Spectroscopic Studies on Inclusion Properties of Fullerenocalix[4]arene Conjugates with Metal Ions

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Received: November 10, 2004; In Final Form: December 8, 2004

Metal-chelating properties—in the ground and excited states—of fullerenocalix[4]arenes containing two malonamide substituents at the upper rim and four alkyl ester chains at the lower rim have been studied by means of steady-state absorption, fluorescence spectroscopy, and time-resolved transient absorption spectra. In particular, the influence that Ag^+ enforces on the fullerene electronic spectra is due to direct interactions between Ag^+ and the surface of C_{60}. The effects stemming from Na^+, Mg^{2+}, and Ba^{2+}, on the other hand, are indirect and are introduced through chelating the metal ions to the calix[4]arene moiety. They strongly depend on the molecular structure of the fullerenocalix[4]arenes. No spectroscopic evidence was obtained for any influence caused by Mn^{2+}, although the malonamide groups provide good chelating ability even for this transition metal ion.

Introduction

Calixarenes have demonstrated unlimited potential as a versatile receptor platform en route toward multifunctional host−guest architectures.[1−6] Matching the concave surface of cup-shaped molecular nanostructures to the convex shape of, for example, C_{60} is a potent means to gain control over the inherently weak association between a host moiety and a molecular guest.[7] The synopses of in-built shape- and size-specific receptor sites are 2-fold: First, it ensures efficient binding. Second, it exerts a major challenge to find the right match. Prominent instances are nanosized, bowl-shaped molecules or container molecules with curved, open-ended cavities, such as cyclodextrins,[8] benzotri(benzonorbornadienes),[9] calixarenes,[10] calixnaphthalenes,[11] and cyclotriveratrylene.[12] In general, they all form remarkably stable composites with fullerenes, which exhibit high guest selectivity and control of reactivity. Unlike some of the aforementioned classes of containers, the structures of calixarenes allow for much more structural flexibility, which plays a considerable role in their binding affinity. This renders the π-rich cavity of macrocyclic calixarenes ideally suited for the extraction of fullerenes—especially C_{60}—from the carbon soot.[10b,c]

The modification of the upper and lower rims of calixarenes offers limitless incentives to fine-tune the physicochemical properties of the resulting multifunctional host−guest architectures. Well-preorganized cone cavities and inclinations of the benzene rings in the molecular hosts are probably the most central factors regulating the binding affinities, that is, control over selectivity and stability. A similarly strong impact was noted upon varying temperature and/or solvent. From among the leading architectural systems emerged recently a remarkable system that was designed to incorporate metal ions and fullerene molecules at the same time.[13]

Fullerenes covalently linked to calixarenes, namely, fullerenocalixarenes, have also been probed for their complexation properties with metal ions.[14−16] In such supramolecular systems no decisive evidence is, however, given that might shed light on the metal ion/C_{60} communications. In particular, it is not clear if the interactions are due to direct metal ion/C_{60} contacts or if indirectly induced effects, which are mainly mediated through the calixarene framework, are responsible for long-range metal ion/C_{60} interactions.[15] Very interestingly, upon adjusting the polarity of the solvent, which exerts an impact on the fullerene solubility, fullerenocalixarene can form self-inclusion conformers with the fullerene moiety capped by the intramolecular calixarene moiety.[17]

In this paper we present spectroscopic results for the addition of metal ions—Na^+, Ag^+, Mg^{2+}, Ba^{2+}, and Mn^{2+}—to tetrahydrofuran solutions of fullerenocalix[4]arenes **1** and **2**; see Scheme 1. A comparison with their reference compounds (**3** and **4**) leads to the conclusion that Ag^+ ions influence the fullerene electronic spectra through direct Ag^+/C_{60} interactions, while the spectroscopic effects evolving from Na^+, Mg^{2+}, and Ba^{2+} are indirectly inductive through metal ion/calixarene/C_{60}.

Experimental Section

Fullerenocalix[4]arenes **1** and **2**,[18] reference compounds **3** and **4**,[19] and reference compound **5**[20] were synthesized according to published work. Sodium perchlorate (99.0+ %, Aldrich), magnesuim perchlorate (99.0%, Aldrich), barium perchlorate (99.999%, Aldrich), manganese perchlorate (99.0%, Aldrich), silver perchlorate (99.9%, Aldrich), and tetrahydrofuran (THF; 99.5%, Aldrich) were used as received.

Absorption spectra were recorded with a Milton Roy Spectronic spectrometer. Emission spectra were recorded with a SLM 8100 spectrofluorometer. Fluorescence lifetimes were measured using a PTI LaserStrobe fluorescence lifetime spectrometer with a GL-3300 nitrogen laser (0.04 nm bandwidth, 500 ps pulse width) as an excitation source and stroboscopic detection. The time resolution following deconvolution of experimental decays is 100 ps.

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10.1021/jp044845z CCC: \$30.25

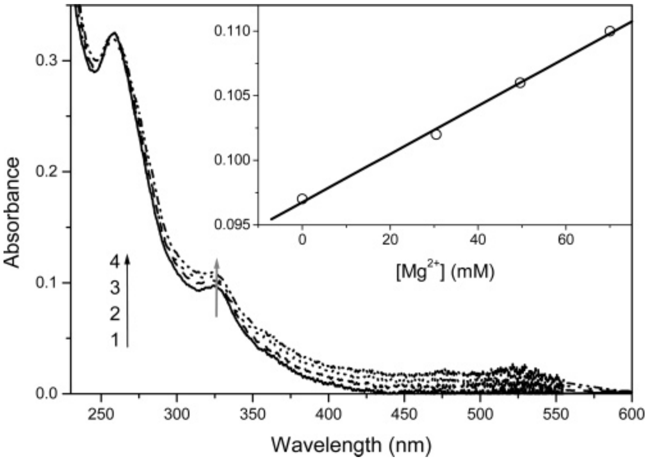
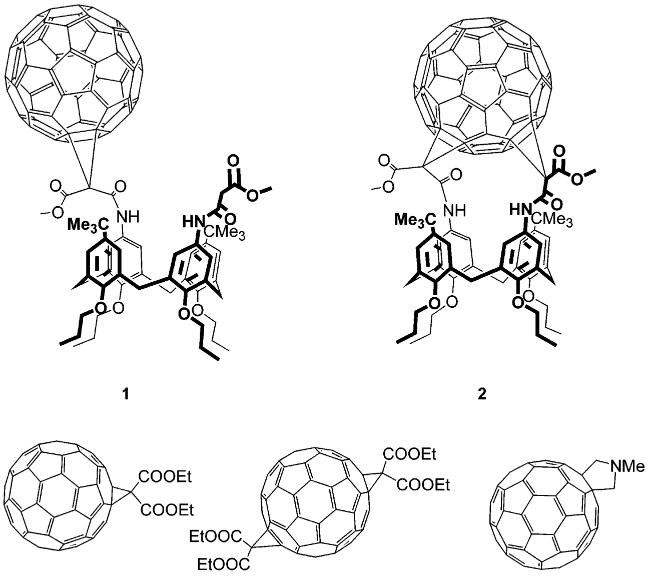


Figure 1. Absorption spectra of **1** (1.8×10^{-2} mM) in THF solution upon addition of $Mg(ClO_4)_2$. The Mg^{2+} concentrations were 0 (1), 30.5 (2), 49.6 (3), and 70.0 mM (4). The insert displays the change of absorbance at 324 nm as a function of Mg^{2+} concentration.

SCHEME 1: Structures of One (1) and Two (2) Fullerene Attached Malonamide Calixarenes and Reference Compounds (3, 4, and 5)



1 2

3 4 5

Nanosecond laser flash photolysis experiments were performed with laser pulses from a nitrogen laser (337 nm, 10 ns pulse width). A monochromator (SPEX) in combination with a Hamamatsu R 5108 photomultiplier was employed to monitor transient absorption spectra.

All the experiments were performed at room temperature. Each spectrum represents an average of at least five individual scans, and appropriate corrections were applied whenever necessary.

Results and Discussion

Titrating variable $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ concentrations to THF solutions of **1** leads to appreciable changes in the absorption and fluorescence spectra of fullerenocalixarene **1**. As exemplified in Figures 1 and 2, both absorption and fluorescence of **1** reveal overall increases. In addition, we see new transitions in the visible region (i.e., 400−600 nm). Please note that especially the absorption spectra of $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ solutions—in the millimolar range—lack any detectable features in part of the UV and the entire visible range of the spectrum. A saturated $Mg(ClO_4)_2$ solution (i.e., ∼80 mM) absorbs only between 200 and 250 nm, and its relative absorption is less than 5% of that of the employed fullerenocalixarene **1**. From these important observations we conclude that the new absorption features in the 450−600 nm range reflect the Mg^{2+} and Ba^{2+} inclusion and emerge as sensitive spectroscopic markers.

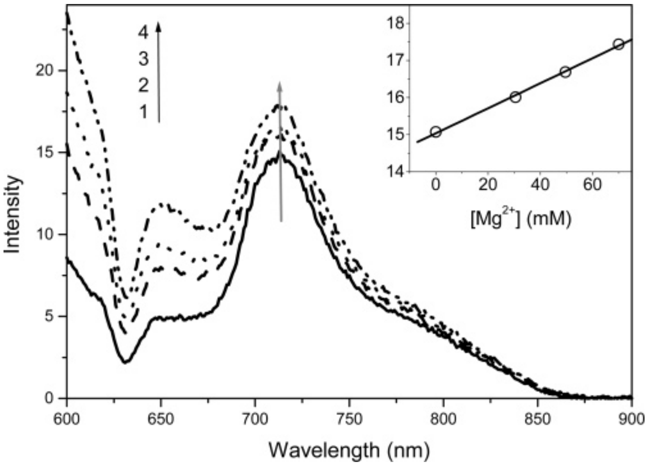


Figure 2. Fluorescence spectra of **1** (1.8×10^{-2} mM) in THF solution upon addition of $Mg(ClO_4)_2$. The Mg^{2+} concentrations were 0 (1), 30.5 (2), 49.6 (3), and 70.0 mM (4). The insert displays the change of fluorescence intensity at 715 nm as a function of Mg^{2+} concentration.

The low solubilities of $Mg(ClO_4)_2$ in THF limit the titration experiments to concentrations less than 80 mM. For $Ba(ClO_4)_2$ concentrations were as high as 285 mM. Within the applied Mg^{2+} concentration regime, both the absorbance at 324 nm, which corresponds to one of the major absorption bands of C_{60}, and the fluorescence intensity at 715 nm, where the overall weak C_{60} fluorescence maximizes, linear relationships were concluded. Similar phenomena were also observed upon titrating Ba^{2+} to THF solutions of **1**. A different behavior was, however, seen at high Ba^{2+} concentrations (i.e., >285 mM), where both absorbance and fluorescence intensities dropped. A potential explanation implies that the inclusion formation is completed in the high concentration regime (i.e., <285 mM) and that further addition of Ba^{2+} causes only intermolecular effects.

By contrast, significant quenching (i.e., up to 50%) of the 715 nm fluorescence was observed when $AgClO_4$ concentrations as high as 300 mM were added to **1**. Important is the fact that the changes of absorbance at 324 nm and also of the 400−600 nm fingerprint constitute only 1/10 of that seen for Ba^{2+} in the same concentration range (i.e., up to ∼300 mM). No appreciable spectroscopic changes were imposed on the absorption or on the fluorescence spectra upon the addition of $NaClO_4$ or $Mn(ClO_4)_2$.

When fullerenocalixarene **2** was tested in THF, a different behavior—with the exception of Mn^{2+} and Ag^+ ions—was concluded. For the former case of Mn^{2+}, no spectroscopic changes, relative to those noted in the absence of any ions, were forced onto the features of **2**. This trend is identical with that seen for **1**. For the case of Ag^+, a similar scenario was also observed: Although the absorption grows slightly upon Ag^+ addition, the fluorescence intensity decreases significantly (i.e., up to 50% at the highest—300 mM—concentration).

Remarkable differences between fullerenocalixarenes **1** and **2** are seen when Mg^{2+} and Ba^{2+} are used: absorption (see Figure 3) and fluorescence lack any appreciable spectroscopic changes.

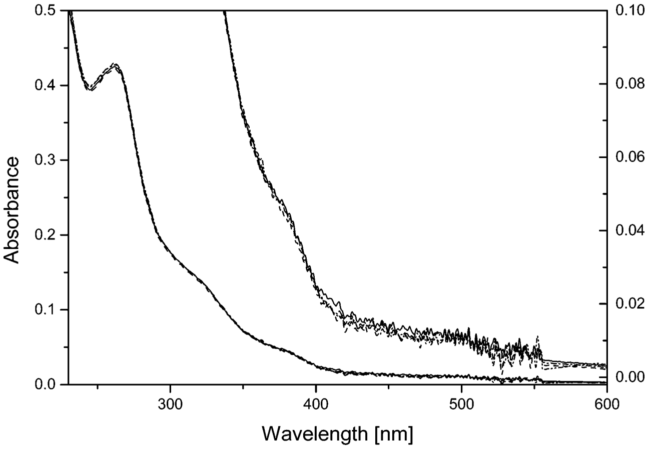


Figure 3. Absorption spectra of **2** (1.8×10^{-2} mM) in THF solution upon addition of $Mg(ClO_4)_2$. The Mg^{2+} concentrations were 0, 19.7, 31.1, and 50.5 mM.

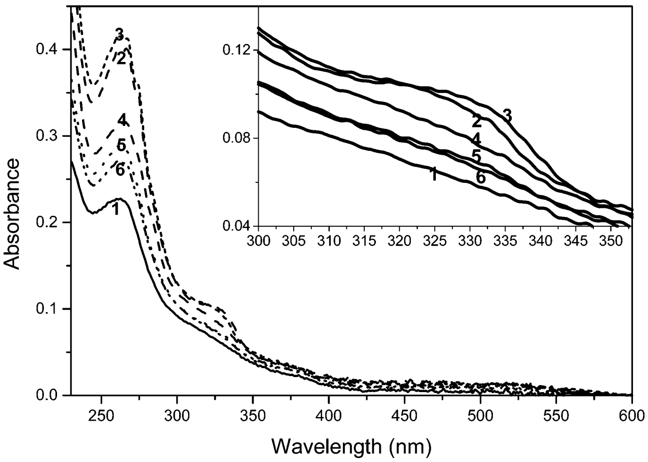


Figure 4. Absorption spectra of **2** (1.9×10^{-2} mM) in THF solution upon addition of $NaClO_4$. The Na^+ concentrations were 0 (1), 44.2 (2), 87.4 (3), 128.8 (4), 168.1 (5), and 266.2 mM (6). The insert displays the extended absorption spectra for the new band varying the addition of Na^+.

As displayed in Figure 4, the addition of Na^+ to **2** led to spectral changes in the absorption spectra that are quite complex. Initially, the absorption features and especially those at 263 and 327 nm increase for $[Na^+]$ concentrations of 0, 44.2, and 87.4 mM, but drops right after adding more Na^+ (i.e., 128.8 and 168.1 mM) before seemingly approaching a plateau value at 266.2 mM. These changes are further accompanied by the grow-in of the 400−600 nm marker, whose development parallels the changes at 263 and 327 nm. The fluorescence spectra that are associated with the Na^+/**2** system show an increase in intensity and are dominated by a dramatic broadening of the features. Interestingly, these changes are seen upon adding similar Na^+ concentrations to **1**, **3**, and **4**.

To distinguish between spectroscopic changes that are due to direct metal ion/C_{60} interactions and those that might evolve from indirectly inductive influences, the absorption and fluorescence spectra of reference compounds **3** and **4** (see Scheme 1) were investigated in the absence and presence of metal ions and compared with the changes seen for **1** and **2**. As might be expected, no appreciable spectroscopic changes were observed in titration experiments with both **3** and **4**, except when adding Ag^+. Once we added Ag^+ ions to **3** and **4**, scenarios for spectroscopic development were observed (i.e., growth of absorption marker in the 400−600 nm and fluorescence quenching) that match those summarized above for **1** and **2**, indicating that Ag^+ interacts with C_{60} through the same mechanism.

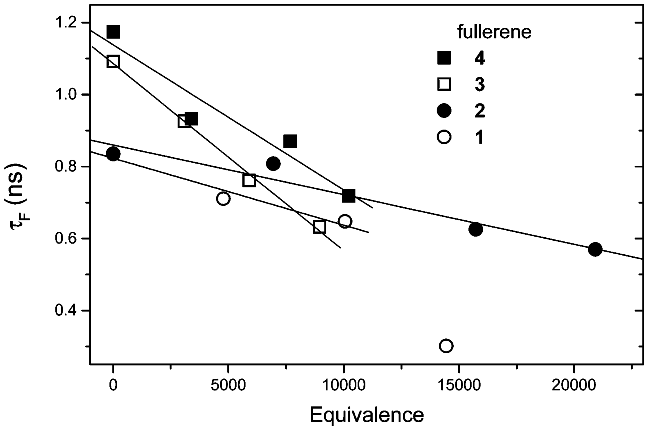


Figure 5. Variations of fluorescence lifetimes (ns) in **1**−**4** when adding variable Ag^+ concentrations.

TABLE 1: Quantum Yield Ratios (Φ^T/Φ_0^T) and Lifetimes (τ_T, μs) of Triplet Excited States of Fullerenocalix[4]arenes (1 and 2) and Fullerene Reference Compounds ((3 and 4) in THF Solution upon Addition of Ag^+ Ions

compd	[Ag+]/[fullerene]	Φ^T/Φ_0^T	τ_T (μs)
1	0	1.00	10.2
	2160	1.22	3.3
	4460	1.69	3.7
	7400	1.73	3.4
2	0	1.00	12.3
	2160	1.05	1.84
	3660	1.13	2.02
	5400	1.47	2.12
3	0	1.00	19.3
	1010		9.33
	1910	0.96	9.24
	2570	0.83	8.83
4	0	1.00	
	2020	0.87	6.71
	3330	0.59	6.46
	4870	0.59	5.99

Finally, we tested another reference compound, namely, **5**, in which the absence of ester groups prevents chelating Ag^+ ions and leaves an indirect inductive mechanism as the sole modus operandi for electronic interactions with C_{60}. Since, even **5** exhibits the same trends, we conclude that Ag^+ ions interact with C_{60} directly.

To gain a better and more comprehensive understanding of the fluorescence deactivation, fullerene fluorescence lifetimes were recorded for fullerenocalix[4]arenes (i.e., **1** and **2**) and their reference compounds (i.e., **3** and **4**) in the absence and presence of Ag^+ ions. In general, the fluorescence lifetimes descend nearly linearly with ascending equivalences of Ag^+ ions—see Figure 5. When comparing, however, the different relationships (i.e., slopes of **1** and **2** versus slopes of **3** and **4**), a trend is evident that suggests stronger interactions for reference compounds **3** and **4**. One of the possible rationales for this observation implies that the presence of Ag^+ ions hosting calix[4]arenes in **1** and **2** weakens the interactions, since Ag^+ ion inclusion confines the effective metal ion/C_{60} distance. Such steric restrains play, on the other hand, only a minor role in **3** and **4**.

As discussed above for the fluorescence deactivation, consequences might also be seen in the triplet features. In fact, the increased/decreased values of Φ^T/Φ_0^T (see Table 1), where Φ^T

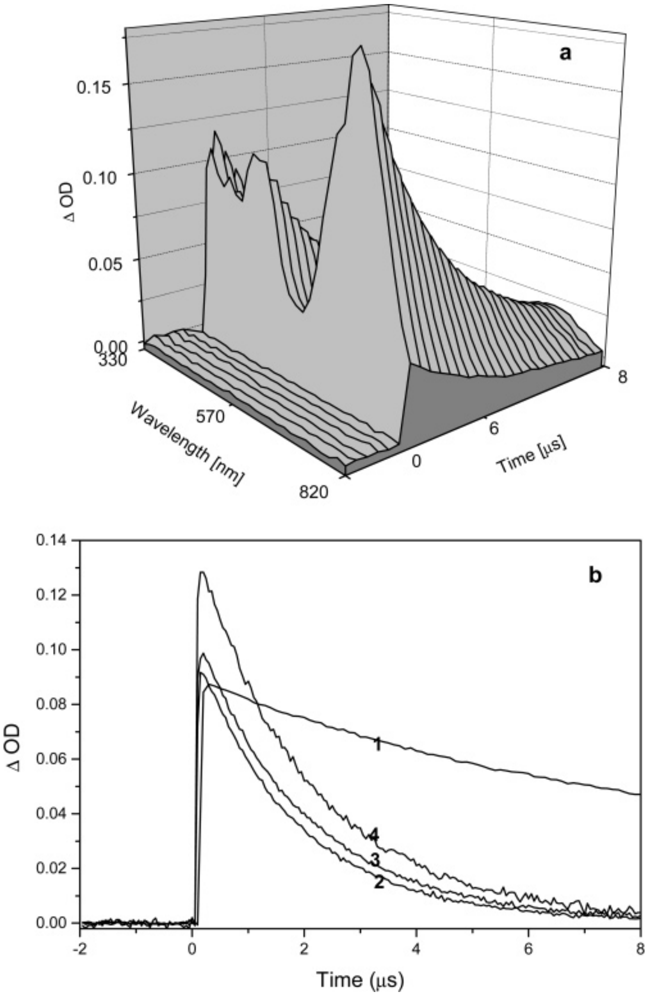


Figure 6. (a) Transient absorption spectra of **2**. (b) Decays of **2** (5.3×10^{-5} M) in THF solutions recorded upon 337 nm laser excitation: 1, [Ag^+] = 0 mM; 2, [Ag^+] = 114.3 mM; 3, [Ag^+] = 193.9 mM; 4, [Ag^+] = 286.0 mM.

and Φ_0^T refer to triplet quantum yields with and without Ag^+, confirm that Ag^+ interacts directly with the surface of C_{60}. The increased Φ^T/Φ_0^T values for **1**, **2**, and **3** after the addition of Ag^+ show a remarkable enhancement of the excited triplet species. The decreased Φ^T/Φ_0^T values in Table 1 suggest that the coupling between C_{60} and Ag^+ for **4** and for **3** at higher [Ag^+] is very strong and results in the intersystem crossing rate to such a fast level that the real Φ^T/Φ_0^T values cannot be obtained under our experiment conditions.

However, looking at the triplet spectra (Figure 6a) and triplet lifetimes (Figure 6b), we gather a different picture. In the presence of Ag^+, the triplet lifetimes for **1** and **2** are substantially shorter than those for **3** and **4**. Very likely, the intersystem crossing dynamics from the triplet excited state back to the singlet ground state are affected more strongly when the Ag^+ ions are incorporated into the calix[4]arene cavity. At first glance this observation appears counterintuitive, since the fluorescence experiments reveal a contrasting trend. It is, however, important to realize that the employed Ag^+ concentrations (see Table 1) are in the 0−300 mM range, which relates to the lower concentration regime in the fluorescence experiments. In fact, a closer analysis of the fluorescence lifetime dependence shows that in this low concentration range the lifetimes are notably longer in the cases of **1** and **2**. This trend is, however, in agreement with the influences seen for the triplet features. Again, our results indicate that the main mechanism for Ag^+ influencing the electronic spectra of C_{60} in **1**−**4** is based on direct Ag^+/C_{60} interactions.

TABLE 2: Quantum Yield Ratios (Φ^T/Φ_0^T) and Lifetimes (τ_T, μS) of Triplet Excited States of Fullerenocalix[4]arene 1 in THF Solution upon Addition of Mg^{2+} and Ba^{2+}

metal ion	[Ag+]/[fullerene]	Φ^T/Φ_0^T	τ_T (μs)
Mg^{2+}	0	1.00	10.2
	200	1.00	8.5
	440	1.03	9.4
	670	1.29	9.5
Ba^{2+}	0	1.00	10.2
	1180	1.11	12.5
	2310	1.27	12.2
	3640	1.26	13.0

As far as the addition of other metal ions (i.e., Na^+, Mg^{2+}, Ba^{2+}, and Mn^{2+}) is concerned, no appreciable spectroscopic variations were observed for **3** and **4**, indicating that any effects occurring from these ions on fullerenocalix[4]arenes **1** and **2** are indirectly inductive through the conformation changes on the metal ion binding, i.e., through metal ions/calix[4]arene/C_{60}. X-ray crystallographic results indicate that the size of the ionophoric hole of calix[4]arene ranges between 3.97 and 4.22 Å,[21] which appears to be a reasonable cavity size to host Na^+, Mg^{2+}, Ba^{2+}, and Mn^{2+}, whose ionic diameters are 1.94, 1.32, 2.68, and 1.60 Å, respectively.[22] Malonamide molecules have been reported as excellent reagents for chelating transition metal ions[23] and lanthanide ions,[24] while ethers have been serving as good reagents to capture alkali and alkaline-earth metal ions from the aqueous solutions.[25]

As shown above, high metal ion concentrations affect the absorption and fluorescence spectra of **1** much more strongly than those of **2**. Both fullerenocalix[4]arenes carry the same functional groups, except that the calix[4]arene moiety was attached to C_{60} in **1** through one and in **2** through two linkage(s). In fullerenocalix[4]arenes **2**, two tethers−connecting C_{60} and calix[4]arenes−largely restrict any movement of the calix[4]arene moiety, while for **1** much higher conformational freedom has to be assumed for the calix[4]arene moiety. Once metal ions are bound to the ether rim of the calix[4]arene moiety in **2**, changes in the molecular conformations of the fullerenocalix[4]arene architecture are minimal. Consequently, appreciable spectroscopic changes are not detected. The exceptional effects that stem from binding Na^+ to **2** might be due to a new molecular conformation, which is formed when Na^+ associates with the malonamide groups. The lack of effects for Na^+ with **1** originates probably from different conformations after Na^+ is bound to the calix[4]arene moiety.[26]

Upon adding Mg^{2+} and Ba^{2+} to THF solutions of **1**, the fluorescence intensity at 715 nm grows nearly linearly as the concentration of metal ions increases. Considering that the malonamide group may partially quench the emission from the C_{60} moiety, the noted increase in fluorescence intensity might be taken as an indicator for the relative distance between the malonamide group and the C_{60} surface. A possible change in distance is induced by the cone-shaped conformation after Mg^{2+} and Ba^{2+} are bound to the ether rim of the calix[4]arene moiety. This notion finds further support when the changes for the lifetimes and quantum yield ratios of the triplet excited state−see Table 2−are considered. In particular, the slight increases in triplet excited-state quantum yields suggest that the enhancement of the singlet excited state of C_{60} moiety−after the addition of Mg^{2+} and Ba^{2+}−leads to higher singlet excited yields, which then intersystem cross to form the triplet manifold. The very close lifetimes of the triplet excited states indicate that Mg^{2+}

and Ba^{2+}, different from the behavior summarized for Ag^+, have little influence on the deactivation of the fullerene triplet excited state.

No appreciable spectroscopic variations were gathered from Mn^{2+} titration experiments for both fullerenocalix[4]arenes **1** and **2**. This suggests that **1** and **2** exhibit no detectable selectivity in terms of binding Mn^{2+}, although malonamide groups are regarded as efficient chelaters for transition metal ions.

The interaction of Ag^+ with fullerene or polycyclic aromatic hydrocarbon has been well described in terms of "cation−π" relations.[27−29] In the gas phase, the clusters of $[Ag_xC_{60}]^+$ with $x = 1-5$ were identified by mass-selected photodissociation experiments.[28] In solution, it has been reported that Ag^+ directly interacts with C═C double bonds on the C_{60} surface to form Ag^+−C_{60} complex with a 1:1 stoichometry.[27] Metal ions—including Na^+, Mg^{2+}, and Ba^{2+}—usually form 1:1 complexes with calix[4]arenes.[30] The complexation assays of **1**/**2** are, however, more complicated, due to the possibility of binding to sites that are located at either the lower rim or, alternatively, the upper rim, or even both binding sites. Currently, we are pursuing ways to probe details of this intriguing aspect, for example, by NMR.

Conclusions

In conclusion, we have shown that Ag^+ affects the electronic states of fullerenocalix[4]arenes through direct Ag^+/C_{60} interactions. However, we cannot exclude the indirectly inductive interactions through Ag^+/calixarene/C_{60} based on our data. Other metal ions, namely, Na^+, Mg^{2+}, and Ba^{2+}, impose their influences on the electronic spectroscopy of fullerene moiety through metal ion/calixarene/C_{60} interactions. The chelating ability of fullerenocalix[4]arenes toward Mn^{2+}, on the other hand, is quite weak.

Acknowledgment. This work was supported by the European Union through grants HPRN-CT-2002-00177 and HPRN-CT-2002-00178, by SFB 583, Funds der chemischen Industrie, and the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Document No. NDRL-4595 from the Notre Dame Radiation Laboratory.

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