

Dendrimers as Ligands. Formation of a 2:1 Luminescent Complex between a Dendrimer with a 1,4,8,11-Tetraazacyclotetradecane (Cyclam) Core and Zn^{2+}

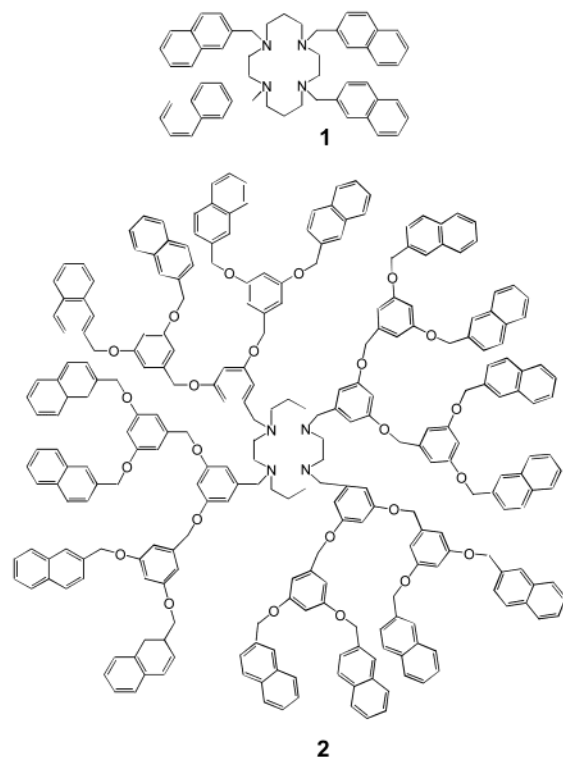
Christophe Saudan,[†] Vincenzo Balzani,^{*,†} Marius Gorka,[‡] Sang-Kyu Lee,[‡] Mauro Maestri,^{*,†} Veronica Vicinelli,[†] and Fritz Vögtle^{*,‡}

Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, Italy, and Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk Strasse 1, D-53121 Bonn, Germany

Received December 16, 2002; Revised Manuscript Received January 28, 2003; E-mail: vbalzani@ciam.unibo.it

Dendrimers¹ are currently attracting great attention because of their unusual and tunable chemical and physical properties and the wide range of potential applications. An important feature of dendrimers is the presence of dynamic internal cavities,² often containing moieties capable of coordinating metal ions. Perhaps surprisingly, exception being made for porphyrin-based dendrimers,³ only a few examples of dendrimers with a well-defined metal-coordinating core have been reported so far.⁴

1,4,8,11-Tetraazacyclotetradecane (cyclam) is one of the most extensively investigated ligands in coordination chemistry because it can coordinate a variety of metal ions to give very stable 1:1 complexes.^{5,6} Currently, cyclam and its derivatives are extensively investigated for medical applications.⁷



We thought that cyclam was a suitable and most interesting core for constructing dendrimers capable of coordinating metal ions. Therefore, we have synthesized⁸ a dendrimer (**2**) consisting of a cyclam core with appended 12 dimethoxybenzene and 16 naphthyl units, and we have investigated its complexation with Zn^{2+} in CH_3-

$CN-CH_2Cl_2$ 1:1 v/v. For comparison purposes, we have also investigated the complexation with Zn^{2+} of 1,4,8,11-tetrakis(naphthylmethyl) cyclam (**1**), which is known to form very stable 1:1 complexes with divalent metal ions.⁹ An important, common feature of model compound **1** and dendrimer ligand **2** is that their potentially fluorescent naphthyl units are quenched by exciplex formation with the cyclam nitrogens.

Complexation with Zn^{2+} , however, engages the nitrogen lone pairs and thereby prevents exciplex formation, with a resulting intense naphthyl fluorescence. This strong fluorescent signal is quite suitable for monitoring the formation of complexes in ligand/metal titration experiments. We have performed such titration experiments, and we have found that the model compound **1** gives a 1:1 complex with Zn^{2+} , $[Zn(\mathbf{1})]^{2+}$, whereas the dendrimer ligand **2** surprisingly gives a complex of 2:1 stoichiometry, $[Zn(\mathbf{2})_2]^{2+}$. This unexpected result has then been confirmed by ¹H NMR titrations.

All of the luminescence measurements were carried out in air-equilibrated $CH_3CN-CH_2Cl_2$ 1:1 v/v solution at 298 K with a Perkin-Elmer LS50 spectrofluorimeter. Compound **1** exhibits an emission band with a maximum around 480 nm, assigned to the formation of exciplexes between amine and excited naphthyl units (Figure 1a). Dendrimer **2** exhibits three types of weak emission bands, assigned to naphthyl-localized excited states ($\lambda_{max} = 337$ nm), naphthyl excimers (λ_{max} ca. 390 nm), and naphthyl-amine exciplexes ($\lambda_{max} = 480$ nm) (Figure 1b).

In $CH_3CN-CH_2Cl_2$ 1:1 v/v, titration of ligand **1** (2.93×10^{-5} M) with Zn^{2+} (as $CF_3SO_3^-$ salt) causes the disappearance of the exciplex emission and the appearance of a strong naphthyl-localized fluorescence (Figure 1a); the titration plot (Figure 2a) is linear and reaches a plateau after the addition of 1 equiv of Zn^{2+} , showing that a 1:1 complex is formed. The abrupt change in the slope of the titration curve at $[Zn^{2+}]/[\mathbf{1}] = 1$ shows that the $[Zn(\mathbf{1})]^{2+}$ complex is a highly stable species. Implementation of the spectral changes in the SPECFIT software¹⁰ yielded a value $>10^7$ M⁻¹ for the association constant, much larger than that exhibited in $CH_3-OH-CHCl_3$ 9:1 v/v.^{9b}

Titration of a (6.65×10^{-6} M) solution of **2** in $CH_3CN-CH_2Cl_2$ 1:1 v/v with Zn^{2+} causes the disappearance of the exciplex band, with a concomitant increase in the excimer and naphthyl-localized emissions (Figure 1b); the titration plot (Figure 2b) is again linear, but in this case it reaches a plateau for 0.5 equiv of Zn^{2+} , showing the unexpected formation of a $[Zn(\mathbf{2})_2]^{2+}$ species. Fitting of the data yielded a value $>10^{13}$ M⁻² for the formation constant of this complex.

¹H NMR experiments were carried out in $CD_3CN-CD_2Cl_2$ 1:1 v/v at 298 K with Bruker 400 MHz equipment on a 6.40×10^{-4} M solution of **2**. Upon addition of Zn^{2+} (as $CF_3SO_3^-$ salt), shifts were observed in the signals of the cyclam hydrogen atoms as well

[†] Università di Bologna.

[‡] Universität Bonn.

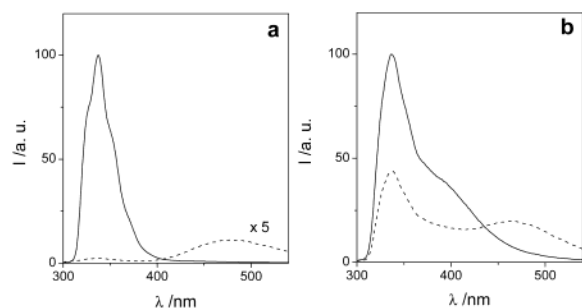


Figure 1. (a) Luminescence spectrum of **1** (2.93×10^{-5} M) before (dashed line) and after (full line) addition of a stoichiometric amount of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ ($\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ 1:1 v/v, 298 K, $\lambda_{\text{exc}} = 275$ nm). (b) Luminescence spectrum of **2** (6.65×10^{-6} M) before (dashed line) and after (full line) addition of a stoichiometric amount of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ ($\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ 1:1 v/v, 298 K, $\lambda_{\text{exc}} = 275$ nm).

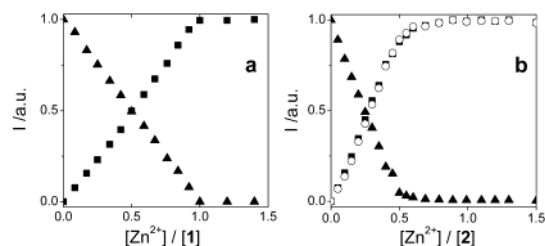


Figure 2. Normalized fluorescence intensity changes observed upon addition of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ to a 2.93×10^{-5} M solution of **1** and a 6.65×10^{-6} M solution of **2** ($\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ 1:1 v/v, 298 K, $\lambda_{\text{exc}} = 275$ nm). Emission intensity was monitored at 337 nm (■), 390 nm (○), and 480 nm (▲).

as on the signals of the $\text{Ar}-\text{CH}_2-\text{N}$ and the $\text{Ar}-\text{CH}_2-\text{O}-\text{Ar}$ hydrogens. All of the observed shifts lead to the conclusion that a $[\text{Zn}(\mathbf{2})_2]^{2+}$ species is indeed formed at the beginning of the titration. For example, in the $\text{Ar}-\text{CH}_2-\text{O}-\text{Ar}$ region, the uncomplexed dendrimer **2** shows a peak at 4.61 ppm, whose intensity decreases on increasing Zn^{2+} concentration and almost disappears for $[\text{Zn}^{2+}]/[\mathbf{2}] = 0.5$. Such a decrease is accompanied by the appearance of a new peak at 4.68 ppm which reaches a maximum for $[\text{Zn}^{2+}]/[\mathbf{2}] = 0.75$ and almost disappears for $[\text{Zn}^{2+}]/[\mathbf{2}] = 1.25$. For $[\text{Zn}^{2+}]/[\mathbf{2}] = 0.75$, a new peak begins to arise at 4.78 ppm, which becomes the most predominant one for $[\text{Zn}^{2+}]/[\mathbf{2}] = 1.25$. The peaks at 4.68 ppm can confidently be assigned to a $[\text{Zn}(\mathbf{2})_2]^{2+}$ complex that, at higher Zn^{2+} concentrations, is gradually replaced by a $[\text{Zn}(\mathbf{2})]^{2+}$ species. In the latter, the coordination sphere of Zn^{2+} is likely completed by counterions, whose concentration, of course, increases with increasing $[\text{Zn}^{2+}]$.

The formation of a highly stable $[\text{Zn}(\mathbf{2})_2]^{2+}$ species has been further confirmed by the fact that, for a solution containing **2** and Zn^{2+} in a 2:1 ratio, addition of trifluoroacetic acid does not cause any increase in the naphthyl-localized fluorescence, showing that all of the dendrimers are engaged with Zn^{2+} .

All of the complexes of cyclam and cyclam derivatives with metal ions reported so far in the literature have 1:1 stoichiometry.¹¹

The unexpected $[\text{Zn}(\mathbf{2})_2]^{2+}$ species formed by the cyclam dendritic ligand **2** shows that the dendrimer branches not only do not hinder, but in fact favor, coordination of cyclam to Zn^{2+} with respect to coordination of solvent molecules or counterions. Two limiting structures can be proposed for the $[\text{Zn}(\mathbf{2})_2]^{2+}$ complex: (i) an “inward” structure, in which the branches of the two coordinated dendrimers are intermeshed, or (ii) an outward structure, in which the branches of the two coordinated dendrimers do not interact. An “inward” structure for $[\text{Zn}(\mathbf{2})_2]^{2+}$ should increase the probability of excimer formation as compared with $[\text{Zn}(\mathbf{2})]^{2+}$. The results obtained (Figure 2b), however, do not show any evidence of increasing number of excimers on increasing Zn^{2+} concentration. It seems, therefore, more likely that the dendrimer branches extend outward and that the cyclam core is forced to adopt a structure in which only three N atoms are available for Zn^{2+} coordination.

The observed dendrimer effect may play an important role in various fields in which cyclam metal complexes and metal-containing dendrimers are currently employed, including abiological applications (e.g., catalysis) and medical diagnosis and therapy. A further motif of interest is offered by the possibility, currently under investigation in our laboratory, of assembling different cyclam-based dendrons around a metal ion to obtain mixed-(dendritic)-ligand complexes that might be very interesting for light-harvesting and multiredox processes.

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