Controlling the Charge Transfer Mechanism and Efficiency by Means of Different C\textsubscript{70} Regioisomeric Adducts

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Dedicated to Professor Rainer Fink on the occasion of his 60th Birthday

Here, differences stemming from two newly synthesized electron donor–acceptor conjugates, α- or β-regioisomeric adducts featuring orthogonal arrangements of an electron-donating free-base porphyrin (H\textsubscript{2}P) and electron-accepting C\textsubscript{70}, are reported. Key to a full-fledged investigation in terms of both experiments and theory is the use of a rigid linker to separate the electron acceptor and donor. Both conjugates are experimentally investigated by means of femtosecond/nanosecond transient absorption measurements, which is further supported by radiation chemical studies based on pulse radiolysis. Significant regioisomeric differences are seen in the charge recombination kinetics, in general, which are as large as 1.4-fold, and in the relative distributions of the charge recombination pathways, in particular, which reach nearly 1.5-fold. Clearly, α-regioisomers of C\textsubscript{70} adducts are much better suited for the construction of future energy conversion systems than β-regioisomers; a fact that relates to the superior electron delocalization within the carbon caps of C\textsubscript{70} made out of “corannulenoid” fragments relative to the equator region of fullerenes featuring extended “phenanthrenoid” rings.

1. Introduction

Ever since the discovery of fullerenes in the 80s,[1] they have attracted considerable attention in chemistry and materials science.[2–4] Key for the far-reaching development of the “chemistry of fullerenes” was preparative methods, which enabled the synthesis of C\textsubscript{60} and C\textsubscript{70} on a large scale.[5] Hand in hand with the gram-scale availability of fullerenes, their chemistry, physics, and materials science rose to the center of attention. This was largely due to C\textsubscript{60}/C\textsubscript{70}’s remarkable properties, including superconductivity,[6] ferromagnetism,[7,8] biological activity,[9,10] and, most importantly, their electron-accepting nature. By virtue of their low reorganization energy in electron transfer reactions, they are used in solar cells[11–13] and artificial photosynthetic systems.[14,15] One of the most promising applications of fullerenes is their incorporation into electron donor–acceptor systems. Here, the incentive is to mimic the photosynthetic solar energy conversion, converting solar energy into either electrochemical energy[16–18] or into chemical energy by means of photocatalytic water splitting[19,20] or the photosynthesis of solar fuels.[21]

In the context of solar energy conversion, an ample amount of work was conducted to implement fullerenes, in general, and C\textsubscript{60}, in particular, into artificial photosynthetic systems to efficiently convert solar energy.[22,23] For C\textsubscript{60} and C\textsubscript{70}, their superior electron acceptor properties, which stem not only from their ability to accept up to six electrons easily, but also from their low reorganization energies in electron transfer reactions, have been demonstrated.[24–30] A look at the literature on the family of fullerenes reveals that the preponderant work has been performed with C\textsubscript{60} so far.[25,31,32] A real bottleneck for C\textsubscript{70} is the higher activation energy and slower reactivity in, for example, cycloaddition reactions with cyclopentadiene.[33] In addition to the more challenging functionalization,[34] larger fullerenes such as C\textsubscript{70} show lower symmetry, which also leads to a larger number of position...
regioisomers, as well as higher costs.[32–35] The two major regioisomers of C70 monoadducts are its α- and β-regioisomers, which disclose, however, no notable differences in terms of their reduction. As a matter of fact, larger fullerences have attracted much less attention, even though they are considered promising structures for the conversion of photochemical energy into storable energy forms.[36–38] Therefore, studies elucidating the mechanistic details of photoinduced electron transfer reactions in covalent electron donor–acceptor systems featuring fullerences, which are larger than C60, are much needed.

By virtue of their absorption cross-section in the visible part of the optical spectrum, their synthetic availability, and their photochemical stability, porphyrins have emerged as the perfect complement to the electron accepting fullerences.[39–43] Porphyrins are, however, not only suitable light harvesters, but also good electron donors.[2,14] Past work in the field has, nevertheless, been almost exclusively conducted with C60-based electron donor–acceptor systems. Considering the limited publications with respect to the buckminsterfullerene, covalently linked electron donor–acceptor architectures based on C70 as the electron acceptor,[30,44,45] on one hand, and porphyrins as the light harvester/electron donor, on the other hand, we report here on two different electron donor–acceptor conjugates featuring a meso-tetraphenyl porphyrin covalently linked to C70. A full-fledged photochemical, radiation chemical, and quantum chemical investigation provides sound insights into the nature of the photoinduced charge separation and recombination.

2. Results and Discussion

2.1. Synthesis and Characterization

An addition of the N-arylaziridine-2,3-dicarboxylates to fullerene C70, described previously,[15] was used for the construction of C70 conjugates with meso-tetraphenylporphyrin (TPP). However, an attempted addition of porphyrinic aziridine 1 with carboxyethyl moieties (Figure 1a), in contrast to previously report for C60,[46] affords totally insoluble products, which led us to introduce solubilizing groups. For this reason, porphyrinic aziridine 2, bearing long and solubilizing alkyl chains, was obtained in the same manner with analogous aziridine 1. Indeed, the introduction of the solubilized carboxy-n-octyl moieties to the porphyrinic aziridine 2 allows us to obtain the desired adduct, soluble enough for purification and characterization.

According to the literature, the addition of such aziridines to fullerences processes as a sequence of concerted stages of aziridine ring opening and 1,3-dipolar cycloaddition with extremely high stereospecificity, while the addition of cis-aziridine affords only trans-adducts.[35,47] In principle, monoaddition to C70 may afford four different position regioisomers, so-called site-isomers. Practically, the reaction mixtures consist of two isomers, namely, a major “α” [1,9] adduct and a minor “β” [7,8] adduct. Both of these isomers are distinguishable by their characteristic patterns in the NMR and UV–vis spectra.

The addition of 2 to C70 under well-established conditions (o-dichlorobenzene, 100 °C) affords a reaction mixture. It contains, according to the 1H NMR spectrum, DL1 and DL2 in 1:2.72 ratio. They are primarily assigned as β- and α-isomers, respectively, on the basis of the chemical shifts known for adducts of the same type.[35] Accordingly, the site selectivity is in sound agreement with previous reports and is due to π-π interactions between C70 and the porphyrin. Seemingly, the isomeric ratio is lower than found recently. High-performance liquid chromatography (HPLC) separation affords the two isomeric DL1 and DL2 in 28% and 24% yields, respectively (Figure 1b). 1H NMR spectra of the products reveal the fingerprints of the individual isomers.[35] These are singlets of pyrrolidine protons at 5.66 and 5.82 ppm for DL1 and 5.82 and 6.15 ppm for DL2, from which we conclude that they are the cis-β and cis-α isomers, respectively. Their absorption spectra, in which only the DL1 isomer shows an absorption maximum typical for cis-β isomers, further support our assignment.

2.2. Density Functional Theory (DFT) Results

Electronically excited states of the C60-porphyrin electron donor–acceptor systems were studied by means of quantum chemical calculations on the model compounds DL1′ and DL2′, related to DL1 and DL2. First of all, the geometries of the ground states were optimized using DFT at the B3LYP/6-31G(d) level of theory. For both isomers, two energy minima corresponding to two different conformers were found. These are, on one hand, the “extended” (e) conformer, in which the porphyrin plane is oriented perpendicular to the tangent plane of the fullerene, and, on the other hand, the “bent” (b) conformer with a significant deviation from perpendicularity (Figure S38, Supporting Information). For DL1′ and DL2′, the extended conformer is ≈5 kcal mol−1 more stable than the bent conformer, and the conformers of DL2′ are ≈3 kcal mol−1 more stable than those of DL1′. In all cases, the HOMOs are localized on the porphyrin, while the LUMOs are localized on C70. The HOMO–LUMO gaps are appreciably larger (0.14 eV) for the bent conformers than for the extended conformers, while only subtle differences (0.06 eV) evolve between the α- and β-isomers (Table S6, Supporting Information).

Next, the electronically excited states of the most stable conformers for DL2′ and DL2′ were computed in four different solvents: toluene, anisole, tetrahydrofuran (THF), and benzonitrile. The first electronically excited state correlates with an excitation of the HOMO on the porphyrin to the LUMO on C70 (Figure S39, Supporting Information) and, represents, in turn, a charge-separated state. In addition, we derived the relative rate constants for charge recombination, kCR, in the four different solvents with the aid of the Marcus theory. A detailed description of the calculations is provided in the Supporting Information. Notably, the quantitative match with the experimental values was poor. A reasonable rationale is based on the time dependency of the solvent relaxation, especially at very short timescales, which is comparable to the dielectric relaxation time. This is unaccounted for by the polarizable continuum model (PCM) model. Still, the correct trend of kCR was found

\[ k_{\text{benzonitrile}} \approx k_{\text{THF}} < k_{\text{anisole}} < < k_{\text{toluene}} \]
2.3. Radiation Chemistry

To establish the transient absorption spectra of the one-electron reduced form of the C\textsubscript{70}-derivatives, pulse radiolytic experiments were performed under reducing conditions with the respective C\textsubscript{70}-R references: C\textsubscript{70}-H, C\textsubscript{70}-Br, and C\textsubscript{70}-CH\textsubscript{3} (Figure 2). The reducing conditions were obtained by irradiating solutions of the C\textsubscript{70}-R references in N\textsubscript{2}-saturated mixtures of toluene, acetone, and isopropanol (8:1:1 v/v/v) with short electron pulses. These conditions led to the formation of the (CH\textsubscript{3})\textsubscript{2}C’(OH) radicals,\textsuperscript{[48,49]} which are known as strong reducing agents (\textasciitilde -1.2 V vs saturated calomel electrode/\textasciitilde -1.1 V vs normal hydrogen electrode),\textsuperscript{[49-51]} and, which are capable of reducing fullerences.\textsuperscript{[52]} As such, (CH\textsubscript{3})\textsubscript{2}C’(OH) radicals are expected to reduce C\textsubscript{70}-H, C\textsubscript{70}-Br, and C\textsubscript{70}-CH\textsubscript{3} to their corresponding one-electron reduced forms. The main reaction pathway includes

\[
\begin{align*}
\text{C}_7\text{H}_8 & \longrightarrow 3^v\text{C}_7\text{H}_8 & (2) \\
3^v\text{C}_7\text{H}_8 + (\text{CH}_3)_2\text{CO} & \rightarrow \text{C}_7\text{H}_8 + 3^v(\text{CH}_3)_2\text{CO} & (3) \\
3^v(\text{CH}_3)_2\text{CO} + (\text{CH}_3)_2\text{HCOH} & \rightarrow 2(\text{CH}_3)_2\text{COH} & (4) \\
\text{C}_{70} + (\text{CH}_3)_2\text{COH} & \rightarrow \text{C}_{70}^{--} + (\text{CH}_3)_2\text{CO} + \text{H}^+ & (5)
\end{align*}
\]

Upon pulse radiolysis of the C\textsubscript{70}-R references, initially after the electron pulse, the transient absorptions of (CH\textsubscript{3})\textsubscript{2}C’(OH) with its featureless band in the UV region of the optical spectrum are discernible. It decays and gives rise to a new set of transient absorptions throughout the UV, visible, and NIR parts of the spectrum.

Figure 1. a) Synthesis of porphyrinic aziridines 1 and 2. b) Addition of aziridine 2 to C\textsubscript{70}.

Figure 2. Structure of the reference C\textsubscript{70} adducts C\textsubscript{70}-H (X=H), C\textsubscript{70}-CH\textsubscript{3} (X=CH\textsubscript{3}), and C\textsubscript{70}-Br (X=Br).
the optical spectrum—Figure 3 for \( \text{C}_{70}-\text{H} \), Figure S8, Supporting Information, for \( \text{C}_{70}-\text{Br} \), and Figure S9, Supporting Information, for \( \text{C}_{70}-\text{CH}_3 \). For example, the transient absorption spectrum of \( (\text{C}_{70}-\text{H})^- \) gives rise to maxima at around 370, 420, and 580 nm, followed by a broad transient absorption throughout the visible and NIR range of the optical spectrum with minor maxima around 740, 810, and 1300 nm. All of the aforementioned is flanked by distinct minima around 400 and 460 nm, where \( \text{C}_{70}-\text{H} \) exhibits ground state absorptions. A closer look at the time evolution of the transient absorption spectra discloses that the initially formed transient absorption of \((\text{CH}_3)_2\text{C}\equiv\text{OH}\) decays and its decay goes hand in hand with the rise of the spectroscopic signature of the one-electron reduced form of the \( \text{C}_{70} \) derivatives. Please compare the time absorption profiles at 390 nm representing the \((\text{CH}_3)_2\text{C}\equiv\text{OH}\) decay and the rise at 1300 nm, where transient absorptions of the one-electron reduced form of the \( \text{C}_{70} \) derivatives evolve in Figure 3b \((\text{C}_{70}-\text{H})\), Figure S8b, Supporting Information \((\text{C}_{70}-\text{Br})\), and Figure S9b, Supporting Information \((\text{C}_{70}-\text{CH}_3)\). The rate constants for the reduction with \((\text{CH}_3)_2\text{C}\equiv\text{OH}\) in toluene, acetone, and isopropanol \((8:1:1 \text{ v/v/v})\) mixtures were determined via analyses of the pseudo-first-order rate constants plotted versus the concentrations of the \( \text{C}_{70}-\text{R} \) references, as shown in Figure 3c. To this end, rate constants of \(6.4 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) \((\text{C}_{70}-\text{H})\), \(1.9 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) \((\text{C}_{70}-\text{Br})\), and \(1.1 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) \((\text{C}_{70}-\text{CH}_3)\) were derived from the linear relationships. These values are quite similar to those previously obtained for \( \text{C}_{60} \). A closer inspection of the time evolution reveals that the one-electron reduced form of the \( \text{C}_{70}-\text{R} \) references further reacts on timescales of hundreds of microseconds. Feasible rationales are dimerization reactions, with an unreacted \( \text{C}_{70}-\text{R} \) to afford \((\text{C}_{70}-\text{R})_2^{2-} \) and/or with another \((\text{C}_{70}-\text{R})_{2-} \) to form \((\text{C}_{70}-\text{R})_2^{2-} \). Such reactions are not unexpected, because they are reported in the literature for \( \text{C}_{60} \)\.[50]

### 2.4. Photophysical Study

First, photophysical studies, namely, steady-state absorption and fluorescence spectroscopy measurements, were performed with the \( \text{C}_{70}-\text{R} \) references in toluene. As a result, extinction coefficients of \(2.3 \times 10^6 \text{ M}^{-1} \text{cm}^{-1} \) and fluorescence quantum yields of 0.0002 were obtained for \( \text{C}_{70}-\text{H} \) (see also Table S3, Supporting Information), which are in sound agreement with previously published values.[53] In addition to the absorption spectra of the \( \text{C}_{70}-\text{R} \) references (see Figure S10, Supporting Information), photophysical studies were performed with the corresponding \( \text{H}_2\text{P} \) (TPP) reference and the electron donor–acceptor conjugates DL1 and DL2. In the case of \( \text{H}_2\text{P} \), absorption spectra in various solvents with different polarities and viscosities, that is, toluene, anisole, THF, and benzonitrile, were investigated.

Absorption spectra exhibit in all cases Soret-band absorptions and a set of Q-band absorptions, which are typical features of \( \mu \text{es} \)-substituted free-base porphyrin derivatives.[54] In all solvents, the Soret-band absorptions are discernible in the range from 420 to 430 nm, followed by four Q-band absorptions in the range between 513 and 650 nm. In the case of DL1 and DL2, an additional band at around 360 nm is observed and it is attributed to the presence of \( \text{C}_{70} \) (see Figure 4).

Figure 3. a) Pulse radiolysis spectrum of \( \text{C}_{70}-\text{H} \) in a nitrogen-saturated mixture of toluene, acetone, and isopropanol \((8:1:1 \text{ v/v/v}) \) saturated with \( \text{N}_2 \), 1.3 \( \mu \text{s} \) after the electron pulse. b) Corresponding time absorption profiles at 390 (black), 450 (red), 750 (blue), and 1300 nm (green dots). The corresponding monoexponential global fits are shown in light blue. c) Plot of the pseudo-first-order rate constant versus \( \text{C}_{70}-\text{H} \) concentration.
Interestingly, the extinction coefficients of DL1 and DL2 are significantly lower compared to the H\textsubscript{2}P reference, which is in line with previously reported porphyrin–fullerene electron donor–acceptor systems and prompts to electronic communication between the photo- and redox-active constituents.\textsuperscript{[55]}

Insights into the electronic interactions between the electron donor and the acceptor came from fluorescence studies. The H\textsubscript{2}P reference exhibits strong emission, in the range between 620 and 760 nm in anisole upon 430 nm photoexcitation into the Soret-band absorption, with maxima at 651 and 718 nm. The fluorescence quantum yield and the lifetime of H\textsubscript{2}P in anisole were found to be 0.116 and 10.74 ns, respectively. Despite the fact that the fluorescence spectra of both electron donor–acceptor systems were identical to those of the H\textsubscript{2}P reference, the fluorescence quantum yields as well as the corresponding lifetimes were significantly quenched. In particular, fluorescence quantum yields of DL1 and DL2 in anisole were found to be 0.0015 and 0.0016, respectively. Relative to the H\textsubscript{2}P reference, these quantum yields correlate to a quenching of ≈99%. In toluene, THF, and benzonitrile the fluorescence quantum yields were calculated to be 0.0008, 0.0011, and 0.0013, respectively, for DL1 and 0.0015, 0.0007, and 0.0009, respectively, for DL2. Such a significant quenching suggests an additional deactivation channel, electron or energy transfer starting from the first singlet excited state of the electron-donating H\textsubscript{2}P.

Next, to reveal the nature of the fluorescence quenching, femtosecond and nanosecond transient absorption spectroscopy measurements were performed photoexciting the electron donor–acceptor compounds DL1 and DL2 as well as H\textsubscript{2}P at 430 nm and the C\textsubscript{70}-R reference compounds at 387 nm. Initially, toluene solutions of the C\textsubscript{70}-R references, that is, C\textsubscript{70}-H, C\textsubscript{70}Br, and C\textsubscript{70}CH\textsubscript{3} were prepared. H\textsubscript{2}P and the electron donor–acceptor compounds DL1 and DL2 were investigated in toluene, anisole, THF, and benzonitrile.

Exemplarily, for C\textsubscript{70}-H upon photoexcitation at 387 nm, the transient absorption changes were analyzed using the Glotaran\textsuperscript{[56]} program with a “two species” kinetic model. After direct photoexcitation, transient maxima at 500 to 800 nm as well as in the NIR region evolve as the first species, that is, the first singlet excited state of C\textsubscript{70}-H. Its lifetime is with 727 ± 3 ps, in perfect agreement with previously reported lifetimes for C\textsubscript{70} derivatives.\textsuperscript{[53,57]}

The singlet excited state decay goes hand in hand with the growth of the second species, for which transient absorption bands at around 590, 619, and 690 nm as well as at in the NIR region at around 1050 nm were observed. Accordingly, the second species is the triplet excited state (Figure S18, Supporting Information), with a lifetime of 38 ± 1 μs.\textsuperscript{[58,59]}

Photoexciting the H\textsubscript{2}P reference at 430 nm, that is, exciting into the Soret-band absorption, several transient absorption maxima in the visible region up to 700 nm and a strong band in the NIR around 1080 nm are seen. These observed spectral features are related to the singlet excited state of the free-base porphyrin, and are not fully decaying within the time range of our femtosecond transient absorption setup (6 ns). Corresponding nanosecond transient absorption measurements were conducted to follow the complete decay of the first excited singlet state of H\textsubscript{2}P and show the known intersystem crossing into the corresponding triplet manifold.\textsuperscript{[60] As a matter of fact, lifetimes of the first excited singlet and triplet state of 11.2 ± 0.1 ns and 18.9 ± 0.3 μs, respectively, were derived in anisole (see also Figure S14–17, Supporting Information, and Table 1 for the spectra and values in other solvents).

Finally, transient absorption spectroscopy measurements based on femtosecond and nanosecond photolysis at 430 nm were performed with the electron donor–acceptor compounds DL1 and DL2 in toluene, anisole, THF, and benzonitrile. Taking a look at the transient absorption spectra, several maxima and minima are observed in the visible and NIR regions. Due to this more complex picture, a three-species model based on target analysis (see Figure S37, Supporting Information) using Glotaran was conducted giving the following results. The transients directly formed after photoexcitation (see Figure 5 and Figure S24–36, Supporting Information) match well the transient absorption spectra of the H\textsubscript{2}P reference first singlet excited state and are thus dedicated to the first singlet excited state located at the free-base porphyrin in DL1 and DL2. The transient absorption of the first singlet excited state decays rapidly, for example, with lifetimes of 49 ± 1 ps for DL1 and 65 ± 2 ps for...
DL2 in anisole (see Figure 5 and Table 1), and gives rise to a new set of spectroscopic features. More precisely, a diagnostic and broad transient absorption band in the NIR region between 1100 and 1400 nm with a maximum at 1300 nm was seen for DL1 and DL2, which is in sound agreement with the radiation chemical reduction of all C70-R references (see Figure 3a and Figure S8a and S9a, Supporting Information) forming C70−. Furthermore, the transient absorption maxima in the visible region at around 450 and 535 to 680 nm are in good agreement with the corresponding one-electron oxidized form of the H2P reference (H2P+). Accordingly, we corroborated a photoinduced electron transfer from H2P to C70 to afford a charge-separated state as the second species (red line). Afterward, the charge-separated state decays, with a lifetime of 559 ± 11 ps, partially back to the ground state as well as partially to the corresponding triplet excited state of H2P; a finding that is in sound agreement with previous findings on C60.[61] Note that no evidence for the triplet excited state of C70 was gathered.

Figure 5. Transient absorption spectra obtained upon femtosecond laser flash photolysis (430 nm) of DL1 in anisole. a) The data matrix analyzed by SVD analysis shows three different components, which relate to the first singlet excited state (S1), the charge-separated state (CSS), and the corresponding triplet excited state (T1). b,c) The fitted spectral and time components, respectively; d) the corresponding kinetic containing the raw data points (grey circles) and the corresponding fit (red line) at 1285 nm obtained by target analysis is shown exemplarily.

Table 1. Singlet excited state (S1), charge-separated state (CSS), and triplet excited state (T1) lifetimes in different solvents at 25 °C. All transient absorption spectra were performed upon photoexcitation at 430 nm.

| Cmpd. | Toluene | Anisole | THF | Benzonitrile |
|-------|---------|---------|-----|-------------|
|       | S1 [ps] | CSS [ps] | T1 [μs] | S1 [ps] | CSS [ps] | T1 [μs] | S1 [ps] | CSS [ps] | T1 [μs] |
| H2P   | 10 487 ± 76 | – | 40.80 ± 0.72 | 11 229 ± 113 | – | 18.90 ± 0.29 | 11 210 ± 103 | – | 13.80 ± 0.32 | 10 800 ± 93 | – | 48.90 ± 0.85 |
| DL1   | 39 ± 2 | 1203 ± 16 | 23.22 ± 0.51 | 49 ± 1 | 559 ± 11 | 4.09 ± 0.11 | 11 ± 1 | 138 ± 2 | 12.80 ± 0.39 | 10 ± 1 | 125 ± 3 |
| DL2   | 48 ± 2 | 1160 ± 19 | 1.23 ± 0.06 | 65 ± 2 | 571 ± 8 | 9.68 ± 0.27 | 12 ± 1 | 195 ± 3 | 20.80 ± 0.43 | 14 ± 1 | 136 ± 4 |

Corresponding singlet and triplet excited state lifetimes were obtained from global analyses by Glotaran. Corresponding singlet excited state, charge recombination, and triplet excited state lifetimes were obtained from target analyses by Glotaran using the model shown in Figure S37, Supporting Information.

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regardless of a parallel or a sequential model. The latter matches the previously obtained triplet excited state of the \( H_2P \) reference (for further details, see also Table S4, Supporting Information). When analyzing the scaling factors from the analysis of the transient absorption matrices, the relative distribution of the corresponding charge recombination pathways changes with the solvent polarity. As a general trend, with increasing solvent polarity the likelihood of the direct decay of the charge-separated state back into the ground state increases (for details, see also Figure S37 and Table S4 and S5, Supporting Information).

Considering that 430 nm photoexcitation of DL1 and DL2 also excites \( C_{70} \), its triplet excited state features are discernable in the NIR region between 870 and 1050 nm. Please note that this pathway is however only contributing less than 5% to the corresponding spectra.

In principle, DL2 is subject to the same photoinduced electron transfer mechanism as DL1. However, DL2 reveals significant longer charge separation lifetimes, especially in viscous anisole and benzonitrile, where the values are 65 ± 2 and 14 ± 1 ps for DL2 relative to 49 ± 1 and 10 ± 1 ps for DL1. In addition, the scaling factors and, in turn, the relative distribution of the corresponding pathways change. \( f_\alpha \), that is, the charge recombination to the ground state, and \( f_\beta \), that is, the charge recombination to the triplet state of the porphyrin, differ strongly in anisole and THF. As a matter of fact, \( f_\beta \) is doubled (see also Figure S37 and Table S4 and S5, Supporting Information) and indicates that the different \( C_{70} \) adduct isomers influence the corresponding pathways significantly. Such differences are related to regioisomeric effects and are documented in similar \( C_{60} \)-based systems, for example, impacting the performance in bulk heterojunction solar cells consisting of different \( C_{60} \) adducts.\(^{[62,63]} \) However, such performance effects in \( C_{60} \)-based devices have been only discussed in terms of the different \( C_{70} \) isomeric adducts affecting the packing on films and altering the performance by this effect, but not by the impact of the different electron transfer rates.\(^{[64]} \)

Potentially, the implementation of electron-donating porphyrins or phthalocyanines into \( C_{60} \)-based solar cells should show differences in the power conversion efficiency performance not only due to structural or packing effects, but also due to the distribution of the corresponding reaction pathways from the charge-separated state. Using different fullerene regioisomeric adducts is an interesting direction toward the control of the distribution of states in advanced electron donor–acceptor systems.

### 3. Conclusion

Here, we report on the synthesis of two new electron donor–acceptor systems containing different isomeric adducts of \( C_{70} \), that is, the \( \alpha \)- and \( \beta \)-regioisomers. The rigid nature of the linker enforces a scenario, in which the porphyrin is locked into “edge to face” configuration relative to the fullerene and, in turn, affords an ideal platform to probe the regioisomeric dependence of electron transfer. Of great relevance is the fact that we documented experimentally the existence of an electron transfer from the electron-donating porphyrins in their excited states to both regioisomeric adducts of the electron-accepting \( C_{70} \) (Figure 6). From our full-fledged investigations we conclude sizeable differences not only in the charge recombination kinetics for the \( \alpha \)- and \( \beta \)-regioisomers, but also in the relative distributions of their charge recombination pathways. Moreover, we demonstrate full control over the charge transfer mechanism by, for example, tuning solvent parameters such as polarity and viscosity. The \( \alpha \)-regioisomeric adducts of \( C_{70} \) are superior, a fact that relates to the unique electron delocalization within the carbon caps of fullerenes. As such, placing the electron acceptor in close proximity to the \( C_{70} \) caps with their “corannulenoid” fragments rather than the equatorial regions made out of “phenanthrenoid” rings is beneficial in terms of suppressing the charge recombination. These findings constitute an intriguing possibility for future bio-inspired and nature-mimicking electron donor–acceptor systems based on fullerenes for solar energy conversion.

### 4. Experimental Section

**General Methods:** NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Fourier-transform infrared spectroscopy (FTIR) spectra were obtained on the Shimadzu IRAffinity-1 in KBr pellets. High resolution mass spectrometry (HRMS) spectra were recorded on a Bruker maXis spectrometer with ESI+ ionization. HPLC was performed on a Shimadzu Prominence LC20 chromatograph with a diode array detector on a Nacalai Cosmopolit PBr column in tolune: dichloromethane (DCM) as an eluant.

Solvents were distilled prior to use. HPLC-grade solvents were used for HPLC. Diethyl ether “extra dry” was used as received. \( C_{70} \) adducts \( C_{60-H}, C_{70-CH_3}, \) and \( C_{70-Br}^{[54]} \) TPP,\(^{[60]} \) and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin,\(^{[60]} \) octyl glyoxylate,\(^{[60]} \) and octyl diazoacetate\(^{[60]} \) were synthesized as described in the literature.

**Diocyl cis-1-[(10,15,20-triphenylporphyrin-5-Yl)phenyl]azidine-2,3-dicarboxylate** 2: A solution of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (50 mg, 0.08 mmol) in toluene (5 mL) of octyl glyoxylate (26 mg, 0.14 mmol) in 2 mL of toluene was added, followed by \( Na_2SO_4 \) (0.2 g), and the reaction mixture was stirred for 30 min at room temperature (RT). The desiccant was filtered off, and the solvent was removed in vacuo.

The residue was dissolved in dry ether (3 mL), five drops of BF\(_3\)\(\cdot\)Et\(_2\)O was added, followed by octyl diazoacetate (18 mg, 91 \( \mu \)mol) in ether (2 mL) was added dropwise. The reaction mixture was stirred for 2 h at RT, then 15 drops of Et\(_3\)N was added, and then the reaction mixture was poured in water and extracted with DCM. The organic layer was separated and dried over \( Na_2SO_4 \). The desiccant was filtered off, the solvent was removed in vacuo, and the product was purified by preparative TLC (SiO\(_2\), PE–DCM 2:1 + 0.1% Et\(_3\)N). As a result, pure porphyrin 2 (27 mg, 28 \( \mu \)mol, 35%) was obtained.

### Figure 6

Simplified energy scheme containing the first singlet excited state of the donor–acceptor systems (blue) and the charge-separated (red) and the triplet excited state (green line). For further detail, please also consider Figure S37, Supporting Information.
2. violet crystals. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: $-2.73$ (s, 2H), $0.80$–$1.00$ (m, 6H), $1.25$–$1.55$ (m, 20H), $1.70$–$1.90$ (m, 4H), $3.50$ (s, 2H), $4.35$ (t, $J$ 6.9 Hz, 4H), $7.46$ (d, $J$ 8.3 Hz, 2H), $7.65$–$7.85$ (m, 9H), $8.16$ (d, $J$ 8.3 Hz, 2H), $8.20$–$8.40$ (m, 6H), $8.80$–$8.95$ (m, 8H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ ppm: $14.3$, $22.8$, $26.0$, $28.7$, $29.3$, $29.4$, $32.0$, $43.5$, $66.4$, $118.6$, $119.5$, $120.3$, $126.8$, $127.9$, $134.7$, $135.4$, $138.2$, $142.3$, $150.6$, $167.2$. FTIR (KBr) $\nu$ cm$^{-1}$: $3316$ (NH), $1734$ (C=O). HRMS (resolution mass spectrometry with electrospray ionisation): m/z calc. for $C_{30}H_{50}O_2$: 467.3521, exp: 467.3531.

**Dyads DL1 and DL2:** Porphyrylaziridine 2 (27 mg, 27 μmol) and fullerene $C_{60}$ (50 mg, 60 μmol) were heated in 1,2-dichlorobenzene (4 mL) at 100 °C for 44 h. The solution was removed in vacuo, and the residue was fractioned by flash chromatography (SiO$_2$, toluene–EtOAc) and purified by HPLC on a PBR column with DCM-toluene as an eluant. As a result, dyads DL1 (14 mg, 7.6 μmol, 28%) and DL2 (12 mg, 6.5 μmol, 24%) were obtained.

**DL1—Brown Powder:** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ ppm: $-2.91$ (s, 2H), $0.50$–$2.00$ (m, 30H), $3.78$ (t, $J$ 6.6 Hz, 2H), $4.25$ (m, 2H), $5.66$ (s, 1H), $5.95$ (s, 1H), $7.15$ (pseudo-d, $J$ 8.2 Hz, 2H), $7.55$–$7.65$ (m, 9H), $7.98$ (pseudo-d, $J$ 8.1 Hz, 2H), $8.01$–$8.11$ (m, 6H), $8.65$–$8.70$ (m, 8H); $^{13}$C NMR could not be recorded due to low solubility of the product in organic solvents.

**DL2—Black Powder:** $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ ppm: $-2.89$ (s, 2H), $0.50$–$2.00$ (m, 30H), $4.03$ (pseudo-d, $J$ 6.7 Hz, 2H), $4.30$–$4.40$ (m, 2H), $5.82$ (s, 1H), $6.15$ (s, 1H), $7.31$ (d, $J$ 8.6 Hz, 2H), $7.55$–$7.65$ (m, 9H), $8.05$–$8.12$ (m, 8H), $8.69$ (pseudo-o, 4H), $8.71$ (d, $J$ 4.8 Hz, 2H), $8.75$ (d, $J$ 4.8 Hz, 2H); $^{13}$C NMR could not be recorded due to low solubility of the product in organic solvents.

**Quantum Chemical Calculations:** All quantum chemical calculations were performed using the Gaussian 16[2018, 2019, 2020] geometry optimization was performed by DFT at B3LYP/6-31G(d) level of theory. The electronically excited states were studied using time-dependent density functional theory (TD DFT) at B3LYP 6-31G(d) level in four different solvents, toluene, anisole, THF, and benzonitrile, with the PCM of solvents. The electronic configuration of each state was analyzed using the CI expansion coefficients.

**Radiation Chemistry:** Pulse radiolysis investigations were conducted with samples dissolved in a toluene/acetone/2-propanol (80/10/10 v/v/v) mixture saturated with N$_2$ and irradiated with high-energy electron pulses (10 MeV, 15 ns duration) by a LINAC-type electron accelerator ELEKTRA-UK03 (Torry, Moscow). The dose delivered per pulse was measured by electron dosimetry.[22] Doses of 30 Cy were selected. The optical detection system consisted of a pulsed 1000 W xenon lamp (Osramp, XBO1000), Suprasil cell (light path 1 cm), high-intensity grating monochromator, photomultiplier, (Hamamatsu Photonics), or a fast InGaAs photodiode and a fast transient recorder (Tektronix, TDS5034).

**UV–Vis Absorption Spectroscopy:** Steady-state absorption spectra were recorded using a Perkin Elmer Lambda 2 UV–vis two-beam spectrophotometer with a slit width of 3 mm and a scan rate of 480 nm min$^{-1}$. A quartz glass cuvette of $10 \times 10$ mm was used.

**Emission Spectroscopy:** Steady-state emission was measured using a Horiba Jobin Yvon Fluoromax-3 spectrometer using a slit width of 3 mm for excitation and emission and an integration time of 0.1 s. A quartz glass cuvette of $10 \times 10$ mm was used. All spectra were corrected for the instrument response. The $C_{60}$R samples were measured at 375 nm, while all other samples were measured upon photoexcitation at 430 nm. The experiments were performed at RT. Fluorescence quantum yields were determined by the comparative method using meso-tetraphenyl porphyrin ($H_{2}P$) and $C_{60}$ in toluene as reference, respectively.

**Singlet Oxygen Calculation:** Triplet quantum yields of the donor–acceptor systems DL1 and DL2 were performed in toluene, anisole, and THF and calculated by the comparative method using pure $C_{60}$ in toluene as the reference system. The emission spectra of the obtained singlet oxygen at around 1275 nm were recorded using a Fluorolog-3 (Horiba Jobin Yvon) spectrometer equipped with a 450 W xenon lamp. NIR accessories, a high-pass filter ($\lambda = 780$ nm), an integration time of 20 s, single-grating monochromators and with a slit width of 3 nm and a quartz glass cuvette of $10 \times 10$ mm. As photoexcitation wavelength 415 nm was chosen.

**Time-Resolved Fluorescence Spectroscopy:** Time-resolved fluorescence spectra were obtained by the time-correlated single-photon counting technique using a Fluorolog-3 emission spectrometer (Horiba Jobin Yvon) together with an R3809U-58 MCP (Hamamatsu) and a SuperK Extreme high-power supercontinuum fiber laser EXB-6 (NKT) photoexciting at 430 nm (pulse width $\leq 150$ ps).

**Femtosecond Transient Absorption Spectroscopy:** Femtosecond transient absorption studies were performed with laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:sapphire laser system (Model CPA 2110, Clark-MXR Inc.; output 775 nm). For excitation wavelengths of 387 and 430 nm, a nonlinear optical parametric amplifier (NOPA) was used to generate ultrashort tunable visible light pulses out of the pump pulses. The transient absorption pump probe spectrometer (TAPPS) can be described as a two-beam setup in which the pump pulse is used as an excitation source for transient species and the delay of the probe pulse is exactly controlled by an optical delay rail. As the probe (white-light continuum), a small fraction of pulses stemming from the CPA laser system was focused by a 50 mm lens into a 2 mm thick sapphire disc. The transient spectra were recorded using fresh argon-saturated solutions in each laser excitation. All experiments were performed at 298 K in a 2 mm quartz cuvette.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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fullerenes, molecular electron donor-acceptors, photoinduced electron transfers, regioisomers, synthetic methods

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