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Effect of protons and metal ions on the fluorescence properties of a polylysin dendrimer containing twenty four dansyl units †

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The interaction of protons, Co^{2+}, Ni^{2+} and Zn^{2+} ions (as nitrate salts) with a polylysin dendrimer, **D**, functionalized in the periphery with 24 5-dimethylamino-1-naphthalenesulfonamido (dansyl) units has been investigated in acetonitrile–dichloromethane solution. The dendrimer consists of a benzene core branched in the 1, 3, and 5 positions. Each branch starts with a (dialkyl)carboxamide-type moiety and carries (i) six aliphatic amide groups and (ii) eight fluorescent dansyl units. For comparison purposes, the behaviour of a monodansyl reference compound (**I**) has also been investigated. The absorption spectrum and the fluorescence properties of the dendrimer are those expected for a species containing 24 non-interacting dansyl units. Both for the model compound and for the dendrimer, protonation causes a shift of the absorption and fluorescence bands towards higher energies; for the dendrimer, however, the changes in fluorescence intensity during the acid titration reveal the occurrence of intradendrimer quenching processes, with signal amplification. Addition of Co^{2+} or Ni^{2+} ions to a basic solution of the model compound **I** does not cause any effect in the absorption and emission properties, whereas in the case of dendrimer **D** a strong fluorescence quenching is observed. At low metal ion concentration each metal ion quenches about 9 dansyl units; the fluorescence quenching takes place by a static mechanism involving co-ordination of metal ions in the interior of the dendrimer. Addition of Zn^{2+} to a basic solution of the dendrimer causes only a very small decrease in the fluorescence intensity. The co-ordinated Co^{2+} and Ni^{2+} ions are fully displaced by addition of Zn^{2+} or H^+ with revival of the dansyl fluorescence. The results obtained show that a dendrimer can exhibit an unusual co-ordinating ability and sensory signal amplification.

Introduction

Dendrimers[1] are well defined macromolecules exhibiting a tree-like structure, first derived by the "cascade molecule" approach.[2] Dendrimer chemistry is a rapidly expanding field for both basic and applicative reasons.[3] Dendrimers containing photoactive components[4–14] can exhibit particularly interesting properties since (i) co-operation among the photoactive units can allow the dendrimer to perform specific functions (*e.g.*, light harvesting by an antenna effect), and (ii) changes in the properties of such units can be exploited to monitor the participation of dendrimers in chemical processes (*e.g.*, electron-transfer reactions). A recent development of dendrimer chemistry concerns the co-ordination of metal ions in the interior branches or in the exterior units.[15–19] When a dendrimer contains photoactive components, interaction with metal ions can result in strong changes of the photochemical and photophysical properties.[20]

Continuing our investigations in the field of photoactive dendrimers,[8,20] we report here the preparation of a polylysin dendrimer functionalized in the periphery with 24 fluorescent 5-dimethylamino-1-naphthalenesulfonamido (dansyl) units, its spectroscopic properties, and its interaction with protons and metal ions in a 5 : 1 v/v acetonitrile–dichloromethane solution. The formula of the dendrimer (**D**) is shown in Fig. 1. The dendrimer consists of a benzene core, branched in the 1, 3, and 5 positions. Each branch starts with a (dialkyl)carboxamide-type moiety and carries six aliphatic amide groups and eight dansyl units in the periphery. For comparison purposes, the behaviour of a monodansyl reference compound (**I**, Fig. 1) has also been investigated. The dansyl chromophoric group, which shows intense absorption bands in the near UV spectral region and a strong fluorescence band in the visible region, is extensively used for sensing or labelling purposes.[21]

The results obtained show that all the 24 dansyl units of the **D** dendrimer can be protonated and that in slightly basic solution the dendrimer can co-ordinate transition metal ions. Profound effects on the fluorescence properties of the dendrimer are observed because of intradendrimer quenching processes occurring with signal amplification.

Experimental

Preparation of 24-Cascade : benzene-(1,3,5)tricarboxamide-[6-*N*, *N*,*N*′,*N*′,*N*″,*N*″] : (3,4-diaza-2-oxohexylidene)[2-1,1] : (2-oxo-3-azapropylidene : 2-oxo-3-azaheptylidene) : *N*-(5′-dimethylaminonaphth-1-ylthiodioxo)amine : *N*-(5′-dimethylaminonaphth-1-ylthiodioxo)butylamine

The dendrimer starting material (24-Cascade : benzene-(1,3,5)-tricarboxamide[6-*N*,*N*,*N*′,*N*′,*N*″,*N*″] : (3,4-diaza-2-oxohexylidene)[2-1,1] : (2-oxo-3-azapropylidene : 2-oxo-3-azaheptylidene) : amine : butylamine) was obtained by courtesy of Schering AG, Berlin, Germany (Dr H. Schmitt-Willich).[22] 0.40 g (0.144 mmol) starting polylysin dendrimer and 0.48 ml (3.46 mmol) triethylamine were dissolved in 150 ml of dry dichloromethane.

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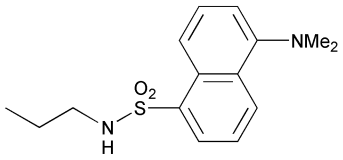
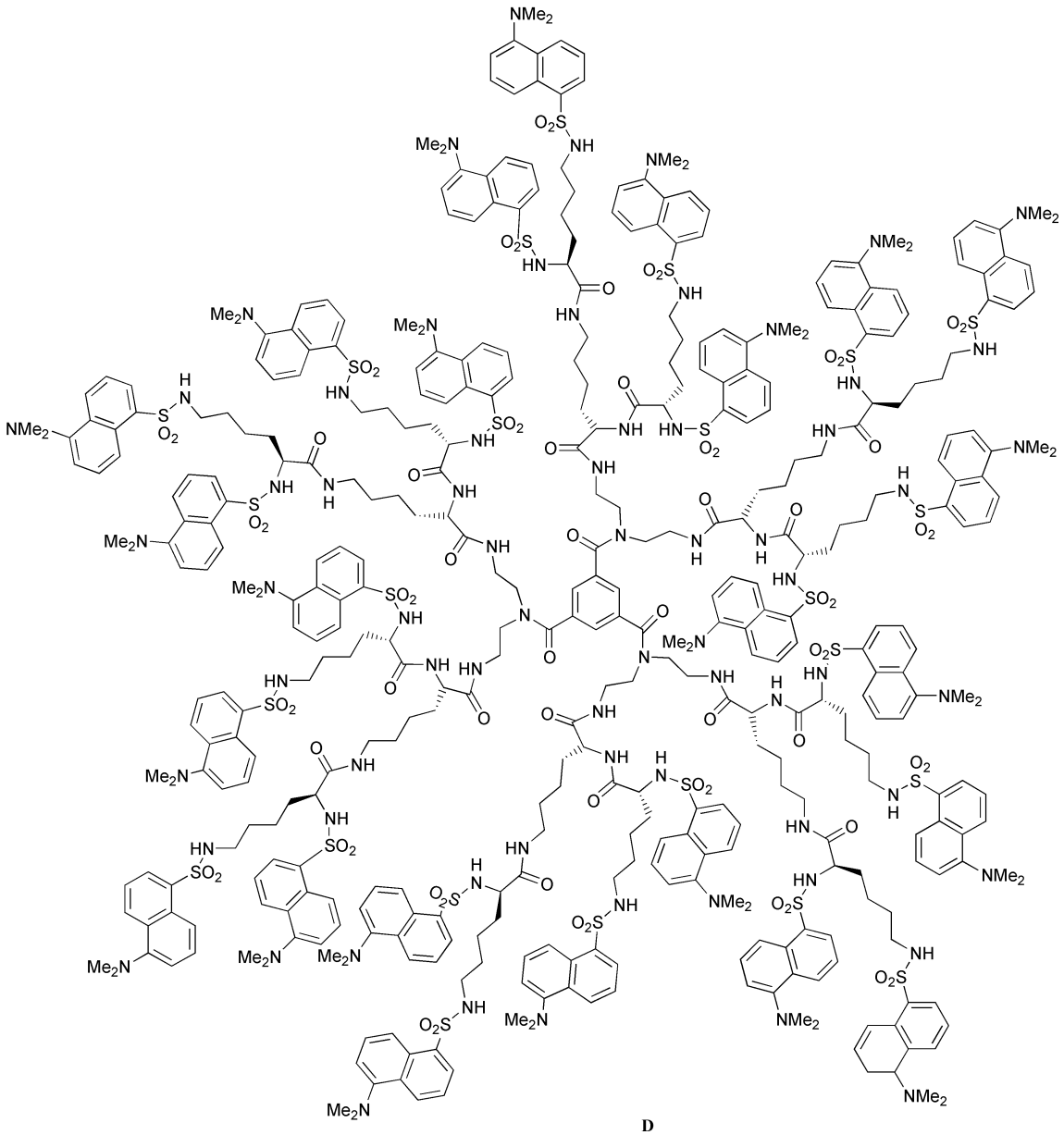


I



D

Fig. 1 Structural formulas of the dendrimer **D** and of the monodansyl reference compound **I**.

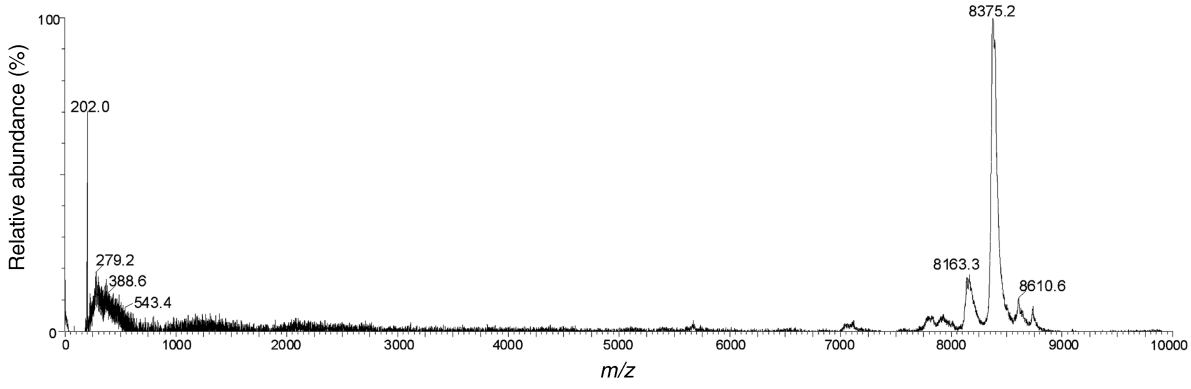


Fig. 2 MALDI-TOF-MS of dendrimer **D**. For more detail, see Experimental section.

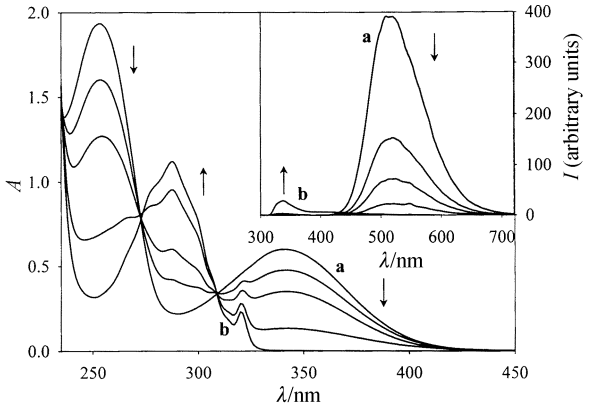


Fig. 3 Absorption and (inset) fluorescence spectra of dendrimer **D** in acetonitrile–dichloromethane solution upon titration with triflic acid (CF_3SO_3H). Curve a is the spectrum of the original solution, b that at the end of the titration. The emission spectra have been obtained by excitation at the isosbestic point at 273 nm.

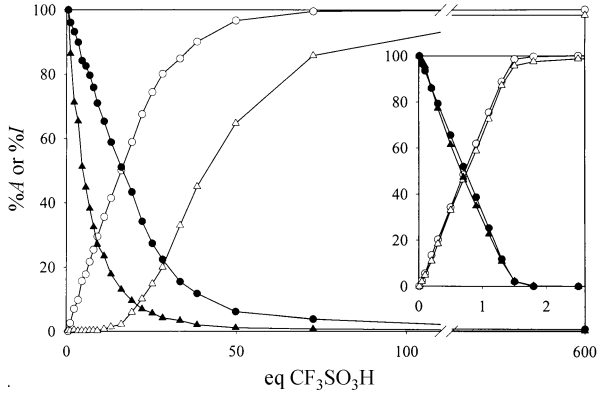


Fig. 4 Normalized changes in absorbance and fluorescence intensity observed for compounds **I** (inset) and **D** upon titration with triflic acid. The changes in absorbance at 339 (unprotonated form) and 286 nm (protonated form) are labelled by (●) and (○), respectively; the changes in the fluorescence intensity at 514 (unprotonated form) and 336 nm (protonated form) are labelled by (▲) and (△), respectively.

To the refluxing mixture a solution of 1.40 g (5.2 mmol) dansyl chloride in 50 ml dichloromethane was added dropwise. After stirring for three days under reflux the mixture was stirred at 25 °C for two days. The solvent was removed *in vacuo* and the residue collected in dichloromethane. After washing with water, aqueous Na_2CO_3 and again with water the organic phase was dried with Na_2SO_4. Further purification was achieved by column chromatography (140 g SiO_2, 40–63 μm, CH_2Cl_2, then CH_2Cl_2–MeOH–Et_3N 100 : 5 : 1) yielding 0.72 g (60%) of a bright yellow solid, mp 180–187 °C. TLC (SiO_2): $R_f = 0.30$ (dichloromethane–methanol–triethylamine 100 : 5 : 1). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.45–1.80 (bm, two maxima at 0.82 and 1.21, 108 H, 18 (NCH(CH_2)$_3$CH_2N)), 2.10 (bm, 24 H, CH_2NSO_2), 2.20 (bm, 12 H, CH_2NHCO), 2.55–4.00 (bm, three maxima at 2.65, 2.75 and 3.47, 186 H, 3 N(CH_2-CH_2NHCO)$_2$, 24 (N(CH_3)$_2$) and 18 (*tert*-CH)), 6.95 (bm, 24 H, CH_{dansyl}), 7.30 (bm, 48 H, CH_{dansyl}) and 7.79–8.42 (bm, 75 H, CH_{dansyl} and CH_{Ph}). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 21.9, 28.5, 31.9, 39.1, 42.6 (CH_2NSO_2), 45.5 ((NCH_3)$_2$), 53.6, 57.1, 115.4, 119.2, 123.3, 128.3 (C_{dansyl}), 128.6 (C_{Ph}), 129.2, 129.7, 129.9, 130.2 (CH_{dansyl}), 130.7 (C_{Ph}), 135.2, 151.8 (C_{dansyl}), 171.6, 172.5 and 172.7 (CONH). MALDI-TOF-MS (Fig. 2; matrix 4-hydroxyazobenzene): *m*/*z* (%) 8375.2 (100, M + H^+), 8140.1 (16, M − dansyl + H^+) and 7905.5 (4, M − 2dansyl + H^+); calc. for $C_{417}H_{519}N_{69}O_{69}S_{24}$: 8371.6.

The absorption spectra and photophysical properties (fluorescence spectra, quantum yields, and excited state lifetimes) were studied in acetonitrile–dichloromethane (5 : 1 v/v) solution. The equipment used has been described elsewhere.[8] Fluorescence quantum yields were measured following the methods of Demas and Crosby[23] (standard used: quinine sulfate in 0.5 M H_2SO_4, $\Phi = 0.55$).[24] The emission intensity was corrected for inner filter effects when necessary.[25] The estimated experimental error is 2 nm on the band maximum, 5% on the molar absorption coefficient, 10% on the fluorescence quantum yield, and 5% on the fluorescence lifetime.

Results and discussion

Absorption and emission properties

In acetonitrile–dichloromethane 5 : 1 v/v solution dendrimer **D** exhibits (Fig. 3) intense absorption bands in the near UV spectral region ($\lambda_{max} = 253$ and 341 nm), practically at the same wavelengths ($\lambda_{max} = 252$ and 338 nm) as those of the model compound **I**. The molar absorption coefficients for the dendrimer **D** ($\varepsilon_{max} = 296\,000$ and 91 800 M^{-1} cm^{-1}) are 24 times the values measured for independent dansyl units, within experimental errors (for **I**: $\varepsilon_{max} = 12\,200$ and 3900 M^{-1} cm^{-1}). The strong fluorescence band (Fig. 3, inset) exhibited by **D** in the visible region has maximum (514 nm), quantum yield (0.28), and lifetime (15 ns) comparable to those of model compound **I** ($\lambda_{max} = 509$ nm, $\Phi = 0.30$, $\tau = 12$ ns). These results show that in the dendrimer the interaction among the 24 dansyl groups is, at most, very small.

The energy of the fluorescent excited state of the unprotonated dansyl unit, as estimated from the onset of the corresponding fluorescence bands, is about 2.76 eV. Electrochemical experiments in acetonitrile solution have shown that compound **I** undergoes a chemically irreversible one-electron oxidation process ($E_{1/2}$ about 0.9 V *vs*. SCE, as estimated by digital simulation), and a one-electron reduction process, reversible only at low temperature (−40 °C) with $E_{1/2} = -2.02$ V (*vs*. SCE). It follows[26] that the fluorescent excited state of the unprotonated dansyl unit is a weak oxidant, E(*dansyl/dansyl$^-$) *ca.* +0.7 V, and a strong reductant, E(dansyl$^+$/*dansyl) *ca.* −1.9 V.

Protonation of the dendrimer

Absorption and fluorescence spectra. The absorption and emission properties of the dansyl group are very sensitive to the addition of acid because of the protonation of the amine subunit.[8f,21d] In the acid titration experiments the concentration of **D** was 6.3×10^{-6} M and that of the reference compound **I** was 24 times higher, in order to have the same number of dansyl units in each solution. The fluorescence intensity values have been obtained by excitation at an isosbestic point ($\lambda = 273$ nm). From a qualitative viewpoint, both the reference compound **I** and the dendrimer **D** exhibit the same behaviour. The spectra of **D** before and after addition of an excess of CF_3SO_3H are shown in Fig. 3. At the end of the acid titration the original absorption bands are no longer present and a new band is formed ($\lambda_{max} = 286$ nm; $\varepsilon_{max} = 6800$ M^{-1} cm^{-1} for **I** and $\lambda_{max} = 288$ nm; $\varepsilon_{max} = 172\,600$ M^{-1} cm^{-1} for **D**). The same isosbestic points are present for both compounds. Besides the changes in absorbance, protonation causes the disappearance of the strong fluorescence band with $\lambda_{max} = 514$ nm and the appearance of a much weaker, shorter lived fluorescence band (Fig. 3, inset) with $\lambda_{max} = 338$ nm, $\Phi = 0.005$, $\tau < 1$ ns for **D**, comparable to that found for the protonated form of **I** ($\lambda_{max} = 336$ nm, $\Phi = 0.002$, $\tau < 1$ ns).

In the case of the model compound **I**, the intensity of the absorption band of unprotonated dansyl at 339 nm decreases linearly with the number of equivalents of acid added (Fig. 4, inset), and it is accompanied by (i) a parallel increase of the absorption band of protonated dansyl at 286 nm, (ii) a parallel decrease of the unprotonated dansyl emission intensity at 514 nm, and (iii) a parallel increase of the protonated dansyl emission intensity at 336 nm. Protonation of 50% of **I** requires

0.7 equivalent of acid, showing that, in the solvent used, the protonated dansyl unit is an acid slightly stronger than triflic acid.

For dendrimer **D** (Fig. 4) the decrease of the absorption band of the unprotonated dansyl units at 339 nm is again accompanied by a parallel increase of the absorption band of the protonated dansyl units at 286 nm, and 50% protonation requires 16 equivalents of acid per dendrimer. Since such a value is about 24 times larger than that required for 50% protonation of the monodansyl reference compound **I** (see above), this result indicates that the 24 dansyl units of **D** behave independently as far as protonation is concerned, at least until 50% of such units have been protonated. When the fraction of protonated dansyl units becomes higher, however, the titration plot is no longer linear (Fig. 4), showing that further protonation of the dendrimer becomes more and more difficult. When the number of equivalents of acid added approaches 100 (which means about 4 protons per dansyl unit), practically all the 24 dansyl units of all the dendrimer molecules are protonated. The protonation reaction is fully reversible upon addition of a base (1,5-diazabicyclo[4.3.0]-non-5-ene, DBN).

Intradendrimer fluorescence quenching. Comparison of the titration curves obtained from fluorescence measurements for compounds **I** and **D** (Fig. 4) shows an important difference. Contrary to what happens for **I**, in the case of dendrimer **D** the changes in the fluorescence intensities of both the unprotonated and protonated species do not parallel the corresponding changes in absorbance. As one can see, the fluorescence intensity of the unprotonated units decreases much faster than expected from the decrease in their concentration, as measured from the change in absorbance at 339 nm. Furthermore, the appearance and the increase in the fluorescence intensity at 336 nm, characteristic of the protonated dansyl units, occur later than expected on the basis of their concentration, as measured from the changes in absorbance at 286 nm. These results show that a mutual quenching takes place of the excited unprotonated species by the ground state protonated species and of the excited protonated species by the ground state unprotonated ones. Although such mutual quenching does not follow a linear behaviour because of the statistical distribution of the protons among the great number of equivalent dansyl units, the data show that, under certain conditions, the number of quenched excited state units is higher than the number of potential quencher units. For example, when the solution contains 80% unprotonated and 20% protonated units, the observed quenching of half of the unprotonated dansyl units (40% of the overall units) shows that, on an average, a protonated unit can quench two unprotonated ones. Such an amplification of the fluorescence quenching effect has previously been reported for another family of dendrimers.[8f,20] We have also found that solutions containing partially protonated dendrimers exhibit multiexponential fluorescence decay.

The energy of the fluorescent excited state of the protonated dansyl unit, as estimated from the onset of the corresponding fluorescence bands, is about 3.88 eV. Electrochemical experiments in acetonitrile solution have shown that for the protonated form of compound **I** no oxidation and reduction process can be observed within the available potential window which, however, is severely restricted by the presence of triflic acid (about −0.8 to +1.6 V *vs.* SCE). Since the amine electron pair in the protonated form is engaged, it can be expected that the protonated dansyl unit is much more difficult to oxidize than the unprotonated dansyl. Reduction of the protonated form, however, should occur at a potential much less negative than that of the unprotonated form (see above). Therefore, taking also into account its high spectroscopic energy, it can be expected that the excited state of the protonated dansyl unit is a strong oxidant.

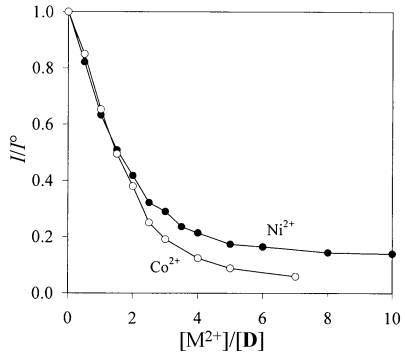


Fig. 5 Titration with Ni^{2+} (●) and Co^{2+} (○) ions of a 6.3×10^{-6} M solution of **D** containing 1.5×10^{-4} M base.

From the data reported above, it follows that: (i) the fluorescent excited state of the unprotonated units can only be quenched by the ground state of the protonated units *via* an oxidative electron transfer; (ii) the fluorescent excited state of the protonated dansyl units (3.88 eV) can be quenched by the ground state of the unprotonated dansyl units (excited state energy, 2.76 eV) by energy transfer and, most likely, also by reductive electron transfer.

In order to elucidate the quenching mechanism of the protonated dansyl units, we recorded the excitation spectra (λ_{em} = 514 nm, a band of the unprotonated dansyl unit) of solutions containing 50% protonated molecules of compounds **I** and **D**. For **I** the excitation spectrum was found to match the absorption spectrum of the unprotonated dansyl units. In the case of dendrimer **D** the excitation spectrum showed some features of the protonated dansyl units, indicating that energy transfer can account, at most, for 20% of the observed quenching.

Metal ion co-ordination

It is known that, in sufficiently basic solution, amide groups,[27] including the dansylamide units,[28] can undergo deprotonation and co-ordination of transition metal ions. Addition of Co^{2+} or Ni^{2+} ions (as $M(NO_3)_2 \cdot 6H_2O$ salts) up to 1.9×10^{-4} M to acetonitrile–dichloromethane (5:1 v/v) solutions of compounds **I** and **D** did not cause any change in the absorption and fluorescence properties. No effect was observed also upon separate addition of tributylamine base. Addition of *both* metal ion *and* base did not cause any effect on the spectroscopic properties of the reference compound **I**, but caused a strong quenching in the fluorescence intensity of the dansyl units in the case of dendrimer **D**. Fig. 5 shows the results obtained upon titration of a 6.3×10^{-6} M solution of **D** containing 1.5×10^{-4} M base with Ni^{2+} or Co^{2+} ions. Dynamic quenching cannot account for the observed quenching since the lifetime of the fluorescent excited state of the dansyl unit is too short (15 ns) and the metal ion concentration (1.9×10^{-4} M) is too low to cause sizeable effects even in the case of a diffusion controlled process.[26] Since addition of metal ions under the same experimental conditions has no effect on the fluorescence of the monodansyl reference compound **I**, the observed quenching must originate from co-ordination of metal ions by a co-operative action of several amide units of the dendrimer. The absorption spectrum of the dendrimer does not show any appreciable change upon metal co-ordination, suggesting that deprotonation, followed by metal ion co-ordination, essentially concerns the aliphatic amide moieties of the dendrimer. With a stronger base (*e.g.*, tetramethylammonium hydroxide), however, spectral evidence of deprotonation of the dansyl amide units has been obtained.

Once metal co-ordination has occurred, quenching can take place by both energy and electron transfer since the excited state of the dansyl unit is a good energy and electron donor (see above) and complexes of Co^{II} and Ni^{II} have several low energy excited states[29] and accessible redox levels.[30]

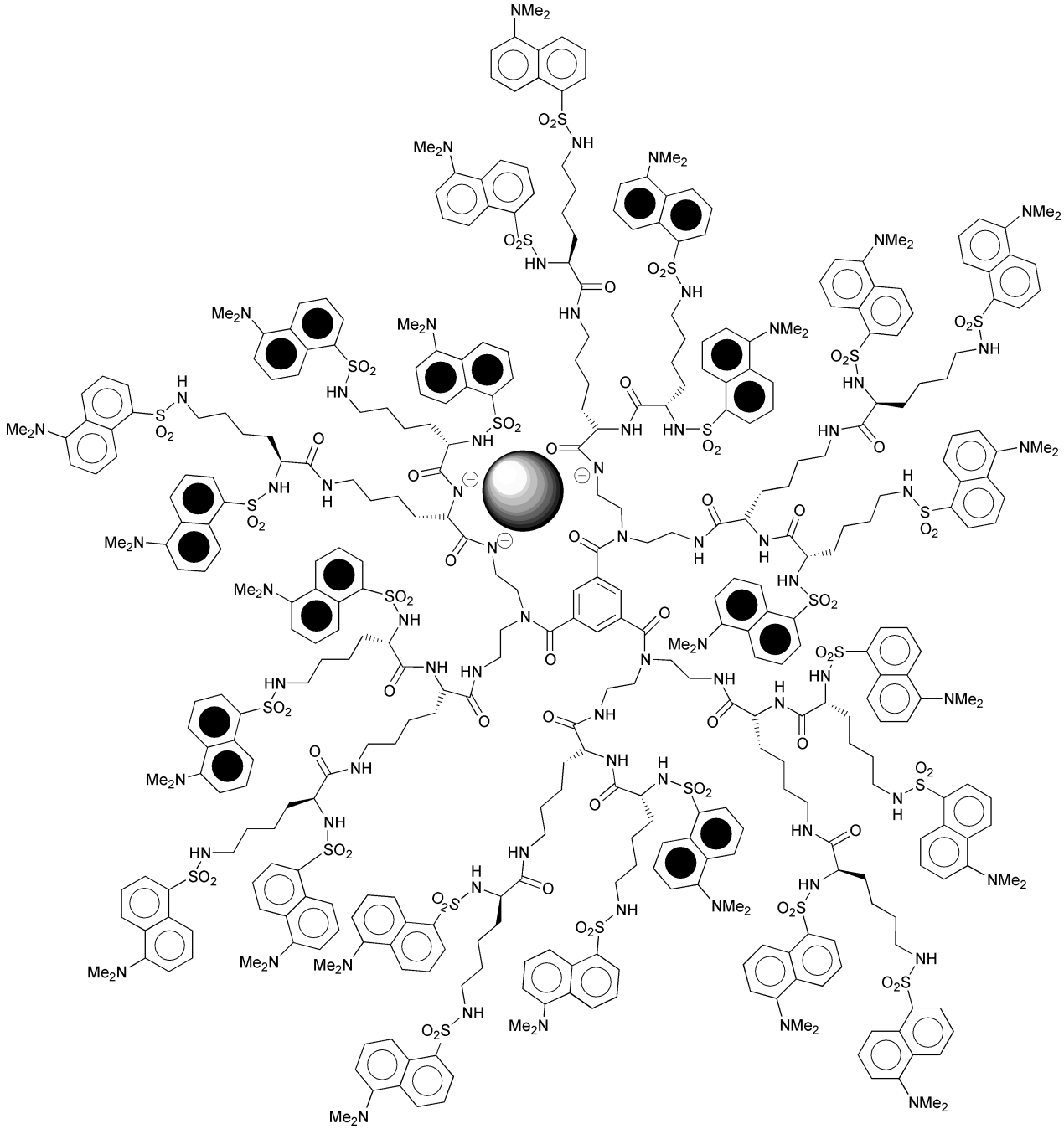


Fig. 6 Schematic representation of the signal amplification effect. A metal ion co-ordinated in the interior of the dendrimer by deprotonated aliphatic amide units (exact location, unknown) can quench the excited state of nine dansyl fluorescent units. For the sake of clarity, the supposedly quenched dansyl units, which are likely those closer to the co-ordinated metal ion, are labelled black.

It is noteworthy that at very low Ni^{2+} or Co^{2+} concentration (Fig. 5), when each dendrimer cannot co-ordinate more than a single metal ion, about 9 dansyl units per metal ion are quenched, as schematically represented in Fig. 6. This is another example of *sensory signal amplification*[31] in the quenching of a fluorescent dendrimer.[20]

It can also be noted that on increasing $M(NO_3)_2{\cdot}6H_2O$ ($M = Co^{2+}$ or Ni^{2+}) concentration the luminescence intensity reaches a plateau, whose value decreases with increasing base concentration. In any case, the plot (Fig. 5) does not go to zero. Such an incomplete quenching can be explained on the basis of limitations imposed on metal ion co-ordination by the dendrimer caused by: (i) incomplete amide deprotonation, (ii) electrostatic repulsion between metal ions, (iii) involvement of dendrimer co-ordination sites in hydrogen bonding with the NO_3^- counter ions,[32] and (iv) the presence of an increasing number of other ligands (water molecules and counter ions).

We have also examined the effect of addition of Zn^{2+} ions as $Zn(NO_3)_2{\cdot}6H_2O$ salt to solutions of compounds **I** and **D**. Up to 1.9×10^{-4} M Zn^{2+} concentration no change was observed in the absorption and fluorescence properties. Addition of *both* Zn^{2+} *and* base caused no effect on **I** and only a very small decrease in the fluorescence intensity of the dansyl units in the case of dendrimer **D** (Fig. 7). Since Zn^{2+} exhibits neither low energy excited states nor accessible redox levels, the observed effect cannot properly be considered as a quenching. Rather, it can be attributed to perturbations (*e.g.*, electrostatic or structural ones) of the dansyl excited state. We have also found that addition of Zn^{2+} to a dendrimer solution containing Ni^{2+} causes a revival of the fluorescence intensity (Fig. 7). This shows that Zn^{2+} displaces Ni^{2+} from the interior of the dendrimer. Accordingly, when Zn^{2+} is first added, successive addition of Ni^{2+} does not cause any effect.

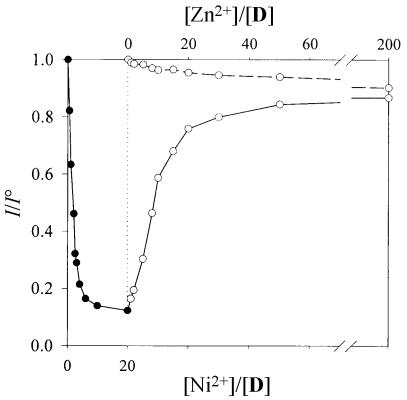


Fig. 7 Titration with Ni^{2+} (●) and, successively, Zn^{2+} (○) ions of a 6.3×10^{-6} M solution of compound **D** containing 1.5×10^{-4} M base (solid line). The dashed curve shows the behaviour observed on addition of Zn^{2+} alone.

Finally, we have found that the Ni^{2+} and Co^{2+} ions can also be displaced by acid addition, as expected because of the reprotonation of the amide units.[27]

Conclusions

We have shown that the polylysin dendrimer **D**, which contains 24 dansyl units in the periphery and 18 aliphatic amide units in the interior, can reversibly bind protons and transition metal ions. Protonation takes place on the amine moiety of the dansyl groups, whereas metal co-ordination takes place by a co-operative action of deprotonated (in basic solution) aliphatic amide units. Both protonation and Ni^{2+} and Co^{2+} co-ordination cause a quenching of the fluorescence emission of the dansyl units, with a significant signal amplification (*e.g.*, 9 dansyl units are quenched by one co-ordinated metal ion). Zn^{2+} ions do not quench the fluorescence intensity and can replace Ni^{2+} and Co^{2+} in the interior of the dendrimer, thereby causing a revival of the dansyl fluorescence. These results indicate that (i) a dendrimer containing several potential ligand sites can exhibit unusual co-ordinating ability[33] and (ii) in a dendritic structure it is possible to obtain signal amplification effects which might prove useful for the design of very sensitive fluorescent chemosensors.[34]

Acknowledgements

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References

1 D. A. Tomalia and H. D. Durst, *Top. Curr. Chem.*, 1993, **165**, 193; J. M. J. Fréchet, *Science*, 1994, **263**, 1710; N. Ardoin and D. Astruc, *Bull. Soc. Chim. Fr.*, 1995, **132**, 875; E. C. Constable, *Chem. Commun.*, 1997, 1073; G. R. Newkome, C. Moorefield and F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH, Weinheim, 1996; F. Zeng and S. C. Zimmerman, *Chem. Rev.*, 1997, **97**, 1681; M. Venturi, S. Serroni, A. Juris, S. Campagna and V. Balzani, *Top. Curr. Chem.*, 1998, **197**, 193; C. Gorman, *Adv. Mater.*, 1998, **10**, 295; J.-P. Majoral and A.-M. Caminade, *Top. Curr. Chem.*, 1998, **197**, 79; O. A. Matthews, A. N. Shipway and J. F. Stoddart, *Prog. Polym. Sci.*, 1998, **23**, 10; D. K. Smith and F. Diederich, *Chem. Eur. J.*, 1998, **4**, 1353; H.-F. Chow, T. K.-K. Mong, M. F. Nongrum and C.-W. Wan, *Tetrahedron*, 1998, **54**, 8543; M. Fischer and F. Vögtle, *Angew. Chem., Int. Ed.*, 1999, **38**, 884; A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665; G. R. Newkome, E. He and C. Moorefield, *Chem. Rev.*, 1999, **99**, 1689; A. D. Schlüter and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2000, **39**, 864.

2 E. Buhleier, W. Wehner and F. Vögtle, *Synthesis*, 1978, 155.

3 R. Dagani, *Chem. Eng. News*, February 8, 1999, 33; M. Freemantle, *Chem. Eng. News*, November 1, 1999, 27.

4 S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto and V. Balzani, *Chem. Eur. J.*, 1995, **1**, 211; S. Serroni, A. Juris, M. Venturi, S. Campagna, I. R. Resino, G. Denti, A. Credi and V. Balzani, *J. Mater. Chem.*, 1997, **7**, 1227; V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759; V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26.

5 P. Bharathi, U. Patel, T. Kawaguchi, D. J. Pessac and J. S. Moore, *Macromolecules*, 1995, **28**, 5955; C. Devadoss, P. Bharathi and J. S. Moore, *J. Am. Chem. Soc.*, 1996, **118**, 9635; M. R. Shorttreed, S. F. Swalle, Z. Y. Shi, W. Tan, Z. Xu, C. Devadoss, J. S. Moore and R. Kopelman, *J. Phys. Chem. B*, 1997, **101**, 6318; C. Devadoss, P. Bharathi and J. S. Moore, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1633.

6 G. M. Stewart and M. A. Fox, *J. Am. Chem. Soc.*, 1996, **118**, 4354.

7 D. M. Junge and D. V. McGrath, *Chem. Commun.*, 1997, 857; D. M. Junge and D. V. McGrath, *J. Am. Chem. Soc.*, 1999, **121**, 4912.

8 (*a*) J. Issberner, F. Vögtle, L. De Cola and V. Balzani, *Chem. Eur. J.*, 1997, **3**, 706; (*b*) A. Archut, F. Vögtle, L. De Cola, G. C. Azzellini, V. Balzani, P. S. Ramanujam and R. H. Berg, *Chem. Eur. J.*, 1998, **4**, 699; (*c*) A. Archut, G. C. Azzellini, V. Balzani, L. De Cola and F. Vögtle, *J. Am. Chem. Soc.*, 1998, **120**, 12187; (*d*) M. Plevoets, F. Vögtle, L. De Cola and V. Balzani, *New J. Chem.*, 1999, 63; (*e*) F. Vögtle, M. Plevoets, M. Nieger, G. C. Azzellini, A. Credi, L. De Cola, V. De Marchis, M. Venturi and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 6290; (*f*) F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, L. De Cola and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 12161.

9 T. Aida and D.-L. Jiang, *Nature* (*London*), 1997, **388**, 454; D.-L. Jiang and T. Aida, *J. Am. Chem. Soc.*, 1998, **120**, 10895; T. Sato, D.-L. Jiang and T. Aida, *J. Am. Chem. Soc.*, 1999, **121**, 10658.

10 A. Bar-Haim and J. Klafer, *J. Am. Chem. Soc.*, 1997, **119**, 6197; A. Bar-Haim and J. Klafer, *Phys. Chem. B*, 1998, **102**, 1662.

11 K. W. Pollak, J. W. Leon, J. M. J. Fréchet, M. Maskus and H. D. Abruna, *Chem. Mater.*, 1998, **10**, 30; S. L. Gilat, A. Andronov and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 1999, **38**, 1422; A. Andronov, S. L. Gilat, J. M. J. Fréchet, K. Ohta, F. V. R. Neuwahl and G. R. Fleming, *J. Am. Chem. Soc.*, 2000, **122**, 1175.

12 S. A. Vinogradov, L.-W. Lo and D. F. Wilson, *Chem. Eur. J.*, 1999, **5**, 1338.

13 J. Hofkens, L. Latterini, G. De Belder, T. Gensch, M. Maus, T. Vosch, Y. Karni, G. Schweitzer, F. C. De Schryver, A. Hermann and K. Mullen, *Chem. Phys. Lett.*, 1999, **304**, 1; T. Gensch, J. Hofkens, A. Heirmann, K. Tsuda, W. Verheijen, T. Vosch, T. Christ, T. Basché, K. Mullen and F. C. De Schryver, *Angew. Chem., Int. Ed.*, 1999, **38**, 3752.

14 N. Maruo, M. Uchiyama, T. Kato, T. Arai, H. Akisada and N. Nishino, *Chem. Commun.*, 1999, 2057.

15 M. F. Ottaviani, S. Bosmann, N. J. Turro and D. A. Tomalia, *J. Am. Chem. Soc.*, 1994, **116**, 661; M. F. Ottaviani, F. Montalti, N. J. Turro and D. A. Tomalia, *J. Phys. Chem. B*, 1997, **101**, 158.

16 M. Zhao, L. Sun and R. M. Crooks, *J. Am. Chem. Soc.*, 1998, **120**, 4877; M. Zhao and R. M. Crooks, *Adv. Mater.*, 1999, **11**, 217; M. Zhao and R. M. Crooks, *Angew. Chem., Int. Ed.*, 1999, **38**, 364.

17 L. Balogh and D. A. Tomalia, *J. Am. Chem. Soc.*, 1998, **120**, 7355.

18 E. M. M. de Brabander-van der Berg and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1308; A. W. Bosman, A. P. H. J. Schenning, R. A. J. Jansen and E. W. Meijer, *Chem. Ber./Recueil*, 1997, **130**, 725.

19 R. J. M. Klein Gebbink, A. W. Bosman, M. C. Feiter, E. W. Meijer and R. J. M. Nolte, *Chem. Eur. J.*, 1999, **5**, 65.

20 V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka and F. Vögtle, *Chem. Commun.*, 2000, 853.

21 (*a*) G. De Santis, L. Fabbrizzi, M. Licchelli, N. Sardone and A. H. Velders, *Chem. Eur. J.*, 1996, **2**, 1243; (*b*) H. Ikeda, M. Nakamura, N. Ise, N. Oguma, A. Nakamura, T. Ikeda, F. Toda and A. Ueno, *J. Am. Chem. Soc.*, 1996, **118**, 980; (*c*) M. Schuster and M. Sandor, *Fresenius J. Anal. Chem.*, 1996, **356**, 326; (*d*) H. F. M. Nelissen, F. Venema, R. M. Uittenbogaard, M. C. Feiters and R. J. M. Nolte, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2045; (*e*) T. Ikunaga, H. Ikeda and A. Ueno, *Chem. Eur. J.*, 1999, **5**, 2698; (*f*) L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, *Chem. Eur. J.*, 1999, **5**, 445.

22 W. Krause, N. Hackmann-Schlichter, F. K. Maier and R. Müller, *Top. Curr. Chem.* (*Dendrimers II*), ed. F. Vögtle, 2000, in the press; Dr H. Schmitt-Willich, lecture at the 1st International Dendrimer Symposium, Frankfurt (M.), October 5th, 1999.

23 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

24 S. R. Meech and D. Phillips, *J. Photochem.*, 1983, **23**, 193.
25 L. Prodi and A. Credi, *Spectrochimica Acta*, *Part A*, 1998, **54**, 159.
26 A. Gilbert and J. Baggot, *Essentials in Molecular Photochemistry*, Blackwell, London, 1991, ch. 5; S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Dekker, New York, 1993.
27 L. Fabbrizzi, F. Forlini, A. Perotti and B. Seghi, *Inorg. Chem.*, 1984, **23**, 807; L. Fabbrizzi, M. Licchelli, P. Pallavicini, A. Perotti, A. Taglietti and D. Sacchi, *Chem. Eur. J.*, 1996, **2**, 75; V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Perotti and A. Taglietti, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 185.
28 L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, *Eur. J. Inorg. Chem.*, 1999, 455.
29 C. K. Jorgensen, *Adv. Chem. Phys.*, 1963, **5**, 33.
30 F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry*, Wiley, New York, 4th edn., 1980, ch. 21, pp. 766–798.
31 For sensory signal amplification effects in polymers, see: T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
32 For anion binding by poly(propylene amine) dendrimers, see: H. Stephan, H. Spies, B. Johannsen, L. Klein and F. Vögtle, *Chem. Commun.*, 1999, 1875.
33 For an unusual ability in the anion sensing by dendrimers containing peripheral cationic units, see: C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 1997, **119**, 2588; C. Valério, E. Alonso, J. Ruiz, J.-C. Blais and D. Astruc, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1747.
34 For reviews on fluorescent chemosensors, see: R. A. Bissell, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, C. P. McCoy and K. R. A. S. Sandanayake, *Top. Curr. Chem.*, 1993, **168**, 223; A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; M. D. Ward, *Chem. Ind.*, 1997, 640; J. P. Desvergne and A. W. Czarnik (Editors), *Chemosensors of Ion and Molecule Recognition*, Kluwer, Dordrecht, 1997; P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71; L. Fabbrizzi, M. Licchelli and P. Pallavicini, *Acc. Chem. Res.*, 1999, **32**, 846; L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, *Coord. Chem. Rev.*, in the press.