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Tuning intramolecular electron and energy transfer processes in novel conjugates of La$_2$@C$_{80}$ and electron accepting subphthalocyanines

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A series of two conjugates with La$_2$@C$_{80}$ and subphthalocyanine (SubPc) have been prepared and characterized by means of cyclic voltammetry, absorption, fluorescence, and femtosecond resolved transient absorption spectroscopy. The strong electron-donating character of La$_2$@C$_{80}$ is essential to power an intramolecular electron-transfer in the La$_2$@C$_{80}$-SubPc conjugates upon photoexcitation.

In the present work, we report on the synthesis and the properties of conjugates 1a and 1b (Scheme 1) that comprise La$_2$@C$_{80}$ as electron donor and (dodecafluoro) /hexa(pentylsulfonyl)SubPc as electron acceptors. We will demonstrate that, despite negligible interactions in the ground-state, electron-transfer events occur between SubPc and La$_2$@C$_{80}$ in the excited state. Whereas in conjugates 2a and 2b, only energy transfer events take place.

Conjugates 1a, 1b were synthesized according to the procedure previously reported for 2a. Briefly, 1a, 1b were obtained in 25% or less via Prato reaction of La$_2$@C$_{80}$ and SubPc 3a, b (Scheme 1). The formation of 1a or 1b as major products was revealed by HPLC and they were isolated via a multi-step HPLC procedure (Figure S1-3). The composition of 1a and 1b was confirmed by MALDI-TOF mass spectrometry (Figure S5-7).

To shed light onto the structural feature of 1a, VT$^1$H NMR studies were conducted. As shown in Figure S8, the $^1$H NMR spectrum measured at 283 K exhibits two sets of signals: those originating from pyrrolidine protons at 5.2 ppm and those from phenyl protons at 8-5.5 ppm, indicating the presence of at least two conformers of 1a in a 3:1 ratio. In each set, a pair of doublets, which are assigned to the geminal protons on the pyrrolidine, is discernable. Confirmation for this assignment was obtained by COSY experiments, revealing a reasonable cross coupling relationship between the doublets (Figure S9).

In addition, the chemical shifts as well as the chemical shift differences ($\Delta\delta=1.2-1.3$ ppm) of these geminal protons are in a good agreement with those reported previously. An increase of the temperature from 283 to 313 K resulted only in a broadening of the NMR signals in 1a (Figure S8) ruling out the possibility of conformational conversion in this temperature range. Characterization of 1b by $^1$H NMR was, however, hampered by the small amounts of the isolated material and its poor stability.

To further investigate the structural and electronic features of 1a, DFT-calculations were performed using a Gaussian 09 package.

Owing to the [5,6]-addition pattern and the unsymmetrical pyrrolidine substitution, 1a adopts at most four different conformations – FigureS13. Among them, conformer I, in which both, the pyrrolidine and the substituted phenoxy unit, are approaching a 5-member ring, has the lowest formation energy (Table S1) at the M06-2X/3-21G ~ 6-31G* ~ sdd level.

Importantly, they do not aggregate owing to their conical shape and are known as strong fluorophores. SubPcs bearing on their periphery electron-withdrawing substituents are well-known electron acceptors. Thus, electron-deficient SubPcs have been considered as promising complements to fullerenes.
comparison, conformer III, in which both the pyrrolidine and the substituted phenoxyl group are aligned close to a 6-member ring, is 2.3-3.3 kcal/mol less stable than conformer I. Conformers III and IV possess the least stability, namely 5.3 kcal/mol less than conformer I. Therefore, we hypothesize the presence of conformers I and II in purified 1a with a ratio of 3:1.

Electrochemical studies with 1a and 2a were carried out by means of CV and DPV. In the range from -2.0 to 1.2 V, 2a reveals four reversible one-electron reductions at -1.06, -1.18, -1.57, and -1.79 V and two irreversible one-electron oxidations at +0.99 and +1.08 V (Table 1 and Figure S12). The first oxidation, the first and third reductions are $C_{60}$ centered, while the second oxidation, the second and forth reductions are centered on SubPc. As for 1a, the electrochemical patterns of the [5,6]-pyrroldine La$_2$@C$_{80}$ and perfluorinated SubPc are clearly distinguishable.$^{12,15}$ In particular, the first and second reductions, which are seen as a one-electron process at -0.47 and -1.12 V, coincide well with the reductions of La$_2$@C$_{80}$ and SubPc, respectively. The third reduction at -1.80 V appears as a two-electron process, involving the second reduction of La$_2$@C$_{80}$ and the second reduction of SubPc. In addition, three oxidations are visible. The first and second are fully reversible one-electron processes, which agree well with of La$_2$@C$_{80}$. The third oxidation is a two-electron process, corresponding to the first oxidation of SubPc and the third oxidation of La$_2$@C$_{80}$. Our electrochemical assays prompt to the fact that ground state interactions between the electroactive constituents of 1a are negligible. The remarkable oxidative features of 1a underline the strong electron donor character of La$_2$@C$_{80}$, which $C_{60}$ in 2a lacks.

Complementary DFT calculations further underline the electrochemical data. As shown in Figure S14, the calculated HOMO of 1a is mainly delocalized on La$_2$@C$_{80}$, while the LUMO and LUMO+1 are localized on the endohedral La$_2$ cluster and on perfluorinated SubPc, respectively.

Table 1. Redox potentials$^{d}$ of La$_2$@C$_{80}$-SubPc conjugate 1a and reference compounds, $E_{p/2}$ vs Fe/Ce$^+$, V.

<table>
<thead>
<tr>
<th></th>
<th>$E_{p/2}^0$</th>
<th>$E_{p/2}^{-}$</th>
<th>$E_{p/2}^{+}$</th>
<th>$E_{p/2}^{-}$</th>
<th>$E_{p/2}^{+}$</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.97</td>
<td>0.58</td>
<td>0.20</td>
<td>-0.47</td>
<td>-1.12</td>
<td>-1.80</td>
</tr>
<tr>
<td>2a</td>
<td>1.08</td>
<td>0.59</td>
<td>0.20</td>
<td>-0.44</td>
<td>-1.18</td>
<td>-1.79</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>0.59</td>
<td>0.20</td>
<td>-0.44</td>
<td>-1.18</td>
<td>-2.13</td>
</tr>
</tbody>
</table>

$^d$Values obtained from DPVs. $^e$Two-electron process; $^f$Data from ref. 15. $^g$[5,6]-pyrroldine La$_2$@C$_{80}$; La$_2$@C$_{80}$-CNTrt (Trt = triphenylmethyl).

Insights into the excited state deactivation in 4, 3a, 3b, 2a, 2b, 1a, and 1b, in general, and into the corresponding photoproducts, in particular, came from transient absorption measurements following femtosecond and nanosecond excitation. Excitation of 4 at 387 nm leads to the population of the La$_2$@C$_{80}$ singlet excited state (1.4 $\pm$ 0.2 eV), which features ground state bleaching at 465 nm and well-resolved fine structure with absorption spectrum of 1a-b is best described as a simple superposition of the spectra of the individual components, namely SubPc and [5,6]-pyrroldine La$_2$@C$_{80}$ (Figure S10-11). Detailed comparison between 1a and 1b suggests that the absorption maxima of 1b are 4 nm red-shifted relative to that of 1a, thus, inferring the stronger electron-acceptor properties of sulfonated SubPcs than of fluorinated one. Despite the presence of [5,6]-pyrroldine La$_2$@C$_{80}$, the absorption maximum of SubPc undergoing no shift as compared with that of SubPc 3a and 3b, indicating the lack of ground-state interaction between the individual components.
maxima at 516, 466, 614, 735, 800, and 900 nm. The latter is subject to a fast intersystem crossing – 60 ± 30 ps – to the triplet manifold due to the presence of the (La$_2$)$_{12}$ cluster, which promotes efficient spin orbit coupling. Following the singlet excited state decay, a weak and broad absorption in the 800–1200 nm region, along with broad features that taper at 550 nm, are discernible. These features relate to the La$_2$(C$_{60}$) triplet excited state (1.0 ± 0.1 eV).

Figure 1. In line with the reference experiments, namely with 720 nm as well as transient minima at 575 and 635 nm – absorption changes in the form of transient maxima at 450, 600, and 720 nm, which peaks around 710 nm. These features relate to the singlet excited state (2.16 eV) of SubPc. Laser excitation of 1a in toluene, 2.2 ± 0.2 ps (THF), and 2.0 ± 0.2 ps (benzonitrile).

Simultaneously, new transitions develop in the visible and the nearCinfrared regions. Importantly, the new transients do not discernible. These features relate to the La$_2$(C$_{60}$) excited state decay, a weak and broad absorption in the 800–1200 nm region, along with broad features that taper at 550 nm, are discernible. These features relate to the La$_2$(C$_{60}$) triplet excited state (1.0 ± 0.1 eV).

Figure 2. Differential absorption spectra (visible and nearCinfrared) obtained upon femtosecond flash photolysis (530 nm) of 2a (10$^{-3}$ M) in argon-saturated THF with several time delays between 0.1 and 7500 ps at room temperature. Insert – time-absorption profiles of the spectra shown at the top at 545, 635, and 1025 nm monitoring the energy transfer.

Commencing with the conclusion of the 530 nm excitation, SubPc 3b reveals differential absorption changes in the form of transient maxima at 424, 474, 623, 660 nm, a broad tail extending far into the near infrared, as well as transient minima at 533 and 583 nm – Figure S16. In addition, a broad near-infrared feature spans from 650 to 1200 nm, which peaks around 710 nm. These features relate to the singlet excited state (2.16 eV) of 3a, which transforms with 1.9 ± 0.1 ns into the corresponding triplet excited state (1.4 eV). Transient absorption spectra of the latter maximize at 470 and 610 nm and minimize at 532 and 570 nm.

Likewise, 530 nm excitation of F$_2$SubPc–C$_{60}$ 2a results in the exclusive formation of the SubPc singlet excited state – Figure 2. In particular, transient maxima at 450, 600, and 720 nm as well as transient minima at 515, 575, and 635 nm are formed and decay rapidly with 1.5 ± 0.3 ps (toluene), 1.5 ± 0.3 ps (THF), and 1.4 ± 0.3 ps (benzonitrile). As the SubPc singlet excited state decay comes to an end a broad near-infrared transient, which maximizes at 910 nm, is noted, suggesting a C$_{60}$ singlet excited state. Interestingly, we did not find the characteristic C$_{60}$ triplet feature at 700 nm at the end of the C$_{60}$ singlet excited state deactivation.

On the contrary, maxiama at 470 and 615 nm as well as a minimum at 575 nm were concluded, pointing to the SubPc triplet excited state. From this we infer that the C$_{60}$ triplet excited state (1.5 eV) undergoes a thermodynamically allowed transfer of triplet excited state energy to SubPc (1.4 eV). The kinetics at the 470 and 615 nm maxima further furnishes the kinetic assignment, namely the rate-determining step in the SubPc triplet excited state formation is the C$_{60}$ centered intersystem crossing. A global analysis reveals kinetics that are very similar (1.6 ± 0.1 ns) to the inherent intersystem crossing dynamics seen for C$_{60}$. In this context, it is reassuring that the transients seen at the end of the femtosecond experiments matches that at the beginning of the nanosecond experiment. Moreover, maxiama at 470 and 610 nm, minima at 532 and 570 nm match the signature of the SubPc triplet excited state.

Laser excitation of 1b in benzonitrile at 568 nm results immediately after excitation in differential absorption maxima at 485 and 623 nm and a minimum at 583 nm – Figure S18. Although these transient features relate to the singlet excited state of SubPc they decay ultrafast with a lifetime of 1.4 ± 0.1 ps. New transients evolve, which maximize at 480 and 610 nm and minimize 583 nm. A spectral comparison with the results from the pulse radiolytic investigations supports the notion that the new transients are attributed to the π-radical anion – ((SO$_2$C$_2$H$_5$)$_2$)SubPc$^-$. Taking the aforementioned into concert, we postulate an electron transfer from La$_2$(C$_{60}$) to the SubPc singlet excited state to afford (La$_2$(C$_{60}$))$^-$(SO$_2$C$_2$H$_5$)$_2$SubPc$^+$. Taking the aforementioned into concert, we postulate an electron transfer from La$_2$(C$_{60}$) to the SubPc singlet excited state to afford (La$_2$(C$_{60}$))$^-$(SO$_2$C$_2$H$_5$)$_2$SubPc$^+$. The latter is centered in the near infrared is hampered by the thermal decomposition of SubPc. This is seen to form a product with absorptions in the 700–850 nm range. Nevertheless, the metastable (La$_2$(C$_{60}$))$^-$(SO$_2$C$_2$H$_5$)$_2$SubPc$^+$ radical ion pair state decays with 28 ± 2 ps to the singlet ground state.
nm, and an excited state lifetime of 36 µs without oxygen perfectly agree with the SubPc triplet excited state of 3a. Likewise, singlet oxygen quantum yields of 2a were found as high as 0.28 (toluene), 0.13 (THF), and 0.41 (benzonitrile) and support the assignment that the triplet excited state evolves as the product of charge recombination. Please note that the singlet oxygen yields in 3a are as high as 0.35.

When turning to 2b, excitation at 530 nm is accompanied by the formation of its singlet excited state – Figure S19. Evidence stems from monitoring maxima at 427, 474, 623, and 660 nm and minima at 535 and 585 nm. These decay in the presence of C60 rapidly with 1.5 ± 0.3 ps (toluene), 1.5 ± 0.3 ps (THF), and 1.4 ± 0.3 ps (benzonitrile) to form accordingly the C60 singlet excited state with its 910 nm maximum. Like for 2a, we did not find the characteristic C60 triplet feature. Instead, maxima at 470 and 625 nm as well as minima at 535 and 585 nm of the SubPc triplet excited state were concluded. In other words, the triplet excited state of SubPc (1.4 eV) evolves from a thermodynamically allowed transfer of triplet excited state. The kinetics at the 470 and 625 nm maxima and the 585 nm minimum document that the rate-determining step is C60 centered intersystem crossing (1.6 ± 0.1 ns). In the absence of oxygen, the SubPc triplet excited state lifetime is 20 ± 5 µs in agreement with what was found for in 3b.

Conclusions

Electron accepting SubPcs have been used in combination with La2@C80 to prepare a series of novel La2@C80-SubPc electron donor-acceptor conjugates to mimic the photosynthetic apparatus. Our results in terms of electrochemical and steady-state absorption reveal no appreciable electronic interactions between SubPc and La2@C80 in the ground state. This changed in the excited state, where an intramolecular electron-transfer evolves from La2@C80 to photo excited SubPc. In comparison, reference conjugates of C60 and SubPcs feature only a singlet-singlet energy transfer from SubPc to C60. Thus, replacing C60 by La2@C80 provides a promising way to tune energy transfer versus electron transfer. Furthermore, considering the short separations between the electron donors and acceptors, optimizing the charge-separated state lifetimes seems achievable via the tailored design of linkers between La2@C80 and SubPc.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, complete characterizations of 1a, 1b, and selected transient absorption spectra. See DOI: 10.1039/b000000x/

14. In the reaction mixture, besides 1a, a minor product 1a was also isolated and identified as a [6,6]-pyrrolidine adduct using MALDI-TOF mass and UV-vis-NIR absorption spectra (Figures S6, S9).