Multiple Recognition of Barbiturate Guests by Hamilton-Receptor-Functionalized Dendrimers

Anouk Dirksen,[a] Uwe Hahn,[b] Frank Schwanke,[b] Martin Nieger,[c] Joost N. H. Reek,[a] Fritz Vögtle,*[b] and Luisa De Cola*[a]

Abstract: The well-known unsubstituted "Hamilton receptor" was monofunctionalized with an amino group and attached at the periphery of poly(propyleneamine) dendrimers through the use of an activated ester. Four generations of Hamilton-receptor-functionalized dendrimers (HR-dendrimers) were synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry. The photophysical properties of the HR-dendrimers were investigated by UV/Vis as well as with steady-state and time-resolved fluorescence spectroscopy. The dendrimers were used as multivalent hosts for the barbiturate guests Barbital (**7**) and [Re(Br)(CO)$_3$(barbi-bpy)] (**8**; barbi-bpy = 5-[4-(4′-methyl)-2,2′-bipyridyl]methyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione). The stable adducts formed between the dendritic architectures (the hosts) and the barbiturate guests **7** and **8** were investigated by ^{1}H NMR spectroscopy and photophysical methods. The binding constants of the barbiturate guests for binding to reference compound **2** (with a single receptor unit) in chloroform were found to be $1.4\times10^3\,\text{M}^{-1}$ and $1.5\times10^5\,\text{M}^{-1}$ for **7** and **8**, respectively. Binding of **7** to the dendrimers enhances the weak emission of the Hamilton receptor. This increase in emission is also generation dependent; it was found to be most pronounced in the case of **2** and the least in the case of the fourth-generation dendrimer **6**. The unexpected increase in the quantum yield of emission from the HR-dendrimers with increasing generation could be caused by the rather rigid conformation of the Hamilton receptors in later-generation compounds, which is a result of intramolecular aggregation and steric hindrance at the periphery of the dendrimer. The photoinduced energy transfer from the excited state of the HR-dendrimers to the lower-lying excited state of the guest **8** was used to probe the formation of host–guest complexes. The rate of energy transfer was calculated to be $3.6\times10^{10}\,\text{s}^{-1}$. Energy transfer in **2**⊂**8** only occurred in the presence of a strong base, which shows that the basic amine core in the HR-dendrimers is crucial for this photoinduced process. The binding of **8** to the dendrimers is completely reversible: **8** can be exchanged with a competitive guest such as **7** and the emission of the HR-dendrimer is restored.

Keywords: barbiturate receptors · dendrimers · energy transfer · host–guest systems · rhenium

Introduction

An important area of supramolecular chemistry is the assembly of multiple components in a predefined way to enable them to perform specific functions, such as photoinduced energy or electron transfer processes.[1–18] Generally, self-assembly and molecular recognition involve the use of a mono- or bifunctionalized host or guest. Multibinding events within the same molecule are very rare in artificial systems, especially when hydrogen bonds are used to glue the complementary components together. Dendrimers have proven to be suitable supramolecular hosts for guest molecules.[19–40] As a result of their monodispersed, highly branched three-dimensional structure, a microenvironment is created within each dendrimer in which guest molecules can be encapsulated through topological entrapment (hydro-

[a] Dr. A. Dirksen, Dr. J. N. H. Reek, Prof. Dr. L. De Cola
Institute of Molecular Chemistry
Universiteit van Amsterdam, Nieuwe Achtergracht 166
1018 WV Amsterdam (The Netherlands)
Fax: (+31) 20-5256454
E-mail: ldc@science.uva.nl

[b] Dr. U. Hahn, Dr. F. Schwanke, Prof. Dr. F. Vögtle
Kekulé-Institut für Organische Chemie und Biochemie
der Universität Bonn
Gerhard-Domagk Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228-735662
E-mail: voegtle@uni-bonn.de

[c] Dr. M. Nieger
Institut für Anorganische Chemie
der Universität Bonn
Gerhard-Domagk Strasse 1, 53121 Bonn (Germany)

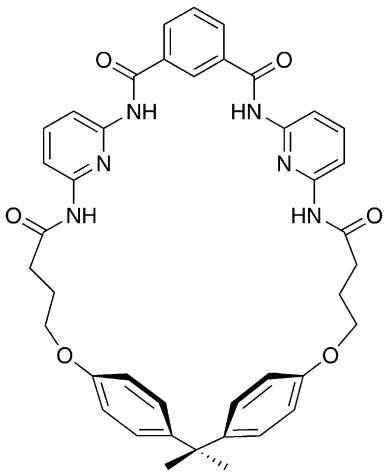
DOI: 10.1002/chem.200305461

philic/hydrophobic interactions).[19–34] Such nonbonding interactions are unspecific and even the encapsulation of solvent molecules can be considered as a form of topological entrapment.

Since dendrimers can be built up very regularly, it is possible to incorporate receptor sites into the core, into the branches, or at the periphery.[19–24,35–40] These receptors might recognize their targets based on acid–base, electrostatic, or hydrogen-bonding interactions. The organization of binding sites in specific parts of a dendritic structure allows the formation of multiple, stable host–guest systems within one molecule.

The creation of large structures that can selectively bind a certain class of compounds contributes to the development of artificial systems closely resembling those found in proteins.[41–43] Particularly interesting are host–guest systems in which the binding of a guest can promote new functions, such as energy, electron, and proton transfer processes. The use of dendrimers containing multiple chromophoric units or receptor sites is extremely appealing since there is a great need for well-characterized systems in which it is possible to simultaneously perform sensor functions and immobilize biological substrates.[44]

Herein we discuss poly(propyleneamine) "POPAM" (also called poly(propylenimine), or PPI)[24] dendrimers substituted at the periphery with receptors that can bind barbiturates and their derivatives through six hydrogen bonds.[45] Such a receptor, whose target binding is based on multiple hydrogen bonds and which contains 2,6-diaminopyridine, was introduced in 1988 by Hamilton et al. (Scheme 1).[45]



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Scheme 1. The barbiturate receptor **1** published in 1988 by Hamilton et al.[45]

Since then, several papers have appeared reporting the ability of this receptor to substract barbiturates from serum[46,47] and its use as a model for enzyme catalysis,[48–50] as a building block in supramolecular materials,[51] and as a receptor in photoactive hydrogen-bond-based assemblies.[11,52,53] From these studies it is clear that the receptor can be a powerful tool for the creation of stable supramolecular assemblies containing barbiturates, even in solvents that compete for the receptor site.[54]

Herein we report the synthesis and characterization of four generations (**G*x***, $x = 1,2,3,4$) of poly(propyleneamine) dendrimers (**3**–**6**) substituted at the periphery with barbiturate receptors, which we will call "Hamilton receptors" (Scheme 2). We discuss the photophysical properties of the Hamilton receptor itself in detail for the first time, as well as the photophysical properties of the Hamilton-receptor-functionalized dendrimers (HR-dendrimers).

Two barbiturate derivatives were also prepared and were studied as guests, namely Barbital[55] (**7**) and [Re(Br)(CO)$_3$(barbi-bpy)] (**8**; barbi-bpy = 5-[4-(4′-methyl)-2,2′-bipyridyl]-methyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione),[53] which are both able to form host–guest complexes with the HR-dendrimers, as depicted in Scheme 3. The binding constants for binding of the barbiturate guests **7** and **8** to the Hamilton receptor could be determined by ^{1}H NMR and fluorescence spectroscopy, respectively.

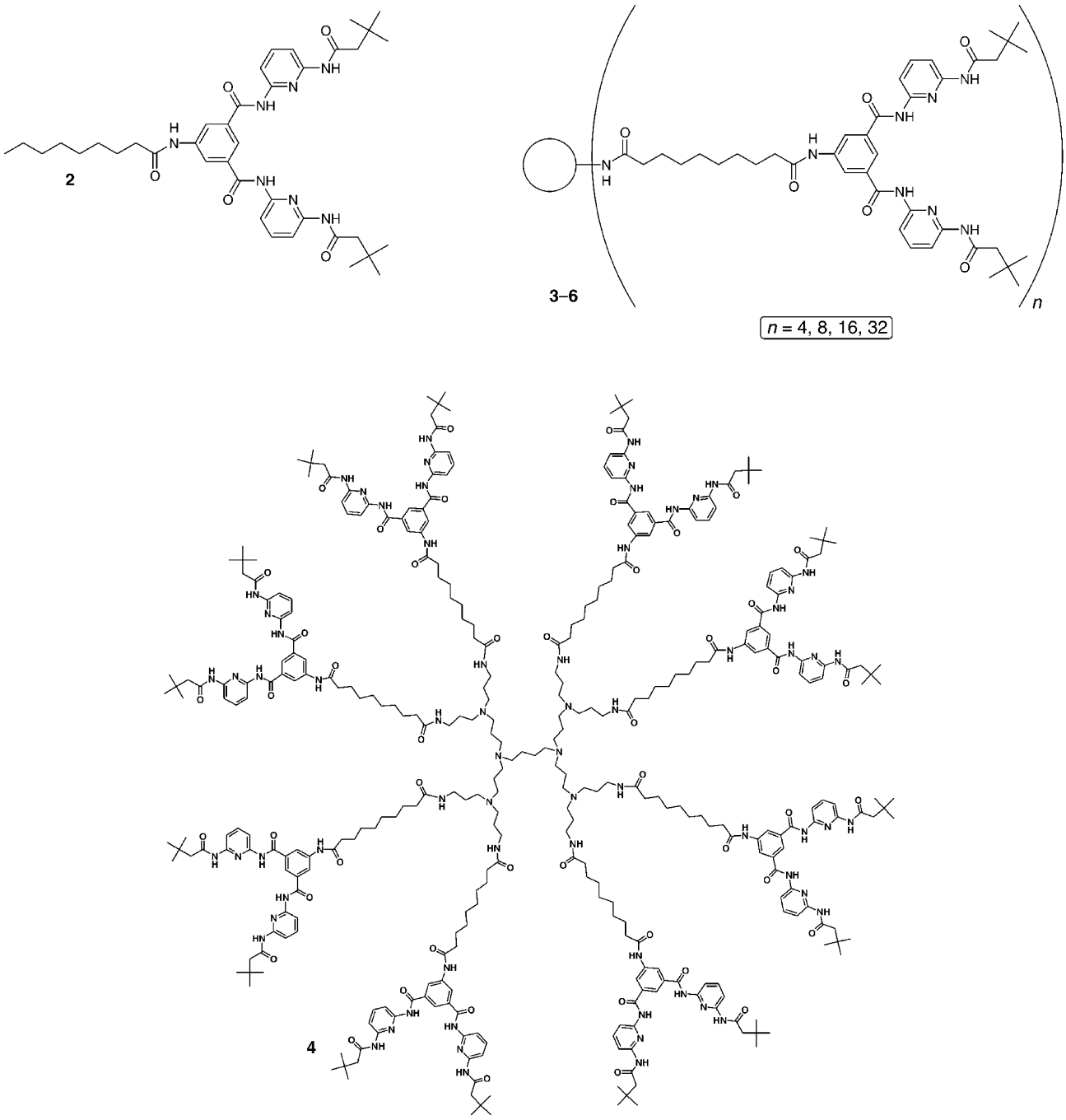
Finally, we showed that the receptor itself can be used as a chromophore and upon excitation can transfer energy to the guest across hydrogen bonds. Compound **8** is very suitable for this purpose as it has a triplet excited state, a metal-to-ligand charge transfer state (^{3}MLCT state), at lower energy than the excited state of the Hamilton receptor. The energy transfer process was studied by both steady-state and time-resolved fluorescence spectroscopy.

Results and Discussion

Synthesis and characterization of the HR-dendrimers: Four generations of HR-dendrimer were synthesized as shown in Scheme 4.

In the first step of the synthesis, the hitherto unknown monomeric receptor **12**, which has an amino group at the 5-position of the isophthalic acid unit, was prepared. This functionalized receptor was subsequently allowed to react in a 1:1:1 ratio with the diacid dichloride **14** and pentafluorothiophenol (PTFE, **13**). The PTFE ester **15** obtained by this synthetic route was used instead of the free acid chloride to ensure full substitution of the periphery of the dendrimers, a strategy used previously by Meijer et al. for the preparation of functionalized POPAM dendrimers.[56] The complete functionalization of the dendrimers can be confirmed by MALDI-TOF spectrometry, as demonstrated for **5** in Figure 1. All generations of dendrimers were characterized by using ^{1}H and ^{13}C NMR spectroscopic and mass spectrometric techniques.

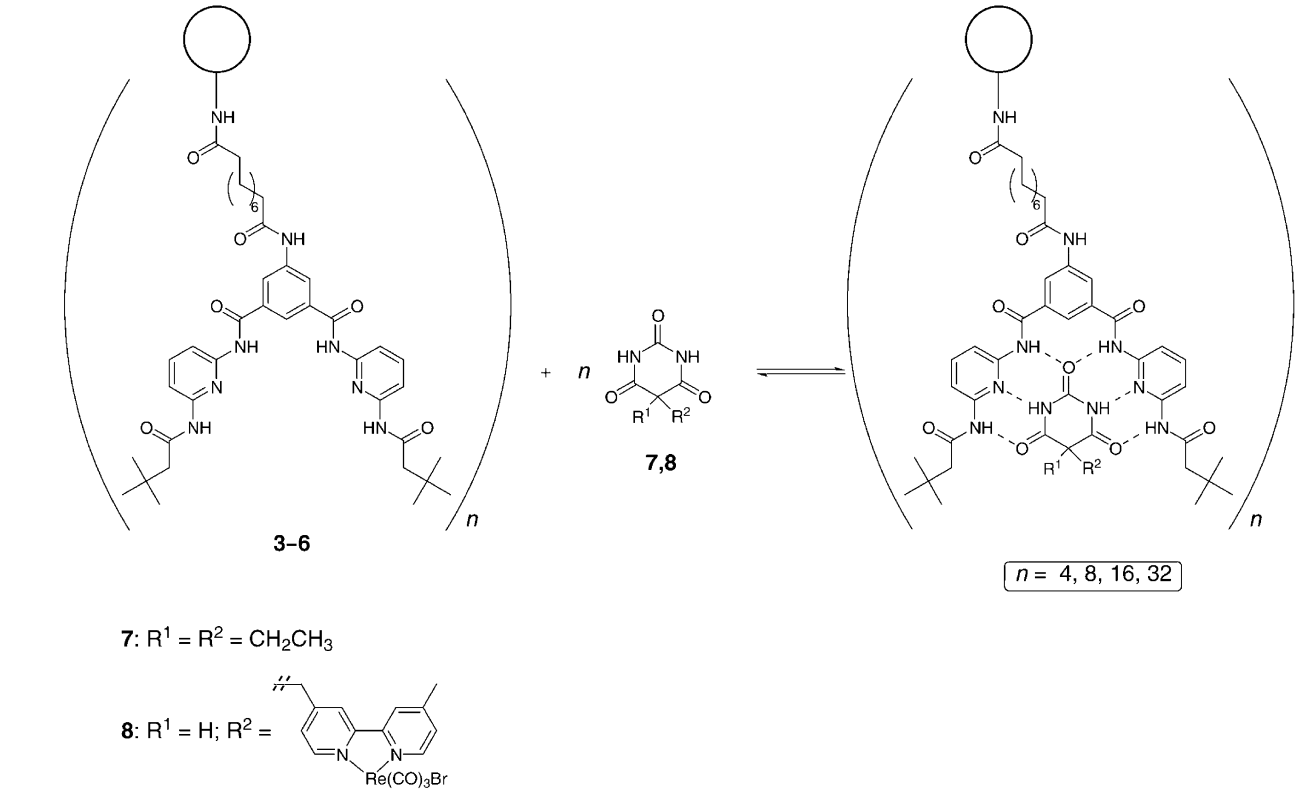
Determination of the association constants (K_{ass}): To gain more insight into the association of the host–guests systems, titrations were performed on **2** to determine its association constants (K_{ass}) with Barbital (**7**) and [Re(CO)$_3$(Br)(barbi-bpy)] (**8**). The association constant of **2**⊂**7** (in $CDCl_3$) was determined by using ^{1}H NMR spectroscopy. A K_{ass} value of $1.4 \times 10^3\,\text{M}^{-1}$ was calculated from the change in chemical shift of selected proton signals of **2** upon addition of **7**. The association constant of **2**⊂**8** (in $CHCl_3$) could be determined by



Scheme 2. A schematic representation of the HR-dendrimers **3–6** and the structures of **2** (reference compound) and **4**.

using fluorescence spectroscopy and exciting **8** at 435 nm. From the changes in the emission intensity of **8** upon addition of **2**, the association constant was calculated to be $1.5 \times 10^5\,\text{M}^{-1}$. The association constants found for **7** and **8** are in good agreement with those found previously by Isied et al., for nondendritic Hamilton receptors, who ascribed the large difference in binding constants to the ability of the barbiturate to form a keto-enol-enolate equilibrium.[57] The association constants of the dendritic host–guest systems cannot be determined exactly because of the wide variety of equilibrating species. However, based on their identical behavior in fluorescence titration experiments (see below), we assume that the binding constant is similar for each receptor site and resembles that of **2**.

Photophysical properties of 2 and the HR-dendrimers 3–6: Several studies have focused on the Hamilton receptor and its complexation of barbiturates and their derivatives. In particular, the assembly of the two units has been investigated by X-ray crystallography and by NMR, UV/Vis, and fluorescence spectroscopies.[11,44–53] However, the photophysical properties of the receptor itself have never been studied in detail. Hamilton et al. reported an absorption maximum in the UV/Vis spectrum at 303 nm for the Hamilton receptor



Scheme 3. Formation of host–guest complexes between the HR-dendrimers **3–6** and the guest molecules **7** and **8**.

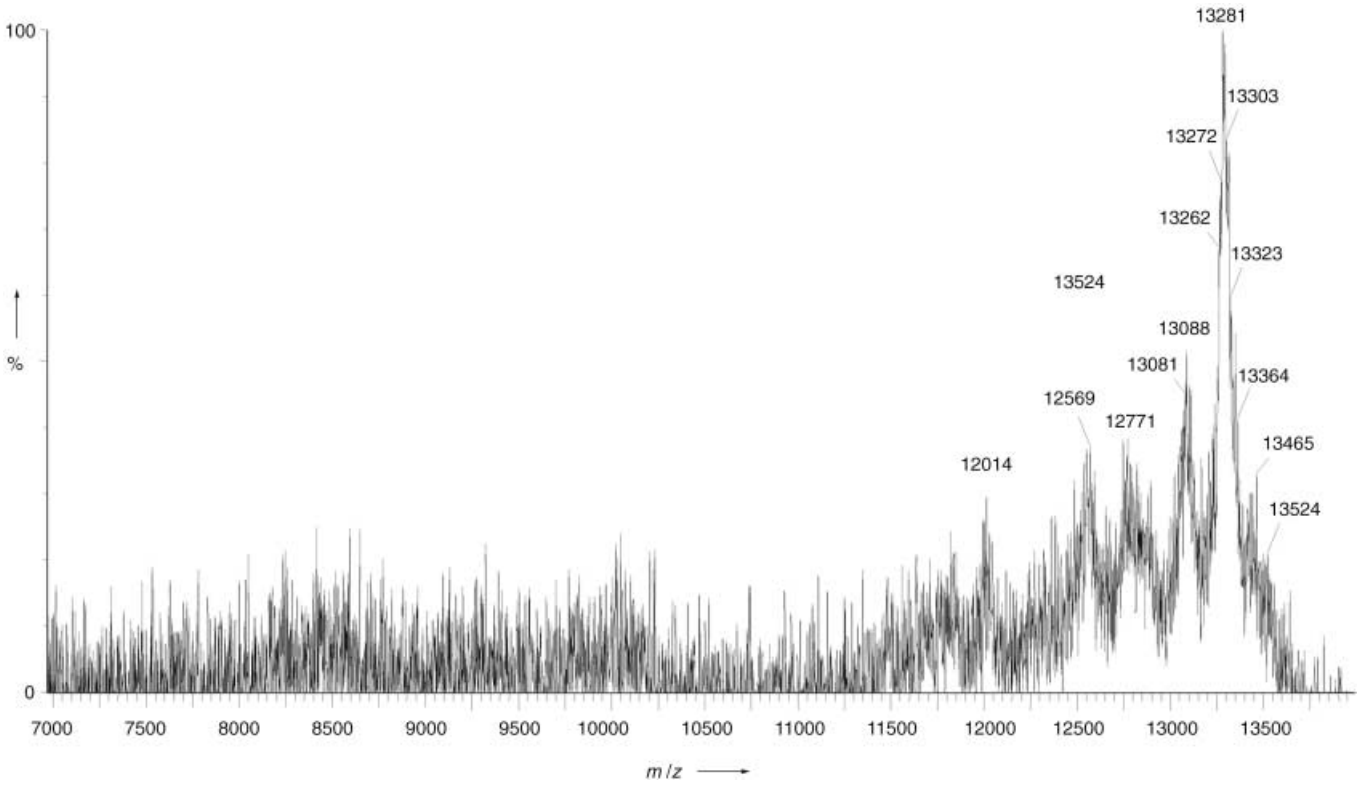
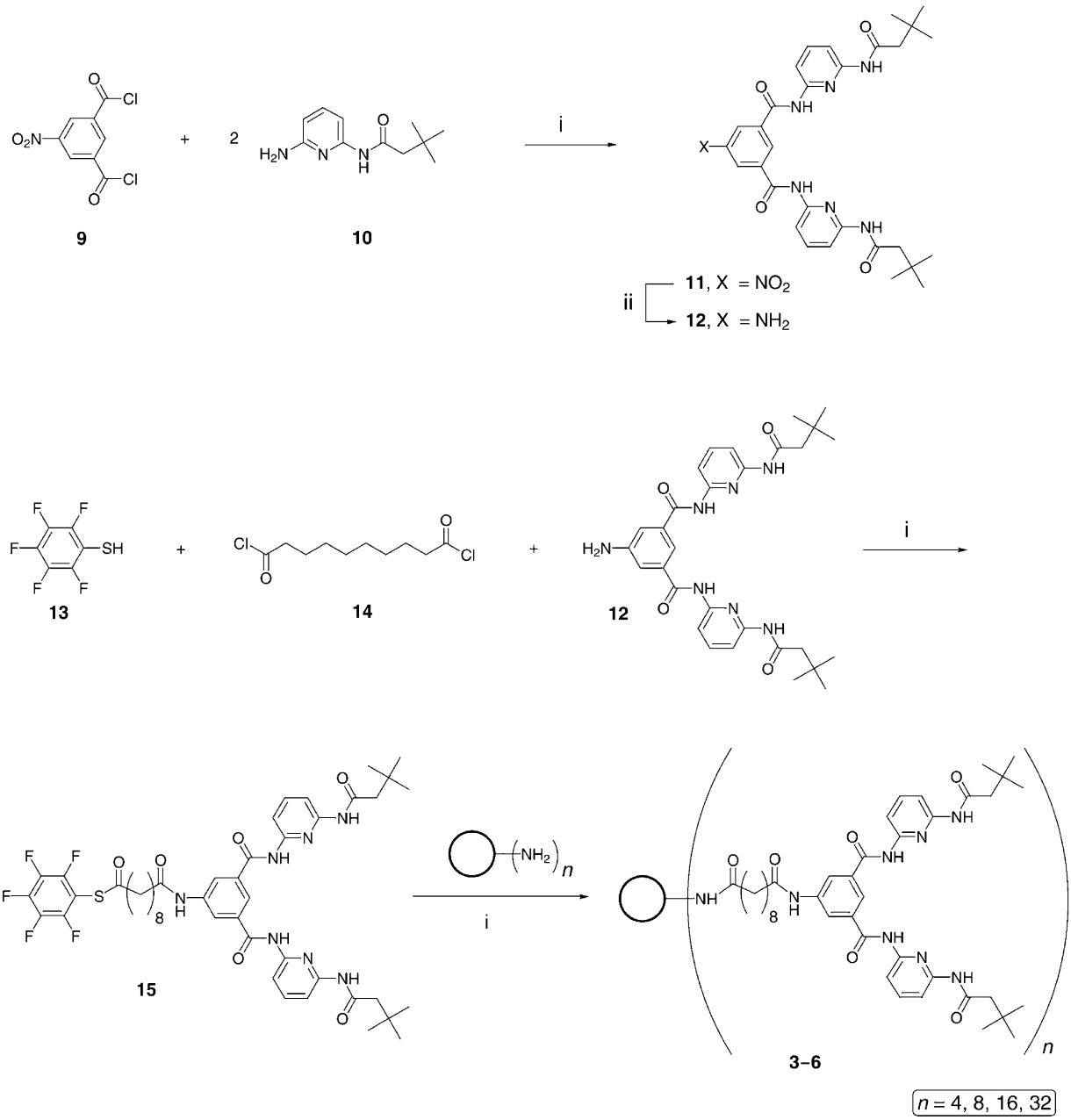


Figure 1. MALDI-TOF mass spectrum of **5** (mass calcd. for **5**: 13292.0).

and an emission maximum at 461 nm.[52] A binding-induced increase in both the absorption and the emission bands of the receptor was also reported.[52]

Like reference compound **2**, which contains a single receptor, the HR-dendrimers **3–6** have an absorption maximum at 302 nm in $CHCl_3$ (Figure 2a). The molar extinction



Scheme 4. Synthesis of HR-dendrimers **3–6**: i) NEt_3, tetrahydrofuran (THF), RT, 12 h; ii) $PtO_2{\cdot}H_2O$, EtOH, 4 bar, RT, 24 h.

coefficient is linearly related to the number of Hamilton receptors attached to the periphery of the poly(propyleneamine) dendrimer. However, the molar extinction coefficient of the Hamilton receptor within the HR-dendrimers **3–6** was found to be significantly lower per Hamilton unit than that within **2** (Table 1). Excitation of the dendrimers at 310 nm gives a dual emission, with a maximum at 440 nm and a shoulder at lower energy centered at about 500 nm for all dendrimers. In the case of **2**, a distinguishable band is observed at 540 nm, although the emission intensity is much lower for **2** than for **3–6** (Figure 2b). All the photophysical data are summarized in Table 1.

The emission shows a double exponential decay for all generations of dendrimer in $CHCl_3$, with a short lifetime component of 400 ps and a longer lifetime of 1.5 ns (Table 1). Remarkably, the quantum yield of emission is larger for the later-generation than for the earlier-generation compounds (Table 1). This trend is probably related to the aggregation of the Hamilton receptors at the periphery of the dendrimer. Steric hindrance becomes greater with increasing dendrimer generation number since the periphery of the molecule becomes more crowded with receptor moieties. The number of possibilities for receptor intra- or intermolecular interaction therefore becomes greater with increasing generation of dendrimer. At the low concentrations used in our experiments, (10^{-5} M receptor concentration), we can assume that intramolecular processes are predominant. Aggregation introduces rigidity to the Hamilton receptor, which results in a higher quantum yield of emission since radiationless deactivation is reduced.

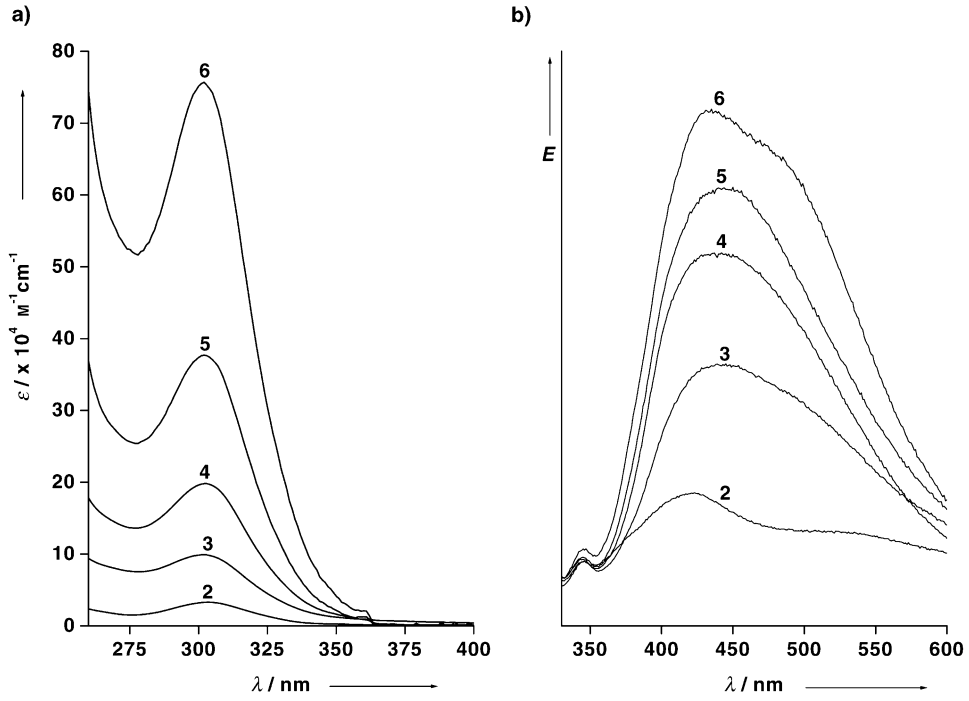


Figure 2. Absorption (a) and emission (b) spectra ($\lambda_{exc}=310$ nm) of **2**–**6** in $CHCl_3$.

Table 1. The photophysical properties of **2**–**6** in $CHCl_3$.

Sample	n[a]	ε [$M^{-1}cm^{-1}$][b]	Ratio ε[c]	Φ_{em}	τ_1 [ps^{-1}][d]	τ_2 [ns][d]
2	1	32900	1.3	0.0024	374	1.46
3	4	99000	4	0.0103	408	1.51
4	8	198000	8	0.0151	408	1.57
5	16	377000	15.2	0.0180	369	1.48
6	32	785000	31.7	0.0211	429	1.38

[a] n = number of Hamilton receptors. [b] Calculated at the maximum at 302 nm. [c] Ratio ε = ratio between the ε values correlated to the number of chromophores. [d] $\lambda_{exc}=356$ nm and $\lambda_{probe}=480$ nm.

Since conformational evidence to support these findings is so far lacking, the binding of guest molecules was used as an alternative strategy to rigidify the structure of the Hamilton receptor to allow validation of the concept described above. The binding of a barbiturate guest such as **7** "fixes" the Hamilton receptor in a certain conformation and in this way reduces the degrees of freedom of the chromophore. Since **7** is an "innocent" guest (i.e. no absorption or emission from **7** occurs at the excitation wavelength used), all changes in the emission of the receptors as a result of the addition of **7** can be attributed to conformational changes of the receptor upon binding the guest.

As can be seen in Figure 3a, the quantum yield of emission from **2** increases dramatically upon addition of **7**, and the maximum shifts to lower energy (450 nm). Such a shift can be explained by considering that the insertion of **7** into **2** causes planarization of the receptor and greater delocalization within the system. As a result of the binding of **7** (a large excess of 100 equiv was used because of the low binding constant), the long-lived component (1.5 ns) of the excited-state lifetime of **2** disappears, so that only the 400-ps component remains (Figure 4). This result indicates that the two different lifetimes belong to two different conformations of the receptor; one in which the receptor arms are not in the same plane (long lifetime), and another in which the receptor arms are in the same plane (short lifetime). The three possible conformations of the receptor in **2**, namely *cis-cis*, *cis-trans*, and *trans-trans*, are depicted in Scheme 5. Detailed theoretical calculations of such *cis-trans* behavior in *meta*-substituted benzenes and 2,6-substituted pyridines were carried out within the frame of our investigations into template syntheses of molecular knots (knotanes) in cooperation with the Theoretical Chemistry Department of the University of Bonn.[58,59] Upon binding of a barbiturate guest, the receptor is always forced into an in-plane *cis-cis* configuration.

Interestingly, an increase in emission and a slight shift of the emission maximum to lower energy is also observed for the HR-dendrimers **3**–**6** upon binding of **7**. This effect becomes smaller with increasing dendrimer generation (Figure 3b). This trend can only be explained if the Hamilton receptors already have restricted conformational freedom in the later-generation dendrimers as a result of the aggregation or steric hindrance at the periphery of the dendrimer.

Energy transfer in the complexes 2⊂8, 3⊂8, 4⊂8, 5⊂8, and 6⊂8: Metal complexes such as $[Ru(bpy)_3]$ and $[Os(bpy)_3]$, but also $[Re(CO)_3(X)(bpy)]$ (X = Cl, Br, I), are often used as energy or electron donors or acceptors in photoinduced processes.[60–65] The use of these complexes is often dictated by their photophysical and redox properties, which are suitable for the study of photoinduced processes. In the complex $[Re(CO)_3Br(bpy)]$, the lowest excited state is a luminescent triplet metal-to-ligand charge transfer state. In a separate study, we have shown that $[Re(CO)_3(Br)(barbi\text{-}bpy)]$ (**8**) forms a stable host–guest complex with the Hamilton receptor.[53] Comparison of the energy levels of the HR-dendrimers **3**–**6** with those of the rhenium guest shows that the ^{3}MLCT state of **8** is at lower energy (17730 cm^{-1}, 564 nm) than the lowest excited state of the HR-dendrimers (27397 cm^{-1}, 365 nm). As a result of the different absorption properties of the separate components of the dendrimer–**8** complexes (Figure 5), it is possible to selectively excite the HR-dendrimers. Excitation at 330 nm predominantly excites the Hamilton receptor. At this excitation wavelength, the

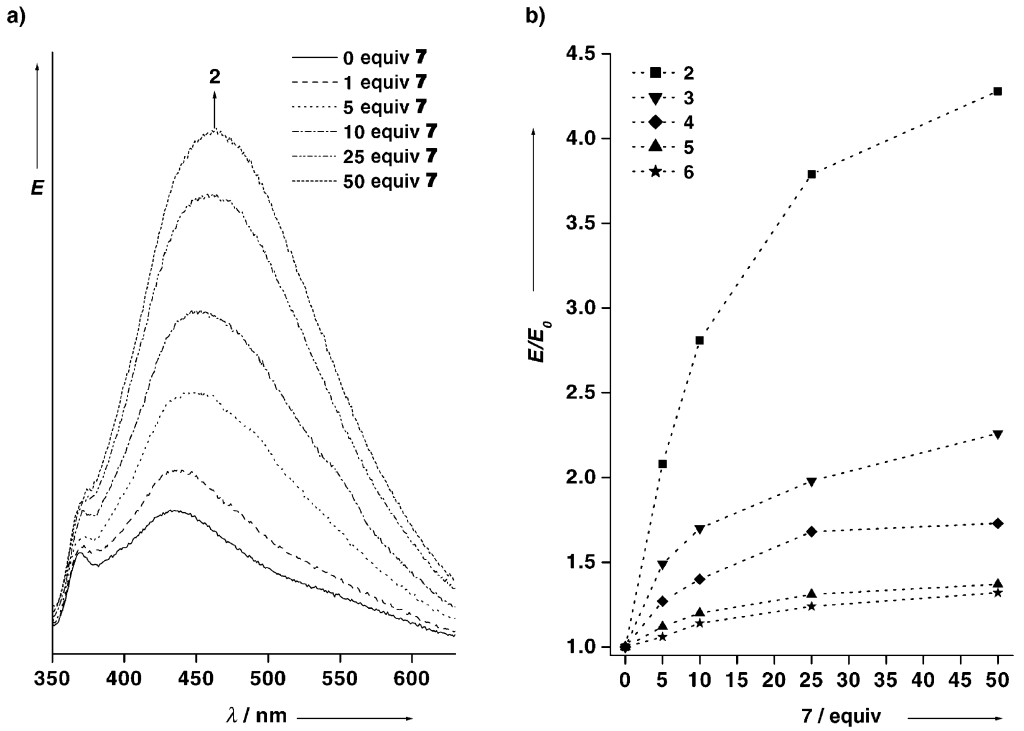


Figure 3. a) Titration of **2** with **7** as observed by fluorescence spectroscopy (in $CHCl_3$; $\lambda_{exc}=330$ nm); a binding-induced increase in the emission of **2** can be seen. b) The binding-induced increase in the emission (in $CHCl_3$; $\lambda_{exc}=330$ nm) of HR-dendrimers **3**–**6** as a result of the addition of **7**, plotted relative to the original emission (E_0).

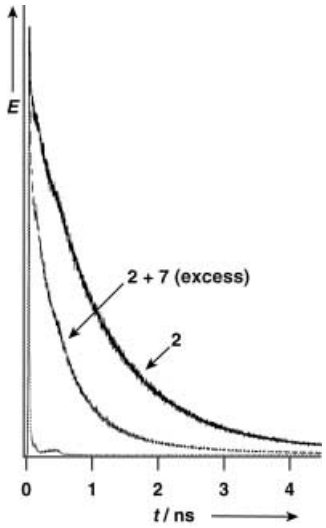


Figure 4. The emission decay (probed at 480 nm) of **2** in the absence and in the presence of a large excess of **7** (100 equiv in CH_2Cl_2; $\lambda_{exc}=$ 324 nm).

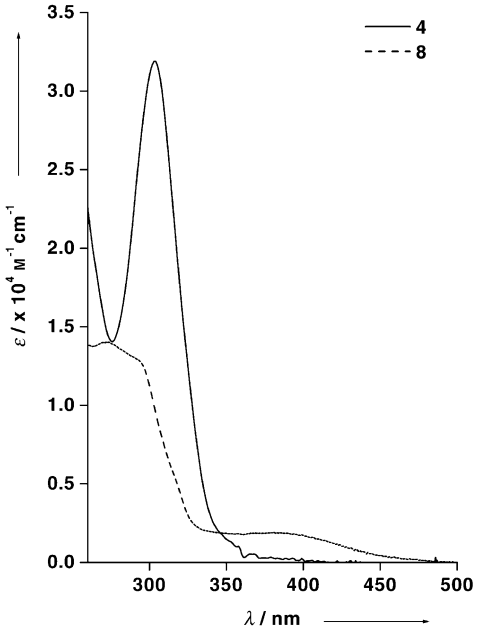
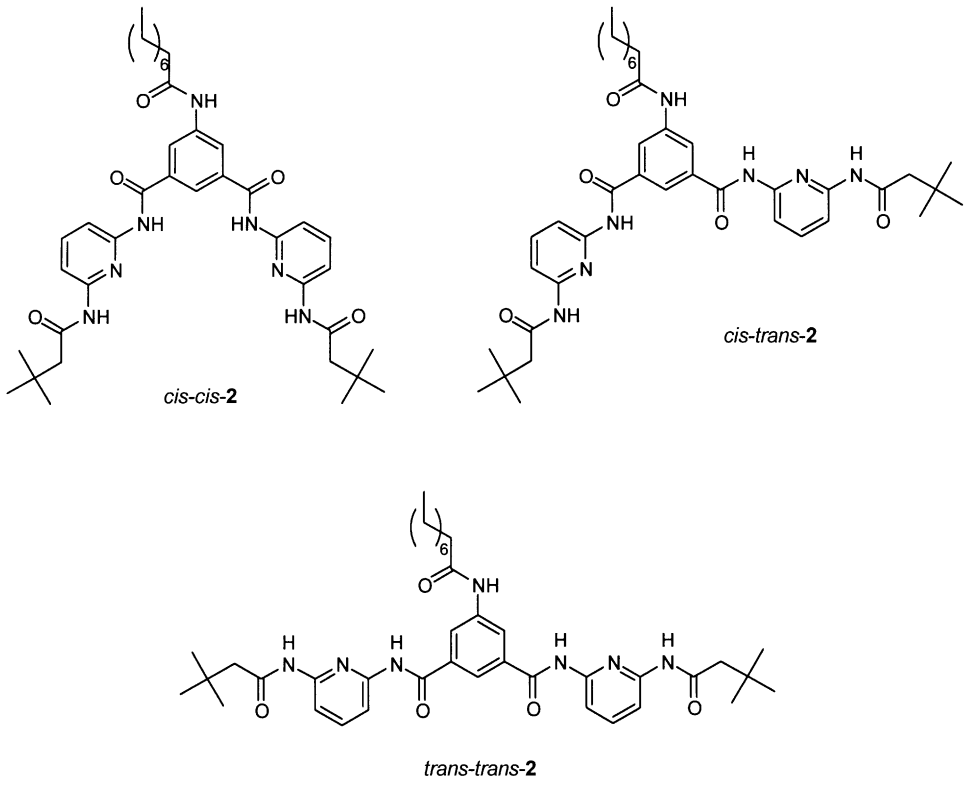


Figure 5. The absorption spectra of **4** (scaled to ε per HR) and **8** in $CHCl_3$.

contribution of **8** to the overall absorption is around 15% in an equimolar solution.

The association of the two components is expected to lead to a very exergonic photoinduced energy transfer ($\Delta G=-1.20$ eV) from the selectively excited ($\lambda_{exc}=330$ nm) Hamilton receptor to **8** (Figure 6b). Indeed, upon addition of the guest, quenching of the excited state ($\lambda_{max}=450$ nm) of the Hamilton receptor, as well as sensitization of the rhenium emission ($\lambda_{max}=564$ nm) was observed, as shown for dendrimer **4** in Figure 6a. No isosbestic point was observed, which indicates that two different processes occur simultaneously. The first process is the quenching of the excited state of the Hamilton receptor by **8** through energy transfer. The second process, discussed in detail below, is the deprotonation of the barbituric acid moiety attached to the bipyridine



Scheme 5. The structures of the *cis-cis*, *cis-trans*, and *trans-trans* configurations of **2**.

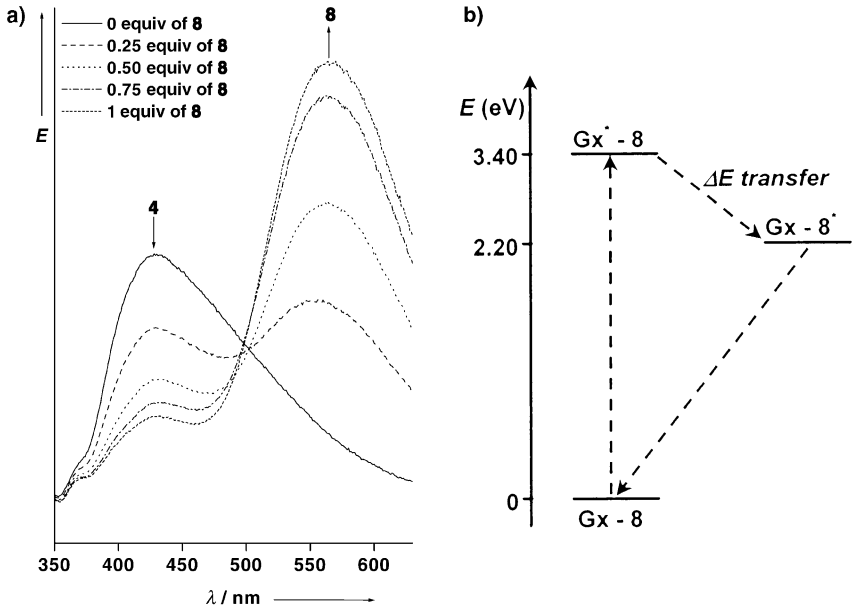
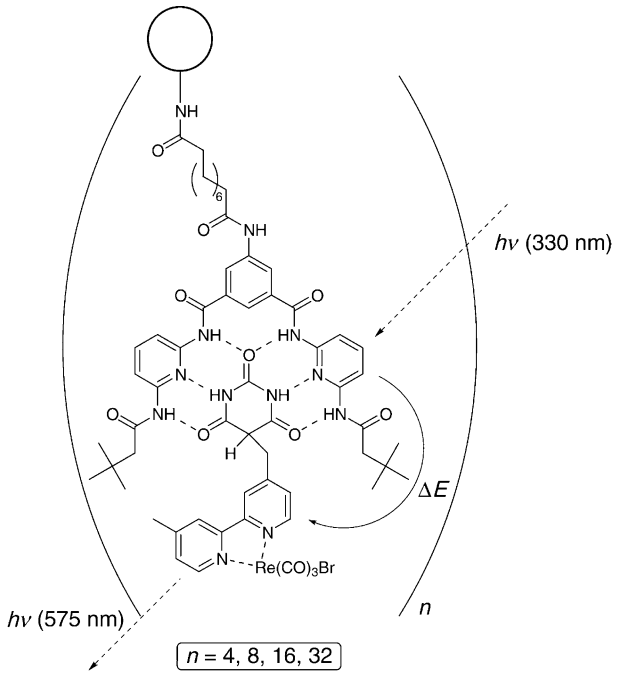


Figure 6. a) Titration of **4** with **8** as observed by fluorescence spectroscopy (in $CHCl_3$; $\lambda_{exc}=330$ nm); an energy transfer from the excited state of **4** to **8** occurs. b) A schematic representation of the energy diagram.

ligand of **8**, which causes a blue shift (from 610 to 564 nm) and an increase in intensity of the emission of **8**.

Time-resolved fluorescence spectroscopy revealed that the emission lifetime of 400 ps, which corresponds to the excited state of the Hamilton receptor, was reduced to 30 ps upon binding of **8**. A long-lived component is also present in the emission of the complex as a result of the population of the ^{3}MLCT state ($\tau=109$ ns) of **8** through energy transfer. From this quenched lifetime, the rate of energy transfer from the Hamilton receptors at the periphery of the dendrimer to **8** was calculated to be $3.6\times10^{10}\,s^{-1}$. The same rate was found for this photoinduced process in all generations of dendrimer (**3**–**6**), as expected. A schematic overview of the photophysical processes occurring in **3**⊂**8**, **4**⊂**8**, **5**⊂**8**, and **6**⊂**8** is given in Scheme 6.

Upon complexation of **8** with HR-dendrimers **3**–**6**, the **8**-based emission is blue-shifted from 610 nm to 564 nm. This shift in the emission of **8** can be attributed to deprotonation of the barbituric acid to produce its enolate form, which is negatively charged. Since the bipyridine ligand is involved in the MLCT as an electron acceptor, the presence of the electron-rich barbiturate would cause the MLCT state to rise to a higher energy. The addition of third-generation poly(propyleneamine) dendrimer (DAB-*dendr*-Am_{16}; DAB = diaminobutane, dendr = dendrimer, Am = amine), which can only act as a base, to a solution of **8** in $CHCl_3$ causes the same shift in emission. Furthermore, an increase in the quantum yield of emission from **8** was observed upon complexation. This result is in accordance with the "Energy Gap Law," which states that if the energy difference between the lowest excited state and the ground state increases, nonradiative decay to the ground state decreases. In the case of the dendrimer–**8** complexes, an increase in the energy gap between the ground state and the lowest excited state (^{3}MLCT state) of **8** upon binding would cause a blue shift and an increase in emission from **8**. Another possible explanation for the increased quantum yield of emission from **8** lies in the change in conformation of **8** upon depro-



Scheme 6. A schematic representation of the energy transfer between HR-dendrimers **3**–**6** and guest compound **8**.

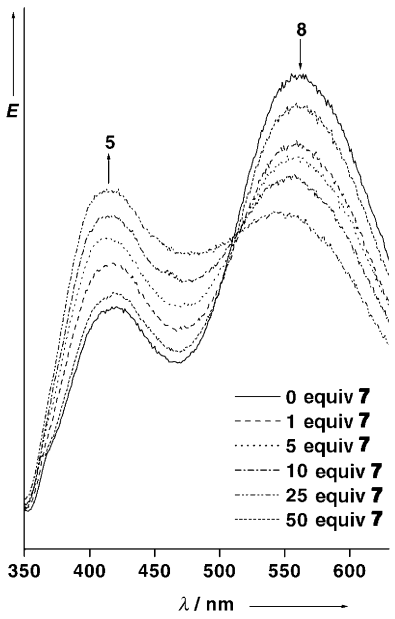


Figure 7. Titration of **8**⊂**5** with **7** in $CHCl_3$, as observed by fluorescence spectroscopy ($\lambda_{exc}=330$ nm). The exchange of **8** with **7** results in the recovery of the emission of **5** and a decrease in the emission of **8**.

tonation. The barbiturate ring in deprotonated **8** lies in-plane with the bipyridine ring as a result of the change in hybridization of the deprotonated carbon atom from sp^3 to sp^2, which improves the conjugation between the binding moiety and the rhenium complex.

The deprotonation of the barbituric acid moiety of **8** proved to be essential for the energy transfer from the excited state of the receptor to the excited state of **8**. No energy transfer was observed within the host–guest complex **2**⊂**8**; only an increase in the quantum yield of emission from **2** was caused by guest binding. Upon addition of a strong base, such as DAB-*dendr*-Am_{16}, the receptor emission was quenched and strong emission from **8** was observed. This result proves that the presence of the basic poly(propyleneamine) core is absolutely necessary for the energy transfer to occur, even though the energy gap between the lowest excited state of the receptor and the lowest excited state of **8** does not increase, but rather decreases upon binding, reducing the driving force for the energy transfer process (see above). The reason for the occurrence of the efficient energy transfer must therefore be an improvement in electronic coupling between the receptor and **8**. The excited state of the receptor is very short-lived (only 400 ps), so that a strong electronic coupling between the energy donor and the energy acceptor is crucial for fast energy transfer to occur.

Competition between 8 and 7: To show that the binding of **8** to the Hamilton receptor causes a photoinduced energy transfer and that the exchange of guest molecules is a clean and reversible process, a competition experiment was performed with compounds **8** and **7**.

Upon addition of a large excess of **7** to a solution containing **3**⊂**8**, **4**⊂**8**, **5**⊂**8**, and **6**⊂**8** (Hamilton receptor:**8**, 1:1), the emission of the Hamilton receptors at 450 nm was restored, while the emission from **8** at 564 nm decreased (at the excitation wavelength almost no direct excitation of the rhenium complex was possible). These results show clearly that **8** was replaced by **7** (Figure 7). The exchange of guests is a clean and reversible process, as demonstrated by the presence of an isosbestic point at 512 nm.

Conclusion

The results presented herein show that the new "Hamilton-receptor"-functionalized dendrimers synthesized in this study can be used as multiple-emitting sensors to probe the presence of barbiturates. The emission from the Hamilton receptor is strongly related to the rigidity of the chromophoric system. The emission quantum yield was found to be dependent on the dendrimer generation (dendritic effect). The emission intensity increases with dendrimer generation because of the increasing aggregation of receptors and steric hindrance at the periphery of the dendrimers. The binding of an "innocent" guest, such as Barbital (**7**), forces the receptor into a "fixed" conformation, which results in an increase in its emission. Binding of the barbiturate guest [Re(CO)$_3$(Br)(barbi-bpy)] (**8**), which has an excited state at a lower energy than those of the HR-dendrimers, results in an energy transfer from the Hamilton receptors to **8** at a rate of $3.6\times10^{10}\ s^{-1}$. The emission of **8** shifts towards higher energy upon binding to the HR-dendrimers as a result of deprotonation of the barbituric acid attached to the bipyridine ligand. Deprotonation is necessary to obtain good electronic coupling between the receptor and **8** to allow an efficient and fast energy transfer. Exchange of **8** with **7** results

in the recovery of the receptor emission and a decrease in the emission of **8**.

By using the Hamilton receptor as a binding motif at the periphery of poly(propyleneamine) dendrimers, stable supramolecular host–guest complexes can be formed in which photophysical processes such as energy transfer can be observed. The emission of the Hamilton receptor was successfully used in binding studies to probe the complexation of guest molecules and can be regarded as a multiple sensor for barbiturates. Careful design of the interior of the dendrimer could allow the assembly of different guests in desired parts of the dendritic structure. Such a structure would make *intradendritic* processes possible and could allow a more complicated function of the molecule, such as the release of one of the guests induced by light excitation.

Experimental Section

Solvents and starting materials: All reagents were obtained from commercial sources and used without additional purification unless otherwise indicated. Solvents were dried according to known procedures. Deuterated solvents were used as obtained from Merck KGaA. $CDCl_3$ was freshly distilled from CaH_2 onto 4-Å molecular sieves prior to use in the binding study.

Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WM 250, DPX 300, and DPX 400 spectrometers. The ^{1}H NMR binding study was performed on a Varian Inova500 spectrometer at 499.86 MHz. EI spectra were recorded on an AEI MS-30 or MS-50 spectrometer, positive-ion FAB mass spectra were collected on a Kratos Concept 1H spectrometer, and MALDI-TOF mass spectra were collected on a Micromass TofSpec E spectrometer. Melting points were recorded on a Büchi SMP 20 apparatus. Thin-layer chromatography (TLC) was carried out on DC-Fertigplatten Kieselgel 60 F254 from Merck KGaA. Column chromatography was performed on silica gel 60, 40–63 mesh, or silica gel 100, 63–100 mesh from Merck KGaA. UV/Vis absorption spectra were recorded on a diode-array HP8453 spectrophotometer at 293 K. Fluorescence spectra were recorded on a SPEX fluorometer. The lifetime of the emission of the HR-dendrimers was determined by single photon counting with a picosecond laser.

Determination of the quantum yields of emission: The quantum yields of emission of the HR-dendrimers in $CHCl_3$ were determined with quinine sulfate in 0.05 M H_2SO_4 (aq) as a reference. The solutions were optically dilute, that is, they had an absorption between 0.05 and 0.15 at the excitation wavelength ($\lambda_{exc}=310$ nm).

Determination of the binding constant for binding of 7 to 2 by ^{1}H NMR spectroscopy: A solution of **7** (28 mM) in $CDCl_3$ was added in aliquots of 10 μL (0.2 equiv **7**) to a solution of **2** (1 mL, 2.5 mM) in $CDCl_3$. The binding constant could be calculated from the change in chemical shift of selected proton signals of **2** upon addition of **7** by using a Scatchard plot.

Determination of the binding constant for binding of 8 to 2 by fluorescence spectroscopy: A solution of **2** (1.2 mM) in $CHCl_3$ was added in aliquots of 5–50 μL (5 μL contains 0.2 equiv **2**) to a solution of **8** (3 mL, 1×10^{-5} M) in $CHCl_3$. The fluorescence intensity at the emission maximum ($\lambda_{max}=618$ nm) of **8** was probed, with excitation at 435 nm. The binding constant could be calculated from the decrease in emission intensity by using a Scatchard plot.

Energy transfer study of G*x* (*x* = 1,2,3,4) dendrimers complexed with 8: A solution of **G*x*** dendrimer (1×10^{-5} M HR) in $CHCl_3$ and a solution of **G*x*** dendrimer (1×10^{-5} M HR) and **8** (2×10^{-5} M) in $CHCl_3$ were mixed in various ratios. In this way, solutions were obtained containing **G*x*** dendrimer (1×10^{-5} M HR) and increasing amounts of **8** per HR. Fluorescence spectra were recorded with excitation at 330 nm and corrected for the small increase in absorption caused by the addition of **8**.

Competition experiment with 7 and 8: A solution of **7** (15 mM) in $CHCl_3$ was added in aliquots of 5–10 μL (10 μL contains 5 equiv **7**) to a solution of **G*x*** dendrimer (3 mL, 1×10^{-5} M HR) and **8** (1 equiv per HR) in $CHCl_3$. Fluorescence spectra were recorded with excitation at 330 nm.

5-Nitroisophthaloyl dichloride (9): A solution of 5-nitroisophthalic acid (18.0 g, 85.0 mmol) in thionyl chloride (30 mL) and *N*,*N*′-dimethylformamide (five drops) was refluxed for 6 h under dry conditions with subsequent vacuum distillation of the thionyl chloride excess. The residue was dried under high vacuum and yielded a colorless solid (21.1 g, 100%): ^{1}H NMR ($CDCl_3$): $\delta=8.68$ (s, 1H; H_{ar}), 8.70 ppm (s, 2H; H_{ar}); ^{13}C NMR ([D_6]dimethyl sulfoxide): $\delta=127.1$, 133.0, 134.8, 148.1, 164.5 ppm.

***N*-(6-Aminopyridin-2-yl)-3,3-dimethylbutyramide (10)**: A solution of 3,3-dimethylbutyryl chloride (12.7 g, 91.6 mmol) in dry THF (50 mL) was added to a solution of 2,6-diaminopyridine (10.0 g, 91.6 mmol) and triethylamine (12.8 mL, 91.6 mmol) in dry THF (100 mL) at 0 °C under an argon atmosphere over a period of 2 h. The solution was stirred for 60 h at RT, the residue filtered off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (CH_2Cl_2/ethyl acetate (4:1) as eluent) gave a colorless solid (8.7 g, 46%): M.p.: 114–115 °C; ^{1}H NMR ($CDCl_3$): $\delta=1.05$ (s, 9H; ($C(CH_3)_3$), 2.18 (s, 2H; ($CH_2C(CH_3)_3$), 4.35 (br s, 2H; NH_2), 6.23 (dd, 1H, $^3J_{H,H}=7.88$, $^4J_{H,H}=0.74$ Hz; H_{py}), 7.42 (dd, 1H, $^3J_{H,H}=7.88$ Hz; H_{py}), 7.55 (d, 1H, $^3J_{H,H}=7.88$ Hz; H_{py}), 7.77 ppm (br s, 1H, CONH); ^{13}C NMR ($CDCl_3$): $\delta=29.8$, 31.3, 51.6, 103.3, 104.2, 140.2, 149.9, 157.1, 170.3 ppm; EI: *m*/*z* (%): 207 (15), 192 (5), 151 (4), 136 (8), 109 (100), 82 (19).

***N*,*N*′-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-nitro-isophthalamide (11)**: A solution of diacid dichloride **9** (2.74 g, 9.6 mmol) in dry THF (40 mL) was added dropwise to a solution of monosubstituted diaminopyridine **10** (4.0 g, 19.3 mmol) and triethylamine (2.7 mL, 19.3 mmol) in dry THF (40 mL) at 0 °C under an argon atmosphere. The solution was stirred at RT for 12 h, the residue filtered off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (CH_2Cl_2/ethyl acetate (2:1) as eluent) gave a yellowish solid (5.4 g, 97%): M.p.: 184 °C; $R_f=0.7$ (CH_2Cl_2/ethyl acetate (2:1 *v*/*v*)); ^{1}H NMR ($CDCl_3$): $\delta=1.10$ (s, 18H; $C(CH_3)_3$), 2.29 (s, 4H; $COCH_2$), 7.71 (t, $^3J_{H,H}=8.0$ Hz, 2H; H_{py}), 7.88 (d, $^3J_{H,H}=8.0$ Hz, 2H; H_{py}), 7.95 (d, $^3J_{H,H}=8.0$ Hz, 2H; H_{py}), 7.98 (br s, 2H; CONH), 8.74 (m, 3H; H_{ar}), 8.82 ppm (br s, 2H; CONH); ^{13}C NMR ($CDCl_3$): $\delta=29.8$, 31.4, 51.5, 109.9, 110.8, 125.2, 131.6, 136.4, 140.9, 148.5, 148.7, 149.9, 162.2, 170.8 ppm. FAB: *m*/*z*: 590 (100), 492 (12), 394 (14). X-ray structure analysis of **11**: $C_{30}H_{41}N_7O_9$ ($C_{30}H_{35}N_7O_6\cdot3H_2O$): colorless crystals, crystal dimensions $0.10\times0.30\times0.50$ mm^3; $M_r=643.70$; triclinic, space group $P\bar{1}$ (no. 2), $a=9.3024(1)$, $b=13.3131(2)$, $c=14.1360(3)$ Å, $\alpha=105.161(1)$, $\beta=103.689(1)$, $\gamma=100.292(1)$°, $V=1586.79(4)$ Å^3, $Z=2$, $\mu(Mo_{K\alpha})=0.101$ mm^{-1}, $T=123(2)$ K, $F(000)=684$. 10711 reflections up to $2\theta_{max}=50$° were measured on a Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation, 5572 of which were independent and used for all calculations. The structure was solved by direct methods and refined to F^2 anisotropically; the H atoms were refined with a riding model. The final quality coefficient $wR2(F^2)$ for all data was 0.2032, with a conventional $R(F)$ value of 0.0782 for 446 parameters and 16 restraints.[66]

5-Amino-*N*,*N*′-bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl] isophthalamide (12): Platinum(IV) oxide hydrate (100 mg) was added to a solution of the nitrocompound **11** (5.4 g, 9.2 mmol) in dry ethanol (100 mL). The suspension was hydrogenated at RT and 4.0 bar with stirring for 24 h. The catalyst was filtered off over celite and the solvent removed under reduced pressure. Recrystallization from ethanol gave a yellowish solid (5.0 g, 97%): M.p.: 191–192 °C; $R_f=0.72$ (ethyl acetate); ^{1}H NMR ($CDCl_3$): $\delta=1.11$ (s, 18H; $C(CH_3)_3$), 2.23 (s, 4H; $CH_2C(CH_3)_3$), 4.17 (s, 2H; NH_2), 7.08 (br s, 2H; H_{ar}), 7.52 (br s, 1H; H_{ar}), 7.72 (br s, 2H; H_{py}), 7.79, 7.85 (br s, 4H; H_{py}), 8.52 (s, 2H; CONH), 8.54 ppm (s, 2H; CONH); ^{13}C NMR ($CDCl_3$): $\delta=29.8$, 31.4, 51.0, 109.6, 110.5, 114.9, 117.2, 135.5, 140.6, 147.8, 149.1, 150.0, 171.8, 174.4 ppm; FAB: *m*/*z* (%): 560 (100), 503 (6), 462 (8), 353 (19).

9-{3,5-Bis[6-(3,3-dimethylbutyrylamino]-pyridin-2-ylcarbamoyl]-3-phenylcarbamoyl}nonanethioic acid pentafluorophenyl ester (PFTP ester; 15): A solution of the amine-functionalized receptor **12** (3.0 g, 5.4 mmol) and pentafluorothiophenol **13** (1.07 g, 5.4 mmol) in dry THF (150 mL) and a solution of sebacoyl dichloride **14** (1.29 g, 5.4 mmol) in dry THF (150 mL) were added simultaneously to a solution of triethylamine (1.5 mL, 10.8 mmol) in dry THF (150 mL) over 12 h under an argon atmosphere. The suspension was stirred for 12 h at RT, the residue filtered

off, and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol (50:50:1) as eluent) gave a yellowish solid (1.50 g, 30%): M.p.: 118°C; R_f=0.51 (petroleum ether/ethyl acetate (1:1 *v*/*v*)); ^{1}H NMR ($CDCl_3$): δ=1.06 (s, 18H; $(CH_3)_3$), 1.22 (brs, 8H; $CH_2(CH_2)_4CH_2$), 1.62 (brs, 4H; CH_2CH_2CO), 2.35 (s, 4H; $CH_2C(CH_3)_3$), 2.43 (m, 2H; CH_2CO), 2.63 (t, $^3J_{H,H}$=7.4 Hz, 2H; CH_2CO), 7.51 (t, $^3J_{H,H}$=8.3 Hz, 2H; H_{py}), 7.69 (d, $^3J_{H,H}$=7.1 Hz, 2H; H_{py}), 7.83 (brs, 2H; H_{py}), 7.90 (brs, 1H; H_{ar}), 8.28 (brs, 3H; H_{ar} + CON*H*), 8.89 (brs, 2H; CON*H*), 8.96 ppm (brs, 2H; CON*H*); ^{13}C NMR ($CDCl_3$): δ=25.3, 25.4, 28.7, 29.0, 29.1, 29.2, 29.8, 31.5, 37.6, 43.6, 50.9, 109.4, 110.6, 121.5, 137.8 (d, $^1J_{C,F}$= 247 Hz; C_{ar}–F), 139.3, 140.2 (d, $^1J_{C,F}$=240 Hz; C_{ar}–F), 146.9 (d, $^1J_{C,F}$= 243 Hz; C_{ar}–F), 148.8, 150.1, 171.9, 173.5, 192.4 ppm; FAB: *m*/*z* (%): 926 (100).

***N,N'*-Bis-[6-(3,3-dimethyl-butyrylamino)-pyridin-2-yl]-5-octanoyl-amino-isophthalamide (2)**: Octanoylchloride (0.087 mL, 0.509 mmol) was added dropwise to a solution of the amine-functionalized receptor **12** (300 mg, 0.536 mmol) and triethylamine (0.074 mL, 0.536 mmol) in dry dichloromethane (15 mL) at 0°C under an argon atmosphere. The solution was stirred for 3 h at RT and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (CH_2Cl_2/MeOH (100:1, 50:1, and 20:1) as eluent) gave **2** (250 mg, 72%) as a light-yellow solid: M.p.: 231–232°C; R_f=0.56 (CH_2Cl_2/methanol (20:1 *v*/*v*)); ^{1}H NMR ($CDCl_3$): δ=0.82 (t, 3H, $^3J_{HH}$=7.1 Hz; CH_2CH_3), 1.06 (s, 18H; $C(CH_3)_3$), 1.20–1.39 (m, 8H; CH_2), 1.68 (dt, 2H, $^3J_{H,H}$=7.5, $^3J_{H,H}$=7.5 Hz; $CH_2CH_2CH_2CO$), 2.22 (s, 4H; $CH_2C(CH_3)_3$), 2.40 (t, 2H, $^3J_{H,H}$=7.5 Hz; CH_2CH_2CO), 7.62 (t, 2H, $^3J_{H,H}$=8.1 Hz; H_{py}), 7.72 (d, 2H, $^3J_{H,H}$=8.1 Hz; H_{py}), 7.83 (d, 2H, $^3J_{H,H}$=8.2 Hz; H_{py}), 8.11 (s, 1H; H_{ar}), 8.20 ppm (s, 2H; H_{ar}); ^{13}C NMR ($CDCl_3$/CD_3OD (10:1 *v*/*v*)): δ=15.1, 23.8, 26.9, 30.3, 30.5, 30.8, 32.5, 33.0, 38.3, 52.1, 111.1, 111.2, 123.2, 123.7, 137.0, 140.7, 141.5, 151.3, 151.6, 167.0, 173.2, 175.1 ppm; FAB: *m*/*z* (%): 686.4 (100).

Typical procedure for dendrimers containing Hamilton receptors (5): Triethylamine (0.03 mL, 0.22 mmol) was added to a solution of DAB-*dendr*-Am_{16} (22 mg, 0.013 mmol) in chloroform (10 mL). A solution of the PFTP ester **15** (200 mg, 0.22 mmol) in chloroform (5 mL) was added slowly over a period of 5 minutes. The solution was stirred for four days under an argon atmosphere. The product was precipitated by dropwise addition of *n*-hexane, filtered, and dried in vacuo to yield **5** (150 mg, 85%) as a brownish product. M.p.: 140°C; ^{1}H NMR ($CDCl_3$): δ=1.03 (s, 288H; $C(CH_3)_3$), 1.47 (brs, 192H; CH_2), 1.58 (brs, 60H; CH_2CH_2N), 2.10 (s, 84H; NCH_2), 2.32 (s, 64H; $CH_2C(CH_3)_3$), 2.60 (m, 64H; $COCH_2$), 3.11 (brs, 32H; $CONCH_2$), 7.45 (brs, 48H; H_{ar}), 7.67 (brs, 32H; H_{py}), 7.82 (brs, 64H; H_{py}), 8.29 (brs, 64H; $CONHC_{py}$), 9.12 ppm (brs, 32H; CON*H*); ^{13}C NMR ($CDCl_3$): δ=10.5, 29.1, 29.3, 29.8, 29.9, 30.9, 31.4, 37.3, 45.9, 51.1, 110.1, 111.2, 121.1, 136.8, 140.3, 149.3, 150.8, 172.9, 176.1 ppm; MALDI-TOF MS: calcd for $C_{728}H_{1024}N_{142}O_{96}$: 13292.0; found: 13291.1.

3: M.p.: 180°C; ^{1}H NMR ($CDCl_3$): δ=1.03 (s, 72H; $C(CH_3)_3$), 1.45 (s, 48H; CH_2), 1.55 (brs, 12H; CH_2CH_2N), 2.05 (s, 12H; NCH_2), 2.35 (s, 16H; $CH_2C(CH_3)_3$), 2.65 (m, 16H; $COCH_2$), 3.15 (brs, 8H; $CONCH_2$), 7.45 (brs, 12H; H_{ar}), 7.71 (brs, 8H; H_{py}), 7.85 (brs, 16H; H_{py}), 8.30 (brs, 16H; $CONHC_{py}$), 9.10 ppm (brs, 8H; CON*H*); ^{13}C NMR ($CDCl_3$): δ= 10.5, 25.8, 26.2, 29.0, 29.8, 31.4, 37.0, 46.0, 50.8, 109.6, 111.6, 121.7, 122.1, 136.0, 140.6, 149.1, 150.5, 163.5, 171.9, 175.4, 177.8 ppm; MALDI-TOF MS: calcd for $C_{176}H_{244}N_{34}O_{24}$: 3217.9; found: 3219.2.

4: M.p.: 135°C; ^{1}H NMR ($CDCl_3$): δ=1.03 (s, 144H; $C(CH_3)_3$), 1.40 (brm, 96H; CH_2), 1.60 (brs, 20H; CH_2CH_2N), 2.05 (s, 36H; NCH_2), 2.35 (s, 32H; $CH_2C(CH_3)_3$), 2.90 (m, 32H; $COCH_2$), 3.10 (brs, 16H; $CONCH_2$), 7.47 (brs, 24H; H_{ar}), 7.68 (brs, 16H; H_{py}), 7.82 (brs, 32H; H_{py}), 8.33 (brs, 32H; $CONHC_{py}$), 9.08 ppm (brs, 16H; CON*H*); ^{13}C NMR ($CDCl_3$): δ=8.8, 25.6, 29.0, 29.3, 29.8, 31.4, 37.3, 45.7, 51.6, 109.8, 111.1, 122.1, 136.1, 140.8, 149.0, 150.9, 172.7, 176.5 ppm; MALDI-TOF MS: calcd for $C_{360}H_{504}N_{70}O_{48}$: 6575.9; found: 6577.2.

6: M.p.: 220°C; ^{1}H NMR ($CDCl_3$): δ=1.03 (s, 576H; $C(CH_3)_3$), 1.48 (brs, 384H; CH_2), 1.58 (brs, 124H; CH_2CH_2N), 2.10 (s, 180H; NCH_2), 2.32 (s, 128H; $CH_2C(CH_3)_3$), 2.62 (m, 128H; $COCH_2$), 3.11 (brs, 64H; $CONCH_2$), 7.45 (brs, 96H; H_{ar}), 7.66 (brs, 64H; H_{py}), 7.81 (brs, 128H; H_{py}), 8.29 (brs, 128H; $CONHC_{py}$), 9.09 ppm (brs, 64H; CON*H*); ^{13}C NMR ($CDCl_3$): δ=10.6, 29.2, 29.3, 29.8, 29.9, 31.4, 37.1, 41.5, 45.9, 51.0, 109.8, 111.2, 136.6, 136.8, 140.6, 148.3, 150.8, 172.9 ppm.

Synthesis of the guest molecules: Barbital[55] (**7**) and [Re(Br)(CO)$_3$(barbi-bpy)][53] (**8**) were synthesized according to literature procedures.

Acknowledgment

We thank Cornelis J. Kleverlaan and Derk J. Stufkens for valuable discussions, S. Bitter and S. Buschbeck for measurement of the MALDI-TOF spectra, and Jeroen van Heyst and René M. Williams for their contribution to the photophysical measurements. This work was financially supported by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) and a Cooperation in the Field of Scientific and Technical Reasearch (COST) grant (Grant no.: D11/0007).

[1] J.-M. Lehn, *Science* **2002**, *295*, 2400–2403.
[2] D. N. Reinhoudt, M. Crego-Calama, *Science* **2002**, *295*, 2403–2407.
[3] C. J. Chang, J. D. K. Brown, M. C. Y. Chang, E. A. Baker, D. G. Nocera in *Electron Transfer in Chemistry Vol. 3* (Ed.: V. Balzani), Wiley-VCH, Weinheim, Germany, **2001**, p. 409.
[4] *Supramolecular Chemistry* (Eds.: V. Balzani, F. Scandola), Horwood, Chichester, England, **1991**.
[5] A. D. Hamilton in *Advances in Supramolecular Chemistry* (Ed.: G. W. Gokel), JAI, London, England, **1990**, p. 1.
[6] V. Balzani, F. Scandola in *Comprehensive Supramolecular Chemistry Vol. 10* (Ed.: D. N. Reinhoudt), Pergamon, Oxford, England, **1996**, p. 687.
[7] J.-M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, Germany, **1995**.
[8] *Molecular Self-Assembly. Organic versus Inorganic Approaches. Structure and Bonding Vol.96* (Ed.: M. Fujita), Springer, Berlin, Germany, **2001**.
[9] *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. Davies, D. D. MacNicol, F. Vögtle), Pergamon/Elsevier, Oxford, England, **1996**.
[10] J. L. Sessler, M. Sathiosatham, C. T. Brown, T. A. Rhodes, G. Wiederrecht, *J. Am. Chem. Soc.* **2001**, *123*, 3655–3660.
[11] T. H. Ghaddar, E. W. Castner, S. S. Isied, *J. Am. Chem. Soc.* **2000**, *122*, 1233–1234.
[12] D. A. Williamson, B. E. Bowler, *J. Am. Chem. Soc.* **1998**, *120*, 10902–10911.
[13] A. Osuka, R. Yoneshima, H. Shiratori, T. Okada, S. Tanigushi, N. Mataga, *Chem. Commun.* **1998**, 1567–1568.
[14] Y. Q. Deng, J. A. Roberts, S.-M. Peng, S. K. Chang, D. G. Nocera, *Angew. Chem.* **1997**, *109*, 2216–2219; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2124–2127.
[15] J. P. Kirby, J. A. Roberts, D. G. Nocera, *J. Am. Chem. Soc.* **1997**, *119*, 9230–9236.
[16] W. Krause, N. Hackmann-Schlichter, F. K. Maier, R. Muller, *Top. Curr. Chem.* **2000**, *210*, 261–308.
[17] L. C. Sun, L. Hammarstrom, B. Akermark, S. Styring, *Chem. Soc. Rev.* **2001**, *30*, 36–49.
[18] M. Kercher, B. Konig, H. Zieg, L. De Cola, *J. Am. Chem. Soc.* **2002**, *124*, 11541–11551.
[19] M. W. P. L. Baars, E. W. Meijer, *Top. Curr. Chem.* **2000**, *210*, 131–182.
[20] R. M. Crooks, B. I. Lemon III, L. Sun, L. K. Yueng, M. Zhao, *Top. Curr. Chem.* **2001**, *212*, 81–135.
[21] V. V. Narayanan, G. R. Newkome, *Top. Curr. Chem.* **1998**, *197*, 19–77.
[22] F. W. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681–1712.
[23] D. K. Smith, F. Diederich, *Top. Curr. Chem.* **2000**, *210*, 183–227.
[24] *Dendrimers and Dendrons* (Eds.: G. R. Newkome, C. N. Moorefield, F. Vögtle), Wiley-VCH, New York, **2001** and references therein.
[25] a) J. F. G. A. Jansen, E. W. Meijer, *J. Am. Chem. Soc.* **1995**, *117*, 4417–4418; b) J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, *265*, 1226–1229.

[26] M. W. P. L. Baars, R. Kleppinger, M. H. J. Koch, S.-L Yue, E. W. Meijer, *Angew. Chem.* **2000**, *112*, 1341–1344; *Angew. Chem. Int. Ed.* **2000**, *39*, 1285–1288.
[27] S. Hecht, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2001**, *123*, 6959–6960.
[28] D. M. Watkins, Y. Sayed-Sweet, J. W. Klimash, N. J. Turro, D. A. Tomalia, *Langmuir* **1997**, *13*, 3136–3141.
[29] J.-F. Eckert, D. Byrne, J.-F. Nicoud, L. Oswald, J.-F. Nierengarten, M. Numata, A. Ikeda, S. Shinkai, N. Armaroli, *New J. Chem.* **2000**, *24*, 749–758.
[30] A. W. Kleij, R. van de Coevering, R. J. M. Klein Gebbink, A.-M. Noordman, A. L. Spek, G. van Koten, *Chem. Eur. J.* **2001**, *7*, 181–192.
[31] G. Pistolis, A. Malliaris, D. Tsiourvas, C. M. Paleos, *Chem. Eur. J.* **1999**, *5*, 1440–1444.
[32] F. Ortega-Caballero, J. J. Giménez-Martínez, L. García-Fuentes, E. Ortiz-Salmerón, F. Santoyo-González, A. Vargas-Berenguel, *J. Org. Chem.* **2001**, *66*, 7786–7795.
[33] F. Köhn, J. Hofkens, U.-M. Wiesler, M. Cotlet, M. van der Auweraer, K. Müllen, F. C. De Schryver, *Chem. Eur. J.* **2001**, *7*, 4126–4133.
[34] R. M. Crooks, M. Zhao, L. Sun, V. Chechnik, L. K. Yueng, *Acc. Chem. Res.* **2001**, *34*, 181–190.
[35] A. Archut, G. C. Azellini, V. Balzani, L. De Cola, F. Vögtle, *J. Am. Chem. Soc.* **1998**, *120*, 12187–12191.
[36] C. Larré, B. Donnadieu, A.-M. Caminade, J.-P. Majoral, *Chem. Eur. J.* **1998**, *4*, 2031–2036.
[37] H. Stephan, H. Spies, B. Johannsen, K. Gloe, M. Gorka, F. Vögtle, *Eur. J. Inorg. Chem.* **2001**, 2957–2963.
[38] D. de Groot, B. F. M. de Waal, J. N. H. Reek, A. P. H. J. Schenning, P. C. J. Kamer, E. W. Meijer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2001**, *123*, 8453–8458.
[39] M. Santo, M. A. Fox, *J. Phys. Org. Chem.* **1999**, *12*, 293–307.
[40] D. K. Smith, A. Zingg, F. Diederich, *Helv. Chim. Acta* **1999**, *82*, 1225–1241.
[41] A. D. Hamilton, *Nature* **2002**, *418*, 375–376.
[42] S. C. Zimmerman, M. S. Wendland, N. A. Rakow, I. Zharov, K. S. Suslick, *Nature* **2002**, *418*, 399–403.
[43] For an example of an x-ray structure of a recognition site in a protein, see: H. Pelletier, J. Kraut, *Science* **1992**, *258*, 1748–1755.
[44] B. H. Weigl, R. L. Bardell, C. R. Cabrera, *Adv. Drug Delivery Rev.* **2003**, *55*, 349–377.
[45] S.-K. Chang, A. D. Hamilton, *J. Am. Chem. Soc.* **1988**, *110*, 1318–1319.
[46] J. N. Valenta, R. P. Dixon, A. D. Hamilton, S. G. Weber, *Anal. Chem.* **1994**, *66*, 2397–2403.
[47] S. Li, L. F. Sun, Y. S. Chung, S. G. Weber, *Anal. Chem.* **1999**, *71*, 2146–2151.
[48] R. Kluger, B. Tsao, *J. Am. Chem. Soc.* **1993**, *115*, 2089–2090.
[49] P. Tecilla, V. Jubian, A. D. Hamilton, *Tetrahedron* **1995**, *51*, 435–448.
[50] P. Tecilla, S.-K. Chang, A. D. Hamilton, *J. Am. Chem. Soc.* **1990**, *112*, 9586–9590.
[51] a) V. Berl, M. Schmutz, M. J. Krische, R. G. Khoury, J.-M. Lehn, *Chem. Eur. J.* **2002**, *8*, 1227–1244; b) V. Berl, M. J. Krische, I. Huc, J.-M. Lehn, M. Schmutz, *Chem. Eur. J.* **2000**, *6*, 1938–1946.
[52] P. Tecilla, R. P. Dixon, G. Slobodkin, D. S. Alavi, D. H. Waldeck, A. D. Hamilton, *J. Am. Chem. Soc.* **1990**, *112*, 9408–9410.
[53] A. Dirksen, C. J. Kleverlaan, J. N. H. Reek, L. De Cola, unpublished results.
[54] A. S. Salameh, T. Ghaddar, S. S. Isied, *J. Phys. Org. Chem.* **1999**, *12*, 247–254.
[55] *A Textbook of Practical Organic Chemistry* (Ed.: A. I. Vogel), Longman Group, London, **1956**, p. 1002.
[56] a) A. P. H. J. Schenning, C. Elissen-Román, J.-W. Weener, M. W. P. L. Baars, S. J. van der Gaast, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 8199–8208; b) M. W. P. L. Baars, S. H. M. Söntjens, H. M. Fischer, H. W. I. Peerlings, E. W. Meijer, *Chem. Eur. J.* **1998**, *4*, 2456–2466.
[57] T. Chin, Z. Gao, I. Lelouche, Y. K. Shin, A. Purandare, S. Knapp, S. S. Isied, *J. Am. Chem. Soc.* **1997**, *119*, 12849–12858.
[58] W. Reckien, S. D. Peyerimhoff, *J. Phys. Chem. A* **2003**, *107*, 9634–9640.
[59] P. Ghosh, C. A. Schalley, unpublished results.
[60] F. Scandola, C. Chiorboli, M. T. Indelli, M. A. Rampi in *Electron Transfer in Chemistry Vol. 3* (Ed.: V. Balzani), Wiley-VCH, Weinheim, Germany, **2001**, p. 337.
[61] L. De Cola, P. Belser, *Coord. Chem. Rev.* **1998**, *177*, 301–346.
[62] F. Barigelletti, L. Flamigni, *Chem. Soc. Rev.* **2000**, *29*, 1–12.
[63] D. J. Stufkens, A. Vlèek, Jr., *Coord. Chem. Rev.* **1998**, *177*, 127–179.
[64] C. J. Kleverlaan, M. T. Indelli, C. A. Bignozzi, L. Pavanin, F. Scandola, G. M. Hasselman, G. J. Meyer, *J. Am. Chem. Soc.* **2000**, *122*, 2840–2849.
[65] E. H. Yonemoto, G. B. Saupe, R. H. Schmehl, S. M. Hubig, R. L. Riley, B. L. Iverson, T. E. Mallouk, *J. Am. Chem. Soc.* **1994**, *116*, 4786–4795.
[66] CCDC-219531 (**11**) contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambrigde CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: August 18, 2003
Revised: November 24, 2003 [F5461]

