

Excimer emission induced by metal ion coordination in 1,8-naphthalimide-tethered iminopyridine ligands

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Received 22nd July 2003, Accepted 10th September 2003

First published as an Advance Article on the web 25th September 2003

Ligands **2–5**, containing the light-emitting subunit 1,8-naphthalimide, have been prepared and their photophysical properties studied by absorption and emission spectroscopy. Ligand **2** interacts in solution with several cations according to a 1 : 2 (metal : ligand) stoichiometry, the 1 : 3 species being not favoured probably because of steric hindrance, while ligands **3–5** form 1 : 3 adducts with all the investigated metal ions. The interaction of ligands **2–5** with metal ions induces considerable variations on the photophysical properties of the light-emitting subunit. The coordination of genuine transition metal ions (Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}) causes the emission intensity to decrease in all the investigated systems, while Zn^{II} or Cd^{II} induce a fluorescence enhancement (system **2**) or the formation of a new band in the emission spectra (systems **3–5**) which can be ascribed to an intramolecular excimeric species. Excimeric emission is not observed in the complexes of **2**, possibly because the ethylenic chain bridging the naphthalimide and the iminopyridine units is too short to allow the intramolecular interaction. The excimeric species disappears on increasing the metal ion (Zn^{II} or Cd^{II}) concentration, as a result of the “disassembling” of the 1 : 3 complexes and the consecutive formation of 1 : 2 and 1 : 1 species, in which the intramolecular interaction is less probable or no longer possible. The appearance and disappearance of an excimer band in the emission spectrum can be described as a convenient way to monitor a metal-driven assembling/disassembling process.

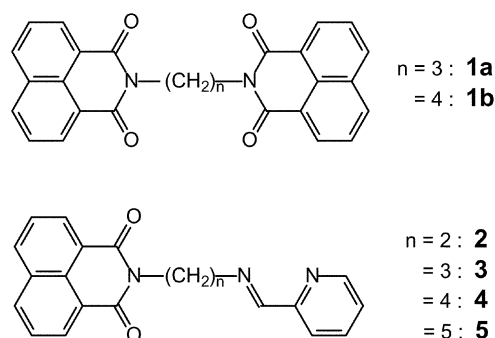
Introduction

Derivatives of 1,8-naphthalimide have been extensively studied in recent decades owing to their interesting photophysical properties¹ and the wide range of their applications in different chemical and biochemical areas. Many naphthalimide chromophores, characterised by both strong absorption and good fluorescence yields were prepared in the last century and used as dyes² or brighteners.³ Several 1,8-naphthalimide-containing compounds have been described as photo-induced DNA-cleaving agents⁴ and tumoricidals,⁵ some of them entering into clinical trials⁶ owing to their strong anticancer activity. Moreover, similar derivatives have been proposed as good candidates for the photochemical inhibition of enveloped viruses in blood and blood products,⁷ and for the fluorescent probing of hypoxic cells.⁸

The 1,8-naphthalimide moiety has also been used to design fluorescent molecular probes sensitive to variations of pH⁹ or metal ion concentration.¹⁰

Although the photophysical properties of 1,8-naphthalimides have been widely studied, the formation of excimeric species has been reported only in a few cases.^{1d,11,12} In particular, a broad emission band, ascribed to an intramolecular excimer, was observed in the fluorescence spectra displayed by compound **1** in which two subunits of naphthalimide are linked together by an aliphatic chain.¹¹ An excimeric emission was also observed when naphthalimide was appended by ethylenic spacers on the aliphatic chains of a poly(allylamine) polymer.¹²

In this paper we report the synthesis of systems **2–5** in which the 1,8-naphthalimide moiety is connected by aliphatic spacers to an iminopyridine bidentate coordinating fragment. The effects on the absorption and emission properties displayed by compounds **2–5** induced by their interaction with different metal ions is discussed; particular attention is focused on the formation of intramolecular excimers due to the coordination of metal ions such as Zn²⁺ and Cd²⁺. The results obtained by crystallographic studies performed on ligands **2** and **3**, and on



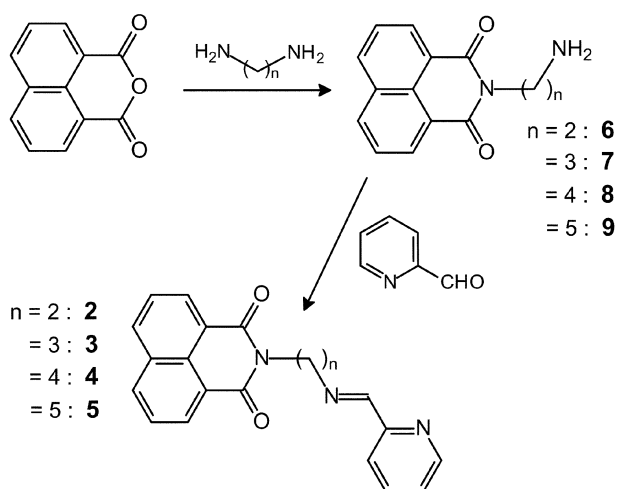
the complexes formed by **2** with zinc(II) and copper(II) are also reported.

Results and discussion

Synthesis and crystal structures of ligands and metal complexes

Ligands **2–5** were prepared according to a two-step synthetic pathway as shown in Scheme 1.

The amino intermediates **6–9** were obtained by reacting an aqueous suspension of the commercially available 1,8-naphthalic anhydride in the presence of excess diamine, according to a modification of a literature method.¹³ Although the yields were not quantitative (ranging between 52.8 and 84.6%), products were pure enough and did not require any chromatographic purification before the following step. Attempts to prepare **6** under homogeneous conditions (*i.e.* with ethylenediamine as the solvent) afforded an impure product (column chromatography was necessary) and lower yields (about 40%) than the heterogeneous method. Compounds **6–9** were easily transformed into the corresponding ligands **2–5** by performing a Schiff condensation in MeOH or CH₂Cl₂ in the presence of a slight excess of 2-pyridinecarbaldehyde. No attempts to



Scheme 1 Schematic representation of the synthetic procedure for systems **2–5**.

improve the yields (in the range 49–80%) of this step were made, since all starting materials are low-cost commercially available products.

Ligands **2** and **3** were isolated in crystalline form, as pale yellow crystals, after slow diffusion of diethyl ether into dichloromethane solutions. Systems **4** and **5** containing the more flexible tetra- and pentamethylene spacers were never obtained as crystals.

The molecular structures of ligands **2** and **3** were determined by means of X-ray single-crystal diffraction and did not reveal any unusual features. The corresponding ORTEP diagrams are reported in Fig. 1. In both cases, the 1,8-naphthalimide moieties are planar as expected. The mean deviations from the best plane calculated using all 15 atoms are 0.045 and 0.025 Å for **2** and **3**, respectively, while the largest deviations are 0.100(2) and 0.059(3) Å. The 1,8-naphthalimide fragments belonging to different molecules are parallel and face each other, with shortest distances of 3.584(3) and 3.448(3) Å for **2** and **3**, respectively. In ligand **2**, due to the presence of a shorter aliphatic spacer, the angle formed by the 1,8-naphthalimide with the iminopyridine mean plane is smaller (114.8°) than in **3** (130.9°); moreover the two sub-units are in an *anti* conformation with respect to the C7–C8 bond, as illustrated in Fig. 1(a).

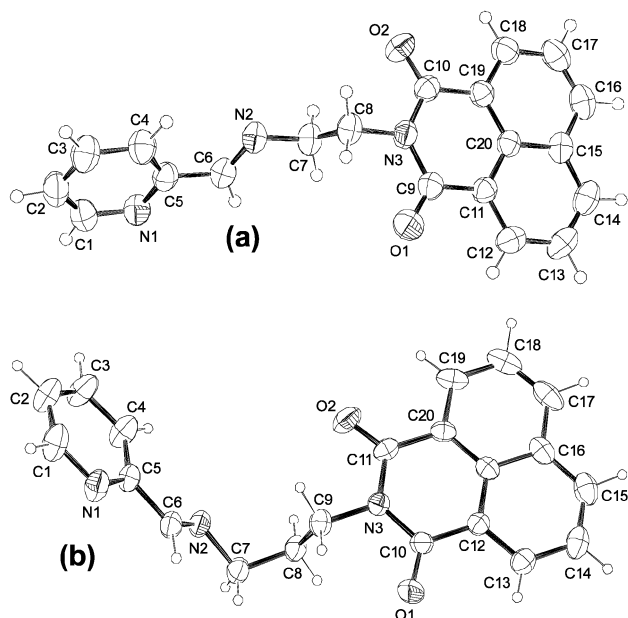


Fig. 1 ORTEP views of (a) ligand **2** and (b) ligand **3** with thermal ellipsoids drawn at 30% probability level.

Several attempts to isolate metal complexes in crystalline form were performed by allowing very slow evaporation of MeCN solutions containing the envisaged metal ion and ligand in 1 : 2 or 1 : 3 molar ratio. The slow diffusion of diethyl ether (or diisopropyl ether) on similar MeCN solutions was attempted as well. In most cases the precipitates were not good enough for X-ray diffraction purposes, and sometimes they were non-crystalline. Crystals of good quality for the X-ray crystallographic studies were obtained (by slow diffusion of diethyl ether in MeCN solutions) only for the trifluoromethanesulfonate salt of $[\text{Zn}^{\text{II}}(\mathbf{2})_2]^{2+}$. In the case of $[\text{Cu}(\mathbf{2})_2]^{2+}$ the quality of the crystals was not as good as for $[\text{Zn}(\mathbf{2})_2]^{2+}$ (see details in the Experimental section), but still sufficient to allow the determination of the molecular structure of the complex.

The crystal structure of the $[\text{Zn}^{\text{II}}(\mathbf{2})_2(\text{CF}_3\text{SO}_3)_2]$ complex, as determined by X-ray diffraction methods, is shown in Fig. 2. The Zn^{II} cation is hexa-coordinated, bonding to two nitrogen atoms from the iminopyridine bidentate fragments of two different ligands **2**, and to one oxygen atom from each triflate anion. The overall geometry at the metal centre can be described as a quite regular octahedron. The Zn–N distances reflect the different hybridization states of the nitrogen atoms [average Zn–N(py) 2.099 Å; average Zn–N(imine) 2.142 Å]. The average Zn–O(triflate) distance is 2.203 Å. It is worth noting that the two ligands adopt a different conformation: in fact, looking straight down the C–C bonds of the aliphatic spacers, the 1,8-naphthalimide and the iminopyridine groups are in an *anti* conformation in one case (see atoms N2 and N3 in Fig. 2), and in a *gauche* conformation in the other case (see atoms N5 and N6 in Fig. 2). The latter conformation allows one of the oxygen atoms of the carbonyl groups to be closer to the metal centre: $\text{Zn} \cdots \text{O4}$ is in fact 3.654 Å, while $\text{Zn} \cdots \text{O2}$ is 5.903 Å. The proximity of O4 to the coordination sphere of Zn^{II} forces the N5–Zn1–N2 angle to the value of 111.3(2)°, which represents the largest discrepancy from the octahedral geometry. The crystal is maintained by van der Waals forces.

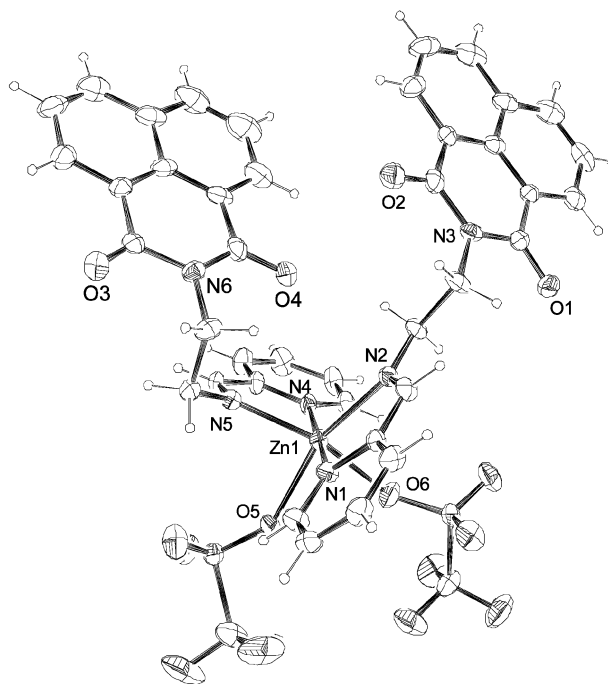


Fig. 2 ORTEP view of $[\text{Zn}^{\text{II}}(\mathbf{2})_2(\text{CF}_3\text{SO}_3)_2]$ with thermal ellipsoids drawn at 20% probability level. Selected bond lengths (Å) and angles (°): Zn1–N1 2.112(6), Zn1–N2 2.159(6), Zn1–N4 2.086(7), Zn1–N5 2.125(6), Zn1–O5 2.269(5), Zn1–O8 2.137(6); N1–Zn1–N2 78.7(2), N1–Zn1–N4 175.3(3), N1–Zn1–N5 98.0(3), N1–Zn1–O5 93.0(2), N1–Zn1–O8 95.0(3), N2–Zn1–N4 99.5(3), N2–Zn1–N5 111.3(2), N2–Zn1–O5 162.2(2), N2–Zn1–O8 87.1(2), N4–Zn1–N5 78.5(3), N4–Zn1–O5 89.9(2), N4–Zn1–O8 89.2(3), N5–Zn1–O5 85.3(2), N5–Zn1–O8 159.2(2), O5–Zn1–O8 77.9(2).

An ORTEP diagram of the $[\text{Cu}^{\text{II}}(\mathbf{2})_2]^{2+}$ molecular cation is reported in Fig. 3. Unfortunately, the poor quality of the crystallographic data (see Experimental section) does not allow an accurate analysis of the structural model. At any rate, a comparison with the analogous Zn^{II} complex can be made on the basis of these preliminary data. The crystal structure of $[\text{Cu}^{\text{II}}(\mathbf{2})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ consists of separated $[\text{Cu}^{\text{II}}(\mathbf{2})_2]^{2+}$ molecular cations and triflate anions which do not interact with the metal centre. Moreover, one MeCN molecule and one water molecule are present in the crystal structure and they do not interact with Cu^{II} . In the $[\text{Cu}^{\text{II}}(\mathbf{2})_2]^{2+}$ molecular cation, the 1,8-naphthalimide and the iminopyridine sub-units of both the ligands are in a *gauche* conformation with respect to the C–C bond of the aliphatic spacer. This implies that two oxygen atoms, one from each ligand, are quite close to Cu^{II} [Cu–O(carbonyl) 2.69(2) Å], leaving no more room for the triflate anions in the coordination sphere of the metal centre. Coordination at the metal centre can therefore be described as 4 + 2, Cu^{II} bonding also to two nitrogen atoms from the iminopyridine groups of two different ligands [Cu–N(py) 1.98(2) Å; Cu–N(imine) 2.01(2) Å].

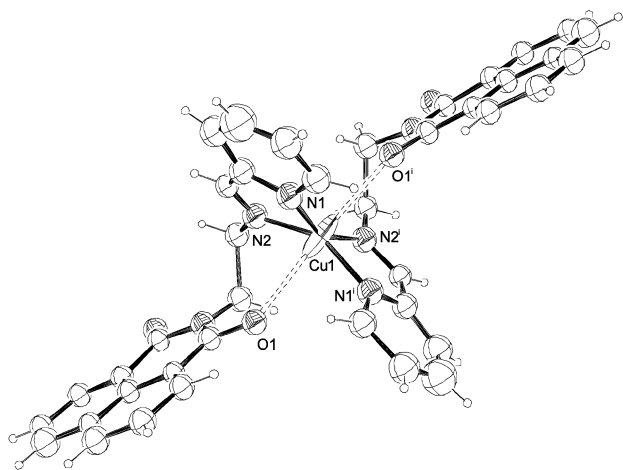


Fig. 3 ORTEP view of $[\text{Cu}^{\text{II}}(\mathbf{2})_2]^{2+}$ molecular cation with thermal ellipsoids drawn at 20% probability level. The triflate anions, as well as MeCN and H_2O molecules, have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Cu1–N1 1.98(2), Cu1–N2 2.01(2); N1–Cu1–N1ⁱ 104(1), N1–Cu1–N2 86.7(9), N1–Cu1–N2ⁱ 152.2(7), N2–Cu1–N2ⁱ 95(1), O1–Cu1–O1ⁱ 165.7(7). Symmetry code: $i - y, -x, -z + 1/2$.

Absorption and emission properties of ligands 2–5

1,8-Naphthalimide and its derivatives are well known chromophores and fluorophores and their photophysical properties have been the object of detailed studies.¹ Ligands **2–5** display spectroscopic properties in acetonitrile solution which resemble very closely those reported for similar compounds such as *N*-methyl-^{1d} and *N*-propyl-naphthalimide.¹² Absorption and emission data are summarized in Table 1.

The electronic spectra of all the examined systems show a band centered at 272 nm ascribed to the iminopyridine moiety and the typical bands due to the naphthalimide chromophore with maxima at 234, 332 and 346 nm whose intensities (see ϵ values in Table 1) are very close to those reported for *N*-methyl-naphthalimide taken as reference. Naphthalimides **2–5** fluoresce in the 350–450 nm range with a maximum at about 380 nm, and their spectra have a mirror image relationship with the long-wavelength absorption bands. The weak emission (fluorescence quantum yields are quite coincident with the values reported for the reference compound)^{1d} of 1,8-naphthalimides has been already explained in terms of fast ISC from the excited π, π^* singlet state to a close-lying n, π^* triplet state.^{1d,14}

The fluorescence lifetimes detected for **2–5**, are lower than 1 ns (see τ values in Table 1) as already observed for *N*-methyl-

naphthalimide and other related compounds^{1d,10d,12} and confirm the existence of very short-lived excited species for all the examined systems. No concentration dependence of the emission spectrum and, in particular, no bands ascribable to excimeric species were observed for all ligands, similarly to *N*-alkylnaphthalimides,^{11,12} for which no intermolecular excimer emission was found up to a concentration value of ca. 10^{-3} M.¹¹

Interaction with metal ions

The behaviour of ligands **2–5** in the presence of metal ions in solution was studied at first by spectrophotometric titration experiments in order to assess the stoichiometry of the complex species. MeCN solutions (5×10^{-5} M) of the ligand were titrated with the envisaged metal ions (Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II}) and absorption spectra were taken after each addition of metal. Similar titration experiments combined with spectrofluorimetric measurements, allowed to evaluate the effects induced by the coordination of metal ions on the emission properties displayed by **2–5**. MeCN was chosen as the solvent for all the measurements since it guarantees a good solubility of metal salts, ligands and complexes. The results for system **2** are quite different from those obtained for the other ligands and therefore are discussed in a separate section.

Behaviour of 2. The addition of metal ions induces in each case a substantial variation of the electronic spectrum: the band at 272 nm, due to the absorption of the iminopyridine moiety, directly involved in the coordination process, shifts to higher wavelengths (280–290 nm) and undergoes a distinct intensity increase. An isosbestic point is observed at about 270 nm. The absorption band related to the π, π^* transition of the naphthalimide moiety experiences only very slight variations, *i.e.* a small red shift ($\Delta\lambda \leq 2$ nm) and a slight intensity increase. These changes were observed until 0.5 equivalents of metal ion were added. As an example, absorption spectra registered during the titration of **2** with nickel(II) trifluoromethanesulfonate are reported in Fig. 4. Similar families of spectra were obtained from the titrations with the other examined metal ions.

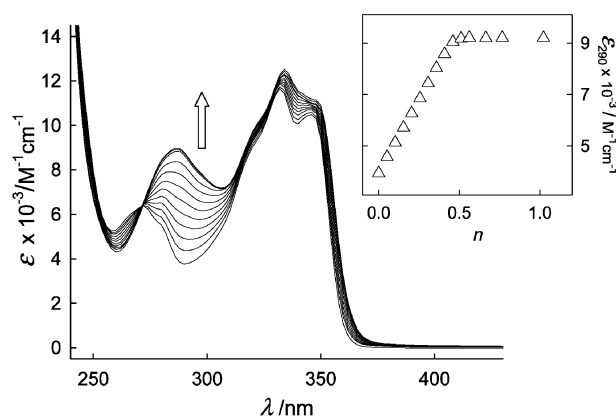


Fig. 4 Absorption spectra recorded during the titration of a MeCN solution of **2** (5×10^{-5} M) with nickel(II). Titration profiles reported in the inset show the formation of a 1 : 2 adduct ($n = \text{equiv. of metal ion/ equiv. of } \mathbf{2}$).

The titration profiles obtained by plotting the molar absorbance (ϵ) values determined at 290 nm *vs.* n (metal equiv./ligand equiv.), clearly indicate the formation of adducts with a 1 : 2 stoichiometry (see inset of Fig. 4). Least-squares analysis of the spectral data gives $\log\beta$ values of 11.47 ± 0.21 and 11.66 ± 0.11 for $[\text{Zn}(\mathbf{2})_2]^{2+}$ and $[\text{Cd}(\mathbf{2})_2]^{2+}$, respectively. Similar values were obtained for the other metal complexes. The examination of the titration profiles does not provide any clear evidence about the formation of complex species with 1 : 3 stoichiometry, which

Table 1 Absorption and emission data for **2–5** and the reference compound in acetonitrile

	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Φ	τ/ns
<i>N</i> -Methylnaphthalimide ^a	234	49700	376	0.027	0.14
	332	12500			
	345	11600			
2	234	49800	376	0.026	0.2 ^b
	272	6800			
	332	12500			
	346	11400			
3	234	49900	377	0.032	0.8 ^b
	272	6950			
	332	12100			
	346	11200			
4	234	49780	378	0.031	0.4 ^b
	272	6700			
	332	11700			
	346	10800			
5	234	48600	378	0.030	0.3 ^b
	272	7050			
	332	10950			
	346	10050			

^a Data from ref. 1d. ^b Excitation wavelength was 335 nm; the fluorescence decays were monitored at 380 nm.

could be prevented by the relatively short length of the ethylenic chain bridging the chelate to the chromophoric subunits. This may disfavour a comfortable positioning of three bulky naphthalimide moieties around the metal center with a resulting enhanced stability of the 1 : 2 species. Moreover, the six-coordinate arrangement could also be reached by interaction of the coordinated ion with the carbonyl groups of the naphthalimide moieties, forming seven-membered chelate rings, as indicated in the solid state by the X-ray structure obtained for [Cu(**2**)](CF₃SO₃)₂. As an alternative, the coordination spheres of the metal ions interacting with **2** may be completed by involving less sterically hindering anionic ligands or solvent molecules. In the case of zinc(II) such a possibility is also confirmed in the solid state by the structure determined on [Zn(**2**)-(CF₃SO₃)₂] in which two trifluoromethanesulfonate anions are bound to the metal center.

A more careful examination of the spectra collected during the titration experiments with Zn^{II} and Cd^{II} reveals that further small spectral changes take place also after the addition of 0.5 equivalents of the metal ion. In particular, the isosbestic point at 270 nm is lost and the absorbance in the 300–310 nm range, which had increased until 0.5 equiv. of metal ion had been added, decreases again until the 1 : 1 ratio is reached (see Fig. 5). Such a situation suggests the formation of a new complex species (with a 1 : 1 metal : ligand stoichiometry) in solution when

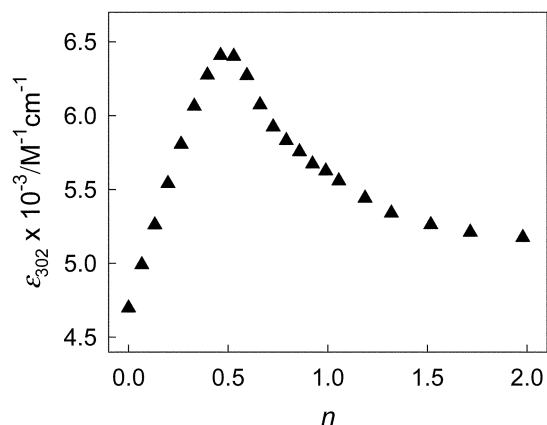
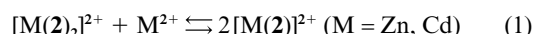


Fig. 5 Variation of the molar absorbance at 302 nm during the titration of a MeCN solution of **2** (5×10^{-5} M) with zinc(II): on increasing the metal ion concentration the 1 : 2 complex disassembles yielding a 1 : 1 species. The process is not clearly revealed by variations in any other part of the spectrum.

the metal ion (Zn^{II} or Cd^{II}) concentration exceeds the 1 : 2 ratio according to the following equilibrium:



Similar spectroscopic evidence for the formation of the 1 : 1 species after the addition of excess metal ion is not observed in the case of the other investigated ions.

The changes in the emission properties displayed by the naphthalimide moiety observed upon metal ion addition depend on the nature of the added metal ion. Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} cause the intensity of the emission band, I_F , at 380 nm to decrease to 10–30% of the original value, depending on the metal ion. The emission spectra registered during the titration with nickel(II) trifluoromethanesulfonate are reported in Fig. 6.

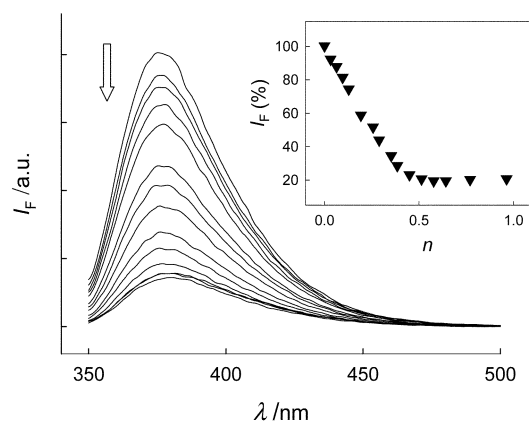


Fig. 6 Emission spectra recorded during the titration of **2** (5×10^{-5} M in MeCN) with nickel(II). The titration profile in the inset indicates 1 : 2 stoichiometry for the complex species in solution (n = equiv. of metal ion/equiv. of **2**).

Iron(II), d⁶, cobalt(II), d⁷, nickel(II), d⁸, copper(II), d⁹, as well as other transition metal ions with partially filled d orbitals, are known to induce fluorescence quenching through photoinduced electron transfer (eT) or energy transfer (ET) mechanisms.¹⁵ The titration profiles obtained by plotting I_F , vs. n generally confirm the 1 : 2 stoichiometry, already observed in the spectrophotometric titrations (see inset in Fig. 6).

On the contrary, the emission band displayed by ligand **2** at 380 nm undergoes an intensity enhancement following the addition of Zn²⁺ or Cd²⁺ by a factor of 6 and 7, respectively, until

0.5 equiv. of metal ion is added (see Fig. 7). The small variation of I_F in the $0.5 < n < 1$ range supports the existence in solution of the 1 : 1 species, as already observed in the spectrophotometric experiments.

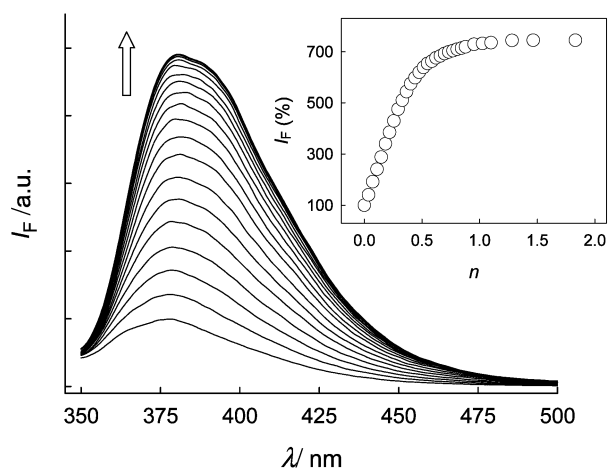


Fig. 7 Emission spectra recorded during the titration of **2** (5×10^{-5} M in MeCN) with cadmium(II). The titration profile is reported in the inset (n = equiv. of metal ion/equiv. of **2**).

The fluorescence enhancement can be explained on the basis of the possible interaction of the metal ion with the C=O groups belonging to the naphthalimide moieties of the coordinated ligands. The interaction with the n orbitals of the dicarboxyimide fragment should increase the energy of the n, π^* excited state and prevent the fast ISC process through which non-radiative deactivation of the excited π, π^* singlet state takes place in the free ligands. This results in a fluorescence enhancement in the presence of the d^{10} cations Zn^{2+} and Cd^{2+} , which, differently from genuine transition metal ions, do not have features to induce the fluorescence quenching through an eT or ET mechanism. A similar hypothesis has been proposed to explain the fluorescence intensity increase of *N*-methyl-naphthalimide in the presence of protic solvents able to interact with the n orbitals on the dicarboxyimide groups *via* H-bonding.¹⁴

Behaviour of ligands 3–5 and excimer formation. The changes induced in the absorption spectra by the addition of any of the considered metal ions to MeCN solutions containing ligands 3–5 are very similar to those described in the previous section for ligand **2**. Nevertheless, the titration profiles generally indicate the formation of adducts with a 1 : 3 stoichiometry, which was not observed for the complexes formed by **2**. Such a difference could be mainly ascribed to the different length of the aliphatic chains in the examined systems: the longer and more flexible spacers in 3–5 lead to less crowding around the metal center in the 1 : 3 complexes. Moreover, the interactions of the metal ion with the carbonyl groups of the naphthalimide moieties which possibly complete the six-coordinate geometry in the 1 : 2 complexes formed by ligand **2**, in the case of 3–5 cannot help to stabilize the 1 : 2 species, since they would originate eight- to ten-membered chelate rings which are highly disfavoured.¹⁶

Least-squares analysis of the spectral data obtained in the titration experiments gives $\log \beta$ values in the range 15–17 (e.g. $\log \beta = 15.61 \pm 0.07$ for $[Cd(3)_3]^{2+}$).

Although the spectrophotometric titrations performed with either zinc(II) or cadmium(II) trifluoromethanesulfonate indicate the formation of 1 : 3 complex as the prevailing species, the small spectral variations in the 300–310 nm range, observed on increasing the metal ion concentration, suggest the formation of complex species with different metal : ligand ratios (*i.e.* 1 : 2 and 1 : 1), in analogy to ligand **2**. On the other hand, these

spectral variations are not observed in the case of the other ions.

As expected, Fe^{II} , Co^{II} , Ni^{II} and Cu^{II} cause the intensity of the emission band at 380 nm to decrease by a factor of 5–10, depending on the metal ion and the ligand. However, no clear correlation between the fluorescence quenching extent and the length of the polymethylene spacer has been found.

The results obtained from the spectrofluorimetric titration experiments with Zn^{2+} or Cd^{2+} are very different from those described above for the related system **2**: the addition of zinc(II) or cadmium(II) trifluoromethanesulfonate to MeCN solutions of ligands 3–5 induces the appearance in the emission spectra of an extra band centered at 470 nm whose relative intensity increases until the metal ion concentration corresponds to a 1 : 3 stoichiometric ratio, then decreases again and almost disappears when the metal ion concentration exceeds the value corresponding to the 1 : 1 stoichiometry. The emission spectra registered during the titration of **4** with Zn^{II} triflate are reported in Fig. 8. Similar families of spectra were obtained from the titration experiments performed on **3** and **5**. The broad red-shifted band is very similar to the emission band reported for compound **1** in acetonitrile or methanol (with a maximum at 470 nm)¹¹ and can be ascribed to an excimeric species deriving from the intramolecular interaction between the naphthalimide moieties in the complex species.

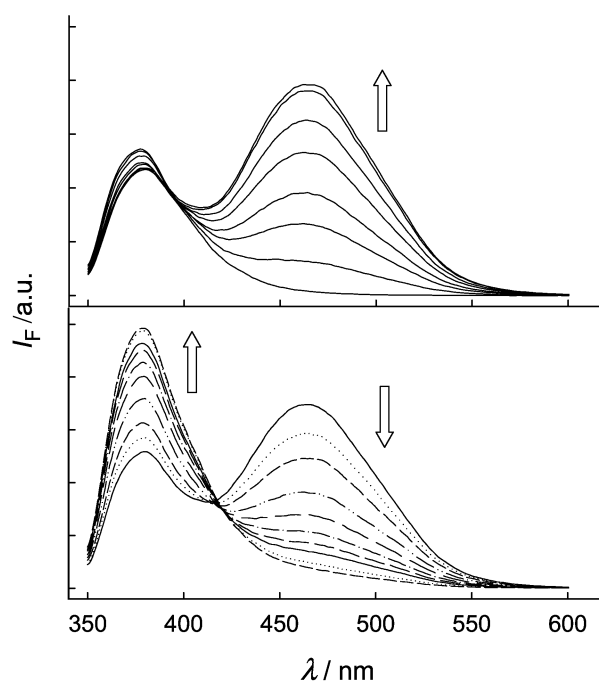


Fig. 8 Emission spectra taken during the titration of **4** (5×10^{-5} M in MeCN) with zinc(II): (above) the intensity of the broad band at 470 nm increases as n (equiv. of Zn^{II} /equiv. of **4**) is increased from 0 to 0.33; (below) the band at 470 nm decreases as n becomes greater than 0.33.

The disappearing of the excimeric species in the presence of excess metal ion can be accounted for by the consecutive formation of complex species with 1 : 2 and 1 : 1 stoichiometry. Octahedral tris-chelate complexes of zinc(II) and cadmium(II) are likely to exist in solution as two isomers, the *fac* and *mer* forms, as a rapidly interconverting mixture, owing to their lability. However, the intramolecular interaction between the fluorophore subunits which provides the excimer formation is allowed in both forms since three or two naphthalimide moieties, respectively, are in a *cis* arrangement. Similar considerations were reported a few years ago by Fages and co-workers when discussing the behaviour of a pyrene-labeled hydroxamate ligand in the presence of Ga^{III} .¹⁷ In 1 : 2 complexes formed by 3–5 the probability of an intramolecular

Table 2 Excimer-to-monomer fluorescence intensity ratios and excimer lifetimes determined for 1 : 3 complexes of zinc(II) and cadmium(II) with systems 3–5

	3		4		5	
	Zn ^{II}	Cd ^{II}	Zn ^{II}	Cd ^{II}	Zn ^{II}	Cd ^{II}
I_E/I_M^a	0.719	0.544	1.658	1.465	1.242	0.896
τ^b/ns	19.5	20.9	23.5	23.1	23.9	23.7

^a Emission intensity values measured at 378 and 470 nm for monomer and excimer, respectively. ^b Monitored at 520 nm, $\lambda_{\text{exc}} = 335$ nm.

interaction is obviously lower and in 1 : 1 species it is no longer possible, so that the progressive dissociation of the 1 : 3 complexes (following an increase of the metal ion concentration) causes the intensity of the excimeric band to decrease.

The efficiency of the excimer formation can be estimated by the values of excimer-to-monomer fluorescence intensity ratio (I_E/I_M), *i.e.* the ratio of the emission intensities at 470 and at 380 nm, for all 1 : 3 complex species (see Table 2).

The highest I_E/I_M values are observed for the complexes formed by ligand 4, suggesting that the tetramethylene chain displays the best features in terms of length and conformational flexibility in order to maximize the interaction (in the excited state) between two aromatic subunits.

Moreover, for each ligand, zinc(II) induces a more efficient excimer formation (*i.e.* higher I_E/I_M values) than cadmium(II), indicating an influence of the cation size beside that of the spacer length and flexibility.

The influence of the chain length and flexibility on the formation of intramolecular excimers, has been pointed out in several systems comprised of two aromatic nuclei (*e.g.* naphthalene, anthracene, pyrene) bridged together in various ways.¹⁸

The interaction of the investigated ligands with Zn²⁺ and Cd²⁺ was also studied by time-resolved fluorescence measurements, observing the effects on the fluorescence decay behaviour.

The free ligands 3–5 display single exponential fluorescence decays at 380 nm, with lifetimes shorter than 1 ns, as mentioned above (see Table 2). When zinc(II) or cadmium(II) trifluoromethanesulfonate are added to a MeCN solution containing one of the systems 3–5 (5×10^{-5} M), the fluorescence decay profiles at 380 nm can only be fitted by employing two exponential terms and reveal the presence of a double lifetime. The relative weight of the long-lived component increases with the concentration of the metal ion until the 1 : 3 stoichiometry is reached. As an example, the following values were obtained for ligand 3 with Zn²⁺: $\tau_1 = 0.6$ ns (88.8%), $\tau_2 = 4.1$ ns (11.2%) and Cd²⁺: $\tau_1 = 0.8$ ns (95.4%), $\tau_2 = 4.6$ ns (4.6%). On further addition of Zn²⁺ or Cd²⁺, the abundance of the long-lived species decreases again owing to the progressive formation of the 1 : 1 complex species and the consequent disappearing of the intramolecular excimer.

The fluorescence decays were also monitored at 520 nm where a 100% contribution of the excimeric emission was expected. The corresponding lifetimes, which are summarized in Table 2, are in all cases higher than 20 ns and in good accordance with the value reported for the intramolecular excimer formed by compound 1 (22–23 ns in methanol).¹¹

Conclusions

The formation of intramolecular excimers resulting from coordination processes has been often exploited in the last years for sensing purposes: several molecular probes mainly based on the well known monomer/excimer dual emission properties of pyrene have been proposed for the sensing of different metal ions, in particular alkali and alkali-earth cations.¹⁹ The study described in this paper shows that coordinative interactions can

favour the formation of excimers even in the case of fluorophores, such as naphthalimide, for which, differently from pyrene, excimeric emission is not very common.

The formation of intramolecular excimers in the naphthalimide derivatives 2–5 is influenced by the nature of the metal ion involved in the coordination process and by the length of the aliphatic chain bridging the chelating iminopyridine and naphthalimide units. In particular, genuine transition metals induce only a decrease of the monomer fluorescence intensity, according to their common quenching behaviour, while zinc(II) or cadmium(II), which are innocent from a photophysical point of view, induce the appearance of an excimeric band in the spectrum of ligands 3–5.

The excimer emission is not observed in the complexes of 2 since the coordination of Zn^{II} and Cd^{II} induces only an enhancement of the monomer fluorescence. The different emission properties displayed by ligand 2 can be ascribed to the relatively short length of the ethylenic bridge which prevents the interaction between the aromatic moieties. The behaviour of 2, whose fluorescence is simply quenched or enhanced depending on the nature of the metal ion, resembles that commonly observed in ON/OFF or OFF/OFF fluorescent chemosensors, which have been widely reported in the literature.²⁰

On the contrary, the behaviour of systems 3–5 in the presence of Zn^{II} or Cd^{II} can be described as an example of metal-driven assembling/disassembling process²¹ which is monitored by the appearance and disappearance, respectively, of a new fluorescent signal: in fact, the intensity of the excimer emission increases with the concentration of Zn^{II} or Cd^{II} until a 1 : 3 adduct is formed (assembling) and decreases again at higher metal ion concentration values owing to the consecutive formation of 1 : 2 and 1 : 1 adducts (disassembling).

In conclusion, the results obtained in the present work can contribute to both the design of novel molecular sensors for metal ions based on naphthalimide derivatives, which are currently investigated in our laboratory, and the study of self-signalling assembling/disassembling processes sensitive to the concentration of metal ions, which are potentially applicable to the development of more sophisticated (supra)molecular devices.

Experimental

Unless otherwise stated, commercially available reagent grade chemicals were used as received, except 2-pyridincarbalddehyde that was freshly distilled prior to use. Cadmium(II), cobalt(II), iron(II) and nickel(II) trifluoromethanesulfonates were prepared according to literature methods.²² Spectrophotometric or fluorimetric grade solvents were used for spectroscopic measurements.

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

UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array or on a Varian Cary 100 spectrophotometer; emission spectra were taken on a Perkin-Elmer LS-50B luminescence spectrometer.

NMR spectra were recorded on a Bruker AMX400 spectrometer.

Mass spectra were obtained using an LCQ DECA ion trap mass spectrometer equipped with electrospray ionization (ESI) ion source and controlled by Xcalibur software 1.1 (Thermo-Finnigan).

Spectrophotometric and spectrofluorimetric titrations were performed on 10 ml samples of solutions of the ligand (5×10^{-5} M) in CH₃CN, by microadditions of CH₃CN stock solutions of metal triflate. In each experiment the overall addition was limited to about 200 μ l, so that volume increment variation was not significant.

The fluorescence decay curves were recorded on an Edinburgh Instruments Model FL900 time-correlated single

photon counting spectrometer, at the Centro Grandi Strumenti (Università di Pavia). The instrument was operated using a flash lamp filled with H₂ at a pressure of 0.4 atm, with a frequency of 40 kHz and a pulse-width of 1.0 ns.

The relative quantum yields of fluorescence were obtained through the optically diluted method,²³ using anthracene ($\Phi = 0.27$ in EtOH) as a reference.²⁴

Complexation constants were determined by using the HyperQuad software package.²⁵

Syntheses

***N*-(2-Aminoethyl)-1,8-naphthalimide, 6.** *Method A.* 1,8-naphthalic anhydride (1.00 g, 5.05 mmol) was added in small portions to ethylenediamine (30 ml, 0.4 mol) under magnetic stirring and the resulting solution was refluxed overnight. The reaction mixture was concentrated (to about 10 ml) to give a yellow precipitate, which was filtered off, washed with diethyl ether and purified by liquid chromatography [SiO₂, CH₂Cl₂-MeOH-ammonia solution (97 : 2 : 1)] (0.81 g, 40.3%) (Found: C, 69.53; H, 4.92; N, 11.35. C₁₄H₁₂N₂O₂ requires C, 69.99; H, 5.03; N, 11.66%). δ_{H} (CD₃OD): 8.55 (2H, d), 8.29 (2H, d), 7.79 (2H, t), 4.15 (2H, t) 2.85 (2H, t).

Method B. A suspension of 1,8-naphthalic anhydride (5 g, 25 mmol) in water (25 ml) was slowly added to an aqueous solution of ethylenediamine (11.1 ml, 0.17 mol in 60 ml) which was stirred and heated at 70 °C. The resulting suspension was heated at 80 °C for 10 min, then a light brown precipitate formed (corresponding to the byproduct containing two naphthalimide moieties) which was eliminated by filtration. The filtered solution was allowed to remain at room temperature overnight. Pale yellow crystals were obtained (4.65 g, 77.5%) (Found: C, 69.12; H, 4.95; N, 11.97. C₁₄H₁₂N₂O₂ requires C, 69.99; H, 5.03; N 11.66%). δ_{H} (CDCl₃): 8.60 (2H, d), 8.21 (2H, d), 7.75 (2H, t), 4.28 (2H, t), 3.07 (2H, t); *m/z* 241 (MH⁺, 100%), 224 (M - NH₂, 11).

Ligand 2. A solution of 2-pyridinecarbaldehyde (0.13 ml, 1.37 mmol) in MeOH (10 ml) was added dropwise to a stirred solution of **6** (0.303 g, 1.26 mmol) in MeOH (30 ml). The resulting solution was stirred at room temperature for 3 h. The white precipitate formed was isolated by *in vacuo* filtration (0.270 g, 65.1%). (Found: C, 72.60; H, 4.46; N, 12.10. C₂₀H₁₅N₃O₂ requires C, 72.94; H, 4.59; N, 12.76%). δ_{H} (CDCl₃): 8.61 (3H, m), 8.43 (1H, s), 8.23 (2H, d), 8.00 (1H, d), 7.75 (3H, m), 7.30 (1H, t), 4.61 (2H, t), 4.06 (2H, t); *m/z* 352 (M + Na⁺, 8%), 330 (MH⁺, 100).

***N*-(3-Aminopropyl)-1,8-naphthalimide, 7.** Same experimental procedure as reported for **6**, method B (4.41 g, 69.36%) (Found: C, 70.55; H, 5.32; N, 10.88. C₁₅H₁₄N₂O₂ requires C, 70.85; H, 5.55; N, 11.02%). δ_{H} (CD₃OD): 8.55 (2H, d), 8.35 (2H, d), 7.81 (2H, t), 4.23 (2H, t), 2.70 (2H, t), 1.91 (2H, m); *m/z* 255 (MH⁺, 52%), 238 (M - NH₂, 100).

Ligand 3. Same experimental procedure as described for **2**, starting from intermediate **7** (0.204 g, 49.1%) (Found: C, 73.43; H, 4.97; N, 12.11. C₂₁H₁₇N₃O₂ requires C, 73.45; H, 4.99; N, 12.24%). δ_{H} (CDCl₃): 8.60 (3H, m), 8.40 (1H, s), 8.20 (2H, d), 7.85 (1H, d), 7.75 (2H, t), 7.61 (1H, t), 7.25 (1H, t), 4.37 (2H, t), 3.81 (2H, t), 2.23 (2H, m); *m/z* 366 (M + Na⁺, 6%), 344 (MH⁺, 100).

***N*-(4-Aminobutyl)-1,8-naphthalimide, 8.** A suspension of naphthalic anhydride (5 g, 25 mmol) in water (25 ml) was added to an aqueous solution of 1,4-diaminobutane (17 ml, 0.17 mol in 60 ml) at 70 °C over a period of 30 min. Then the resulting mixture was heated at 80 °C for 15 min and the light brown solid formed was filtered off. The filtered solution was cooled to room temperature and then at 4 °C, giving, after a week, a light

brown-silverish precipitate, which was collected and washed with water (2.20 g, 32.80%) (Found: C, 71.46; H, 5.95; N, 10.15. C₁₆H₁₆N₂O₂ requires C, 71.62; H, 6.01; N, 10.44%). δ_{H} (CDCl₃): 8.55 (2H, d), 8.17 (2H, d), 7.73 (2H, t), 4.16 (2H, t), 2.74 (2H, t), 1.75 (2H, m), 1.55 (2H, m); *m/z* 269 (MH⁺, 100%).

Ligand 4. A solution of 2-pyridinecarbaldehyde (0.09 ml, 0.95 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a stirred solution of **8** (0.240 g, 0.89 mmol) in CH₂Cl₂ (50 ml). The resulting mixture was stirred for 24 h: the solvent was evaporated and the oily product was dried *in vacuo*. The oil solidified at room temperature to give a waxy product (0.242 g, 75.7%) (Found: C, 72.89; H, 5.40; N, 11.60. C₂₂H₁₉N₃O₂ requires C, 73.93; H, 5.36; N, 11.76%). δ_{H} (CDCl₃): 8.59 (1H, d), 8.54 (2H, d), 8.40 (1H, s), 8.34 (2H, d), 7.99 (1H, d), 7.89 (1H, t), 7.81 (2H, t), 7.47 (1H, t), 4.23 (2H, t), 3.77 (2H, t), 1.85 (4H, m); *m/z* 380 (M + Na⁺, 16%), 358 (MH⁺, 100), 252 (M - NCHC₃H₄N, 7).

***N*-(5-Aminopentyl)-1,8-naphthalimide, 9.** Same experimental procedure as reported for **8** (2.05 g, 84.64%) (Found: C, 71.96; H, 5.90; N, 9.60. C₁₇H₁₈N₂O₂ requires C, 72.32; H, 6.43; N, 9.92%). δ_{H} (CDCl₃): 8.58 (2H, d), 8.20 (2H, d), 7.74 (2H, t), 4.18 (2H, t), 2.69 (2H, t), 1.75 (2H, m), 1.49 (4H, m); *m/z* 283 (MH⁺, 100%).

Ligand 5. Same experimental procedure as described for **4**, starting from intermediate **9** (0.273 g, 80.9%) (Found: C, 73.41; H, 5.69; N, 11.34. C₂₃H₂₁N₃O₂ requires C, 74.37; H, 5.70; N, 11.31%). δ_{H} (CDCl₃): 8.62 (1H, d), 8.59 (2H, d), 8.36 (1H, s), 8.20 (2H, d), 7.96 (1H, d), 7.73 (3H, m), 7.29 (1H, t), 4.19 (2H, t), 3.69 (2H, t), 1.81 (4H, m), 1.52 (2H, m); *m/z* 382 (MH⁺, 100).

X-Ray structure determinations

Details on the crystallographic study carried out on ligands **2** and **3**, and on the complexes formed by Zn^{II} and Cu^{II} with ligand **2**, are reported in Table 3. Data on crystal [Cu(2)₂](CF₃SO₃)₂·(CH₃CN) are not of good quality; the relevant structural investigation must be considered as preliminary and it will be revised as soon as better crystals are available. Nevertheless, it is reported here since the molecular conformation of the complex was revealed and this allowed to make a comparison with the analogous Zn^{II} complex.

Intensity data were obtained for all the crystals on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were determined by least-squares fitting of 25 centred reflections. Calculations were performed with the WinGX-97 software.²⁶ Empirical absorption correction²⁷ was applied in all cases except for **2**, for which no suitable reflection for a ψ -scan was found in the 80 < χ < 90° range. All the structures were solved by direct methods (SIR92)²⁸ and refined on F^2 by full-matrix least-squares using SHELXL-97.²⁹ In particular, for both ligands, non-H atoms were refined with anisotropic displacement parameters, and H atoms were located in the difference-Fourier maps and refined with isotropic displacement parameters. For [Zn(2)₂](CF₃SO₃)₂, non-H atoms were refined with anisotropic displacement parameters, while H atoms were inserted in calculated positions with isotropic displacement parameters proportional to those of their neighbouring atoms and not refined. As stated above, the poor quality of the [Cu(2)₂](CF₃SO₃)₂·CH₃CN·H₂O crystal did not allow to achieve a good resolution for the structural model. In order to reduce the number of parameters to be refined, only the Cu atom was refined anisotropically. All other non-H atoms were refined isotropically while the H atoms were inserted in calculated positions and not refined. Disorder at the triflate anion, which was refined with alternative positions and with the use of geometrical constraints, and the likely presence of one MeCN molecule and one

Table 3 Details on the crystallographic studies

	Ligand 2	Ligand 3	[Zn ^{II} (2) ₂ (CF ₃ SO ₃) ₂]	[Cu ^{II} (2) ₂](CF ₃ SO ₃) ₂ ·CH ₃ CN·H ₂ O
Formula	C ₂₀ H ₁₅ N ₃ O ₂	C ₂₁ H ₁₇ N ₃ O ₂	C ₄₂ H ₃₀ F ₆ N ₆ O ₁₀ S ₂ Zn	C ₄₄ H ₃₀ CuF ₆ N ₆ O ₁₁ S ₂
<i>M_r</i>	329.35	343.38	1022.21	1060.43
Crystal colour	Yellow	Pale yellow	Colourless	Blue
Crystal size/mm	0.34 × 0.56 × 0.70	0.14 × 0.34 × 0.63	0.14 × 0.14 × 0.21	0.10 × 0.14 × 0.14
Crystal system	Monoclinic	Triclinic	Triclinic	Tetragonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 4 ₃ 2 ₁ 2
θ range for cell determination/ $^{\circ}$	6.51–10.58	5.43–11.00	4.89–9.64	5.53–9.84
<i>a</i> / \AA	9.756(3)	8.038(6)	9.357(4)	17.810(80)
<i>b</i> / \AA	13.355(6)	9.247(4)	14.954(5)	17.810(80)
<i>c</i> / \AA	12.837(6)	12.334(3)	16.129(3)	14.150(60)
α / $^{\circ}$	90	81.09(3)	77.93(2)	90
β / $^{\circ}$	109.57(3)	74.06(4)	84.33(3)	90
γ / $^{\circ}$	90	77.20(5)	79.44(3)	90
<i>V</i> / \AA^3	1575.9(12)	855.3(8)	2165.3(12)	4488(34)
<i>D_c</i> /g cm ⁻³	1.388	1.333	1.568	1.569
μ /mm ⁻¹	0.092	0.088	0.755	0.673
<i>T_{min}</i> , <i>T_{max}</i>	–	0.964, 0.988	0.881, 0.900	0.910, 0.935
Scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
θ range/ $^{\circ}$	2–30	2–30	2–30	2–25
Reflections measured	–13 < <i>h</i> < 13 0 < <i>k</i> < 18 0 < <i>l</i> < 18	–11 < <i>h</i> < 11 –12 < <i>k</i> < 12 0 < <i>l</i> < 17	–13 < <i>h</i> < 13 –21 < <i>k</i> < 21 0 < <i>l</i> < 22	0 < <i>h</i> < 21 0 < <i>k</i> < 21 0 < <i>l</i> < 16
Total reflns. measured	4769	5170	13017	4393
Unique reflns.	4585	4956	12582	2296
<i>R_{int}</i> ^a	0.0193	0.0141	0.1322	0.1691
<i>R₁</i> ^b (reflns.)	0.0469 (2609)	0.0536 (1920)	0.0882 (3220)	0.1677 (720)
<i>R_{all}</i>	0.1144	0.1778	0.3634	0.4202
<i>wR</i> _{2all}	0.1415	0.1671	0.2741	0.5012
GOF ^c	1.024	1.007	0.913	1.289
Refined parameters	286	303	604	116
Weighting scheme ^d	1/[$\sigma^2 F_o^2 + (0.055P)^2 + 0.242P$]	1/[$\sigma^2 F_o^2 + (0.060P)^2 + 0.018P$]	1/[$\sigma^2 F_o^2 + (0.095P)^2 + 0.00P$]	1/[$\sigma^2 F_o^2 + (0.200P)^2 + 0.00P$]
(Shift/esd) _{max}	0.000	0.000	0.000	0.005
Max., min. $\Delta\rho$ /e \AA^{-3}	0.185, –0.191	0.158, –0.162	0.700, –0.905	0.719, –0.534

^a $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (calculated on reflections with $I > 2\sigma(I)$). ^c $\text{GOF} = S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{0.5}$, where n is the number of reflections and p is the total number of parameters refined. ^d $P = [\text{Max}(F_o^2, 0) + 2F_c^2] / 3$

water molecule, not precisely located, contribute to the high final discrepancy factors. Attempts to refine the structure in lower-symmetry space groups were unsuccessful due to the low number of observed reflections. The crystal structure was described in the chiral space group $P4_32_1$; nevertheless, due to the low quality of data, Friedel's opposites were merged and no attempts to refine the Flack parameter were made.

Atomic scattering factors were taken from ref. 30. Diagrams of the molecular structures were produced by the ORTEP program.³¹

CCDC reference numbers 215887–215890.

See <http://www.rsc.org/suppdata/dt/b3/b308439f/> for crystallographic data in CIF or other electronic format.

Acknowledgements

The financial support by the Ministero dell'Istruzione, Università e Ricerca (MIUR–PRIN “Dispositivi Supramolecolari”) is gratefully acknowledged. The Authors thank Prof. L. Fabbri for fruitful discussions.

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