Metal-Induced Assembling/Disassembling of Fluorescent Naphthalenediimide Derivatives Signalled by Excimer Emission

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Abstract: The new quadridentate bischelating ligands **2** and **3** display in solution the typical absorption and emission properties expected for naphthalenediimide derivatives. Spectrophotometric studies show that systems **2** and **3** interact with Zn^{II}, Cd^{II} and Cu^{I} in CHCl$_3$ or MeCN according to an apparent 1:1 stoichiometry. Molecular modelling, ESI-MS and ^{1}H NMR experiments indicate that the complex species formed in the presence of stoichiometric amounts of metal ion are nonhelical [2+2] adducts. The metal-induced self-assembling process is signalled by an intense excimer-type emission caused by the intramolecular interaction of two naphthalenediimide subunits that face each other in the [2+2] adduct, as shown by molecular modelling studies. In the presence of excess metal ion, a disassembling process takes place, leading to a dinuclear complex with a 2:1 metal/ligand stoichiometry, in which the intramolecular excimer is no longer allowed to form because the interaction between the naphthalenediimide subunits has been lost. Thus, the overall metal-induced assembling/disassembling process is signalled by the appearance and disappearance of the excimer band in the emission spectrum.

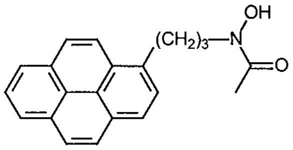
Keywords: excimers · fluorescence · naphthalenediimides · N ligands · self-assembly · zinc

Introduction

The application of metal–ligand interactions to self-assembling processes has proved to be a fruitful strategy to prepare discrete supramolecular species.[1] Complex molecular architectures, such as helicates,[2] knots,[3] catenanes,[4] grids[5] and cylinders[6] have been produced in the last years by the self-assembly of multidentate ligands that is promoted by metal ions. Owing to their particular features, several of these metal-containing supramolecular assemblies find application in molecular recognition (host–guest chemistry)[1f–h, 7] and in the design of supramolecular devices that display a variety of functions.[8]

In several cases, the self-assembled species involve light-emitting components whose photophysical properties can be exploited for different applications, including molecular sensing. For instance, tri- and tetrametallic assemblies that contain rhenium(I)tricarbonyl subunits, either at the corners of a triangle[7c] or of a square,[7c, 9] have been described as luminescent hosts for molecules of different size.

A recent paper by Fages[10] reports the self-assembly of the fluorescent pyrene-containing hydroxamate ligand **1** driven by Ga^{3+} or Fe^{3+} ions. The formation of the self-assembled system, in the case of gallium(III), is signalled by an intense pyrene excimer emission, which is attributed to an intramolecular excimeric excited species.



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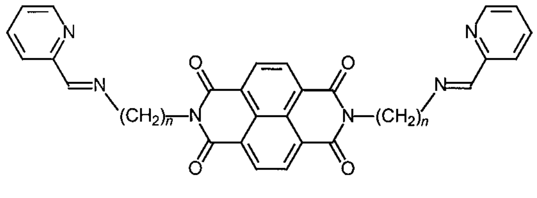

$n = 2$: **2** $n = 3$: **3**

Examples of self-assembled systems that involve d^{10} cations (e.g., Cu^{I}, Zn^{II}, Cd^{II}) and quadridentate ditopic ligands that contain potentially fluorescent aromatic spacers (e.g. naphthalene, pyrene) have been reported by Harding et al.[11] In

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these cases, the assembling process was investigated mainly by NMR studies and the possible effects induced by the interaction with metal ions on the photophysical properties displayed by the ligands were not mentioned.

This paper describes the metal-directed assembling process involving the naphthalenediimide derivatives **2** and **3**, whose photophysical properties are strongly affected by interactions with metal ions. In particular, the interaction with Zn^{II} (or Cd^{II}) according to a 2:2 stoichiometry brings the two naphthalenediimide subunits in a face-to-face position that favours the formation of an intramolecular excimer; this is signalled by a specific fluorescent emission. Moreover, addition of an excess of metal ion causes the disassembling of the [2+2] adduct to give the complex with 2:1 metal/ligand stoichiometry and the disappearance of the excimeric species.

Thus, the assembling and disassembling processes can be monitored by the increase and decrease, respectively, of the intensity of a characteristic and intense band in the emission spectrum.

Experimental Section

General remarks: Unless otherwise stated, commercially available reagent grade chemicals were used as received. Cadmium(II) trifluoromethane sulfonate[12] and tetraacetonitrilecopper(I) perchlorate[13] were prepared according to literature methods. Monoprotected derivatives of ethylenediamine and 1,3-diaminopropane, BOC-en and BOC-pn respectively, were obtained as previously described.[14]

Column chromatography was carried out on silica gel 60 (Merck 9385).

Spectrophotometric or fluorimetric grade solvents were used for spectroscopic measurements.

UV/Vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer; emission spectra were recorded on a Perkin–Elmer LS-50B luminescence spectrometer.

NMR spectra were recorded on a Bruker AMX 400 spectrometer.

Mass spectra were obtained with an LCQ DECA ion trap mass spectrometer equipped with an electrospray ionization (ESI) ion source and controlled by Xcalibur software 1.1 (Thermo-Finnigan). For sample injection, the instrument syringe pump was used at a flow rate of 5 $\mu L\,min^{-1}$. Experiments with solutions containing equimolecular amounts of metal ion (Zn^{II} or Cu^{I}) and ditopic ligand (**2** or **3**) in acetonitrile were carried out under constant instrumental conditions: source voltage 0.5 kV, capillary voltage 41 V, sheet gas flow 60 (arbitrary units), capillary temperature 100 °C, tube lens voltage -20 V. Resolution was usually set at 10000 to obtain high-resolution spectra.

Spectrophotometric and spectrofluorimetric titrations were performed on 10 mL samples of solutions of the bis-chelate ligand (10^{-5} M) in $CHCl_3$ or CH_3CN, by microadditions of CH_3CN stock solutions of $Zn(CF_3SO_3)_2$, $Cd(CF_3SO_3)_2$ or $[Cu(CH_3CN)_4]ClO_4$. In each experiment, the overall addition was limited to $\approx 200\,\mu L$, so that both volume increment and solvent polarity variation were not significant.

The fluorescence decay curves were recorded on an Edinburgh Instruments Model FL 900 time-correlated single-photon counting spectrometer, at the Centro Grandi Strumenti (Università di Pavia). The instrument was operated with a flash lamp filled with H_2 at a pressure of 0.4 atm, with a frequency of 40 kHz and a pulse-width of 1.0 ns.

The relative fluorescence quantum yields were obtained by the optically diluted method,[15] with anthracene ($\Phi = 0.27$ in EtOH) as a reference.[16]

***N,N'*-Bis(*tert*-butoxycarbonylaminoethyl)-1,8:4,5-naphthalenetetracarboxylicdiimide (4)**: BOC-en (1.46 g, 9.1 mmol) and Et_3N (0.7 mL, 5 mmol) were added to a mechanically stirred suspension of 1,8:4,5-naphtalene dianhydride (1.20 g, 4.55 mmol) in *i*PrOH (70 mL). The resulting mixture was refluxed for 72 h. After cooling to room temperature, a white solid formed that was filtered, washed with MeOH and purified by liquid chromatography (SiO_2, $CHCl_3$/MeOH 98:2, $R_f = 0.62$). Yield: 81.3%; ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta = 1.3$ (s, 18H; CH_3), 3.4 (t, 4H; CH_2), 4.3 (t, 4H; CH_2), 7.0 (t, 2H; NH), 8.7 (s, 4H; ArH); MS (ESI): *m/z* (%): 575.2 (100) $[M^+ + Na]$, 519 (12); elemental analysis calcd (%) for $C_{28}H_{32}N_4O_8$: C 60.84, H 5.84, N 10.14; found: C 59.89, H 5.6, N 9.49.

***N,N'*-Bis(*tert*-butoxycarbonylaminopropyl)-1,8:4,5-naphthalenetetracarboxylicdiimide (5)**: Diimide **5** was obtained by the procedure described for compound **4**, starting with BOC-pn. Yield: 58.7%; ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta = 1.3$ (s, 18H; CH_3), 1.7 (m, 4H; CH_2), 3.0 (m, 4H; CH_2), 4.0 (t, 4H; CH_2), 6.8 (t, 2H; NH), 8.7 (s, 4H; ArH); MS (ESI): *m/z* (%): 603.3 (100) $[M^+ + Na]$, 554.7 (26), 547.3 (14).

***N,N'*-Bis(aminoethyl)-1,8:4,5-naphthalenetetracarboxylicdiimide (6)**: Trifluoroacetic acid (15 mL) was added dropwise to a stirred suspension of **4** (1.98 g, 3.6 mmol) in CH_2Cl_2 (15 mL). The resulting pale yellow solution was stirred for 2 h. The solvent was removed on a rotary evaporator. The residue was treated with *n*-heptane (2×50 mL), and the azeotropic mixture trifluoroacetic acid/*n*-heptane was evaporated in vacuo[17] to afford a yellow solid, which is the trifluoromethanesulfonate salt of diamine **6** and was used as a reagent in the following step. Yield: 86.6%; ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): $\delta = 3.1$ (m, 4H; CH_2), 4.3 (t, 4H; CH_2), 7.8 (brs, 6H; NH_3^+), 8.7 (s, 4H; ArH); MS (ESI): *m/z* (%): 353.1 (100) $[M^+ + H]$, 177.1 (25).

***N,N'*-Bis(aminopropyl)-1,8:4,5-naphthalenetetracarboxylicdiimide (7)**: Diimide **7** was obtained from **5** by the procedure described for compound **6**. Yield: 97.8%; ^1H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 2.15$ (m, 4H; CH_2), 3.1 (t, 4H; CH_2), 4.3 (t, 4H; CH_2), 8.7 (s, 4H; ArH); MS (ESI): *m/z* (%): 761.0 (24) $[2M^+ + H]$, 381.1 (100) $[M^+ + H]$, 364.2 (39).

***N,N'*-Bis[(2-pyridylmethylene)aminoethyl]-1,8:4,5-naphthalenetetracarboxylicdiimide (2)**: A solution of 2-pyridinecarboxyaldehyde (previously distilled under reduced pressure, 0.164 mL, 1.72 mmol) and Et_3N (0.240 mL, 1.72 mmol) in dry MeOH (50 mL) was added dropwise to a solution of **6** (0.5 g, 0.86 mmol) in dry MeOH (100 mL). The resulting mixture was stirred for 4 h, and the formation of a white precipitate was observed. The solid product was filtered off and washed with diethyl ether. Yield: 98.6%; ^1H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 4.0$ (t, 4H; CH_2); 4.5 (t, 4H; CH_2); 7.35 (m, 2H; ArH); 7.8 (t, 2H; ArH); 7.9 (d, 2H; ArH); 8.35 (s, 2H; CH); 8.55 (d, 2H; ArH); 8.7 (s, 4H; ArH); MS (ESI): *m/z* (%): 553.3 (45) $[M^+ + Na]$, 531.3 (100) $[M^+ + H]$, 442.4 (29); elemental analysis calcd (%) for $C_{30}H_{22}N_6O_4$: N 15.84, C 67.92, H 4.18; found: N, 16.13, C 67.79, H 3.91.

***N,N'*-Bis[(2-pyridylmethylene)aminopropyl]-1,8:4,5-naphthalenetetracarboxylicdiimide (3)**: The bis-chelate ligand **3** was prepared from compound **7**, by the procedure described for **2**. Yield: 62.4%; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 2.25$ (m, 4H; CH_2), 3.8 (t, 4H; CH_2), 4.4 (t, 4H; CH_2), 7.3 (m, 2H; ArH), 7.6 (t, 2H; ArH), 7.75 (s, 4H; ArH) 7.8 (d, 2H; ArH), 8.4 (s, 2H; ArH), 8.55 (d, 2H; ArH), 8.8 (s, 4H; ArH); MS (ESI): *m/z* (%): 559.3 (100) $[M^+ + H]$, 470.3 (11), 280.1 (55); elemental analysis calcd (%) for $C_{32}H_{26}N_6O_4$: N 15.04, C 68.81, H 4.69; found: N, 14.79, C 68.91, H 4.55.

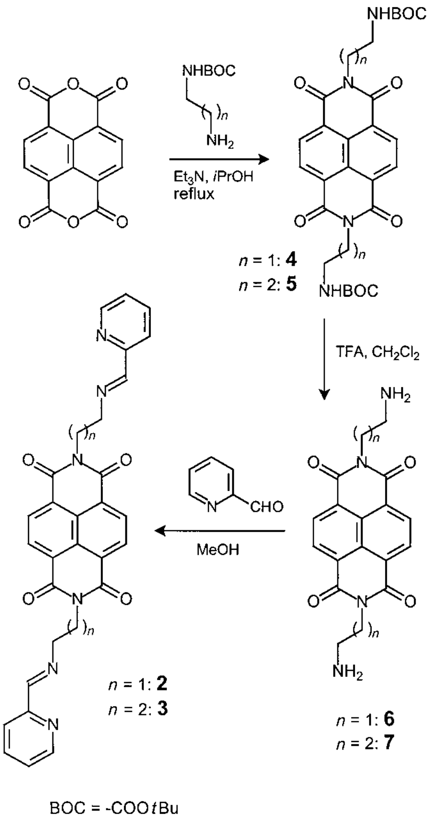
$[Zn_2(2)_2](CF_3SO_3)_4$: A solution of $Zn(CF_3SO_3)_2$ (68 mg, 0.188 mmol) in MeCN (20 mL) was addded dropwise to a solution of **2** (0.1 g, 0.188 mmol) in $CHCl_3$ (180 mL). The solution became cloudy and the pale yellow precipitate, formed after stopping the magnetic stirring, was collected by filtration. Yield: 72.1%; ^1H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 3.85$ (t, 8H; CH_2); 4.1 (t, 8H; CH_2); 7.9 (m, 4H; ArH); 8.1 (d, 4H; ArH); 8.3 (s, 8H; ArH); 8.35 (t, 4H; ArH); 8.6 (d, 4H; ArH); 8.9 (s, 4H; CH); MS (ESI): *m/z*: 1694.7 $[M^+ - CF_3SO_3]$; elemental analysis calcd (%) for $C_{64}H_{44}F_{12}N_{12}O_{20}S_4Zn_2$: N 9.40, C 42.99, H 2.48; found: N, 9.69, C 43.18, H 2.61.

$[Zn_2(3)_2](CF_3SO_3)_4$: The dizinc(II) complex formed by **3** was obtained by the same procedure described for $[Zn_2(2)_2](CF_3SO_3)_4$. Yield: 64.5%; MS (ESI): *m/z*: 1638.8 $[M^+ - CF_3SO_3]$; elemental analysis calcd (%) for $C_{68}H_{52}F_{12}N_{12}O_{20}S_4Zn_2$: N 9.13, C 44.35, H 2.85; found: N, 8.94, C 44.18, H 2.97.

Results and Discussion

Syntheses: Systems **2** and **3** were prepared according to the general synthetic pathway shown in Scheme 1.

The diamino derivatives **6** and **7** could be obtained, in principle, by direct reaction of 1,8:4,5-naphthalene dianhy-



Scheme 1.

dride with excess diamine (ethylenediamine or 1,3-diaminopropane), but all attempts to carry out this synthesis always gave mixtures of unidentified products, possibly oligomeric species. Therefore, the syntheses of the diamines **6** and **7** were performed by a two-step procedure consisting of 1) reaction of 1,8:4,5-naphthalene dianhydride with the monoprotected diamine (mono-BOC-ethylenediamine, BOC-en or mono-BOC-1,3-diaminopropane, BOC-pn previously prepared) in the presence of a basic catalyst (e.g. Et_3N); 2) deprotection of the bis-BOC adducts **4** and **5** to afford the diamines as their trifluoromethanesulfonate salts. The isolation of **6** and **7** as neutral products was not necessary and their salts were directly used in the final step, a Schiff condensation in MeOH, in the presence of an equimolar amount of base (Et_3N). The bis-chelate systems **2** and **3** were obtained with overall yields of 70 and 36%, respectively.

Zn^{II} complexes were isolated as pale yellow microcrystalline compounds by slow evaporation of solutions containing equimolecular amounts of the metal ion and the ditopic ligand in MeCN. Although several attempts to grow X-ray quality crystals by slow diffusion of diethyl ether in solutions of complexes in $CHCl_3$ or MeCN afforded pale yellow needles, these were not of satisfactory quality for crystallographic investigations.

Cu^I complexes were isolated as dark red solids that slowly turned greenish-brown when exposed to air. The low stability of copper(I) complexes could result from oxidation by dioxygen and subsequent imine hydrolysis induced by copper(II).

Absorption and emission properties of systems 2 and 3: The derivatives of naphthalenediimide are well-known chromophores and fluorophores that display typical absorption and emission spectra, and their photophysical properties have been extensively studied.[18] The spectroscopic properties of systems **2** and **3** are very similar to those reported in the literature for analogous derivatives (see, for instance, *N,N'*-dibutyl naphthalenediimide, **8**).[18] Absorption and emission data are summarised in Table 1.

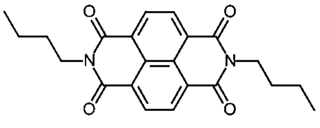


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Table 1. Absorption and emission data for systems **2**, **3** (in $CHCl_3$) and for reference compound **8** (in CH_2Cl_2).[18b]

	λ_{abs} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{em} [nm][a]	Φ
2	274	12600	386	0.0018
	360	19900	409	
	382	24100		
3	280	14600	387	0.0018
	360	20800	409	
	382	25300		
8	357	23500	386	0.0019
	377	28300	407	

[a] λ_{exc}: 351 nm (for **2** and **3**) and 330 nm (for **8**).

The electronic absorption spectra of the naphthylamides **2** and **3** (the spectrum of **2** in $CHCl_3$ is reported in Figure 1) show a band centred at $\lambda = 270-280$ nm, ascribed to the π-conjugated iminopyridine moiety, and the typical bands in the range $\lambda = 330-390$ nm, attributed to the diimido-aromatic system, whose intensities (see ε values in Table 1) are very close to those reported for the reference compound *N,N'*-dibutylnaphthalenediimide **8**.

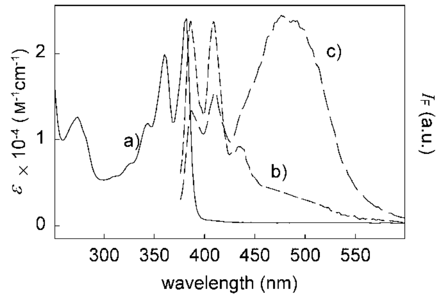

Figure 1. Absorption and emission spectra of system **2**: a) absorption spectrum in $CHCl_3$ (10^{-5} M); b) emission spectrum in $CHCl_3$ (10^{-5} M); c) emission spectrum in $CHCl_3$ (2.5×10^{-5} M).

The emission spectra, which are the mirror images of the corresponding long-wavelength absorption bands (see Figure 1), show a weak intensity, and the low quantum yield values ($\Phi = 0.0017-0.0018$) are in agreement with those reported for related naphthalenediimides (e.g., $\Phi = 0.0018$ in MeCN and 0.0019 in CH_2Cl_2 has been found for compound

8[18b]). Fluorescence lifetimes for compounds **2** and **3** were not measured, because they are shorter than the resolution of our equipment; however, in any case, experimental results indicate that τ_f values are lower than 1 ns, in agreement with the value reported for similar derivatives (< 20 ps[18a]).

The poor emissivity and the very short lifetimes should be caused by a fast deactivation of the singlet $\pi\pi^*$ state to a close-lying triplet state, as previously observed for the reference naphthalenediimide **8**[18b] and other related compounds.[19]

An interesting feature arises from the ability of naphthalenediimide systems to form excimeric species, even in dilute solutions (e.g. $> 2 \times 10^{-5}$ M for the dibutyl derivative in MeCN).[18b] Systems **2** and **3** display similar behaviour as a broad band centred at $\lambda = 480$ nm appears in their emission spectra at concentration values higher than 10^{-5} M (see Figure 1).

Interaction of system 2 with metal ions—spectrophotometric ESI-MS and ^{1}H NMR studies: The interaction with different metal ions in solution was initially studied with spectrophotometric titration experiments in order to assess the stoichiometry of the assembled species. Solutions (10^{-5} M) of the ditopic ligands in $CHCl_3$ or MeCN were titrated with metal ions (Cu^I, Zn^{II}, Cd^{II}) and the absorption spectra taken after each addition of metal. In each case, a substantial variation of the initial spectrum was observed: the band at $\lambda = 274$ nm, assigned to the absorption of the iminopyridine moiety and directly involved in the coordination process, underwent both a red shift (by ≈ 12 nm) and a distinct intensity increase. The absorption bands ascribed to the naphthalenediimide moiety experienced a less clear red-shift (2–4 nm) and an intensity decrease. These changes are observed until one equivalent of metal ion is added, then less evident spectral changes take place; in particular, a small intensity decrease of the band at $\lambda = 286$ nm is observed.

Absorption spectra registered during the titration experiment of **2** with zinc(II) triflate are reported in Figure 2.

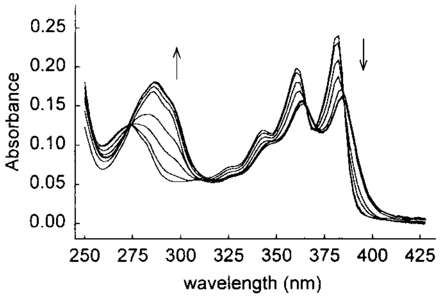

Figure 2. Absorption spectra recorded during the titration of a $CHCl_3$ solution of **2** (10^{-5} M) with zinc(II).

The titration with copper(I) also induces the appearance and the development of a new broad band in the visible range (maximum at $\lambda = 470$ nm, $\varepsilon_{max} = 5990$); this kind of absorption band is very common in copper(I) complexes of ligands containing donor sp^2 nitrogen atoms and can be ascribed to an MLCT transition.[8e, 20]

The titration profiles (see Figure 3) obtained by plotting the absorbance value at 390 nm versus n (metal equiv/ligand equiv) indicate the formation of adducts with an apparent 1:1 stoichiometry in all cases. However, the slight spectral changes observed at higher metal ion concentrations (i.e. the intensity variation of the iminopyridine band) and the loss of the distinct isosbestic points towards the end of the titrations cannot exclude the formation of complexes with different stoichiometry, when excess metal ion is present in solution.

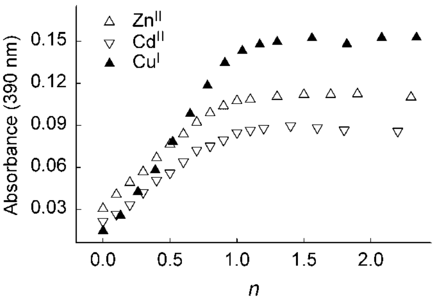

Figure 3. Profiles obtained in the spectrophotometric titration experiments of **2** (10^{-5} M) in $CHCl_3$ with Cu^I, Zn^{II} and Cd^{II} (n = equiv of added metal ion/equiv of **2**).

These results can be interpreted at first on the basis of molecular modelling studies, which lead to the conclusion that the formation of a complex species with an actual 1:1 stoichiometry is sterically disfavoured because the rigidity of the naphthalenediimide spacer prevents the ditopic ligand from wrapping around a single metal ion. Molecular models clearly indicate that dinuclear complexes, namely [2+2] species, are highly favoured for all the considered metal ions. Figure 4 shows the energy-minimized structures obtained with the HyperChem software package for the two adducts $[Cu_2(\mathbf{2})_2]^{2+}$ and $[Zn_2(\mathbf{2})_2(MeCN)_4]^{4+}$.

The formation of [2+2] adducts satisfies the coordinative demands of tetrahedral copper(I), while anionic ligands or

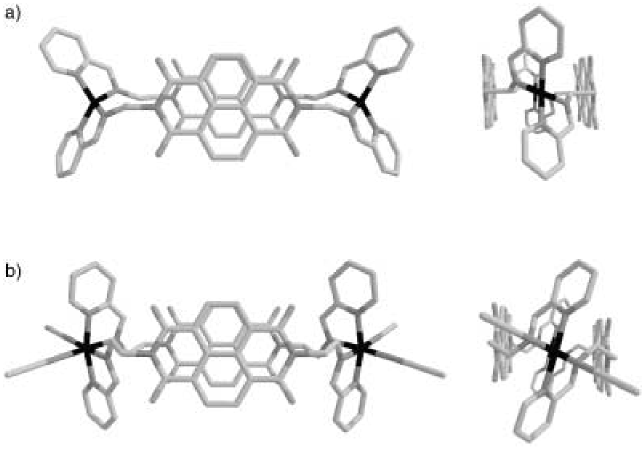

Figure 4. Molecular models for a) $[Cu_2(\mathbf{2})_2]^{2+}$ and b) $[Zn_2(\mathbf{2})_2(MeCN)_4]^{4+}$, which were obtained by the HyperChem software package (MM+ force field). Two perspective views, elaborated by SymApps software (Bio-Rad laboratories), are reported for each adduct to show the face-to-face position of the naphthalenediimide moieties. Hydrogen atoms are omitted for clarity.

solvent molecules can complete the coordination spheres of zinc(II) and cadmium(II), which more usually form five- or six-coordinate complexes. However, the apparent 1:1 stoichiometry determined by titration experiments could correspond to the formation of other oligonuclear complexes: in principle, [3+3] or [4+4] adducts may coexist in solution with the dinuclear species.

In order to assess more clearly the identity of the complex species formed in solution by the ditopic ligand **2**, further investigations have been performed by electrospray ionization mass spectroscopy (ESI-MS). In recent years, the ESI-MS technique has been successfully used for the detection of supramolecular species in solution and has been particularly helpful for identifying polynuclear metal complexes.[21]

The ESI-MS spectrum of a solution containing equimolecular amounts of zinc(II) triflate and **2** (5×10^{-5} M) in acetonitrile is shown in Figure 5. It shows peaks at *m/z* 1638.9 (corresponding to $[Zn_2(\mathbf{2})_2(CF_3SO_3)_3{}^+]$) and 745.2 ($[Zn_2(\mathbf{2})_2(CF_3SO_3)^{2+}]$, base peak). Peaks of lower intensity have been also observed at *m/z* 447.4 ($[Zn_2(\mathbf{2})_2CF_3SO_3{}^{3+}]$) and 297.9 ($[Zn_2(\mathbf{2})_2{}^{4+}]$). The charge-state determination of the peaks was performed by high-resolution scan experiments. A peak separation of 0.5 is observed in the high-resolution spectrum corresponding to the main peak at *m/z* 745.2 (see Figure 5), confirming the authenticity of the dinuclear complex species $[Zn_2(\mathbf{2})_2(CF_3SO_3)^{2+}]$. Moreover, peak separations of 0.33 and 0.25 have been observed in the isotopic distributions corresponding to the peaks at *m/z* 447.4 and 297.6, respectively, as expected for the tri- and tetrapositive ions to which they have been assigned.

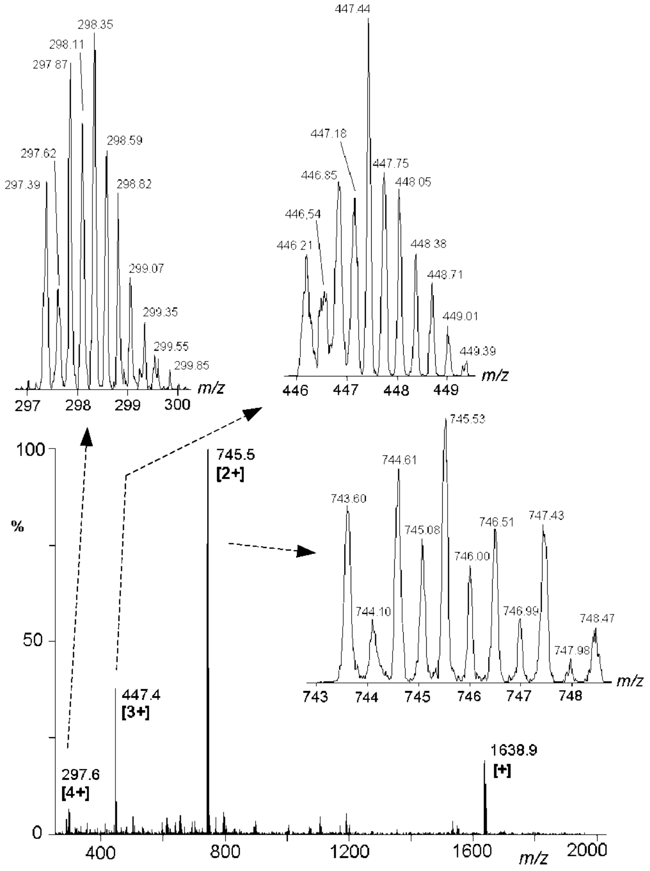

Figure 5. ESI-MS spectrum of an equimolar mixture of **2** and $Zn(CF_3SO_3)_2$ in acetonitrile (5×10^{-5} M). The high-resolution spectra, reported in the insets, show typical peak separations (0.5, 0.33 and 0.25 for [2+], [3+] and [4+] species, respectively) which confirm the multiple charge states of the depicted ions. [+]:$[Zn_2(\mathbf{2})_2CF_3SO_3)_3{}^+]$; [2+]: $[Zn_2(\mathbf{2})_2(CF_3SO_3)_2{}^{2+}]$; [3+]: $[Zn_2(\mathbf{2})_2CF_3SO_3{}^{3+}]$; [4+]: $[Zn_2(\mathbf{2})_2{}^{4+}]$.

ESI-MS spectrum of solutions containing equimolecular amounts of $[Cu(MeCN)_4]ClO_4$ and **2** (5×10^{-5} M) in acetonitrile exhibits peaks at *m/z* 1287.6 (corresponding to $[Cu_2(\mathbf{2})_2ClO_4{}^+]$, base peak) and 594.5 ($[Cu_2(\mathbf{2})_2{}^{2+}]$; peak separation in the high-resolution spectrum: 0.5). Moreover, a peak of lower intensity (≈10%) has been observed at *m/z* 1980.7. It can be ascribed to the $[Cu_3(\mathbf{2})_3(ClO_4)_2{}^+]$ species, showing that, in the case of copper(I), the [3+3] adduct is present in solution as a minor component, in equilibrium with the main species, the dinuclear complex.

Tetradentate bis-chelating ligands, as previously reported in analogous examples,[8e, 11] can form, in principle, either helical or nonhelical [2+2] complexes with tetrahedral or octahedral metal centres. The stereochemistry of the possible adducts has been assessed for copper(I) complexes: the helical form can exist as a couple of enantiomers (*S,S* and *R,R* configurations), while the nonhelical form is represented by the two superimposable *meso* isomers (*R,S* and *S,R* configurations).[11a] Analogous considerations can be made for complexes with nontetrahedral metal centres (e.g., Zn^{II} or Cd^{II}).[11]

Although molecular models indicate that the nonhelical (or *box* form) is preferred for all the complexes formed by **2**, NMR studies have been performed in order to gain a better insight on which stereoisomer (or mixture of stereoisomers) exists in solution.

The spectra of the free ligand **2** and of its adduct $[Zn_2(\mathbf{2})_2]^{4+}$ in CD_3CN are reported in Figure 6.

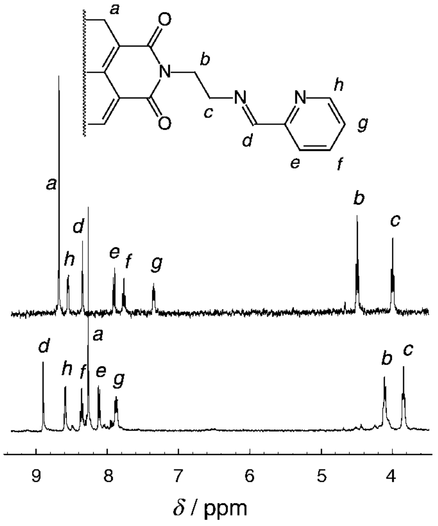

Figure 6. ^1H NMR spectra of **2** (top) and $[Zn_2(\mathbf{2})_2]^{4+}$ (bottom) in CD_3CN (25 °C, 5×10^{-4} M).

The spectrum pertaining to the zinc(II) complex can be measured either on a solution of $[Zn_2(\mathbf{2})_2](CF_3SO_3)_2$ (5×10^{-4} M) or **2** (5×10^{-4} M) and an equimolecular amount of $Zn(CF_3SO_3)_2$ in CD_3CN. The identical results obtained from the two measurements indicate that the same species (or mixture of species) is present in solution both when the preformed complex is dissolved in CD_3CN and when **2** and the metal ion are allowed to react in situ. The low solubility of the complex in $CHCl_3$ prevents analogous ^1H NMR measurements in $CDCl_3$ from being carried out.

When compared to the spectrum of **2**, the spectrum of the zinc(II) complex shows a downfield shift of the resonances of the protons belonging to the iminopyridine moieties that are directly involved in the interaction with the metal ion, and an upfield shift for naphthalene and aliphatic protons. If the two aromatic spacers are forced to face each other by the coordination of the two metal ions, as predicted by molecular models (see Figure 4), this shielding effect can be interpreted in terms of a ring-current effect exerted by each naphthalenediimide system on the protons belonging to the other ligand molecule.

The much less intense series of signals in the spectrum of the complex can be ascribed to the existence of small amounts of other species in equilibrium with the [2+2] adduct.

Particular attention should be devoted to the signals from the naphthalene and ethylene protons (a singlet and a double triplet, respectively, in both spectra) for which no significant multiplicity variation is observed upon metal ion coordination.

Previous studies carried out on different metal helicates (Cu^I, Ag^I or Zn^{II}) containing [2+2] adducts[11a, 22] showed that ^1H NMR spectra of the complexes, when compared with the spectra of the uncoordinated ligands, display an increased complexity. In particular, the diastereotopic nature of the methylene protons close to a stereogenic metal centre results in an increased multiplicity of their signals.

The interaction of **2** with Zn^{II} does not induce any detectable variation in the multiplicity of the signals attributed to the potentially diastereotopic methylene protons, and this allows us to exclude the formation of helical species in solution. Indeed the single set of signals displayed by the $[Zn_2(\mathbf{2})_2]^{4+}$ spectrum, on the NMR timescale at room temperature, is consistent with the existence in solution of only one main species (the presence of undetectable amounts of other isomers cannot be excluded), namely, the highly symmetrical nonhelical [2+2] adduct.

More information on the interaction of **2** with metal ions has been obtained by performing NMR measurements on solutions of the ditopic ligand in the presence of an increasing amount of zinc(II) triflate (0.5, 1.0, 1.5, 2.0, 4.0 equiv) in CD_3CN. The spectral variations observed for the signals from the aliphatic protons are summarized in Figure 7.

The spectrum obtained in the presence of 0.5 equivalents of zinc(II) is more complex than those of the simple system **2** and of the [2+2] adduct, as expected for the occurrence in solution of more than one species.

Interesting considerations arise from an analysis of the spectra obtained in the presence of excess metal ion. The signals ascribed to the $-CH_2-CH_2-$ chain change from two triplets (at $\delta = 3.84$ and 4.10) to four triplets (at $\delta = 3.84$, 4.10, 4.17 and 4.51), as two new signals at lower fields appear when the metal/ligand ratio, *n*, is increased from 1 to 1.5 (see Figure 7). The relative intensity of the new triplets increases with the metal ion concentration and they are the only signals pertaining to the aliphatic protons when a fourfold excess of zinc(II) is added. This suggests the formation of a new complex species in solution when the metal ion concentration exceeds the 1:1 ratio according to the disassembling process described in Equation (1):

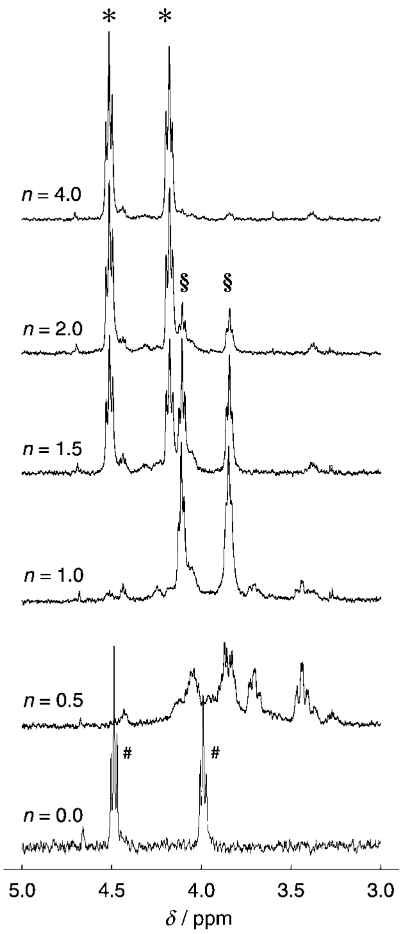

Figure 7. ^1H NMR spectra of a solution of **2** in CD_3CN (25 °C, 5×10^{-4} M) in the presence of increasing amounts of zinc(II) where n = equiv of Zn^{II}/equiv of **2**. Signals corresponding to aliphatic protons (labelled as *b* and *c* in Figure 6) are reported. (#): free ligand **2**; (§): $[Zn_2(\mathbf{2})_2]^{4+}$ ([2+2] adduct); (*): $[Zn_2(\mathbf{2})]^{4+}$.

$$[Zn_2(\mathbf{2})_2]^{4+} + 2\,Zn^{2+} \rightleftharpoons 2\,[Zn_2(\mathbf{2})]^{4+} \qquad (1)$$

As in the disassembled species, the ring-current effect is no longer active (the two naphthalenediimide moieties are now separated from each other), and the resonances of the aliphatic protons undergo a downfield shift; this accounts for the appearance of the new set of signals.

Similar considerations can be made by observing the history of the singlet pertaining to the naphthalene protons. The signal at $\delta = 8.68$ gradually disappears as a new singlet at $\delta = 8.26$ grows, when the assembling process takes place; the resonance of this signal is again shifted to lower fields ($\delta = 8.74$) as the increase of metal ion concentration induces the disassembling of the [2+2] adduct, confirming the role of the face-to-face interaction between the naphthalenediimide moieties.

Probing the assembling and disassembling processes by steady-state and time-resolved spectrofluorimetry: The effects of the metal-ion coordination on the emission properties of **2** were studied by carrying out spectrofluorimetric titration experiments. Figure 8 shows the emission spectra registered during the titration of a $CHCl_3$ solution of **2** with zinc(II): a broad band centred at $\lambda = 480$ nm appears and its intensity increases until one equivalent of metal ion is added; at higher concentrations of zinc(II), the intensity of this band decreases (it almost disappears after the addition of 4 equiv of metal ion).

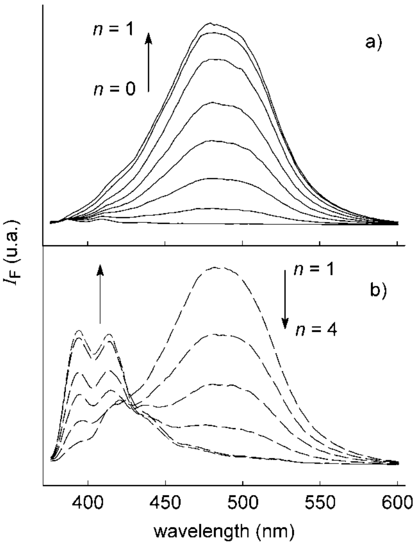

Figure 8. Emission spectra recorded during the titration of **2** (10^{-5} M in $CHCl_3$) with zinc(II): a) the intensity of the broad band at $\lambda = 480$ nm increases as *n* (equiv of Zn^{II}/equiv of **2**) is increased from 0 to 1; b) the band at $\lambda = 480$ nm decreases as *n* becomes higher than 1.

The addition of cadmium(II) induces similar spectral variations, in a similar manner to the addition of zinc(II), whereas, in the case of copper(I), no substantial change in the emission spectrum of the ligand was observed.

The following considerations can be made on the basis of these results:

1) The formation of [2+2] adducts (1:1 formal stoichiometry) is confirmed.
2) The broad emission band at $\lambda = 480$ nm formed upon metal ion (Zn^{II} or Cd^{II}) addition is very similar to the excimeric band observed for concentrated solutions of the ligands and can be ascribed to an excimeric species derived from the intramolecular interaction between the two naphthalenediimide moieties, which in the [2+2] assemblies lie on parallel planes facing each other, as shown by molecular models (see Figure 4).
3) The decrease of the excimeric emission intensity at metal concentration values exceeding the 1:1 stoichiometry can be accounted for by the disassembling of the [2+2] species according to Equation (1). It should be noted that this process is not clear on the basis of the spectrophotometric titration results, since only slight variations in the absorption spectrum of **2** were observed when metal ions in solution exceeded the 1:1 ratio (see above).
4) The absence of the excimer band in emission spectra of the copper(I) complex could be ascribed to an auto-absorption process, since the complex displays the strong MLCT absorption band in same the spectral region ($\lambda_{max} = 480$ nm); however, addition of excess Cu^+ ion results in a disassembling process and a consequent slight enhancement of the locally excited state emission ($\lambda = 380$–420 nm).

The solution behaviour of system **2** in the presence of zinc(II) or of cadmium(II) can be summarized by commenting on the titration profile in which the emission intensity at $\lambda = 480$ nm is plotted versus the equivalents of metal ion (see Figure 9). The plots can be imagined as being split into two parts: 1) the left (rising) arm (with $0 < n < 1$) in which the assembling process takes place; the formation of the [2+2] adduct is signalled by the formation of an excimeric species and the development of its characteristic emission band; 2) the right (decreasing) arm ($n > 1$), in which the [2+2] species gradually disassembles as the metal ion concentration increases in solution. The disassembling process is signalled by the disappearance of the excimer and of its emission band.

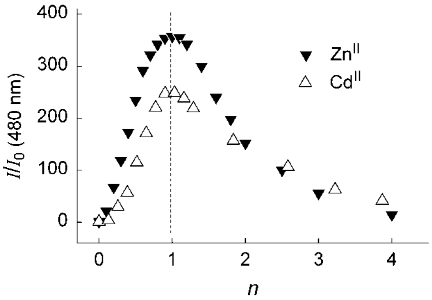

Figure 9. Profiles obtained in the spectrofluorimetric titration of **2** (10^{-5} M in $CHCl_3$) with zinc(II) and cadmium(II): assembly and disassembly of the [2+2] adduct are signalled by the increasing (left-hand part of the plot) and decreasing (right-hand part) of the excimeric band intensity. *n* = equiv of added metal ion/equiv of **2**.

The overall assembling/disassembling process for the system Zn^{2+}/**2** was also investigated by time-resolved fluorescence measurements, observing the effects on the fluorescence decay behaviour of system **2** induced by its interaction with metal ions.

The free ligand **2** displays a single exponential fluorescence decay, with a lifetime shorter than 1 ns, as mentioned above for all derivatives studied.

When the metal ion (Zn^{2+} or Cd^{2+}) is added to a solution containing **2** (10^{-5} M) in $CHCl_3$, the fluorescence decay profile can only be fitted by employing two exponential terms and reveals the presence of a double lifetime ($\tau_1 < 1$ ns and $\tau_2 = 15.9$ ns, respectively): the longer lifetime can be ascribed to the expected intramolecular excimer. The abundance of the long-lived component increases (up to 70%) with the concentration of the metal ion until 1:1 stoichiometry is reached. On further addition of Zn^{2+}, the abundance of the long-lived species decreases and it is equal to 19% when two equivalents have been added.

The roughly bell-shaped profile obtained by plotting the abundance values of the long-lived species versus the

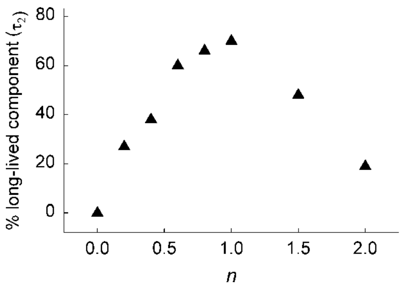

Figure 10. Effect of the interaction with Zn^{II} on the fluorescence decay of **2**: the abundance of the long-lived component ($\tau_2 = 15.9$ ns) increases up to 70% in the $0 < n < 1$ range (n = equiv of added metal ion/equiv of **2**), as expected for the formation of an intramolecular excimer from the [2+2] adduct; the disassembling process and consequent excimer disappearance is confirmed by the decrease of the long-lived component abundance when $n > 1$.

equivalents of added metal ion (see Figure 10) again represents the overall assembling/disassembling process which system **2** undergoes in the presence of zinc(II).

Solution behaviour of system 3: The interaction of bis-chelate **3** with metal ions in solution has been studied mainly by spectrophotometric and spectrofluorimetric experiments. The results are quite similar to those already described for system **2**, indicating that the variation of the length of aliphatic chains between the iminopyridine fragments and the naphthalenediimide moiety (tri- rather than dimethylene spacers are present in system **3**) does not induce particular effects on the solution behaviour of the quadridentate ditopic ligand. In fact, bis-chelate **3** forms complexes with Cu^{I}, Zn^{II} and Cd^{II} according to an apparent 1:1 stoichiometry (see the spectrophotometric titration profile in Figure 11).

ESI-MS experiments have been carried out on solutions containing **3** and the metal ion (Zn^{II} or Cu^{I}) in acetonitrile in order to identify the complex species present in solution.

In the case of zinc(II), the ESI-MS spectrum (Figure 12) shows peaks at m/z 1695.0 ($[Zn_2(\mathbf{3})_2(CF_3SO_3)_3{}^{+}]$) and 773.3 ($[Zn_2(\mathbf{3})_2(CF_3SO_3)^{2+}]$, base peak). Low-intensity peaks are also observed at m/z 465.5 ($[Zn_2(\mathbf{3})_2CF_3SO_3{}^{3+}]$) and 311.5 ($[Zn_2(\mathbf{2})_2{}^{4+}]$). The authenticity of the multiple charged species (di-, tri- and tetrapositive ions) are confirmed by the high-resolution spectra in which peak separations of 0.5, 0.33 and 0.25, respectively, are observed.

The ESI-MS spectrum obtained in the case of copper(I) exhibits peaks at m/z 1343.1 (corresponding to

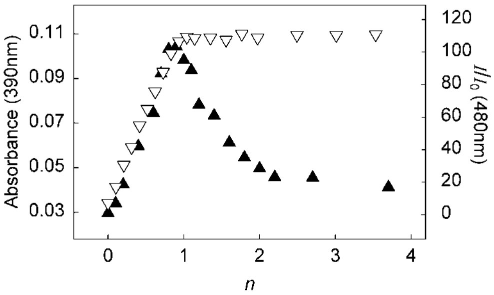

Figure 11. Profiles obtained in the spectrophotometric (▽) and spectrofluorimetric (▲) titrations of **3** (10^{-5} M in $CHCl_3$) with zinc(II). The assembling process (the formation of the adduct with a 1:1 stoichiometry) is signalled by an increase of the excimeric fluorescence intensity ($0 < n < 1$ range) while the disassembling process induces a decrease ($n > 1$).

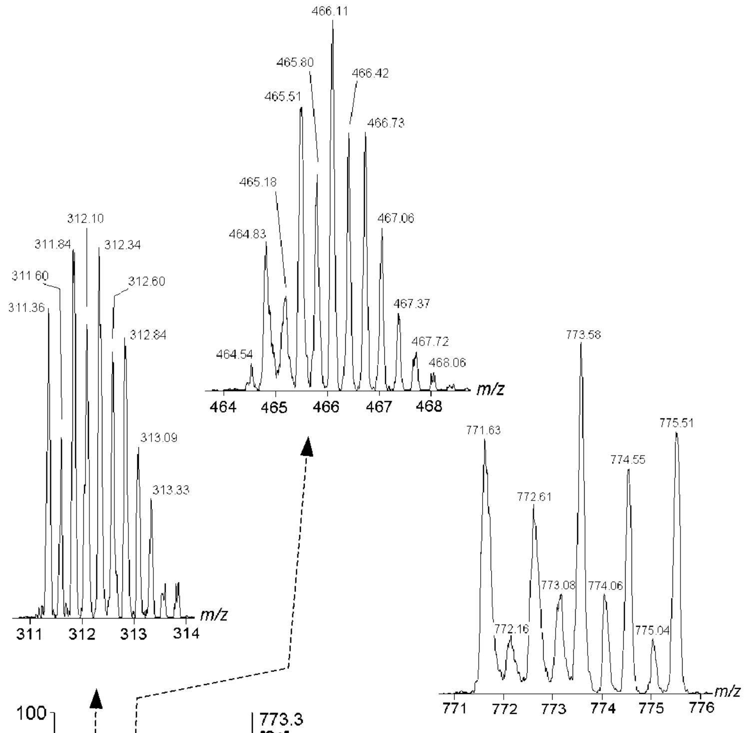

Figure 12. ESI-MS spectrum of an equimolar mixture of **3** and $Zn(CF_3SO_3)_2$ in acetonitrile (5×10^{-5} M). Typical peak separations (0.5, 0.33 and 0.25 for [2+], [3+] and [4+] species, respectively) are observed in the high-resolution spectra, reported in the insets, confirming the multiple charge states of the depicted ions. [+]: $[Zn_2(\mathbf{3})_2(CF_3SO_3)_3{}^{+}]$; [2+]: $[Zn_2(\mathbf{3})_2(CF_3SO_3)_2{}^{2+}]$; [3+]: $[Zn_2(\mathbf{3})_2CF_3SO_3{}^{3+}]$; [4+]: $[Zn_2(\mathbf{3})_2{}^{4+}]$.

[$Cu_2(\mathbf{3})_2ClO_4^+$], base peak) and 621.6 ([$Cu_2(\mathbf{2})_2^{2+}$]; peak separation in the high-resolution spectrum: 0.5). Low-intensity peaks at m/z 2065.3 (10%) and 2786.7 (15%), which can be ascribed to the trinuclear ([$Cu_3(\mathbf{3})_3(ClO_4)_2^+$]) and tetranuclear complex ([$Cu_4(\mathbf{3})_4(ClO_4)_3^+$]), respectively, have been also observed. These results suggest that the polynuclear species (i.e., the [3+3] and/or [4+4] adducts) form in solution, as minor species, when the metal ion is the tetrahedral copper(I), but they are not favoured (as observed also in the case of system **2**) when the assembling process is driven by zinc(II) and, in any case, the [2+2] adduct represents the main, if not the unique, assembled species in solution.

Spectrofluorimetric measurements show that the interaction of **3** with Zn^{II} or Cd^{II} induces the appearance of the strong excimeric band centred at $\lambda = 480$ nm in the emission spectrum of the ligand. The intensity of this band, as already described for system **2**, increases until a 1:1 metal/ligand ratio is reached and decreases when excess metal ion is added (see the spectrofluorimetric titration profile in Figure 11).

This behaviour indicates, as in the case of **2**, the formation of a [2+2] adduct in which an intramolecular interaction between the two naphthalenediimide subunits can generate an excimer excited species. Again, the assembling and the disassembling of the [2+2] adduct, which are controlled by the concentration of the metal ion (Zn^{II} or Cd^{II}) in solution, can be therefore signalled by the appearance and the disappearance, respectively, of the excimeric band in the emission spectrum.

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