.) or ligand-to-metal (l.m.c.t.)]. For complexes of metal ions in normal oxidation states with phenanthroline-type ligands such an approach is generally valid.[23] This simplified picture, however, is no longer applicable if there is a large degree of covalency in the metal–ligand bonds of the ground state complex and if excited-state configurations of different nature are sufficiently close in energy to be intermixed. In cyclometallated complexes the metal–C^- bonds are expected to exhibit a high degree of covalency and the l.c. and m.l.c.t. excited configurations may lie very close in energy. For these reasons, the localized molecular-orbital approach can only be used as a first approximation scheme for the orthometallated palladium(II) complex.

Let us consider the energy position of the m.c. excited states. The cations Li^+, Cu^+, Ag^+, Zn^{2+} and Cd^{2+} have closed-shell electronic configuration, so that their m.c. excited states lie at very high energies. By contrast, Co^{2+} and Ni^{2+}, which have d^7 and d^8 electronic configurations, respectively, possess low energy excited states.[24] For example, the lowest energy excited state for the Co^{2+} and Ni^{2+} aqua ions lies at 8100 and 8500 cm^{-1}, respectively. The Pd^{2+} ion has a d^8 electronic configuration as does Ni^{2+}, but its m.c. excited states are expected to lie at higher energy since Pd^{2+} belongs to the second transition series and C^- has a stronger ligand field than N. Electronic transitions from the ground state to m.c. excited states are symmetry forbidden. The corresponding absorption bands, therefore, are very weak and can only be observed in concentrated solutions.

All the metal catenates contain dap-type chromophoric units and thus are expected to exhibit l.c. bands in the UV region due to spin allowed $\pi \longrightarrow \pi^*$ transitions.[16] The absorption spectrum of L is twice as intense as that of dap in the whole spectral region since the two chromophoric units do not interact, being remote from each other[25] (Fig. 1). In the entwined topography of the metal complexes, however, the phenoxy group of a moiety lies very close and parallel to the phenanthroline ring of the other moiety;[14,26] under such circumstances, ligand-to-ligand charge transfer (l.l.c.t.) transitions from the phenoxy electron-donor groups to the metal-co-ordinated phenanthroline electron-acceptor groups can take place, as has been demonstrated to occur in similar systems.[26] The luminescence properties of L are very similar to those of dap, which again indicates a lack of interaction between the two chromophoric groups. Luminescence is due to the lowest $^1(\pi\pi^*)$ and $^3(\pi\pi^*)$ levels which are respectively responsible for the fluorescence band (400 nm at room temperature, 382 nm in rigid matrix at 77 K) and for the phosphorescence band (524 nm at 77 K).

The occurrence of m.l.c.t. and l.m.c.t. bands in metal complexes at low energies is related to the redox properties of the metal and ligands.[22] The co-ordinating site of metal catenates is moderately difficult to reduce and very difficult to oxidize.[15] Among the investigated complexes, only $[CuL]^+$ has a metal ion that can be easily oxidized and therefore only for this complex are low energy m.l.c.t. bands present,[27,28] as for any other copper(I) complex of phen-type ligands.[12,29,30] Some of the examined complexes contain metals that can be easily reduced,[15] so that l.m.c.t. bands could also occur at low energy.

On the basis of the above considerations, we can now discuss the absorption and luminescence properties of the various catenates.† The complex $[LiL]^+$ is expected to exhibit only l.c. absorption bands. One can see, however, that its absorption spectrum (Fig. 5) looks quite different from that of L (Fig. 2). Such differences, which mainly concern the relative intensities of the l.c. bands at 240, 285 and 323 nm are caused by the perturbation induced by the metal ion on the $\pi \longrightarrow \pi^*$ l.c. transitions.[31] No evidence for l.l.c.t. bands is present, but it should be recalled that such bands are expected to be much weaker than the l.c. bands and could thus be masked. The luminescence properties of $[LiL]^+$ are almost identical to those of L, indicating that the lowest energy $^1(\pi\pi^*)$ and $^3(\pi\pi^*)$ levels responsible for the luminescence of L are still the lowest excited states, and that the presence of the metal ion and the consequent

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† In previously reported preliminary results[15] very weak bands apparently due to impurities or photoproducts were wrongly assigned as emission bands of the silver(I), nickel(I) and cadmium(II) catenates.

different topography do not play an important role in the energy and in the decay rate constants of these levels.

The absorption and emission properties of $[CuL]^+$ have already been discussed.[27,28] The absorption spectrum of $[CuL]^+$ in the UV region is similar but not identical to that of $[LiL]^+$, suggesting that m.l.c.t. transitions can contribute to the observed bands. Most important, the absorption spectrum of $[CuL]^+$ (Fig. 5) shows a broad, weak band in the visible region that can be straightforwardly assigned to spin-allowed m.l.c.t. transitions.[27] The lowest ^{3}m.l.c.t. level, which is the lowest excited state of the system, is responsible for the observed red luminescence (Table 1, Fig. 8). The corrected excitation spectrum shows that all the upper excited states undergo radiationless decay to the lowest excited state with unitary efficiency, as usually happens in complexes containing heavy metals.

In $[AgL]^+$ the lowest excited state is still a ^{3}l.c. level, as shown by the presence, in a rigid matrix at 77 K, of an intense, structured emission band at 498 nm (Fig. 9) with $\tau = 0.012$ s. Lifetimes in this range are typical of heavy-atom perturbed ^{3}l.c. levels.[32] The lack of ^{3}l.c. emission in fluid solution at room temperature is an expected result for intrinsically long-lived excited states because of the occurrence of quenching processes related to diffusion (triplet–triplet annihilation, quenching by impurities). The lack of l.c. fluorescence can be attributed to a fast intersystem crossing induced by the heavy-metal ion. This is also consistent with the high intensity of the ^{3}l.c. emission at 77 K (about 10 times higher than that of the corresponding emission of $[LiL]^+$).

The absorption spectra of the catenates of Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} (Fig. 6) are similar but not identical. The l.m.c.t. bands, and perhaps l.l.c.t. bands, could contribute to the observed absorptions. From the metal-centred reduction potentials (−0.60, −0.18, −0.96 and −1.15 V for the Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} catenates, respectively)[15,†] one can expect that the energy of the l.m.c.t. bands decreases in the order $[CdL]^{2+} > [ZnL]^{2+} > [CoL]^{2+} > [NiL]^{2+}$ but specific assignments are difficult. The weak metal-centred bands of $[CoL]^{2+}$ and $[NiL]^{2+}$ in the visible region can only be seen in concentrated solution. The luminescence bands exhibited by $[ZnL]^{2+}$ and $[CdL]^{2+}$ (Fig. 8, Table 1) can confidently be assigned to l.c. levels which, because of their partial charge-transfer character,[16] are affected by the presence of the positive charge carried by the metal ion. The presence of low-lying non-emissive excited states in Co^{2+} and Ni^{2+} is the cause of lack of luminescence in $[CoL]^{2+}$ and $[NiL]^{2+}$. Such low lying levels, in fact, offer a fast radiationless decay path to the $^1(\pi\pi^*)$ and $^3(\pi\pi^*)$ levels which are responsible for the ligand-centred luminescence.

Finally, the luminescence band shown by $[PdL]^{2+}$ at 77 K ($\lambda_{max} = 555$ nm, Fig. 9; $\tau = 3.0 \times 10^{-4}$ s), cannot be easily assigned. In orthometallated complexes of Pd^{2+} the m.l.c.t. and l.c. excited configurations are mixed.[32] A substantial m.l.c.t. character for the luminescent excited state is indicated by the noticeable red-shift of the luminescence band compared with the l.c. bands of $[AgL]^+$, $[ZnL]^{2+}$ and $[CdL]^{2+}$ as well as by the much shorter lifetime.

Conclusion

The absorption and emission properties of L are strongly influenced by protonation and by co-ordination of metal ions. Comparison with the spectral changes caused by protonation on the simple model compound dap shows that monoprotonation of L results from co-operative action of the two phen-type chelating units yielding a 'proton catenate' species (Fig. 11). Double protonation does not lead to the disentangling of the two chelating sites. The changes caused by protonation or metal co-ordination in the UV spectral region of the absorption spectrum are mainly due to perturbations induced on the ligand-centred transitions, but charge-transfer transitions may also contribute in some cases. For the copper(I) complex, a moderately intense m.l.c.t. band is clearly observed in the visible region. The species L, HL^+, H_2L^{2+}, $[LiL]^+$, $[CuL]^+$ $[AgL]^+$ $[ZnL]^{2+}$ $[CdL]^{2+}$ and $[PdL]^{2+}$ are luminescent, whereas $[CoL]^{2+}$ and $[NiL]^{2+}$ are not, because of the presence of low energy m.c. levels which facilitate radiationless decay processes. The species L, HL^+, H_2L^{2+}, $[LiL]^+$, $[ZnL]^{2+}$ and $[CdL]^{2+}$ exhibit ligand-centred fluorescence (nanosecond time-scale) and phosphorescence (second time-scale at 77 K). The complex $[AgL]^+$ exhibits only a phosphorescence band (10^{-2} s time-scale) at 77 K because the intersystem crossing process is made faster by the presence of the heavy-metal ion. For $[CuL]^+$ the lowest excited state is a ^{3}m.l.c.t. level which is responsible for the luminescence observed in the red region of the spectrum (microsecond time-scale). The orthometallated $[PdL]^{2+}$ shows a phosphorescence band at 77 K (Fig. 9) which can be assigned to a level containing a substantial amount of m.l.c.t. character. Comparison between absorption spectrum and corrected excitation spectrum at 298 K shows that for each luminescent species the emitting level is reached with the same efficiency regardless of the excitation wavelength. The results obtained show that for L it is possible to tune the luminescence over the whole visible spectral region by protonation or by co-ordination of suitable metal ions (Figs. 4, 8 and 9). This property is interesting for analytical purposes. Furthermore, it opens the possibility to the occurrence of energy transfer processes in 3-catenands[33] or higher homologues[34] when they contain different co-ordinated centres.[12] For a 3-catenate containing only one Zn^{2+} ion, a H^+-controlled switching of the direction of energy transfer (from the free catenand moiety to the zinc(II) catenate in neutral solution, and from the zinc(II) catenate moiety to the protonated catenand in acid medium) can also be predicted on the basis of the results obtained (Table 1).

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[†] The observed reduction for the cadmium(II) and zinc(II) catenates could be ligand centred, which could mean that the metal-centred reduction occurs at even more negative potentials.

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