JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Photoswitchable Metal Coordinating Tweezers Operated by Light-Harvesting Dendrimers

Enrico Marchi,[†] Massimo Baroncini,[†] Giacomo Bergamini,[†] Jeroen Van Heyst,[‡] Fritz Vögtle,[‡] and Paola Ceroni*[,†,§]

[†]Department of Chemistry "G. Ciamician", University of Bologna, via Selmi 2, 40126 Bologna, Italy
[‡]Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, Gerhard-Domagk Strasse 1, D-53121 Bonn, Germany
[§]Interuniversity Center for the Chemical Conversion of Solar Energy (SolarChem), Bologna unit, via Selmi 2, 40126 Bologna, Italy

Ⓢ *Supporting Information*

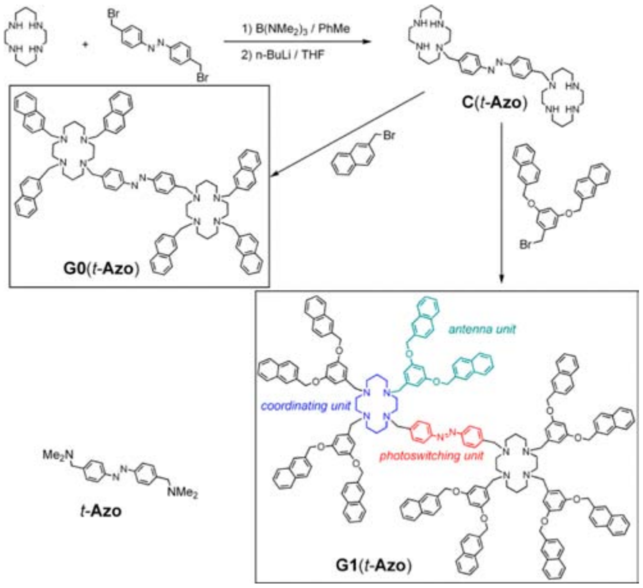
ABSTRACT: A dendrimer bearing two cyclam units linked by an azobenzene moiety, and luminescent naphthalene units at the periphery performs three different functions (light-harvesting, photoisomerization and coordination of metal ions) which can cooperate or interfere depending on the nature of the metal ion. It is thus an example of light controlled molecular tweezers in which Zn(II) coordination allows 100% efficient photosensitization of azobenzene switching, while Cu(II) shuts down azobenzene isomerization.

Artificial supramolecular structures containing multiple units are highly attractive to perform complex functions not exhibited by the single components. The value of these systems relies not only on the total number of components, but also on the diversity of the moieties and on the functions resulting from their mutual interactions.[1] To achieve these goals, a proper organization of the different functional units is vital. Dendrimers,[2,3] a class of multibranched molecules that can—by design—exhibit a high degree of order and complexity, are ideal scaffolds to organize multiple units in a nanoobject. Dendrimers containing photochromic[4,5] or luminescent units[6] or performing as ligands of metal ions[7,8] have been extensively investigated in the past decade. Herein we report on two dendrimers (Scheme 1) containing all the three above-mentioned functions. They bear two coordinating units (1,4,8,11-tetraazacyclotetradecane, hereafter called cyclam), linked by a photoswitching azobenzene moiety, and functionalized at the periphery with 6 or 12 light-harvesting (naphthalene) chromophores in **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**), respectively.

Azobenzene has been chosen because it undergoes an efficient and fully reversible photoisomerization reaction from the *trans* to the *cis* form.[9] For this reason, it has been extensively used to construct photoswitchable devices.[10] Cyclam is one of the most extensively investigated ligands in coordination chemistry,[11] able to strongly bind a wide variety of metal ions.

To the best of our knowledge, the present compounds represent the first example of dendrimers containing photochromic (azobenzene), luminescent (naphthalene) and metal coordinating units (cyclam) and thus performing three different functions: light-harvesting, metal coordination and photoswitching. Because of their proximity, the various functional groups of the dendrimers interact: the azobenzene unit enables to control the distance between the two cyclam moieties upon light stimulation. This leads to different coordination properties for the *cis* and *trans* isomers. Metal coordination and photosensitized isomerization can control each other. Therefore, this is an example of photocontrolled metal coordinating tweezers in which the coordinated metal ion is not only a spectator but it can switch ON/OFF the light-harvesting and photoisomerization functions.

Scheme 1. Synthesis and Structures of the Investigated Compounds, Evidencing the Three Different Functional Units



The synthesis of **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) (Scheme 1) was achieved starting from a common intermediate: **C**(*t*-**Azo**) that was prepared by monoalkylation of 2 equiv of a boron triprotected cyclam[12] with 1 equiv of bis(4-bromomethylphenyl)diazene. **C**(*t*-**Azo**) was reacted with 2-(bromomethyl)naphthalene in DMF for 2 days to afford **G0**(*t*-**Azo**) in

Received: July 31, 2012
Published: September 5, 2012

dx.doi.org/10.1021/ja307522f | *J. Am. Chem. Soc.* 2012, 134, 15277−15280

moderate yield. For the synthesis of **G1**(*t*-**Azo**), an excess of 3,5-bis(2′-naphtalenylmethyloxy)benzylbromide was reacted with **C**(*t*-**Azo**) in DMF for 4 days. Both compounds **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) were fully characterized by ^{1}H and ^{13}C NMR, ESI-MS, and UV−vis absorption spectroscopy.

The absorption spectra of **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) in CH_3CN/CH_2Cl_2 1:1 (v/v) (Figure 1) are similar to those obtained by the sum of the component spectra. They show the characteristic bands of both naphthalene at 275 nm and azobenzene at 336 ($\pi\pi^*$ transition) and 450 nm ($n\pi^*$ transition). The lowest energy excited state is localized on the azobenzene moiety.

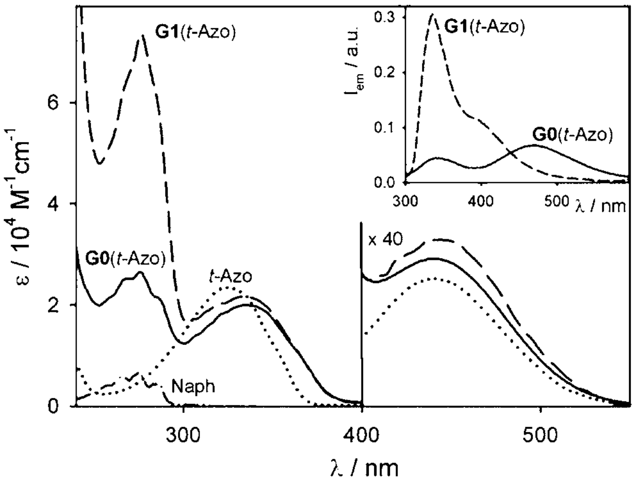


Figure 1. Absorption spectra of **G0**(*t*-**Azo**) (full line), **G1**(*t*-**Azo**) (dashed line), *t*-**Azo** (dotted line) and naphthalene (dashed-dotted line) in CH_3CN/CH_2Cl_2 1:1 (v/v). Inset shows emission spectra of **G0**(*t*-**Azo**) (full line), **G1**(*t*-**Azo**) (dashed line) in CH_3CN/CH_2Cl_2 1:1 (v/v). λ_{ex} = 275 nm. T = 298 K.

By excitation at 275 nm where most of the light is absorbed by the naphthalene chromophores, **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) exhibit a very weak luminescence (Figure 1, inset). The former shows two bands at 335 and 470 nm, and the latter exhibits a maximum at 335 nm together with a shoulder at 400 nm. In analogy with the behavior previously reported for the two dendrimers containing only a cyclam core,[13] we can assign the different emission bands to naphthyl localized excited states (λ_{max} = 335 nm), naphthyl excimers (λ_{max} ca. 390 nm), and naphthyl-amine exciplexes (λ_{max} = 470 nm) as a result of the interaction of an excited naphthalene with an amine group of the cyclam unit. The emission spectrum of **G1**(*t*-**Azo**) does not show the band at 470 nm: this result is likely due to the fact that energy transfer to the azobenzene core (see below) is faster than exciplex formation, while in **G0**(*t*-**Azo**), the close proximity of naphthalene and cyclam nitrogens enable exciplex formation in competition with energy transfer to the azobenzene core. The emission quantum yields of **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) (0.6×10^{-3} and 1.1×10^{-3}, Table S1) are much lower than those previously observed for cyclam-cored dendrimers (3 and 5×10^{-3} for generation 0 and 1, respectively).[14] This result suggests a quenching by the azobenzene unit (see below).

Upon irradiation at 365 nm, where only azobenzene is absorbing light, the absorption spectra of **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) (Figure S1) show a decrease of the $\pi\pi^*$ band at 336 nm and an increase of the $n\pi^*$ band of azobenzene. These spectral changes are characteristic of *trans* → *cis* isomerization. The *cis*-azobenzene species can be converted back to the *trans* isomer by irradiation at 436 nm in the $n\pi^*$ band.

Upon irradiation at 365 nm, the values of the photochemical quantum yield $\Phi_{t\rightarrow c}$ and the percentage of *trans* at the photostationary state of the model compound *t*-**Azo** (Scheme 1) are identical to those obtained for **G0**(*t*-**Azo**), within the experimental errors (Table 1). Small differences are observed for **G1**(*t*-**Azo**): a lower value of $\Phi_{t\rightarrow c}$ upon irradiation at 365 nm, and a somewhat larger fraction of *trans* in the photostationary state reached by irradiation both at 365 (Table 1), is indicative of a higher stability of the *trans* isomer compared to the *cis* one in **G1**(*t*-**Azo**) with respect to the model compound.

Table 1. Most Relevant Photochemical Data of the Investigated Dendrimers and their Zn(II) Complexes as Well as Model Compound Azo in CH_3CN/CH_2Cl_2 1:1 (v/v) Solution at 298 K

	λ_{irr} =275 nm		λ_{irr} =365 nm	
	$\Phi_{t\rightarrow c}$	η_{ET}	$\Phi_{t\rightarrow c}$	% *t*
G0-Azo	0.05	0.2	0.15	5
$[Zn_2($**G0-Azo**$)]^{4+}$	0.08	1.0	0.07	10
$[Cu_2($**G0-Azo**$)]^{4+}$	<0.01	-	0.03	51
G1-Azo	0.04	0.4	0.09	7
$[Zn_2($**G1-Azo**$)]^{4+}$	0.04	0.6	0.06	13
$[Cu_2($**G1-Azo**$)]^{4+}$	<0.01	-	0.06	36
Azo	0.13	-	0.15	5

To elucidate the interaction between naphthalene and azobenzene in the dendritic structures, photoisomerization of azobenzene has been investigated upon selective excitation of the naphthalene at 275 nm, where more than 95% of the light is absorbed by the naphthalene for **G1**(*t*-**Azo**) and **G1**(*c*-**Azo**). The results show that azobenzene isomerization takes place, demonstrating that energy transfer from the naphthalene to the *trans* isomer of the azobenzene core occurs with an efficiency (η_{ET}, Table 1) of 20% and 40% for **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**), respectively.

Upon titration of a 1.8×10^{-5} M solution of **G0**(*t*-**Azo**) in CH_3CN/CH_2Cl_2 1:1 (v/v) solution with $Zn(CF_3SO_3)_2$, the absorption spectrum shows a blue shift and an increase in intensity of the $\pi\pi^*$ band of azobenzene together with a decrease of absorbance at 260 nm with isosbestic points at 268 and 342 nm (Figure 2). The plot of normalized absorption changes at 304 nm versus the amount of Zn(II) (inset of Figure 2) is quite linear and exhibits a plateau at ca. 2.3 equiv of Zn(II) per dendrimer, demonstrating that up to two metal ions can be coordinated, that is, one per cyclam unit. By global fitting of the absorption changes, an estimate of the association constants can be obtained: $K_1 = 7 \times 10^7$ M^{-1}, $K_2 = 5 \times 10^6$ M^{-1} for 1:1 and 2:1 metal/dendrimer stoichiometry. In the 1:1 complex, only one of the two cyclam units is linked to Zn(II) because the *trans*-azobenzene unit keeps the two cyclam units quite far apart (Scheme 2a, left).[15]

Titration with $Zn(CF_3SO_3)_2$ has been performed also on the solution obtained at the photostationary state upon irradiation at 365 nm, where the ratio of *cis* and *trans* isomers is 95:5. The absorbance change at 304 nm reaches a plateau at ca. 1.4 equiv of Zn(II) ions per dendrimer, instead of 2.3 equiv observed in the case of the *trans* isomer (inset of Figure 2). These results can be rationalized on the basis of a structural rearrangement

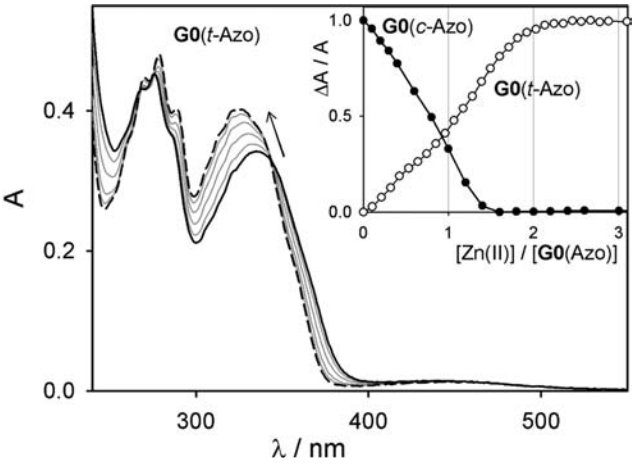
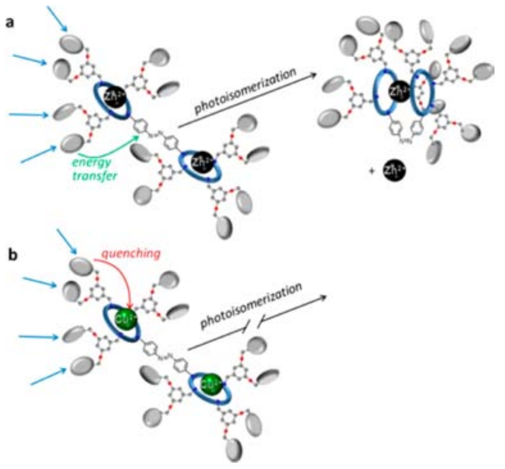


Figure 2. Absorption spectra of a 1.8×10^{-5} M solution of **G0**(*t*-**Azo**) in CH_3CN/CH_2Cl_2 1:1 (v/v) during the titration with $Zn(CF_3SO_3)_2$: 0 equiv (thick solid line), 3 equiv (thick dashed line). Inset shows the normalized absorption changes at 304 nm for **G0**(*t*-**Azo**) (open circles) and **G0**(*c*-**Azo**) (solid circles).

Scheme 2. Schematic Representation of the Functions Performed by G1(Azo)[a]



[a] Different coordination ability by the cyclam moieties (blue circles) of **G1**(*t*-**Azo**) (left) and **G1**(*c*-**Azo**) (right), light-harvesting by naphthalene units (grey ovals) and sensitized photoisomerization of the core azobenzene.

which brings the two cyclam units much closer, so that one Zn(II) ion can be coordinated by both of them (Scheme 2a, right).[16] The coordination of the second Zn(II) ion is highly disfavored by the electrostatic repulsion due to the close proximity of two 2+ ions. By fitting the absorption changes and taking into account the small percentage of *trans* isomer present at the photostationary state, the association constant is estimated as $K_1 = 1 \times 10^8$ M^{-1}. This value is slightly higher than that found for the trans isomer, evidencing a positive effect of the second cyclam unit on the stability constant.[17]

Qualitatively similar results are obtained in the case of **G1**(*t*-**Azo**) upon titration with $Zn(CF_3SO_3)_2$: $K_1 = 7 \times 10^7$ M^{-1}, $K_2 = 1 \times 10^5$ M^{-1}. Upon titration with $Zn(CF_3SO_3)_2$ of the photostationary state of **G1**(*c*-**Azo**) obtained at $\lambda_{irr} = 365$ nm, the plot of absorbance at 304 nm is very similar to that reported for **G0**(*c*-**Azo**). This results demonstrate the formation of a complex with 1:1 metal to dendrimer stoichiometry with $K_1 = 1 \times 10^8$ M^{-1}.

Photochemical experiments on the metal complexes of both dendrimers have been performed upon addition of an excess of Zn(II) ions (6 equiv per dendrimer). The presence of two metal ions per dendrimer in the *trans* isomer disfavors the *trans* → *cis* photoreaction, as demonstrated by the lower value of $\Phi_{t\rightarrow c}$ upon irradiation at 365 nm and higher molar fraction of *trans* isomer at the photostationary state upon irradiation at 365 (Table 1).

Regarding the isomerization sensitized by naphthalene excitation, a strong increase of the efficiency of energy transfer (η_{ET}) from naphthalene to azobenzene is observed (Table 1, Scheme 2a) with unitary values of η_{ET} for metal complexes of **G0**(*t*-**Azo**). This result is consistent with the fact that coordination of Zn(II) to the cyclam prevents exciplex formation.

Similar coordination properties have been observed upon titration of **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) solutions with $Cu(CF_3SO_3)_2$. At variance with Zn(II) complexes, the absorption spectra show the increase of a new band at 330 nm, which can be assigned to a ligand-to-metal charge transfer (LMCT) transition (Figure S2).[18] As expected, the cyclam moiety is able to coordinate both Zn(II) and Cu(II) ions, but profound differences are observed in the photophysical and photochemical properties. Indeed, no sensitized isomerization is observed in the Cu(II) complexes of **G0**(*t*-**Azo**) and **G1**(*t*-**Azo**) upon excitation of the naphthalene units and a lower isomerization quantum yield upon direct excitation of the azobenzene core (Table 1, Scheme 2b). These results are consistent with the quenching of the naphthalene luminescence and, to some extent, the azobenzene isomerization by energy/electron transfer to a coordinated Cu(II) ion.

In conclusion, two dendrimers bearing two cyclam units as coordinating sites for metal ions, a photoisomerizable azobenzene core, and naphthalene light-harvesting units at the periphery have been synthesized. The functions performed by the three components cooperate or interfere depending on the nature of the metal ion: Zn(II) coordination allows 100% sensitization of azobenzene by the light-harvesting antenna, whereas Cu(II) prevents this effect. Zn(II) ions can be released in solution upon photochemical stimulation. For the first generation dendrimer, up to 12 naphthalene units can sensitize the azobenzene isomerization with larger energy transfer efficiency compared to **G0**(*t*-**Azo**). Compared to the pioneering work by Shinkai et al.,[19] the presently investigated systems couple the photocontrolled tweezering function, the light harvesting antenna performed by the dendrons and the possibility to switch ON/OFF the sensitization of azobenzene depending on the nature of the coordinated metal ion (Scheme 2). The cyclam moieties cannot discriminate between Zn(II) and Cu(II) ions, but the resulting complexes can be differentiated on the basis of their photochemical behavior. A Cu(II)-like behavior is expected for all metal ions exhibiting low-lying excited states or easy to oxidize and reduce that can quench naphthalene by energy or electron transfer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for the synthesis and characterization, photochemical isomerization and Cu(II) titration. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

paola.ceroni@unibo.it

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge MAE (DGPSP Italy-China) MIUR (PRIN 20085ZXFEE, FIRB RBAP11C58Y) for financial support and Prof. Vincenzo Balzani for useful discussions.

REFERENCES

(1) Schmittel, M.; Mahata, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5284–5286.

(2) (a) *Designing Dendrimers*; Campagna, S., Ceroni, P., Puntoriero, F., Eds.; Wiley: Hoboken, NJ, 2012. (b) Caminade, A.-M.; Turrin, C.-O.; Laurent, R.; Ouali, A.; Delavaux-Nicot, B. *Dendrimer. Towards Catalytic, Material and Biomedical Uses*; Wiley: Chichester, U.K., 2011. (c) Vögtle, F.; Richardt, G.; Werner, N. *Dendrimer Chemistry*; Wiley-VCH: Chichester, U.K., 2009.

(3) For some recent reviews, see: (a) Franc, G.; Kakkar, A. K. *Chem. Soc. Rev.* **2010**, *39*, 1536–1544. (b) Wilms, D.; Stiriba, S. E.; Frey, H. *Acc. Chem. Res.* **2010**, *43*, 129–141. (c) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857–1959. (d) Jang, W. D.; Selim, K. M. K.; Lee, C. H.; Kang, I. K. *Prog. Polym. Sci.* **2009**, *34*, 1–23. (e) Li, W. S.; Aida, T. *Chem. Rev.* **2009**, *109*, 6047–6076.

(4) Deloncle, R.; Caminade, A.-M. *J. Photochem. Photobiol., C* **2010**, *11*, 25–45.

(5) For examples of dendrimers with azobenzene units, see, e.g.: (a) Nguyen, T.-T.-T.; Turp, D.; Wang, D.; Nolscher, B.; Laquai, F.; Müllen, K. *J. Am. Chem. Soc.* **2011**, *133*, 11194–11204. (b) del Barrio, J.; Tejedor, R. M.; Chinelatto, L. S.; Sanchez, C.; Pinol, M.; Oriol, L. *Chem. Mater.* **2010**, *22*, 1714–1723. (c) Li, Z.; Wu, W.; Li, Q.; Yu, G.; Xiao, L.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 2763–2767. (d) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Vögtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714–10719.

(6) (a) Restani, R. B.; Morgado, P. I.; Ribeiro, M. P.; Correia, I. J.; Aguiar-Ricardo, A.; Bonifácio, V. D. B. *Angew. Chem., Int. Ed.* **2012**, *51*, 5162–5165. (b) Bozdemir, O. A.; Erbas-Cakmak, S.; Ekiz, O. O.; Dana, A.; Akkaya, E. U. *Angew. Chem., Int. Ed.* **2011**, *50*, 10907–10912. (c) Uetomo, A.; Kozaki, M.; Suzuki, S.; Yamanaka, K.; Ito, O.; Okada, K. *J. Am. Chem. Soc.* **2011**, *133*, 13276–13279. (d) Bergamini, G.; Ceroni, P.; Fabbrizi, P.; Cicchi, S. *Chem. Commun.* **2011**, *47*, 12780–12782. (e) Kuroda, D. G.; Singh, C. P.; Peng, Z.; Kleiman, V. D. *Science* **2009**, *326*, 263–267.

(7) (a) Shellaiah, M.; Rajan, Y. C.; Lin, H.-C. *J. Mater. Chem.* **2012**, *22*, 8976–8987. (b) Yang, J.; Lee, S.; Lee, H.; Lee, J.; Kim, H. K.; Lee, S. U.; Sohn, D. *Langmuir* **2011**, *27*, 8898–8904. (c) Ochi, Y.; Fujii, A.; Nakajima, R.; Yamamoto, K. *Macromolecules* **2010**, *43*, 6570–6576. (d) Branchi, B.; Ceroni, P.; Balzani, V.; Klärner, F.-G.; Voegtle, F. *Chem.—Eur. J.* **2010**, *16*, 6048–6055.

(8) For cyclam dendrimers, see: Bergamini, G.; Marchi, E.; Ceroni, P. *Coord. Chem. Rev.* **2011**, *255*, 2458–2468.

(9) For a recent review, see: Bandara, H. M. D.; Burdette, S. C. *Chem. Soc. Rev.* **2012**, *41*, 1809–1825.

(10) (a) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines—A Journey into the Nanoworld*; Wiley-VCH: Weinheim, 2003. (b) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001.

(11) (a) Barefield, E. K. *Coord. Chem. Rev.* **2010**, *254*, 1607–1627. (b) Fabbrizzi, L.; Licchelli, M.; Mosca, L.; Poggi, A. *Coord. Chem. Rev.* **2010**, *254*, 1628–1636.

(12) Bernard, H.; Yaouanc, J. J.; Clément, J. C.; des Abbayes, H.; Handel, H. *Tetrahedron Lett.* **1991**, *32*, 639–642.

(13) Saudan, C.; Balzani, V.; Ceroni, P.; Gorka, M.; Maestri, M.; Vicinelli, V.; Vögtle, F. *Tetrahedron* **2003**, *59*, 3845.

(14) Saudan, C.; Balzani, V.; Gorka, M.; Lee, S.-K.; van Heyst, J.; Maestri, M.; Ceroni, P.; Vicinelli, V.; Vögtle, F. *Chem.—Eur. J.* **2004**, *10*, 899.

(15) HyperChem Professional 7.51 has been used to visualize the geometry of the 1:1 complex.

(16) Since the coordination number of Zn(II) is lower than 8, the two cyclam moieties are forced to adopt a structure in which not all of the four N atoms are coordinated to a Zn(II) at the same time.

(17) Profound changes are observed in the emission spectra, but these results are not discussed because recording an emission spectrum brings about photoisomerization of the azobenzene unit.

(18) Bergamini, G.; Ceroni, P.; Balzani, V.; Cornelissen, L.; van Heyst, J.; Lee, S.-K.; Vögtle, F. *J. Mater. Chem.* **2005**, *15*, 2959.

(19) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111.