Proton-Driven Self-Assembled Systems Based on Cyclam-Cored Dendrimers and [Ru(bpy)(CN)₄]²⁻

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Abstract: 1,4,8,11-Tetraazacyclotetradecane (cyclam), which is one of the most extensively investigated ligands in coordination chemistry, in its protonated forms, can play the role of host toward cyanide metal complexes. We have investigated the acid-driven adducts formed in acetonitrile−dichloromethane (1:1 v/v) solution by [Ru(bpy)(CN)₄]²⁻ with 1,4,8,11-tetrakis(naphthylmethyl)cyclam (**1**) and a dendrimer consisting of a cyclam core appended with 12 dimethoxybenzene and 16 naphthyl units (**2**). [Ru(bpy)(CN)₄]²⁻, **1**, and **2** exhibit characteristic absorption and emission bands, in distinct spectral regions, that are strongly affected by addition of acid. When a solution containing equimolar amounts of [Ru(bpy)(CN)₄]²⁻ and **1** or **2** is titrated by trifluoroacetic acid, or when [Ru(bpy)(CN)₄]²⁻ is titrated with (**1**·2H)²⁺ or (**2**·2H)²⁺, {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·**1**} or {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·**2**} adducts are formed in which the fluorescence of the naphthyl units is strongly quenched by very efficient energy transfer to the metal complex, as shown by the sensitized luminescence of the latter. The {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·**1**} and {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·**2**} adducts can be disrupted (i) by addition of a base (1,4-diazabicyclo[2.2.2]octane), yielding the starting species [Ru(bpy)(CN)₄]²⁻ and **1** or **2**, or (ii) by further addition of triflic acid, with formation of (**1**·2H)²⁺ or (**2**·2H)²⁺ and protonated forms of [Ru(bpy)(CN)₄]²⁻. It is shown that upon stimulation with two chemical inputs (acid and base) both {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·**1**} and {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·**2**} exhibit two distinct optical outputs (a naphthalene-based and a Ru(bpy)-based emission) that behave according to an XOR and an XNOR logic, respectively.

Introduction

Several interesting functions at the supramolecular level can be promoted by light excitation in both natural and artificial systems.[1,2] Photoisomerization reactions are at the basis of the natural visual processes[3] and are often used in artificial nanomachines to promote mechanical movements,[1a,2b,c,4] light signals can be used for information processing in artificial systems;[5−7] energy migration is exploited for light harvesting in natural[8] and artificial[9,10] antenna devices, and finally, photoinduced electron transfer is the basic process for the conversion of light into chemical energy in natural photosynthesis,[11] as well as in attempts to perform artificial photosynthesis.[12]

In most cases, the artificial systems used to produce light-induced functions consist of covalently linked components.[1,2,9,13] Covalent linkages allow preparation of chemically robust species in which the interaction is transmitted through well-defined pathways. Of considerable recent interest, however, is the study of the light-induced processes in assemblies in which the component parts can be self-assembled by exploiting relatively

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weak, noncovalent interactions.[10d,14,15] Molecular self-assembly is, in fact, a central concept to nature's forms and functions.[16]

The challenge for chemists engaged in artificial self-assembly processes resides in the "programming" of the system,[17,18] i.e., in the design of components which carry, within their structures, the pieces of information necessary not only for the construction of the desired supramolecular architecture but also for the performance of the required function. Since the function to be performed upon light excitation is often related to the occurrence of a reversible assembly/disassembly process,[18] the system has to be programmed so as to be able not only to *self-assemble* under thermodynamic control but also to *disassemble* under a suitable energy input. For information processing, even more interesting are those systems that are capable of existing in three or more forms that are interconverted by means of different stimuli.[19,20] In fact, systems which respond to a given combination of multiple stimuli open the way to more complex switches (logic gates) at the molecular scale.[5−7] From this viewpoint, fluorescence is an ideal output because of its ease of detection even at the single-molecule limit.[21] Another remarkable feature of fluorescent signals is that they do not need to be wired to operate. Light can indeed bridge the gap between the world of molecules and our macroscopic world.[22]

Here we report the results of an investigation carried out on the assembly/disassembly of the luminescent dendritic hosts **1** and **2** with the luminescent metal complex $[Ru(bpy)(CN)_4]^{2-}$ (Chart 1). The assembly process is proton driven and leads to formation of $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot \mathbf{1}\}$ and $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot \mathbf{2}\}$ adducts with strong effects on the luminescence properties. The adducts can then be disassembled by addition of either a base, namely, 1,4-diazabicyclo[2.2.2]octane (DABCO), or an excess of triflic acid, giving rise to two different optical outputs that behave according to an XOR and an XNOR logic.

Experimental Section

High-purity trifluoroacetic (CF_3COOH) and triflic (CF_3SO_3H) acids and DABCO were purchased from Aldrich and used without further purification.

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Chart 1

$[Ru(bpy)(CN)_4]^{2-}$

1

2
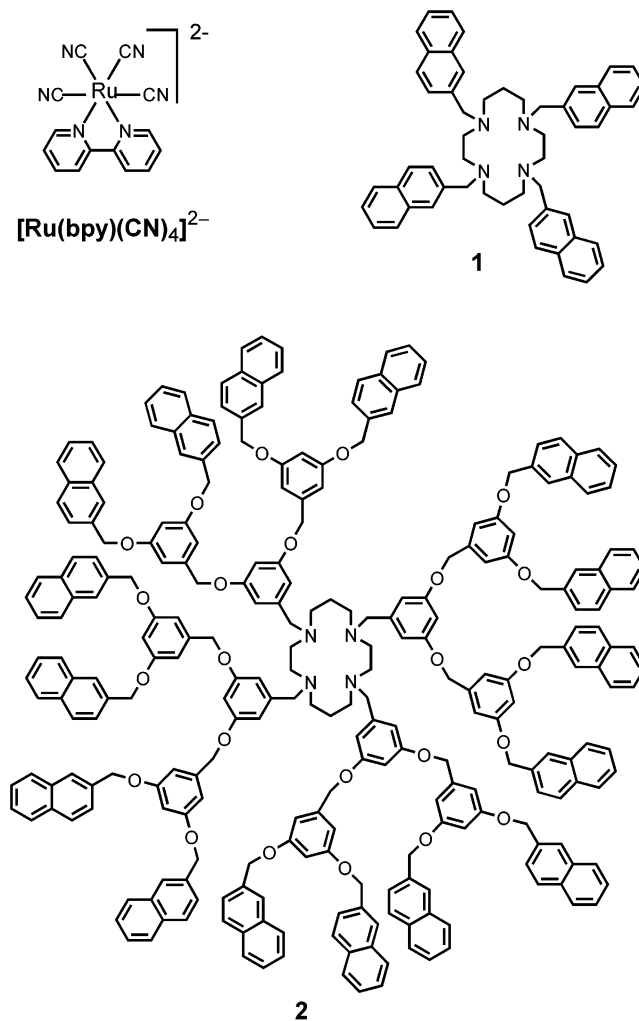
1,4,8,11-Tetrakis(2-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane (**1**) and 1,4,8,11-tetra-3,5-bis[3′,5′-bis(2″-oxymethylnaphthyl)-benzyloxy]benzyl-1,4,8,11-tetraazacyclotetradecane (**2**) have been prepared as previously described.[23]

$[Ru(bpy)(CN)_4]^{2-}$ (as a tetrabutylammonium salt) was kindly supplied by Prof. M. T. Indelli, University of Ferrara.

Photophysical Experiments. The experiments were carried out in air-equilibrated acetonitrile/dichloromethane (1:1 v/v) solution at 298 K. Absorption and emission spectra were recorded by a Perkin-Elmer λ 40 spectrophotometer and a Perkin-Elmer LS50 spectrofluorimeter. Titration curves were obtained by implementing the spectra into the SPECFIT software.[24] The estimated experimental errors are ±2 nm on the band maximum, ±5% on the molar absorption coefficient, and ±10% on the relative luminescence intensity.

Results and Discussion

Dendrimers 1 and 2. Dendrimers **1** and **2** (Chart 1) consist of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core, which is one of the most extensively investigated ligands in coordination chemistry, appended with four naphthyl units (**1**) and 12 dimethoxybenzene and 16 naphthyl units (**2**). The absorption and luminescence spectra of these host compounds in

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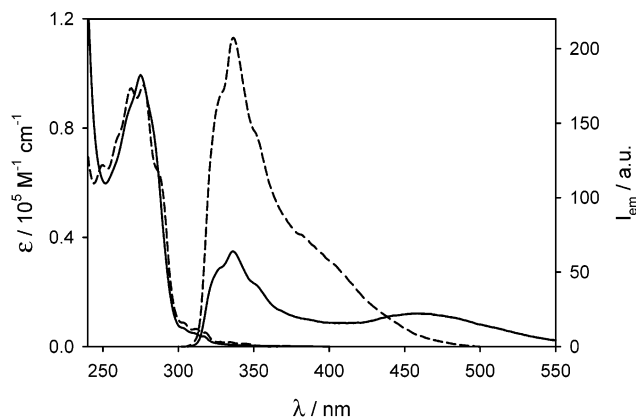
Figure 1. Absorption and emission spectra of dendrimer **2** in acetonitrile−dichloromethane (1:1 v/v) solution at 298 K before (solid line) and after (dashed line) addition of 2 equiv of trifluoroacetic acid. The emission intensities are directly comparable since in all cases the excitation wavelength was 275 nm, the absorbance of the solution at the excitation wavelength was 0.50, and the same experimental setup was used.

Figure 2. Changes observed in the absorption spectrum of $[Ru(bpy)(CN)_4]^{2-}$ (2.25×10^{-5} M) in acetonitrile−dichloromethane (1:1 v/v) solution at 298 K upon addition of trifluoroacetic acid. The thick solid line is the spectrum before acid addition, and the thick dashed line the spectrum obtained after addition of 1 equiv of acid. The inset shows the normalized absorbance changes at 318 (○) and 535 nm (■).

acetonitrile−dichloromethane (1:1 v/v) solution have been previously investigated.[23] In both **1** and **2** the naphthalene-type fluorescence at 335 nm is strongly quenched by the cyclam amine units via formation of intramolecular exciplexes which are responsible for the broad emission bands with a maximum at about 460 nm. The emission spectrum of **2** (Figure 1) shows an additional weak band in the 400 nm region, overlapped with the other two bands, assigned to naphthyl excimers.[23]

Cyclam undergoes protonation in aqueous solution[25] as well as in other solvents.[26] It is well-known that protonation of amines engages the lone pair of the nitrogen atoms and therefore moves the n(N) → π* charge-transfer (CT) transitions to higher energy. The very small change of the absorption spectrum of **2** upon addition of trifluoroacetic acid (Figure 1) shows that the interaction between amine and aromatic moieties in the ground state is negligible. Addition of trifluoroacetic acid, however, causes strong changes in the emission spectra of **1** and **2**. The spectrum obtained at the end of acid titration for dendrimer **2** is shown in Figure 1. Comparison with the spectrum recorded before acid addition shows that protonation causes (i) the disappearance of the exciplex band with a maximum around 460 nm, (ii) a strong increase in the intensities of the naphthyl localized band with $\lambda_{max} = 335$ nm, and (iii) an increase in the intensity of the excimer band around 400 nm. It is worth noting that the spectral changes take place only during the addition of the first 2 equiv of acid. These results show that (i) under our experimental conditions, the tetramine cyclam core undergoes only two protonation reactions under the applied conditions and (ii) addition of 2 equiv of acid prevents exciplex formation. Analysis of the titration plots by the SPECFIT software[24] yielded the following values for the first two acidity constants: $pK_{a1} = 8.0$ and $pK_{a2} = 6.2$ for compound **1**, and $pK_{a1} = 8.0$ and $pK_{a2} = 6.9$ for compound **2**.

$[Ru(bpy)(CN)_4]^{2-}$. The absorption and emission spectra of this complex have been thoroughly investigated by Scandola and co-workers in water and acid solution.[27] The low-energy
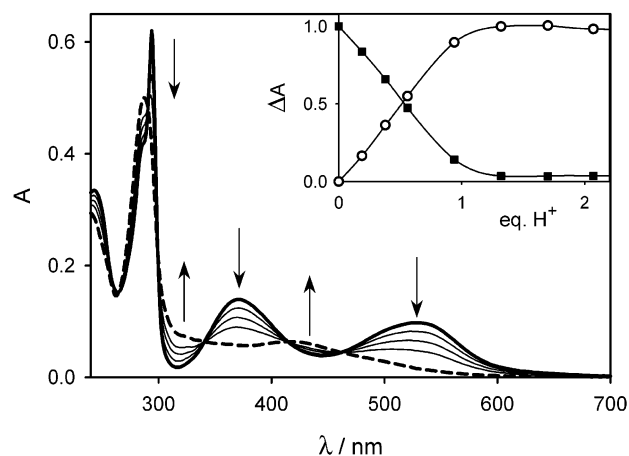
absorption bands and the weak luminescence band exhibited in the visible region are related to metal-to-ligand (bpy) charge-transfer (MLCT) excited states (spin-allowed states for the absorption bands, the lowest spin-forbidden state for the emission band). The energies of these excited states are strongly dependent on the interaction of the CN⁻ ligands with solvents or protons. In aqueous solution, addition of sulfuric acid starting from pH 3 causes successive protonation of the four CN⁻ ligands as shown by the progressive displacement of the absorption and emission bands to higher energies. The four protonation steps, however, are not separable, and no definite emission spectra for the various protonated forms can be obtained.[27b]

In acetonitrile−dichloromethane (1:1 v/v) solution, $[Ru(bpy)(CN)_4]^{2-}$ shows two moderately intense MLCT absorption bands at 373 and 535 nm (Figure 2) and a very weak emission band at 770 nm (Figure 3). Upon titration with trifluoroacetic acid, the absorption bands move to higher energies with an isosbestic point that is maintained until 1 equiv of acid has been added. Strong changes are also observed in the emission spectra (Figure 3) where a band arises at 630 nm upon addition of acid. The intensity of such a band increases linearly up to a plateau value that is reached at about 1 equiv of acid. Addition of large amounts of acid causes further changes in the absorption spectra with a second family of isosbestic points, and the corresponding emission band further shifts to higher energy and increases in intensity. Analysis by the SPECFIT software[24] of the titration plots shown in the insets of Figures 2 and 3 yielded the following values for the first and second acidity constants: $pK_{a1} = 7.1$, $pK_{a2} = $ ca. 4.[28]

Assembly. Formation of adducts between protonated polyazamacrocycles and $[Ru(bpy)(CN)_4]^{2-}$ was previously exploited for promoting intercomponent energy-transfer processes.[29] The

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(28) The reported value for pK_{a2} is a rough estimate since the second protonation step is not well resolved from the following ones.[27c]

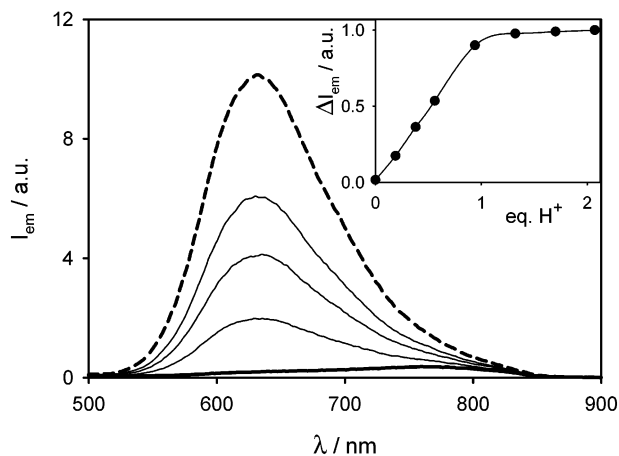**Figure 3.** Changes observed in the emission spectrum of $[Ru(bpy)(CN)_4]^{2-}$ (2.25×10^{-5} M) in acetonitrile−dichloromethane (1:1 v/v) solution at 298 K upon addition of trifluoroacetic acid. The thick solid line is the spectrum before acid addition, and the thick dashed line the spectrum obtained after addition of 1 equiv of acid. The inset shows the normalized intensity changes at 630 nm. $\lambda_{ex} = 300$ nm.

aims of our study were (i) to see whether the cyclam core of dendrimers is accessible to large potential guests, (ii) to understand whether the excitation energy collected by the dendrimer chromophoric units can be funneled to such a guest, and (iii) to explore whether the effect of adduct assembly/disassembly on the luminescence properties could be used for light-signal processing. Since the behaviors of the two examined systems $[Ru(bpy)(CN)_4]^{2-}$ and **1** and $[Ru(bpy)(CN)_4]^{2-}$ and **2** are quite similar, we will mainly concentrate our discussion on that involving dendrimer **2**.

The absorption spectrum of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **2** (3.0×10^{-5} M) is displayed in Figure 4. Comparison with the spectra of the two separated components (Figures 1 and 2) shows that there is no interaction between the two compounds in the ground state. Lack of interaction in the excited state, as well, is demonstrated by the emission spectrum (Figure 5), which exhibits the characteristic bands of the isolated dendrimer (Figure 1) and metal complex (Figure 3).

Titration of the above-mentioned mixture with trifluoroacetic acid causes strong changes in the absorption and emission spectra. In the absorption spectrum (Figure 4) the two bands of $[Ru(bpy)(CN)_4]^{2-}$ at 373 and 535 nm move to higher energies (345 and 476 nm), but less than in the case of protonation (Figure 2), and isosbestic points are maintained up to the addition of 2 equiv of acid. These results suggest that addition of acid promotes association of $[Ru(bpy)(CN)_4]^{2-}$ and **2** and that after addition of 2 equiv of protons a $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot2\}$ adduct is formed, where the two protons bridge the cyclam core of the dendrimer to the CN^- ligands of the metal complex (Figure 7). The behavior of the emission spectrum upon acid addition (Figures 5 and 6) confirms the hypothesis of the proton-driven formation of an adduct between $[Ru(bpy)(CN)_4]^{2-}$ and **2**. Addition of acid up to 2 equiv to the 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **2** causes a decrease of the exciplex band at 450 nm which is accompanied by a decrease of the naphthyl
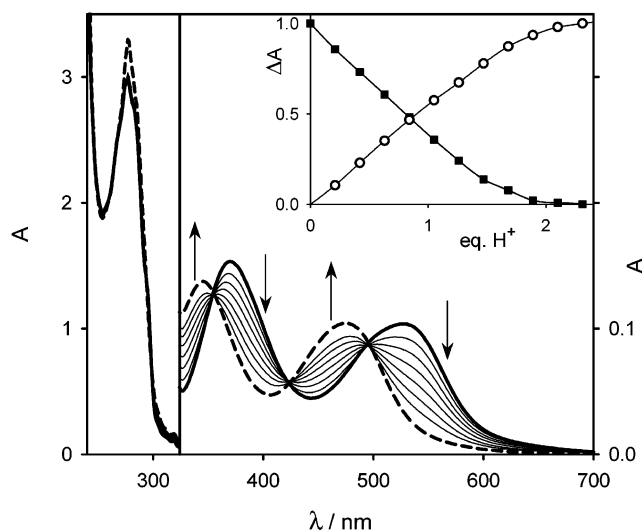
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Figure 4. Changes observed in the absorption spectrum of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **2** (3.0×10^{-5} M) in acetonitrile−dichloromethane (1:1 v/v) solution at 298 K upon addition of trifluoroacetic acid. The thick solid line is the spectrum before acid addition, and the thick dashed line the spectrum obtained after addition of 2 equiv of acid. The inset shows the normalized absorbance changes at 445 (○) and 535 nm (■). Note the different absorbance scales for the left and right parts of the figure.
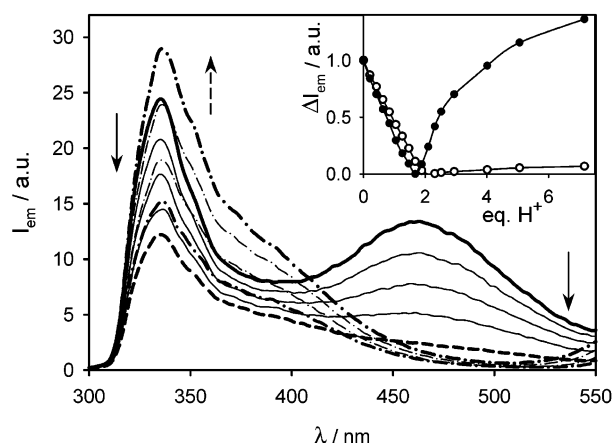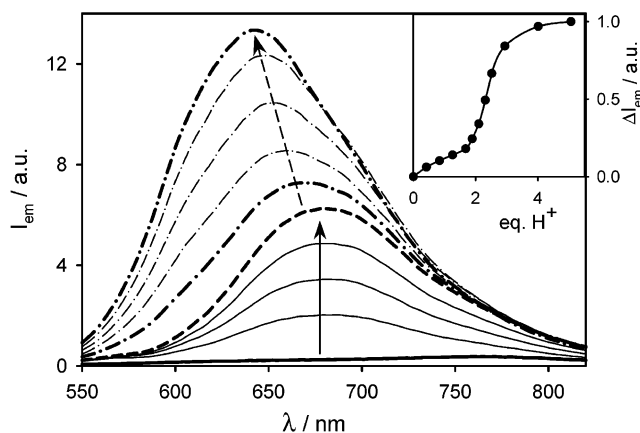

Figure 5. Changes in the emission spectra in the naphthyl region of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **2** (3.0×10^{-5} M) in acetonitrile−dichloromethane (1:1 v/v) solution at 298 K upon addition of trifluoroacetic acid: 0 equiv (thick solid line), 2 equiv (thick dashed line), 2.5−6 equiv (dashed−dotted line). $\lambda_{ex} = 288$ nm. The inset shows the normalized intensity changes at 335 (●) and 460 nm (○).

band at 335 nm (Figure 5; excitation was performed at 288 nm, where ca. 80% of the absorbed light causes naphthyl excitation). Such a behavior is different from that observed upon addition of acid to a solution containing **2** alone (decrease of the exciplex band and increase of the naphthyl band, Figure 1). On excitation at 490 nm (where 100% of the absorbed light causes excitation of the metal complex), addition of acid causes the appearance of a band with a maximum around 680 nm (Figure 6), redshifted compared with the band originated by addition of acid to $[Ru(bpy)(CN)_4]^{2-}$ alone (Figure 3).

We have also performed titrations of $[Ru(bpy)(CN)_4]^{2-}$ solutions by the diprotonated forms of **1** and **2**, namely, $(1\cdot2H)^{2+}$ and $(2\cdot2H)^{2+}$. The results obtained were fully consistent with those reported above. The absorption bands were displaced to higher energies, isosbestic points were observed up to the addition of ca. 1 equiv of $(2\cdot2H)^{2+}$, and the absorption spectrum after addition of 1 equiv of $(2\cdot2H)^{2+}$ was equal to

Figure 6. Changes in the emission spectra in the $[Ru(bpy)(CN)_4]^{2-}$ region of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **2** (3.0×10^{-5} M) in acetonitrile–dichloromethane (1:1 v/v) solution at 298 K upon addition of trifluoroacetic acid: 0 equiv (thick solid line), 2 equiv (thick dashed line), 2.5–6 equiv (dashed–dotted line). $\lambda_{ex} = 490$ nm. The inset shows the normalized intensity changes at 620 nm.
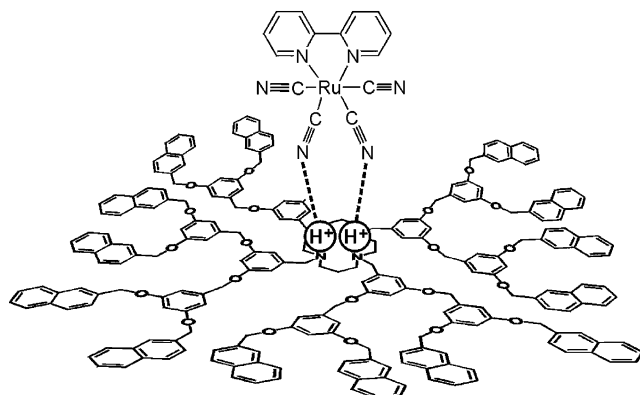

Figure 7. Schematic representation of the $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 2\}$ adduct.

that obtained upon addition of 2 equiv of H^+ to the 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **2** (Figure 4). Similar results were obtained when $(1 \cdot 2H)^{2+}$ was used in the place of $(2 \cdot 2H)^{2+}$.

Indeed, all the results obtained are consistent with formation of $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 1\}$ and $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 2\}$ adducts. In such assemblies, the Ru complex must share the protons with the cyclam core of the dendrimer (Figure 7), which explains why the absorption and emission bands of the metal complex are less shifted to higher energies than those of the protonated metal complex. As far as luminescence is concerned (Figure 5), on adduct formation the exciplex band of the dendrimer decreases because the cyclam core shares protons with the metal complex; however, the intensity of the naphthyl band does not increase, as would be expected upon disappearance of the exciplex, but decreases (to 15% of that of the fully protonated species). This shows that a new deactivation channel, namely, energy transfer to the lower lying excited state of the metal complex, is available for deactivation of the naphthyl units in the adduct. To estimate the energy-transfer efficiency, we prepared two solutions of $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 2\}$ of different concentrations, exhibiting the same absorbances at 287 and 374 nm. Excitation of these solutions mainly in the naphthyl bands (at 287 nm) and in the MLCT bands (at 374 nm) shows a metal complex emission intensity at 680 nm that is 88% lower

in the former compared to the latter case.[30] Taking into account that 20% of the light is directly absorbed by the Ru complex at 287 nm, it follows that the intraadduct energy-transfer efficiency is 85%. In the case of compound **1**, the behavior is qualitatively similar, but the energy-transfer efficiency is higher, ca. 100%. In conclusion, both dendrimers play the role of light-harvesting hosts that, in the adducts, transfer the collected energy to the metal complex guest.

Disassembly. The above-described spectral changes upon acid titration are fully reversed by successive addition of a stoichiometric amount of a base, namely, DABCO, indicating an assembly/disassembly reversible behavior.

We have also found that, upon further addition of an excess of acid to $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 1\}$ and $\{[Ru(bpy)-(CN)_4]^{2-} \cdot (2H^+) \cdot 2\}$, novel spectral changes are observed. For example, the isosbestic points of the absorption spectra disappear, the intensity of the naphthyl-type emission at 335 nm increases (Figure 5), and the metal complex based emission at 680 nm increases in intensity and moves to higher energies (Figure 6). This behavior can be easily explained considering that both $[Ru(bpy)(CN)_4]^{2-}$ and **2** (or **1**) are Lewis bases, so that when excess acid is present they do not need to share protons, but they are stabilized as independent protonated species, namely, $[Ru(bpy)(CN)_{2-n}(CNH)_{2+n}]^{n+}$ (n from 0 to 2) and $(2 \cdot 2H)^{2+}$ or $(1 \cdot 2H)^{2+}$ species. As shown by the inset to Figure 5, adduct formation between $[Ru(bpy)(CN)_4]^{2-}$ and **2** upon acid addition exhibits an *on–off–on* behavior; i.e., the system performs as a luminescent threshold[31] device.

Energy transfer from a dendritic host to guest molecules or metal ions has already been reported,[10d,15a,32] as well as reversible assembly and disassembly of the supramolecular system. For example, in a dendrimer consisting of a hexamine core surrounded by 8 dansyl-, 24 dimethoxybenzene-, and 32 naphthalene-type units,[10d] a very efficient energy transfer takes place from all the chromophoric groups of the dendrimer to an eosin guest molecule. In such a system, assembly requires extraction of eosin from acidic (pH 5–7) aqueous solution by shaking with a dichloromethane solution of the dendrimer, and disassembly requires shaking a dichloromethane solution of the adduct with a basic (pH > 12) aqueous solution. Clearly, the assembly/disassembly process is much easier in the present system.

In conclusion, the $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 1\}$ and $\{[Ru(bpy)-(CN)_4]^{2-} \cdot (2H^+) \cdot 2\}$ adducts can be disrupted (i) by addition of a base (DABCO), yielding the starting species $[Ru(bpy)(CN)_4]^{2-}$ and **1** or **2**, or (ii) by addition of triflic acid, with formation of $(1 \cdot 2H)^{2+}$ or $(2 \cdot 2H)^{2+}$ and protonated forms of $[Ru(bpy)(CN)_4]^{2-}$. This means that the adducts behave as systems that respond to two different chemical inputs.

Light-Signal Processes. Upon 270 nm excitation (90% of the light is absorbed by naphthyl units), a solution of the $\{[Ru(bpy)(CN)_4]^{2-} \cdot (2H^+) \cdot 2\}$ adduct (3.0×10^{-5} M) shows emission bands at 335 and 680 nm (Figures 5 and 6). The intensities of these two optical channels (outputs) change upon addition of base or acid (inputs) as shown in Table 1. Let us

(30) The emission intensity signals were corrected for the number of exciting photons by using $[Ru(bpy)_3]^{2+}$ as a standard.
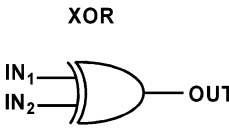
(31) For an interesting example of threshold devices, see, e.g.: Pina, F.; Melo, M. J.; Maestri, M.; Passaniti, P.; Balzani, V. *J. Am. Chem. Soc.* **2000**, *122*, 4496.

(32) (a) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286. (b) Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489. (c) Kawa, M.; Takahagi, T. *Chem. Mater.* **2004**, *16*, 2282.

Table 1. Emission Intensities of {[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} under Different Experimental Conditions in Acetonitrile−Dichloromethane (1:1 v/v) Solution

compound	$I_{335\ nm}$/au	$I_{680\ nm}$/au
{[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**}	12	3.2
{[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} + base[a]	29	0.4
{[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} + acid[b]	76	0.2
{[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} + acid[a] + base[b]	15	2.8

[a] DABCO, 30 equiv. [b] Triflic acid, 30 equiv.
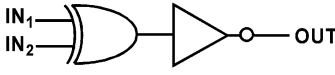
Figure 8. Truth table and symbol of the (a) XOR and (b) XNOR logic gates.

consider first emission at 335 nm. In a binary logic scheme,[5−7] a threshold value of 25 can be fixed for the emission intensity, and in a positive logic convention, a 0 can be used to represent a signal that is below the threshold value and a 1 can be employed to indicate a signal that is above. We can thus write the truth table shown in Figure 8a, which shows that the system behaves as an XOR logic gate. Conversely, one can monitor the emission at 680 nm, establish a threshold value of 1.5 for the emission intensity, and use a 0 and a 1 to indicate intensity values below and above the threshold value, respectively. The truth table reported in Figure 8b shows that using this output channel the system behaves as an XNOR logic gate.

Conclusions

We have shown that the luminescent cyclam-based hosts **1** and **2** can be assembled with the luminescent metal complex [Ru(bpy)(CN)$_4$]$^{2-}$ by a proton-driven process that causes strong changes in the luminescence properties. In the {[Ru(bpy)-(CN)$_4$]$^{2-}$·(2H$^+$)·**1**} and {[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} adducts formed in this way, very efficient energy transfer takes place from the naphthyl units of **1** and **2** to the metal complex.

We have also shown that the {[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**1**} and {[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} adducts can be disrupted by two distinct chemical inputs, namely, addition of DABCO, yielding the starting species [Ru(bpy)(CN)$_4$]$^{2-}$ and **1** or **2**, or addition of triflic acid, with formation of (**1**·2H)$^{2+}$ or (**2**·2H)$^{2+}$ and protonated forms of [Ru(bpy)(CN)$_4$]$^{2-}$. Such processes cause strong changes in the luminescent properties. In particular, in the case of {[Ru(bpy)(CN)$_4$]$^{2-}$·(2H$^+$)·**2**} there are two optical output channels, emission at 335 and 680 nm, that behave as XOR and XNOR logic gates, respectively.

A large number of dendrimers playing the role of antennae for light harvesting have been reported in the literature.[10] The system investigated in this study is an example of a light-harvesting antenna in which the energy-collecting units can be reversibly assembled to/disassembled from the dendrimer core.[29b,c] This behavior introduces more flexibility in view of the construction of systems useful for artificial photosynthesis.