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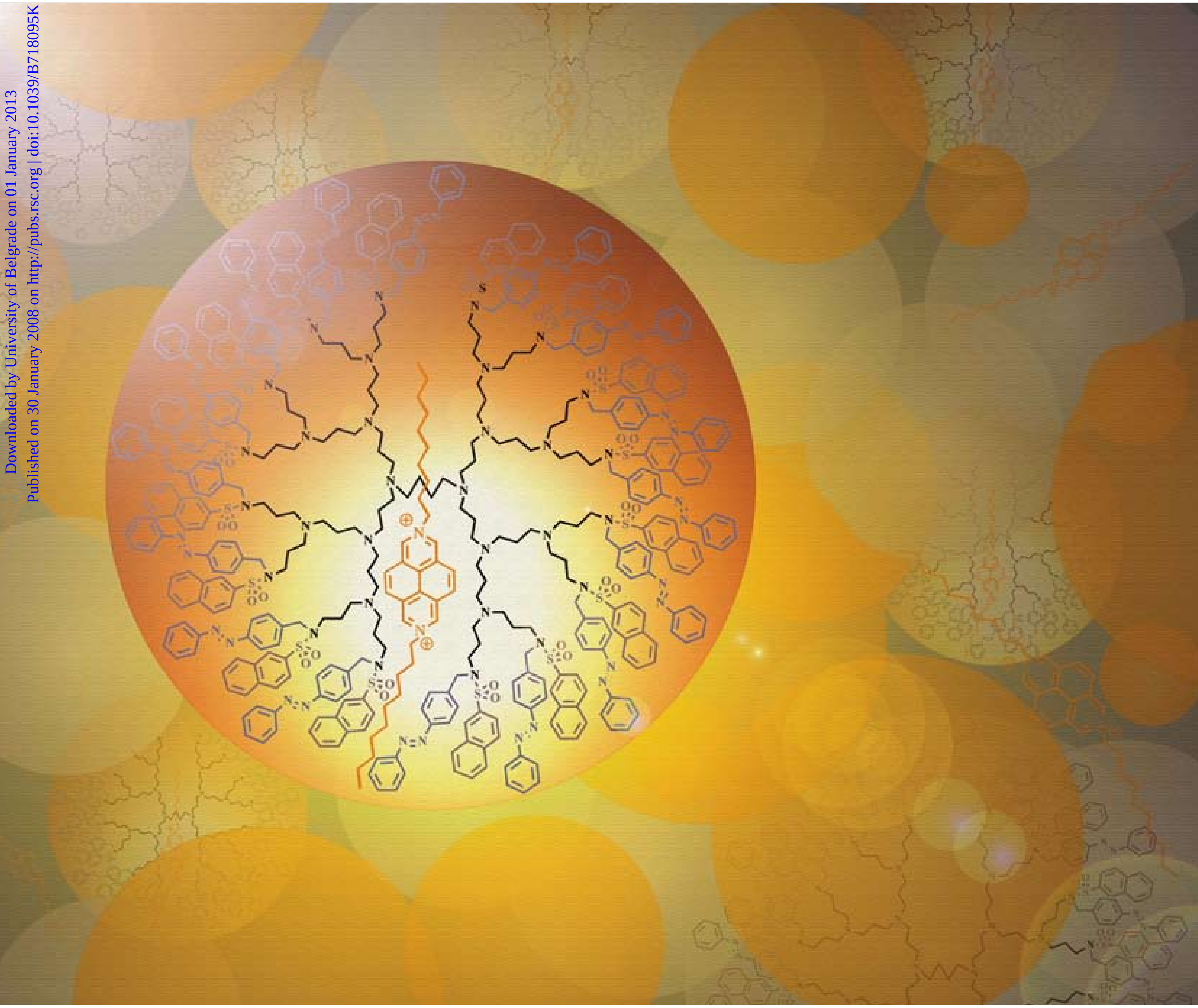

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PAPER

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A fluorescent guest encapsulated by a photoreactive azobenzene dendrimer

A fluorescent guest encapsulated by a photoreactive azobenzene dendrimer

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We have studied the adduct formed by *N*,*N'*-2,7-didecyldiazapyrenium ($\mathbf{P}^{2+}$), as the hexafluorophosphate salt, with a third generation dendrimer (**D**) that comprises 14 tertiary amine units in the interior, and 16 naphthyl and 16 *trans*-azobenzene units in the periphery. A strong charge-transfer interaction between the electron-accepting diazapyrenium dication and electron-donating amine units of the dendrimer interior leads to a host–guest complex with 1 : 1 stoichiometry, namely $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$. The self-assembly process can be easily monitored by strong changes in the absorption and emission spectra: (i) new absorption bands ($\lambda_{max} \approx 445$ and 565 nm) at lower energy compared to the isolated species arise, (ii) a strong quenching of the intense diazapyrenium fluorescence is observed, and (iii) a new broad emission band, typical of the charge-transfer complex, appears with a maximum at 660 nm at 298 K and 600 nm at 77 K. By global analysis of the absorption spectra, an association constant of 1.0×10^6 M^{-1} is obtained for $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$, compared to 3.0×10^4 M^{-1} in the case of the adduct of $\mathbf{P}^{2+}$ with triethylamine under the same experimental conditions. This result demonstrates that the presence of bulky substituents at the dendrimer periphery does not hinder the formation of a stable complex and suggests a cooperative effect due to the multiple amine groups of the dendrimer branching points. No energy transfer from the azobenzene or naphthyl chromophores to the charge-transfer complex has been evidenced. The self-assembly process can be reversed upon addition of an equimolar amount of trifluoromethanesulfonic acid. An adduct with 1 : 1 stoichiometry is formed also between $\mathbf{P}^{2+}$ and **D**(2t14c), a species obtained from **D**(16t) upon irradiation at 365 nm: the corresponding association constant is very similar to that of $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$, showing that the isomeric state of the peripheral azobenzene units does not affect the stability of the adduct.

Introduction

Dendrimers[1] are monodisperse macromolecules in which all bonds emerge radially from the core with a regular branching pattern. They have a well-defined composition; proper chemical units can be placed in their core, branching points or periphery in order to obtain the desired chemical functions. Therefore, dendrimers are currently attracting increasing attention for a wide range of potential applications in such different fields as medicine, biology, chemistry, physics, and engineering.[2]

Because of their tree-like and, usually, quite flexible structure, dendrimers present internal dynamic cavities in which they can host small molecules or ions.[3,4] The self-assembling process may also take advantage of cooperative effects due to multiple interacting units offered by the dendritic structure,[5] compared to a simple host, constituted by a single recognition unit.

The presence of photoactive components in the dendrimer and/or in the encapsulated guest offers numerous advantages:[6] (i) luminescent units are useful to get information on the dendrimer structure and on the self-assembling process; (ii) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting, and sensing with signal amplification, and (iii) photochemical reactions can change the structure and other properties of dendrimers.

In the present work, we have investigated the interaction of a third generation dendrimer of the poly(propylene amine) family functionalized with naphthyl and *trans*-azobenzene units (**D**(16t) in Scheme 1)[7] and *N*,*N'*-2,7-didecyldiazapyrenium ($\mathbf{P}^{2+}$, Scheme 1, hereafter called diazapyrenium), as the hexafluorophosphate salt, to give a self-assembled structure. The investigated dendrimer comprises 14 tertiary amine units in the interior, and 16 naphthyl and 16 *trans*-azobenzene units in the periphery.

Azobenzene units are interesting photoactive components since they undergo an efficient and fully reversible photoisomerization reaction. Furthermore, isomerization of azobenzene units involves a large structural rearrangement, since in

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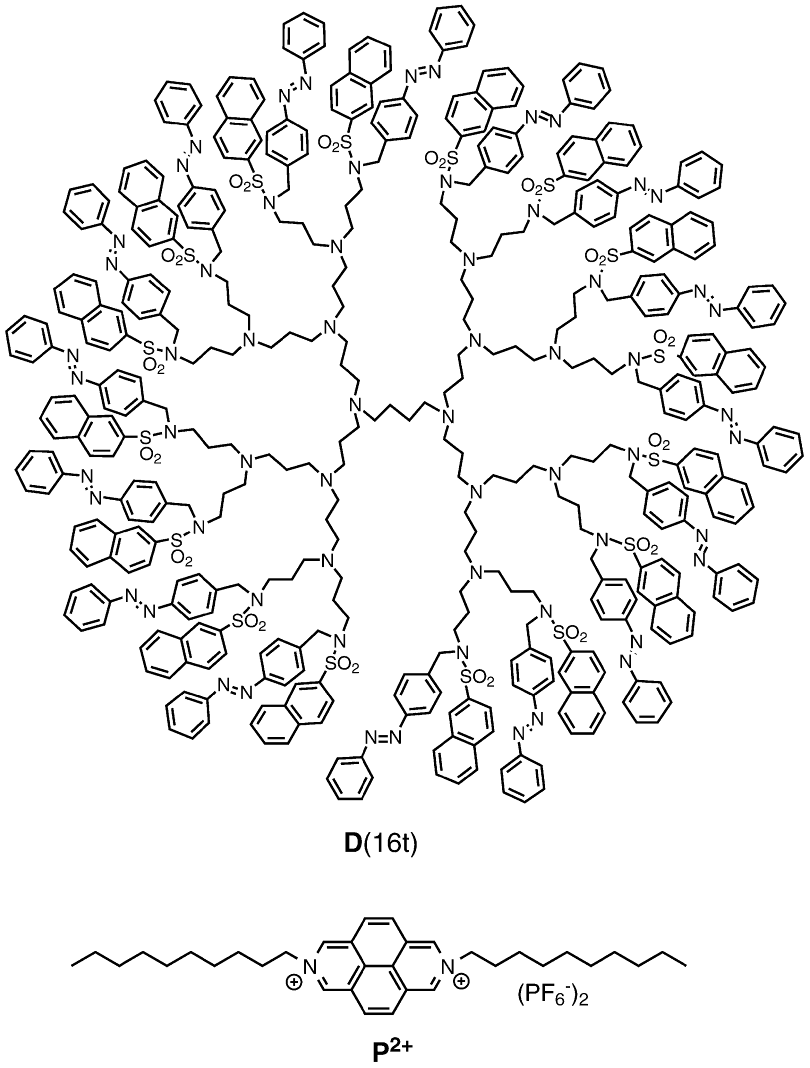

D(16t)

P^{2+}

Scheme 1

going from the *trans* to the *cis* isomer the distance between the *para* carbon atoms of azobenzene decreases from 9 to 5.5 Å and the dipole moment increases from zero (since the *trans* form is planar and symmetric) to 3.0 D.[8] Functionalizing dendrimers with azobenzene groups[9] in the core, branching points or periphery leads to systems able to modify their structure and flexibility according to the isomerization state of the azobenzene units. In particular, structural changes in the peripheral units of a dendrimer can modify the surface properties and cause rearrangements in the internal cavities. In turn, modification of the internal cavities may affect the hosting ability of a dendrimer, as previously observed for the fourth generation dendrimer of the same family acting as a host for dye molecules.[10]

Diazapyrenium chromophore is highly luminescent and presents a very strong electron acceptor character.[11,12] For these reasons it is extensively used in the construction of supramolecular systems, like pseudorotaxanes,[13] catenanes[14] and rotaxane.[14c] It is able to form a complex with amine groups, as a result mainly of charge-transfer interactions. This property, together with the high luminescence quantum yield, has been exploited in the study of the interaction with DNA, and in particular with adenine.[15]

Self-assembly between a diazapyrenium chromophore and a poly(propylene amine) dendrimer functionalized with azobenzene units leads to an interesting supramolecular structure with the possibility of: (i) cooperative effects in the association, (ii) photoinduced energy or electron transfer processes within the adduct, and (iii) modulation of the properties of the resulting adduct upon changing the isomeric state of the peripheral azobenzene units.

Results and discussion

Photophysical properties of dendrimer D(16t) and P^{2+}

Dendrimer **D**(16t) (Scheme 1) contains potentially fluorescent and photoreactive units, naphthyl and azobenzene groups, respectively. Its absorption spectrum (solid line in Fig. 1) is dominated by the azobenzene ππ* ($\lambda_{\max}$ = 325 nm) and nπ* ($\lambda_{\max}$ = 440 nm) absorption bands. The naphthalene chromophore presents structured absorption bands around 270 nm

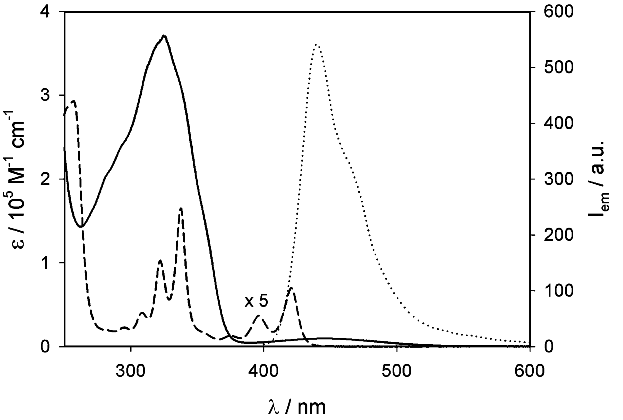

Fig. 1 Absorption spectra of **D**(16t) (solid line) and $\mathbf{P}^{2+}$ (dashed line) in dichloromethane solution. For clarity, the spectrum of $\mathbf{P}^{2+}$ has been multiplied by 5. Emission spectrum of $\mathbf{P}^{2+}$ (dotted line) in dichloromethane solution (λ_{ex} = 360 nm).

($S_0 \rightarrow S_2$ transition) and 310 nm ($S_0 \rightarrow S_1$ transition):[16] the former can be recognized superimposed on the much stronger azobenzene ππ* band at 325 nm, while the latter is completely covered by azobenzene absorption. The fluorescence of the naphthalene units is strongly quenched by the tertiary amines (*via* electron transfer) as well as by the *trans*- and *cis*-azobenzene units (*via* energy transfer).[7]

$\mathbf{P}^{2+}$ shows two intense and structured absorption bands (dashed line in Fig. 1) with maxima at 338 and 421 nm, assigned to ππ* states and an intense and structured fluorescence band with a maximum at 440 nm (dotted line in Fig. 1).[12]

Photochemical properties of dendrimer D

Irradiation at 365 nm of a dichloromethane solution of **D**(16t) at 298 K leads to strong spectral changes, as expected for the *trans* → *cis* photoisomerization of the azobenzene moieties. On continued irradiation, a photostationary state is reached, in which a species containing, as an average, two *trans* and 14 *cis* azobenzene units, **D**(2t14c), is formed. The initial **D**(16t) species can be completely recovered by keeping the solution in the dark. The thermal *cis* → *trans* reaction at 298 K is very slow ($t_{1/2}$ > 24 h), so that the **D**(2t14c) species can be studied as a potential host.

Both *trans* → *cis* photoisomerization quantum yield (upon irradiation at 365 nm) and the kinetics of thermal *cis* → *trans* reaction at 323 K are very similar to those of the model azobenzene compound. This behaviour is expected on the basis of the results previously reported for the larger fourth generation dendrimer.[7]

Adduct formation between D and $\mathbf{P}^{2+}$

Upon titration of a 5 × 10^{-6} M dichloromethane solution of **D**(16t) with a 5 × 10^{-4} M dichloromethane solution of $\mathbf{P}^{2+}$, absorption spectra show a broadening of the lowest energy absorption bands of the $\mathbf{P}^{2+}$ chromophore and the increase of new bands at lower energy ($\lambda_{max} \approx$ 445 and 565 nm) compared to those of both the starting species (Fig. 2). A plot of the absorption changes at 565 nm (inset of Fig. 2) reveals that a plateau is reached upon addition of about one equivalent of $\mathbf{P}^{2+}$ per dendrimer. This behaviour is consistent with the formation of an adduct between **D**(16t) and $\mathbf{P}^{2+}$ with 1 : 1 stoichiometry, which hereafter will be named $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$ because $\mathbf{P}^{2+}$ interacts with the interior units of the dendrimer (see below). Global analysis of the absorption changes using dedicated software (Specfit)[17] leads to an association constant (K_a) of about 1.0 × 10^6 M^{-1}, with a molar absorption coefficient of 6000 M^{-1} cm^{-1} at 565 nm for the adduct. The high value of the association constant demonstrates that bulky substituents at the dendrimer periphery do not prevent the formation of a stable complex. The driving force for the interaction of the dendrimer with the diazapyrenium chromophore has a charge-transfer (CT) character and is related to the strongly electron-accepting diazapyrenium and the electron-donating amine functions of the dendrimer. Indeed, a strong CT interaction between diazapyrenium and aliphatic amines has been previously reported.[13c–e] The interaction may also take advantage of hydrogen bonding to the acidic protons at the α-position in the diazapyrenium dication.[13e]

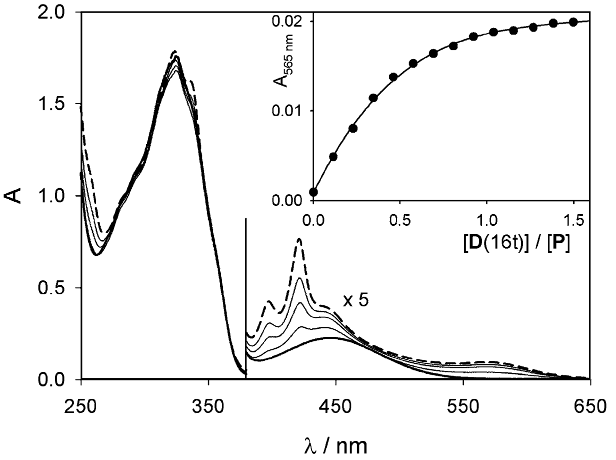

Fig. 2 Absorption spectral changes upon titration of a 5 × 10^{-6} M solution of **D**(16t) with a 5 × 10^{-4} M solution of $\mathbf{P}^{2+}$ in dichloromethane. Dashed line represents the absorption spectrum upon addition of one equivalent of $\mathbf{P}^{2+}$ per dendrimer. Inset shows absorption changes at 565 nm and the corresponding fitting.

A comparative titration of a 2 × 10^{-5} M dichloromethane solution of $\mathbf{P}^{2+}$ with a 5 × 10^{-4} M dichloromethane solution of triethylamine, a model compound for the interior amine function of the dendrimer, shows the formation of a 1 : 1 complex with K_a = 3.0 × 10^4 M^{-1}. The much lower value of the association constant compared to that of the dendrimer suggests a cooperative effect in the case of the dendritic adduct, taking advantage of the multiple amine interacting units.

Emission spectra measured during the titration of $\mathbf{P}^{2+}$ with **D**(16t), upon excitation at 360 nm (Fig. 3), show the appearance of a new broad band at 660 nm, that reaches a plateau at about one equivalent of $\mathbf{P}^{2+}$ per dendrimer. Similar results have been obtained upon titration of a 1 × 10^{-5} M solution of $\mathbf{P}^{2+}$ with **D**(16t) in dichloromethane: in particular, a strong decrease of the diazapyrenium emission band at 440 nm and the concomitant increase of the band at 660 nm are observed. Fig. 3 reports the emission spectra of $\mathbf{P}^{2+}$ before (dotted line)

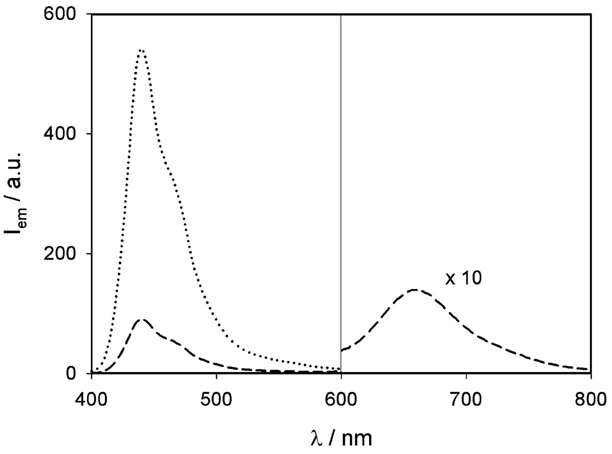

Fig. 3 Emission spectra of a 8 × 10^{-6} M solution of $\mathbf{P}^{2+}$ in dichloromethane before (dotted line) and after (dashed line) addition of one equivalent of **D**(16t). λ_{ex} = 360 nm.

and after (dashed line) addition of one equivalent of **D**(16t). The new band at 660 nm can be attributed to the charge-transfer complex formed. Although an emission from a CT complex is rather unusual, it has been previously reported in the same spectral region for a diazapyrenium–amine complex.[13*b*] The quenching of the diazapyrenium emission intensity upon formation of the 1 : 1 complex is consistent with the presence of a low-lying CT excited state which deactivates the fluorescent diazapyrenium excited state by radiationless transition. An excitation spectrum measured upon setting λ_{em} = 650 nm presents bands with maxima around 280, 450 and 565 nm: this spectrum does not remind one of that of the dendrimer or of the diazapyrenium chromophore, but is very similar to that obtained by subtraction of the absorption spectrum of the $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$ adduct and those of the two separate species. Therefore, the new emission band at 660 nm is clearly due to the absorption features characteristic of the CT complex and no detectable energy transfer from the azobenzene chromophore takes place.[18] This behaviour suggests that the $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$ adduct is formed in the interior of the dendrimer, so that energy transfer from azobenzene to $\mathbf{P}^{2+}$ is too slow to compete with the intrinsic and very fast deactivation of the lowest singlet excited state of the azobenzene.[19] Indeed, no significant change in the *trans* → *cis* photoisomerization quantum yield of **D**(16t) and $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$ upon irradiation at 365 nm has been observed, confirming that no additional deactivation pathway of the lowest singlet excited state of azobenzene is active in the presence of $\mathbf{P}^{2+}$.

The $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$ adduct is still emissive at 77 K in a rigid matrix of CH_2Cl_2–CH_3Cl 1 : 1 (v/v) mixture with the band maximum blue-shifted at 600 nm, showing that the CT excited state responsible for this emission band is destabilized by lack of solvent repolarization, but it is in any case the lower lying excited state.

The $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$ adduct[20] can be disassembled by addition of an equimolar quantity of trifluoromethanesulfonic acid (CF_3SO_3H), as demonstrated by the disappearance of both the absorption band at 565 nm and the emission band at 660 nm and the recovery of the initial $\mathbf{P}^{2+}$ emission intensity. This result demonstrates that the diazapyrenium chromophore interacts mainly with the amine units of the dendrimer. A further proof is the experimental observation that no interaction of $\mathbf{P}^{2+}$ with model compounds containing either naphthalene or azobenzene units and no amine units takes place.

Similar results have been obtained upon addition of $\mathbf{P}^{2+}$ to a solution of **D**(2t14c), obtained upon irradiation at 365 nm, suggesting that the isomeric form of the peripheral azobenzene units does not strongly perturb the association with the diazapyrenium dication.

Conclusions

The self-assembly between a diazapyrenium unit, namely *N*,*N*′-2,7-didecyldiazapyrenium $\mathbf{P}^{2+}$, and a third generation dendrimer of the poly(propylene amine) family containing 14 amine units in the interior and 16 *trans*-azobenzene and 16 naphthyl units at the periphery (**D**(16t)) has been investigated. Strong charge-transfer interactions and possible hydrogen bonding between the electron-accepting diazapyrenium molecule and the electron-donating amine units of the dendrimer lead to an adduct with 1 : 1 stoichiometry, $\mathbf{D}(16t)\supset\mathbf{P}^{2+}$. Dramatic changes of the photophysical properties are caused by the formation of the self-assembled structure: (i) new absorption bands at lower energy compared to the isolated species arise, (ii) a strong quenching of the intense diazapyrenium fluorescence is observed, and (iii) a new broad emission band increases with a maximum at 660 nm. The adduct can be disassembled upon addition of an equimolar quantity of trifluoromethanesulfonic acid.

No significant effect of the isomeric state of the azobenzene units has been observed since an adduct with 1 : 1 stoichiometry and a similar stability constant has been obtained in the interaction of $\mathbf{P}^{2+}$ with **D**(2t14c), a species obtained from **D**(16t) upon irradiation at 365 nm.

It is worth noting that a much higher association constant has been obtained in the case of the dendritic hosts (1.0 × 10^6 M^{-1}), namely **D**(16t) or **D**(2t14c), compared to triethylamine (3.0 × 10^4 M^{-1}), a model compound for the interior amine units of the dendrimer. This demonstrates that the dendritic structure not only does not prevent the formation of a stable complex for the presence of quite bulky azobenzene and naphthalene substituents at the dendrimer periphery, but indeed favours the formation of the adduct with $\mathbf{P}^{2+}$ because of the multiple amine functions present in the dendrimer branching points. Furthermore, no energy transfer from the azobenzene chromophores to the charge-transfer complex has been evidenced, suggesting that $\mathbf{P}^{2+}$ is not close to the azobenzene units of the dendrimer periphery.

Experimental section

Dichloromethane and chloroform for spectroscopy were purchased from Merck. The third generation dendrimer $\mathbf{D}^{7}$ and *N*,*N*′-2,7-didecyldiazapyrenium $(\mathbf{P}^{2+})^{12}$ as the hexafluorophosphate salt were synthesized according to literature procedures.

Photophysical experiments

The experiments were carried out in air-equilibrated dichloromethane solution at 298 K. UV–Vis absorption spectra were recorded with a Perkin Elmer λ40 spectrophotometer, using quartz cells with pathlength of 1.0 cm. Fluorescence spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter equipped with a Hamamatsu R928 phototube. The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient.

Photochemical experiments

Photochemical experiments were performed using a medium pressure mercury lamp. An interference filter (Oriel) was used to select a narrow spectral range with $\lambda_{\max} = 365$ nm. The intensity of the incident light was measured by a ferrioxalate actinometer.[21] The photoisomerization quantum yield ($\Phi_{t\to c}$) was calculated by extrapolation to zero time of the apparent quantum yield values obtained for short irradiation periods. The relative amounts of *cis* and *trans* isomers during photochemical experiments have been calculated on the basis of the previously reported results.[7]

The rate of thermal *cis* → *trans* reaction has been calculated by plotting changes of absorbance, namely $\Delta A = A_\infty - A_t$ (where A_∞ is the absorbance at the end of the reaction, *i.e.* for the all *trans* species), *versus* time and by determining the slope of the corresponding straight line.

The estimated experimental errors are: 10% on the photoreaction quantum yield, 5% on the composition of the photostationary state.

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