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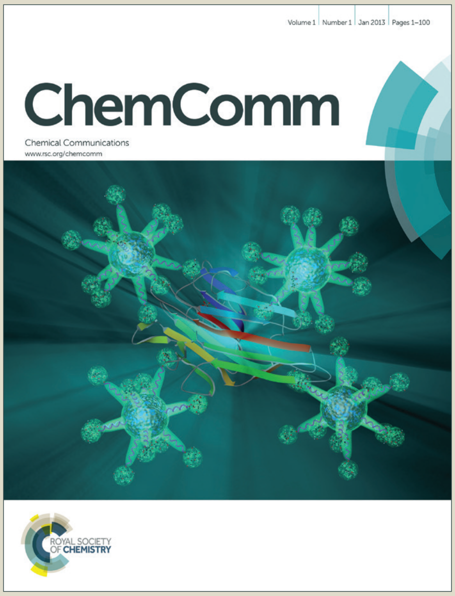

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Reduction-Triggered Aromatic to Aromatic Electronic Structure Switching in a Tribenzotetraazachlorin-Fullerene Conjugate

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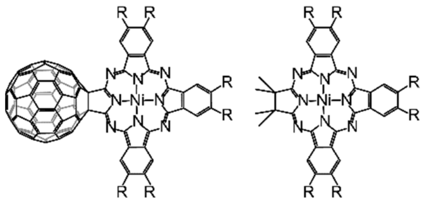
Absorption spectral changes observed during sodium mirror reduction of tribenzotetraazachlorin-fullerene (TBTAC-C_{60}) conjugates have clarified that electronic communication between the TBTAC and C_{60} moieties is switched off upon reduction of the conjugate. The spectroscopy has suggested that the anionic species retains its aromatic character.

Recent developments in chemistry of π-conjugation molecules have enabled us to realize versatile physicochemical properties based on their unique electronic structures.[1-3] For example, the linear or two-dimensional expansion of π-conjugation systems lowers the energy of their lowest singlet excited states, while the spherical arrangement of π-electrons to give such species as C_{60} leads to exceptionally-highly-degenerate frontier molecular orbitals (MOs).[2] More recently, three-dimensionally designed π-electronic molecules have opened a new route to substantialize novel molecular functionalities.[3]



R=OBu : **1**
R=SO_2Bu: **2**

R=OBu : **3**
R=SO_2Bu: **4**

Scheme 1 Structures of TBTAC-C_{60} conjugates (left) and TBTAC derivatives (right) used in this study.

Construction of hybrid π-conjugation systems by using phthalocyanine (Pc) and C_{60} components is of particular interest, since this class of compound possibly exhibits delocalized π-conjugation on the condition that the Pc and C_{60} moieties are arranged in close proximity so that the π oribitals of these moieties can overlap.[4,5] We have demonstrated that the electronic communication in tribenzotetraazachlorin-fullerene (TBTAC-C_{60}) conjugates (Scheme 1) is switched on and off depending on the push-pull nature of the substituents, R, leading to markedly different spectroscopic properties.[6]

In the case R = butyloxy group (OBu), linear combinations of the LUMO and LUMO+1 of the TBTAC and C_{60} moieties, respectively, result in two delocalized unoccupied MOs (LUMO+1 and LUMO+2), because these are energetically close to each other, and belong to the same irreducible representation. As a consequence, the unusual triply split Q-band components appear in the absorption spectrum of **1**. The conjugate having strongly electron withdrawing butylsulfonyl groups (SO_2Bu) as the R, on the other hand, shows no such delocalized MOs due to large energy differences between the relevant MOs of the TBTAC and C_{60} moieties. In addition, we have reported that various related derivatives of **1** exhibit diverse spectroscopic properties arising from their characteristic electronic structures.[7-10] These results indicate that weakly-coupled electronic interactions between the TBTAC and C_{60} moieties are sensitive to the electronic structures of each moiety, and therefore, it is anticipated that the electronic communication present in neutral **1** can be controlled by exertion of electronic perturbation on one of the moieties.

According to the results of DFT calculations, the LUMO of **1** is localized on the C_{60} moiety due to the symmetry mismatch between the LUMO of the C_{60} unit and the unoccupied frontier MOs of the TBTAC.[6] Therefore, it is reasonable to make a hypothesis that one-electron reduction of **1** effectively reduces the C_{60} moiety, i.e. the negative charge localizes formally on the C_{60} moiety, rather than giving rise to delocalized negative charges over the whole molecule. In the present study, on the basis of this hypothesis, the spectroscopic elucidation of chemically reduced species of the TBTAC-C_{60} conjugates, as well as TBTAC derivatives as a reference has been performed.

Compounds **1**–**4** were prepared according to the literature.[6] Absorption and magnetic circular dichroism (MCD) spectra of chemically reduced **1**–**4** were obtained by employing the conventional sodium mirror technique. Dry THF solutions of **1−4**, degassed by the freeze–pump–thaw method under high vacuum in advance, were reduced stepwise by exposure of the solution to the surface of the sodium mirror with monitoring the absorption spectral changes. The presence and disappearance of isosbestic points during the reduction provide a good indication of the termination of each reduction step.

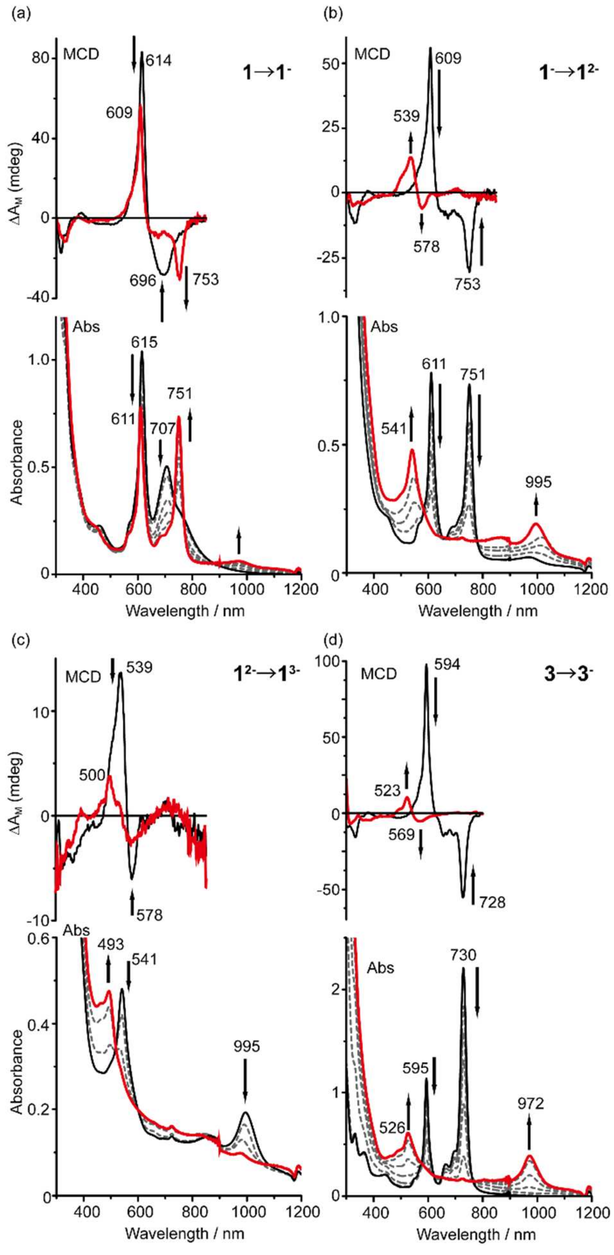


Figure 1. Electronic absorption (bottom) and MCD (top) spectral development upon (a) first, (b) second, and (c) third sodium reduction of **1**, and (d) first sodium reduction of **3** in deaerated THF.

Spectral changes observed in the course of the stepwise reduction of **1** are shown in Figure 1 (a)-(c). Based on the results of TDDFT calculations, the broad absorption component appearing in the longer wavelength region of neutral **1** (ca. 650−900 nm) mainly consists of two electronic transitions, the HOMO to LUMO+1 and HOMO to LUMO+2 transitions. Since the LUMO+1 and LUMO+2 of **1** are delocalized over the molecule, the π-conjugation also extends over both the C_{60} and TBTAC moieties (see ref. 6 for detailed discussion on the electronic structures of the neutral species).

The one-electron reduction process of **1** ($\mathbf{1}\rightarrow\mathbf{1}^{-}$) leads to the loss of the absorption peaks at 615 and 707 nm, of which the former results in a new band at 611 nm. In contrast, the latter band and the shoulder at ca 750 nm are fused into one band at 751 nm for $\mathbf{1}^{-}$. In addition, the $\mathbf{1}^{-}$ species also exhibits broad, relatively weak band components in the region of 900−1200 nm, indicating the formation of the C_{60} anion radical moiety.[11]

It is noteworthy that the MCD spectrum of $\mathbf{1}^{-}$ resembles that of neutral **3** in shape (Figure 1(d)), indicating that the electronic structures of the TBTAP moiety of anionic $\mathbf{1}^{-}$ and neutral **3** are similar. As a consequence, it is likely that the electron additionally introduced into $\mathbf{1}^{-}$ by the reduction is localized mainly on the C_{60} moiety rather than the TBTAC unit, and consequently, the electronic communication between these components disappears because the electronic structures of the C_{60} moiety is perturbed as a result of its reduction to C_{60}^{-}.

In the second reduction step of **1** ($\mathbf{1}^{-}\rightarrow\mathbf{1}^{2-}$), the absorption bands at 751 and 611 nm lose their intensity, and instead, new weaker, broader bands appear at 995 and 541 nm. Interestingly, these spectral changes are quite similar to those observed for the first reduction step of **3** ($\mathbf{3}\rightarrow\mathbf{3}^{-}$), where the sharp absorption bands at 730 and 595 nm disappear, and two new bands gain intensity at 972 and 526 nm (Figure 1(d)). The resulting spectra can be safely attributed to the anionic species of the TBTAC derivatives, and therefore, it can be concluded that the observed spectral changes during the $\mathbf{1}^{-}\rightarrow\mathbf{1}^{2-}$ process correspond to the addition of an electron to the TBTAC moiety rather than the C_{60} unit.

The intensities of the MCD *B*-terms corresponding to the absorption bands at 751 and 615 nm for $\mathbf{1}^{-}$ are comparable to those of neutral **1**, while the other reduced species such as $\mathbf{1}^{2-}$, $\mathbf{2}^{-}$, and $\mathbf{3}^{-}$ exhibit obviously weaker MCD signals. Since the intense MCD signals observed for neutral **1** originally arise from large orbital angular momenta associated with the S_1 states of the pristine phthalocyanine,[12] the intense MCD signals appearing in the $\mathbf{1}^{-}$ species strongly suggest that the TBTAC moiety of $\mathbf{1}^{-}$ retains its aromatic character even after the reduction by confining the introduced electron to the C_{60} moiety.[13] As demonstrated in Figure 1(c), the third reduction step of **1** ($\mathbf{1}^{2-}\rightarrow\mathbf{1}^{3-}$) leads to a featureless absorption spectrum except for the perceivable band at 493 nm, while the corresponding MCD signals are even weaker than those of $\mathbf{1}^{2-}$.

The spectral changes associated with the reduction of **2** differ significantly from those observed for **1** (Figure 2). In contrast to **1**, neutral **2** exhibits sharp, intense absorption bands in the 600−800 nm region because the strong electron withdrawing nature of the substituted SO_2Bu groups of **2** reduces the relative MO energy of the TBTAC with respect to the C_{60} moiety, leading to the interruption of the electronic communication between these moieties.[6] Since DFT calculations predict that, unlike **1**, the LUMO of **2** is TBTAC-centered, it can be anticipated that the one-electron reduction of **2** (**2**→**2**$^{-}$) will barely affect the C_{60} moiety, which however, results in the reduced TBTAC moiety. As demonstrated in Figure 2 (a), the intense bands at 753 and 609 nm indeed lose their intensity upon reduction, to give newly-developed bands at 986 and 565 nm. The observed spectral changes resemble those observed during the **1**$^{-}$→**1**$^{2-}$, **3**→**3**$^{-}$, and **4**→**4**$^{-}$ processes (Figures 1 (b) and (d), and 3 (a), respectively). The **1**$^{2-}$→**1**$^{3-}$ step corresponds to the **2**$^{-}$→**2**$^{2-}$ and **4**$^{-}$→**4**$^{2-}$ steps, where the third electron in **1**$^{3-}$ delocalizes on the TBTAC moiety, to formally give a species consisting of C_{60}^{-} and TBTAC^{2-} components.

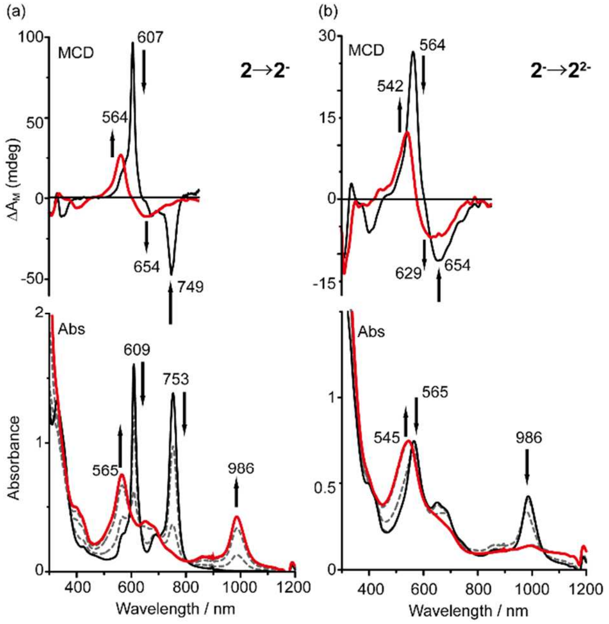


Figure 2. Electronic absorption (bottom) and MCD (top) spectral development upon (a) first and (b) second sodium reduction of **2** in deaerated THF.

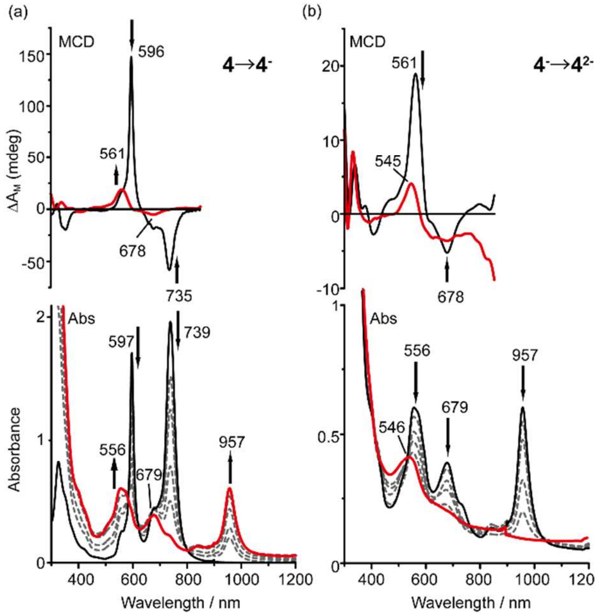
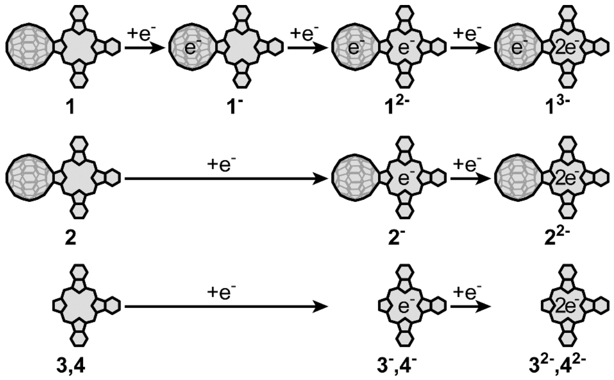


Figure 3. Electronic absorption (bottom) and MCD (top) spectral development upon (a) first and (b) second sodium reduction of **4** in deaerated THF.

The location of the introduced electrons at each reduction step is schematically summarized in Scheme 2. Since the C_{60}-centered LUMO is involved with the reduction only in the case of compound **1**, the one-electron reduced species of **1** can be regarded formally as a conjugate consisting of neutral TBTAC and anionic C_{60}^{-} species. In this case, the electronic structure of the TBTAC moiety of the conjugate is maintained even after the reduction. The second and third reduction steps, to yield **1**$^{2-}$ and **1**$^{3-}$ species, respectively, occur mainly at the TBTAC site. Compounds **2**–**4**, on the other hand, have a TBTAC-centered LUMO, and therefore, the first and second reduction steps of these derivatives correspond to the second and third reduction steps of **1**, respectively. As demonstrated in Figure 4(a), the ESR spectrum of **1**$^{-}$ consists of a sharp signal with a relatively small *g* value (1.9999) and a less intense wing in the higher field side, which is similar to that reported for C_{60}^{-} anion radicals.[14] The *g* value for the **2**$^{-}$ species (2.0035), on the other hand, is typical for π-radicals (Figure 4(b)), consistently supporting our assignments depicted in Scheme 2. These conclusions are also supported by MCD spectroscopy, where the relatively intense MCD *B*-terms at 753 and 614 nm observed for **1**$^{-}$ compared to the MCD signals of the other reduced species shown in this study, imply the presence of aromatic character even after the first reduction process.



Scheme 2 Schematic image for each reduction step of **1**–**4**. Note that both **1** and **1**$^{-}$ are aromatic, while the other reduced species are not.

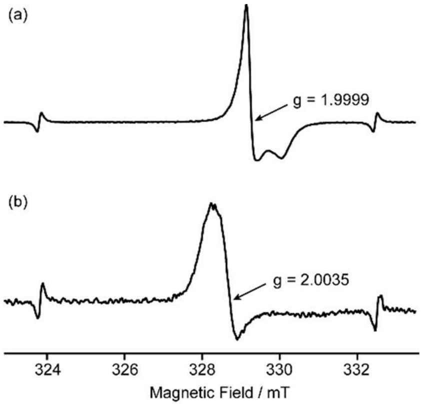


Figure 4. ESR spectra of (a) **1**$^{-}$ and (b) **2**$^{-}$ in deaerated THF at 123 K.

In summary, the present study has demonstrated that the electronic communication between the TBTAC and C_{60} moieties for the neutral **1** can be switched off by sodium mirror reduction. The associated spectral changes, however, indicate that both the **1** and **1**$^{-}$ species maintain an aromatic character. To the best of our knowledge, there have been few previous examples showing the aromatic to aromatic electronic structure switching of π-molecules upon one-electron reduction or oxidation. It is particularly worth noting that these unique electronic properties have been achieved by taking advantage of the weakly coupled electronic communication inherently found for **1**.

Notes and references

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1 E. L. Spitler, C. A. Johnson II, M. M. Haley, *Chem. Rev.* 2006, **106**, 5344.
2 (a) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* 2007, **107**, 718; (b) Z. Chen, R. B. King, *Chem. Rev.* 2005, **105**, 3613; (c) M. Bühl, A. Hirsch, *Chem. Rev.* 2001, **101**, 1153.
3 (a) K. Tahara, Y. Tobe, *Chem. Rev.* 2006, **106**, 5274; (b) R. Herges, *Chem. Rev.* 2006, **106**, 4820; (c) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* 2006, **106**, 4843.
4 (a) G. Bottari, G. de la Torre, D. M. Guldi, T. Torres, *Chem. Rev.* 2010, **110**, 6768; (b) T. G. Linssen, K. Dürr, M. Hanack, A. Hirsch, *J. Chem. Soc., Chem. Commun.* 1995, **31**, 103; (c) H. Mizuseki, N. Igarashi, R. V. Belosludov, A. A. Farajian, Y. Kawazoe, *Synth. Met.* 2003, **138**, 281.
5 (a) T. Fukuda, N. Hashimoto, Y. Araki, M. E. El-Khouly, O. Ito, N. Kobayashi, *Chem. Asian J.* 2009, **4**, 1678; (b) T. Fukuda, Y. Kikukawa, S. Takaishi, N. Kobayashi, *Chem. Asian J.* 2012, **7**, 751.
6 T. Fukuda, S. Masuda, N. Kobayashi, *J. Am. Chem. Soc.* 2007, **129**, 5472.
7 T. Fukuda, S. Masuda, N. Hashimoto, N. Kobayashi, *Inorg. Chem.* 2008, **47**, 2576.
8 T. Fukuda, H. Kaneko, N. Kobayashi, *J. Porphyrins Phthalocyanines*, 2009, **13**, 999.
9 T. Fukuda, I. Sugita, N. Kobayashi, *Chem. Commun.* 2009, **45**, 3449.
10 T. Fukuda, S. Masuda, Md. Wahadoszamen, N. Ohta, N. Kobayashi, *Dalton Trans.* 2009, **38**, 6089.
11 (a) T. Kato, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, Y. Achiba, *Chem. Phys. Lett.* 1991, **180**, 446; (b) T. Nojiri, M. M. Alam, H. Konami, A. Watanabe, O. Ito, *J. Phys. Chem. B* 1997, **101**, 7943.
12 T. Fukuda, E. A. Makarova, E. A. Luk'yanets, N. Kobayashi, *Chem. Eur. J.* 2004, **10**, 117.
13 (a) J. Mack, M. J. Stillman, N. Kobayashi, *Coord. Chem. Rev.* 2007, **251**, 429; (b) J. Mack, N. Kobayashi, M. J. Stillman, *J. Porphyrins Phthalocyanines* 2006, **10**, 1219; (c) J. Mack, N. Kobayashi, *Chem. Rev.* 2011, **111**, 281.
14 M. M. Khaled, R. T. Carlin, P. C. Trulove, G. R. Eaton, S. S. Eaton, *J. Am. Chem. Soc.* 1994, **116**, 3465.

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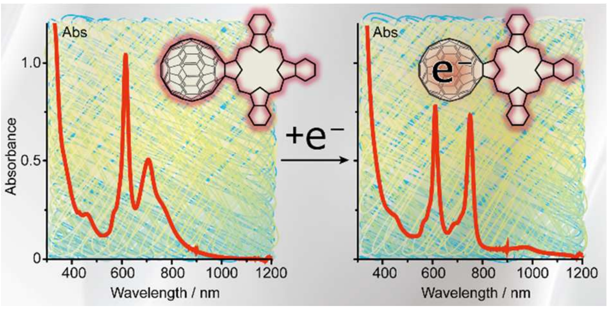

Electronic absorption spectral changes observed during sodium reduction of a tribenzotetraazachlorin-fullerene conjugate have clarified that the aromatic nature of the conjugate has been retained even in the one-electron reduced form.