Decelerating Charge Recombination Using Fluorinated Porphyrins in N,N-Bis(3,4,5-trimethoxyphenyl)aniline—Aluminum(III) Porphyrin—Fullerene Reaction Center Models

Niloofar Zarrabi, Sairaman Seetharaman, Subhajyoti Chaudhuri, Noah Holzer, Victor S. Batista,* Art van der Est,* Francis D’Souza,* and Prashanth K. Doddutoori*

ABSTRACT: In supramolecular reaction center models, the lifetime of the charge-separated state depends on many factors. However, little attention has been paid to the redox potential of the species that lie between the donor and acceptor in the final charge separated state. Here, we report on a series of self-assembled aluminum porphyrin-based triads that provide a unique opportunity to study the influence of the porphyrin redox potential independently of other factors. The triads, BTMPA-Im→AlPorF₃-Ph-C₆₀ (n = 0, 3, 5), were constructed by linking the fullerene (C₆₀) and bis(3,4,5-trimethoxyphenyl)aniline (BTMPA) to the aluminum(III) porphyrin. The porphyrin (AlPor, AlPorF₃, or AlPorF₅) redox potentials are tuned by the substitution of phenyl (Ph), 3,4,5-trifluorophenyl (PhF₃), or 2,3,4,5,6-pentafluorophenyl (PhF₅) groups in its meso positions. The C₆₀ and BTMPA units are bound axially to opposite faces of the porphyrin plane via covalent and coordination bonds, respectively. Excitation of all of the triads results in sequential electron transfer that generates the (PhF₅) groups in its meso positions. Despite the fact that the radical pair is identical in all of the triads, remarkably, the lifetime of the BTMPA radical pair was found to be very different in each of them, that is, 1240, 740, and 56 ns for BTMPA-Im→AlPorF₃-Ph-C₆₀, respectively. These results clearly suggest that the charge recombination is an activated process that depends on the midpoint potential of the central aluminum(III) porphyrin (AlPorF₅).

INTRODUCTION

The generation of long-lived high-energy charge-separated states is an essential component of the conversion of sunlight into chemical energy in natural photosynthesis. To achieve energy conversion with a high quantum yield, the photosynthetic systems use a series of electron transfer reactions along a chain of redox active cofactors. The sunlight energy collected by the light harvesting antenna systems is funneled to the reaction center complex where an extremely fast and highly efficient initial charge separation occurs. The charge separation is then stabilized by a series of secondary electron transfer steps that ultimately generate species that are long-lived enough to allow oxidation and reduction of soluble donors and acceptors to occur on opposite sides of the photosynthetic membrane. In oxygenic photosynthesis, this process generates the energy-rich compounds ATP, NADPH, and O₂ that are used to drive respiration, carbon fixation, and a host of other biochemical processes. The mimicking of the initial steps of photosynthetic energy conversion using synthetic models is important to further our understanding of the intricate details of electron transfer in natural photosynthesis. Most importantly, research in this area holds promise for technological advances in solar energy conversion and storage for future energy needs. In this regard, many reaction center models have been designed and studied to mimic the photoinduced charge separation of natural systems. However, unlike the reaction centers, charge recombination is an important factor because the number of donors and acceptors is smaller, and the complexes are not embedded in a membrane protein. In these model systems, the rate of charge separation and recombination has been studied as a function of the driving force, reorganization energy, and electronic coupling, which depend on the distance between donor and acceptor units, the
Bridge and medium connecting them,37−39 molecular conformation,32,40 etc. By optimizing these factors through careful design of the complexes, sequential charge transfer yielding the desired long-lived charge separated states is achieved.41−44

In many of these synthetic models, substituted porphyrin compounds are used because they share similar structural, physical, and chemical properties with the chlorophyll chromophores of the natural photosystems.45,46 In the artificial complexes, porphyrins are covalently or noncovalently connected to variety of redox active units. In most cases, the donor and acceptor centers are connected to the periphery of the porphyrin ring either through the meso- or pyrrolic (β-) positions. This strategy results in complexes in which the charge separation occurs in the porphyrin plane and is sometimes referred to as horizontal electron transfer. A smaller number of model compounds have been studied in which “vertical” or “axial” electron transfer occurs perpendicular to the porphyrin plane.27,30,47−60 One of the main reasons for this limitation is the use of transition metal ions in the porphyrin cavity that do not allow more than one axial unit.

The most important factor governing biological electron transfer is the electronic coupling between the donor and acceptor, which leads to the linear dependence of the logarithm of the rate on the distance as described by the Moser-Dutton relationship.61 In molecular systems, the electronic coupling depends strongly on the nature of the bonding and the arrangement of the orbitals involved in the electron transfer. Therefore, it is fundamentally important to consider the axial arrangement as an alternative to the more common horizontal arrangement for the artificial model compounds. Moreover, the axial placement of the donor and acceptor units on opposite faces of the porphyrin ensures that they are spatially well separated and that unwanted interactions are minimized. With this objective, recently, we along with others have reported several axial-bonding type reaction center models by exploiting the unique properties of the main group porphyrins.

Among the main group porphyrins, aluminum(III) porphyrins are unique because they can form two different types of axial bonds: (i) covalent Al−O bonds formed through condensation with carboxylic acids and alcohols to form ester and ether linkages, respectively,71−74 and (ii) Al−X coordination bonds (X = N, O) through Lewis acid−base interactions between Lewis bases, such as pyridine and imidazole, and the Al center.35,64 These two types of bonding allow a wide variety of donors and acceptors to be attached on opposite faces of the porphyrin ring. Additionally, AlPor is highly fluorescent indicating that the excited singlet state lifetime is relatively long, which is advantageous if electron transfer is to take place. AlPor also has a rich redox chemistry with two reversible oxidation and reduction processes, allowing it to easily act as both an electron donor and acceptor. Furthermore, the optical and redox properties of AlPor can be tailored by introducing appropriate substituents in meso- or β-positions of the porphyrin cavity for desired applications. The combination of these properties makes AlPor a unique candidate for constructing “axial-bonding” type multicomponent Donor-AlPor-Acceptor systems.

An important factor in determining the lifetime of the charge-separated state is the nature of the charge recombination reaction. In the design of such systems, it is usually assumed that the direct recombination occurs between the donor and acceptor units. However, a more accurate description of the recombination process is that it is mediated by a series of excited states of the porphyrin that can transfer energy to the ground state of the acceptor. This process is believed to be the rate-limiting step in the charge recombination reaction.61

Scheme 1. Construction of the Dyads AlPorF₃-Ph-C₆₀ and Triads BTMPA-Im→AlPorF₃-Ph-C₆₀, n = 0, 3, 5

[Scheme Image]

“Reaction conditions: (i) C₆₀-Ph-COOH, dry CH₂Cl₂ and CH₃OH, stirring at room temperature under nitrogen for 12-18 h. (ii) BTMPA-Im, o-dichlorobenzene (o-DCB), under titration conditions.
radical ions of the final charge separated state and the rate is therefore determined primarily by the electronic coupling between them and to a lesser extent on their midpoint potentials and the reorganization energy. However, stepwise electron transfer or a hopping mechanism is also possible in which case the recombination depends on the energies of the intermediate states. To optimize the lifetime of the final charge separated state, it is therefore important to be able to distinguish between these possible recombination mechanisms.

Here, we report three novel aluminum(III) porphyrin centered triads that allow this question to be addressed by taking advantage of the properties of aluminum(III) porphyrin. The structures of the three triads (BTMPA-Im→AlPor-Ph-C₆₀, BTMPA-Im→AlPorF₅-Ph-C₆₀ and BTMPA-Im→AlPorF₃-Ph-C₆₀) are shown in Scheme 1. The aluminum(III) porphyrin acts as the primary electron donor/acceptor, fullerene is the primary/secondary electron acceptor, and the imidazole-attached N,N-bis(3,4,5-trimethoxyphenyl)aniline (BTMPA) acts as the primary/secondary electron donor. We have selected fullerene as an electron acceptor due to its small reorganization energy for electron transfer. We will show that stabilization of the initial charge separation by secondary electron transfer occurs, and remarkably, the stabilization, as measured by the overall lifetime of the charge separation, is more pronounced in those triads in which aluminum(III) porphyrin is substituted with electron withdrawing PhF₃ and PhF₅ groups which make it a better electron acceptor.

### EXPERIMENTAL SECTION

**Synthesis.** All chemicals, solvents, and chromatographic materials were obtained from Aldrich Chemicals, Fisher Chemicals, or Alfa Aesar and were used as received. The synthesis details of the precursor porphyrins 5,10,15,20-tetraphenylporphyratoaluminum(III) hydroxide (AlPor-OH), 35,65 5,10,15,20-tetrakis(3,4,5-trifluorophenyl)porphyratoaluminum(III) hydroxide (AlPorF₅-OH), 36,77 and their corresponding reference compounds AlPor-Ph₃5,65 and AlPorF₃-Ph₆4,79 are reported elsewhere. The precursor 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (H₂PorF₅), and its aluminum(III) derivative (AlPorF₅-OH) were synthesized using modified literature procedures; for details, see the Supporting Information and Scheme S1. The preparation of the dyad AlPor-Ph-C₆₀ and the reference fullerene (C₆₀-Ph-COOMe) has been reported previously. 65 The electron donor 4-(1H-imidazol-1-yl)-N,N-bis(3,4,5-trimethoxyphenyl)aniline (BTMPA-Im, Scheme S2), the dyads (AlPorF₅-Ph-C₆₀ and AlPorF₃-Ph-C₆₀, Scheme 2), and one of the reference compounds (AlPorF₅-Ph Scheme S1) were prepared as described in the Supporting Information. The self-assembled dyads (BTMPA-Im→AlPorF₅-Ph, n = 0, 3, 5) and triads (BTMPA-Im→AlPorF₅-Ph-C₆₀, n = 0, 3, 5) were constructed by coordinating the BTMPA-Im with AlPorF₅-Ph and AlPorF₃-Ph-C₆₀ respectively; see Schemes 1 and 2. Because these self-assembled dyads and triads are...
formed in a solution equilibrium, they cannot be isolated easily for elemental and mass analysis.

RESULTS AND DISCUSSION

Synthesis. The newly designed secondary electron donor BTMPA-Im, consisting of the electron donor BTMPA bound to the Lewis base imidazole, was synthesized according to Scheme S2. The synthesis and self-assembly of dyads and triads are shown in Schemes 1 and 2. In the dyads AlPorFn-Ph-C\textsubscript{60}, fullerene is bound covalently to the porphyrin by condensation of AlPorFn\textsubscript{−}OH (n = 0, 3, 5) with C\textsubscript{60}-Ph\textsubscript{−}COOH\textsubscript{65} in quantitative yield (see Scheme 1). The Al center in the dyad, AlPorFn-Ph-C\textsubscript{60}, acts as Lewis acid; therefore, Lewis bases such as imidazole appended as BTMPA-Im can be bound via coordination bonding through the free imidazole nitrogen to construct the supramolecular triads BTMPA-Im \rightarrow AlPorFn-Ph-C\textsubscript{60}. A similar strategy was employed to construct the dyads BTMPA-Im \rightarrow AlPorF\textsubscript{n}-Ph starting from the reference compound AlPorF\textsubscript{n}-Ph (see Figure 2).

Preliminary characterization of the covalently bound dyads and reference porphyrins was carried out by ESI High Resolution mass spectrometry. The mass spectra of the dyads and reference porphyrin showed peaks, which corresponds to the mass (m/z) of either [M + H]\textsuperscript{+} or [M – (PhCOO/C\textsubscript{60}-PhCOO)\textsubscript{+}CH\textsubscript{3}CN]\textsuperscript{+}; for details, see the Experimental Section in the Supporting Information as well as Figures S1–S3. The EI mass spectra of BTMPA-Im is shown in Figure S4, and the spectra revealed a [M]\textsuperscript{+} peak at m/z = 491.27 (calculated 491.2056). The melting point studies indicate that all the dyads, AlPorFn-Ph-C\textsubscript{60}, and the reference compounds, AlPorF\textsubscript{n}-Ph and AlPorF\textsubscript{n}-Ph, are stable up to 300 °C. The reference compound, AlPor-Ph, and the secondary electron donor, BTMPA-Im, have melting points of 293.5 – 294.1 °C and 166.6 – 168.5 °C, respectively. The IR spectra of AlPor\textsubscript{−}OH, C\textsubscript{60}-Ph\textsubscript{−}COOH, AlPor-Ph, and AlPor-Ph-C\textsubscript{60} are shown in Figure S5. The AlPor-Ph-C\textsubscript{60} spectrum reveals the peaks from both AlPor and C\textsubscript{60} units. The absence of the carboxylic acid C=O stretching peak at 1695 cm\textsuperscript{−1} and presence of a characteristic C\textsubscript{60} vibrational mode at 527 cm\textsuperscript{−1} confirms formation of the dyad AlPor-Ph-C\textsubscript{60}, i.e., C\textsubscript{60} is connected to AlPor through a carboxylate linker. Similar results were observed from the other two dyads, AlPorF\textsubscript{3}-Ph-C\textsubscript{60} (Figure S6) and AlPorF\textsubscript{5}-Ph-C\textsubscript{60} (Figure S7). The 1H NMR spectra of BTMPA-Im, AlPorF\textsubscript{3}-Ph-C\textsubscript{60} and AlPorF\textsubscript{5}-Ph-C\textsubscript{60} are shown in Figures S8 – S10, respectively. The data obtained from the spectra are summarized in the Experimental Section of the Supporting Information. The upfield shift of the bridging phenyl protons a and b, from 8.07 and 7.87 ppm in free C\textsubscript{60}-Ph–COOH\textsubscript{65} to ~5.12 and ~6.80 ppm, respectively, in the dyads is due to the shielding effect of the porphyrin ring.

Figure 1. (a) Absorption spectra of AlPorF\textsubscript{3}-Ph (red) and AlPorF\textsubscript{3}-Ph-C\textsubscript{60} (green), C\textsubscript{60}-Ph-COOMe (blue) in CH\textsubscript{3}Cl\textsubscript{2}. Absorption titrations of (b) AlPor-Ph-C\textsubscript{60} vs BTMPA-Im: BTMPA-Im was added up to 1.83 \times 10\textsuperscript{−4} M in 10 μL (1.33 \times 10\textsuperscript{−3} M) increments to 1 mL (4 \times 10\textsuperscript{−6} M) solution of AlPor-Ph-C\textsubscript{60}; (c) AlPorF\textsubscript{3}-Ph-C\textsubscript{60} vs BTMPA-Im: BTMPA-Im was added up to 2.47 \times 10\textsuperscript{−5} M in 10 μL (1.37 \times 10\textsuperscript{−4} M) increments to 1 mL (4 \times 10\textsuperscript{−6} M) solution of AlPorF\textsubscript{3}-Ph-C\textsubscript{60}; (d) AlPorF\textsubscript{5}-Ph-C\textsubscript{60} vs BTMPA-Im: BTMPA-Im was added up to 7.69 \times 10\textsuperscript{−6} M in 5 μL (1.36 \times 10\textsuperscript{−4} M) increments to 1 mL (4 \times 10\textsuperscript{−6} M) solution of AlPorF\textsubscript{5}-Ph-C\textsubscript{60}. All the titrations were performed in o-DCB. The inset shows the Benesi–Hildebrand plot.
current at the center of the ring and confirms axial-bonding via the carboxylate spacer. The protons from pyrrolidine ring appear at δ (4.97 ppm), d, ε (4.98, 4.25 ppm), and f (2.77 ppm) in free C60-Ph–COOH.65 In the dyad compounds, AlPorF3-Ph-C60 and AlPorF5-Ph–C60, these peaks were shifted upfield to ~4.77, ~4.48, ~4.00, and ~2.40 ppm, respectively. Figure S11 shows the 1H NMR spectrum of a 1:1 mixture of AlPor-Ph-C60 and BTMPA-Im (bottom) along with the individual spectra of AlPor-Ph-C60 (middle) and BTMPA-Im (top). In the coordination complex, the shielding due to the porphyrin ring also causes an upfield shift of the BTMPA-Im protons on the imidazole unit, bridging phenyl, terminal phenyl, as well as methoxy groups. The magnitude of the shift depends on the distance of the protons from the porphyrin ring, and the imidazole protons display the greatest shift indicating that coordination occurs via the imidazole group. On the benzoate bridging group to the fullerene, the protons, a, closest to the porphyrin ring show an increased upfield shift upon coordination, suggesting that the aluminum(III) center lies out of the porphyrin plane in AlPor-Ph-C60 and is pulled into the plane when BTMPA-Im coordinates. Similar 1H NMR titrations for AlPorF5-Ph-C60 (n = 3, 5) and AlPorF5-Ph (n = 0, 3, 5) with BTMPA-Im give analogous results (data not shown). Thus, the NMR titrations confirm the formation of the triads (BTMPA-Im→AlPorF5-Ph-C60) and the dyads (BTMPA-Im→AlPorF5-Ph) in solution.

UV–Vis Absorption Spectroscopy. The UV–vis spectra of AlPorF5-Ph-C60 and its reference compounds (AlPorF5-Ph and C60-Ph-COOME) were measured in dichloromethane (CH2Cl2), and the spectra are shown in Figure 1a. The band positions (Q-band and B- or Soret band) and their molar extinction coefficients are summarized in Table 1. As shown in Figure 1a, the absorption spectrum of the dyad is essentially a linear combination of its reference compounds and the positions and molar extinction coefficients (ε) of the porphyrin bands are essentially unchanged in the dyad compared to the corresponding monomer porphyrins. Similar spectral features were also observed from the dyads AlPorF5-Ph-C60 (Figure S12a) and AlPorF5-Ph–C60 (Figure S12b). Overall, the absorption studies suggest that any interaction between the porphyrin (AlPorF5) and the linked fullerene (C60) is sufficiently weak that it causes no discernible change in their electronic structure. This can be attributed to their perpendicular orientation which decreases the electronic coupling between their respective π-systems. The imidazole-appended donor, BTMPA-Im, has relatively weak and very broad absorption bands in the ultraviolet region, Figure S12c.

Furthermore, the UV–vis spectra of dyads AlPorF3-Ph-C60 and their reference porphyrins, AlPorF3-Ph, were measured in o-dichlorobenzene (o-DCB), and the spectra are shown in Figure S13. The observed spectral trends and absorption profiles are consistent with CH2Cl2 data, although the C60 band in the dyads was obscured due to the solvent cutoff. The absorption bands of AlPor at 550 and 410 nm have been chosen to excite the AlPor for steady-state fluorescence and transient-absorption studies, respectively.

Axial coordination of ligands to AlPors causes a significant shift of its absorption bands. These shifts can be rationalized as arising from a change in the planarity of the porphyrin ring as the Al center, which lies above the plane of the four pyrrole nitrogen atoms in the dyad, is drawn toward the coordinating ligand. These spectral changes allow the formation of self-assembled dyads and triads (Schemes 1 and 2) to be monitored by absorption titrations, from which the binding constants can be obtained as summarized in Table S1. Figure 1b shows absorption titrations of AlPorF3-Ph-C60 with BTMPA-Im in o-DCB. Upon addition of BTMPA-Im, the Soret and Q bands of the porphyrin 416, 546, and 588 nm are shifted to 422, 561, and 600 nm, which is typical of coordination of nitrogen ligands to AlPor.66,71 Isosbestic points are observed at 426 and 555 nm, indicating the formation of the triad BTMPA-Im→AlPorF3-Ph-C60 Benesi–Hildebrand analysis (Figure 1b, inset) gives a linear plot indicating that a 1:1 complex is formed, and the slope yields a binding constant $K = 1.7 \times 10^4$ M$^{-1}$. Similar spectral changes were observed in titrations of AlPorF5-Ph-C60 vs BTMPA-Im (Figure 1c) and AlPorF5-Ph–C60 vs BTMPA-Im (Figure 1d) confirming the formation of the triads BTMPA-Im→AlPorF5-Ph-C60 and BTMPA-Im→AlPorF5-Ph–C60 respectively. The binding constants differ for the triads and follow the order: $K (\text{AlPorF5-Ph–C60 vs BTMPA-Im}) < K (\text{AlPorF5-Ph-C60 vs BTMPA-Im}) < K (\text{AlPorF3-Ph-C60 vs BTMPA-Im})$. The trend is consistent with the expected increase in the Lewis acidity of the Al center as an increasing number of fluorine atoms are added to the phenyl substituents. Hence, the Al center is the strongest Lewis acid when the porphyrin is substituted with PhF and weakest with Ph. Therefore, it binds the Lewis base most strongly in the PhF substituted porphyrin and most weakly with Ph substituents.

Additional titrations were carried out to establish the formation of the dyads BTMPA-Im→AlPorF5-Ph (n = 0, 3, 5); AlPor-Ph vs BTMPA-Im (Figure S14a), AlPorF3-Ph vs BTMPA-Im (Figure S14b), and AlPorF5-Ph vs BTMPA-Im (Figure S14c). The observed spectral changes were similar to

Table 1. Optical and Redox Data of Investigated Compounds

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidation Potential [V vs Fe]</th>
<th>Reduction Potential [V vs Fe]</th>
<th>Absorption $\lambda_{max}$ [nm] (log (ε [M$^{-1}$ cm$^{-1}$]))</th>
<th>Fluorescence $\lambda_{max}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60-Ph-COOME</td>
<td>−0.33, −0.73, −1.28</td>
<td></td>
<td>256 (5.06), 309 (4.55)</td>
<td></td>
</tr>
<tr>
<td>AlPor-Ph</td>
<td>+1.22</td>
<td>−0.86, −1.23</td>
<td>547 (4.23), 416 (5.65)</td>
<td>596, 648</td>
</tr>
<tr>
<td>AlPor-Ph-C60</td>
<td>+1.19</td>
<td>−0.32, −0.70, −0.88, −1.25</td>
<td>548 (4.43), 416 (5.76), 255 (5.12)</td>
<td>595, 646</td>
</tr>
<tr>
<td>AlPorF3-Ph</td>
<td>+1.39, 1.69</td>
<td>−0.71, −1.09</td>
<td>546 (4.20), 413 (5.56)</td>
<td>594, 646</td>
</tr>
<tr>
<td>AlPorF5-Ph</td>
<td>+1.41, 1.75</td>
<td>−0.36, −0.73, −1.09, −1.31</td>
<td>546 (4.30), 414 (5.60), 256 (4.84)</td>
<td>593, 646</td>
</tr>
<tr>
<td>AlPorF5-Ph-C60</td>
<td>+1.72</td>
<td>−0.49, −0.89</td>
<td>551 (4.30), 418 (5.59)</td>
<td>592, 646</td>
</tr>
<tr>
<td>AlPorF5-Ph-C60</td>
<td>+1.70</td>
<td>−0.34, −0.43, −0.75, −0.95, −1.31</td>
<td>551 (4.36), 418 (5.59), 256 (5.05)</td>
<td>594, 650</td>
</tr>
<tr>
<td>BTMPA-Im</td>
<td>+1.18</td>
<td>−0.20, −0.38</td>
<td>308 (4.95)</td>
<td></td>
</tr>
</tbody>
</table>

*Redox potentials were reported against ferrocene, where $E_{1/2}(\text{Fc/Fc}^+) = 0.84$ V with 0.1 M TBAP in o-DCB in our experimental conditions. 

In CH2Cl2 *In o-DCB.*
those of the corresponding triads; thus, they establish the formation of dyads BTMPA-Im→AlPorF₃-Ph. Furthermore, titrations of AlPorF₃-Ph-C₆₀ (n = 0, 3, 5) with Me-Im (Figure S15) and AlPorFn-Ph (n = 0, 3, 5) with Me-Im (Figure S16) were performed in o-DCB, (Me-Im = 1-methylimidazole). The spectral trends are consistent with their corresponding dyads and triads and were employed as controls in analyzing the excited state properties of the investigated systems. Together with the NMR and absorption titrations, formation of the triads BTMPA-Im→AlPorFn-Ph-C₆₀ (n = 0, 3, 5) and dyads BTMPA-Im→AlPorFn-Ph (n = 0, 3, 5) are established in solution.

**Computation.** The electronic structure of the dyads and triads were studied using Density Functional Theory (DFT). All the complexes (dyads and triads) were optimized at the B3LYP/def2-SVP level of theory using an ultra fine grid in the Gaussian 16 software. The optimizations were performed in a CPCM dielectric continuum solvent model of dichlorobenzene as implemented in Gaussian 16. Figures 2 and S17−S19 show optimized geometries and frontier orbitals of the triads and dyads (plotted with isovalue 0.04). The DFT calculations revealed that the location of the frontier orbitals is sensitive to the meso-substitutions of the porphyrin.

**BTMPA-Im→AlPorF₃-Ph-C₆₀.** As shown in Figure 2, the HOMO, LUMO, and HOMO-1 are localized on the BTMPA-Im, C₆₀, and AlPorF₃, respectively. Unlike the previous triad (BTMPA-Im→AlPor-Ph-C₆₀), the frontier orbitals in this triad are exclusively localized on their respective moieties, and therefore direct electronic interaction can be ruled out between redox centers. Moreover, the angle between N(C₆₀)-N(Im)-N(BTMPA) is found to be 132.9°. The decrease in the angle represents the bent geometry between BTMPA and AlPorF₃ units. The calculated radius for AlPorF₃ was found to be 9.06 Å. The center-to-center distance between BTMPA and C₆₀, BTMPA and AlPorF₃, and between AlPorF₃ and C₆₀ were estimated to be 21.6, 9.5, and 12.3 Å, respectively. In the dyad BTMPA-Im→AlPorF₃-Ph (Figure S19), the HOMO and LUMO are restricted to the BTMPA and AlPorF₃ units, whereas in the dyad AlPorF₃-Ph-C₆₀ (Figure S17), the HOMO-1 and LUMO are on the AlPorF₃ and C₆₀ units, respectively.

**BTMPA-Im→AlPorF₅-Ph-C₆₀.** The HOMO and LUMO are localized on BTMPA-Im and C₆₀, respectively, see Figure 2. The electron withdrawing effect of the pentafluorinated phenyl substituents on the porphyrin lowers the energy of the highest occupied π-orbital of the porphyrin so that it lies below the HOMO-1. Again, the frontier orbitals in this system are also exclusively localized on their respective moieties, and therefore no electronic interaction can be anticipated between redox centers. Moreover, the angle between N(C₆₀)-N(Im)-N(BTMPA) found to be 132.9° which is same as for the BTMPA-Im→AlPorF₃-Ph-C₆₀. The HOMO and LUMO in one of the reference dyads, BTMPA-Im→AlPorF₅-Ph (Figure S19), are confined to the BTMPA and AlPorF₅, respectively. In the second reference dyad, AlPorF₅-Ph-C₆₀ (Figure S17 and S18), the HOMO-5 and LUMO are on the AlPorF₅ and C₆₀ units, respectively. The calculated radius for AlPorF₅ and the center-to-center distance between BTMPA and C₆₀, BTMPA, and AlPor and between AlPor and C₆₀ were measured to be 21.4, 9.6, and 12.4 Å, respectively. The angle between N(C₆₀)-N(Im)-N(BTMPA) was estimated to be 157.1°.

**Figure 2.** Frontier orbitals of BTMPA-Im→AlPor-Ph-C₆₀ (Triad 1), BTMPA-Im→AlPorF₃-Ph-C₆₀ (Triad 2), and BTMPA-Im→AlPorF₅-Ph-C₆₀ (Triad 3).

<table>
<thead>
<tr>
<th>TRIAD 1</th>
<th>TRIAD 2</th>
<th>TRIAD 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO - 1</td>
<td>HOMO</td>
<td>LUMO</td>
</tr>
</tbody>
</table>

F
center-to-center distance between BTMPA and C₆₀, BTMPA and AlPorF₃, and between AlPorF₃ and C₆₀ were found to be 9.07, 21.6, 9.4, and 12.3 Å, respectively.

**Energetics of Dyads and Triads.** Cyclic voltammetry measurements of the newly synthesized compounds were performed in o-DCB with 0.1 M tetrabutylammonium perchlorate (TBA.ClO₄) as supporting electrolyte and ferrocene as an internal standard. The cyclic voltammogram of AlPor-Ph-C₆₀ and its reference compounds AlPor-Ph and fullerene derivative (C₆₀-Ph-COOOMe) are reported elsewhere. Representative voltammograms are shown in Figure 3, and the oxidation and reduction midpoint potentials are summarized in Table 1. The redox processes of all of the compounds are found to be one-electron reversible based on the peak-to-peak separation values and the cathodic-to-anodic peak current ratio. During the cathodic scan, all three dyads (AlPor-Ph-C₆₀, AlPorF₃-Ph-C₆₀, and AlPorF₅-Ph-C₆₀) showed four reduction processes. The observed voltammograms are assigned to the combination of porphyrin and C₆₀ reduction processes. For the dyad AlPor-Ph-C₆₀, the first two processes are assigned to the reduction of C₆₀ and the third process is assigned to the first reduction of the porphyrin. The fourth process is a combination of the third reduction of C₆₀ and the second reduction of the porphyrin. In the case of AlPorF₃-Ph-C₆₀, the first, third, and fourth processes are assigned to the first reduction of C₆₀, second reduction of porphyrin, and third reduction of C₆₀, respectively. Whereas, the second process is assigned to the combination of porphyrin first reduction and C₆₀ second reduction. For AlPorF₅-Ph-C₆₀, the first reduction of porphyrin partially overlaps with the first reduction of C₆₀. The remaining distinct second, third, and fourth processes are assigned to the second reduction of C₆₀, second reduction of porphyrin, and third reduction of C₆₀, respectively. A comparison of the porphyrin reduction potentials in the dyads AlPorFₙ-Ph-C₆₀ and their reference compounds AlPorFₙ-Ph shows that with increasing numbers of fluorine substituents on the phenyl groups, the porphyrin reduction potentials undergo a positive shift as a result of the increasing electron withdrawing ability of the phenyl groups.

The anodic scan of the dyads reveals one or two oxidation processes, which are assigned to the first and second oxidation of porphyrin unit. Again, the potentials follow the same trend as the reduction potentials with a shift to more positive values as the electron withdrawing ability of the porphyrin substituents increases. Comparison of dyads and their reference compounds show that the redox processes in dyads are not strongly perturbed by the addition of the fullerene. The secondary electron donor BTMPA-Im shows a one-electron process in the anodic scan corresponding to its first oxidation. Additionally, the redox potentials of the triads (physical mixtures of the dyads and BTMPA-Im) were measured to evaluate possible effects of the electron donor on the potentials of the porphyrin. The observed voltammogram (not shown) for each triad was found to be just the sum of its corresponding dyad and BTMPA-Im, which indicates that the porphyrin potentials are not perturbed by coordination of the electron donor.

The redox potentials can be used in combination with optical data to construct the energy level diagram of the states involved in possible electron-transfer processes. Figure 4 summarizes the energy levels of the investigated compounds. The energies of the lowest excited singlet states (Eₛₐₚ) of AlPor (2.14 eV), AlPorF₃ (2.14 eV), and C₆₀ (1.75 eV) and the lowest excited triplet states of AlPor (1.61 eV) and C₆₀ (1.55 eV) have been taken from the literature. The singlet and triplet state energies of AlPorF₃ and AlPorF₅ have been calculated from their absorption and emission spectra; see Figure S20. The estimated energies are 2.14, 1.65, and 1.53 eV for ³AlPorF₃*, ³AlPorF₅*, and ³AlPorF₅*, respectively. The energy of the charge-separated states Eₜₚ (relative to the ground state) and the free-energy changes for charge separation (ΔGₜₚ) are estimated using the following equations.

**Figure 3.** Cyclic voltammograms of (a) C₆₀-Ph-COOOMe, (b) BTMPA-Im, (c) AlPorF₃-Ph, (d) AlPorF₃-Ph-C₆₀, (e) AlPorF₅-Ph, and (f) AlPorF₅-Ph-C₆₀ with 0.1 M TBA.ClO₄ in o-DCB. Voltammograms were measured with ferrocene (0.84 V vs Ag wire) as an internal standard. Scan rate 100 mV/s.

**Figure 4.** Energy level diagram of investigated triads BTMPA-Im→AlPorFₙ-Ph-C₆₀ in toluene.
1 and 2 (also see footnotes of Table 2) and are summarized in Table 2.

\[ E_{CS} = E_{i/2}^\text{re}(D) - E_{i/2}^\text{re}(A) + G_S \]  

(1)

Here, \( G_S \) is the ion-pair stabilization and incorporates both the solvent-dependent Coulomb energy change upon ion-pair formation or recombination and the free energy of solvation of the ions, equation 2

\[ G_S = \frac{e^2}{(4\pi\varepsilon_0)}[(1/(2R_\text{a}) + 1/(2R_\text{c}) - 1/R_{D-A})1/\varepsilon_0] \]

\[ - (1/(2R_\text{a}) + 1/(2R_\text{c}))1/\varepsilon_R] \]

(2)

where \( R_a \), \( R_c \), and \( R_{D-A} \) are donor radius, acceptor radius, and the center-to-center distance between donor and acceptor, respectively. \( \varepsilon_0 \) is the dielectric constant of the solvent used for the photophysical studies (9.93 and 2.4 for o-DCB and toluene, respectively). \( \varepsilon_R \) is the dielectric constant of the solvent used for measuring the redox potentials, in this case o-DCB. Using the radii from the DFT calculations, \( G_S \) values of

---

**Table 2. Experimentally Calculated Free Energy Change (\( \Delta G \)) Values of Charge Separation (CS) and Charge Recombination (CR) Processes of the Investigated Dyads and Triads in Toluene**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{CS1} )</th>
<th>( E_{CS2} )</th>
<th>( E_{CS3} )</th>
<th>( \Delta G_{CS1} )</th>
<th>( \Delta G_{CS2} )</th>
<th>( \Delta G_{CR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPor-Ph-C60</td>
<td>1.51</td>
<td>2.10</td>
<td>1.50</td>
<td>-0.63</td>
<td>-0.04</td>
<td>-2.10</td>
</tr>
<tr>
<td>BTMPA-Im→AlPor-Ph</td>
<td>1.51</td>
<td>2.10</td>
<td>1.50</td>
<td>-0.63</td>
<td>-0.04</td>
<td>-1.50</td>
</tr>
<tr>
<td>AlPorF2-Ph-C60</td>
<td>1.77</td>
<td>1.93</td>
<td>1.52</td>
<td>-0.37</td>
<td>-0.21</td>
<td>-1.93</td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF2-Ph</td>
<td>1.77</td>
<td>1.93</td>
<td>1.52</td>
<td>-0.37</td>
<td>-0.21</td>
<td>-1.52</td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF3-Ph</td>
<td>2.04</td>
<td>1.63</td>
<td>1.52</td>
<td>-0.10</td>
<td>-0.51</td>
<td>-1.63</td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF5-Ph</td>
<td>2.04</td>
<td>1.63</td>
<td>1.52</td>
<td>-0.10</td>
<td>-0.51</td>
<td>-1.63</td>
</tr>
</tbody>
</table>

\( a \) CS1: AlPorF_n-C60; CS2: BTMPA*-AlPorF_n; CS3: BTMPA*-AlPorF_n-C60; \( \Delta G_{CS} = E_{CS} - E_{0-0} \); \( E_{0-0} = 2.14 \) eV; \( \Delta G_{CR} = -E_{CS} \)

---

**Figure 5.** Fluorescence spectra of (a) AlPor-Ph (red) and AlPor-Ph-C60 (green), (b) AlPorF3-Ph (red) and AlPorF3-Ph-C60 (green), (c) AlPorF5-Ph (red) and AlPorF5-Ph-C60 (green), (d) AlPor-Ph vs BTMPA-Im: BTMPA-Im was added up to 1.52 \( \times 10^{-4} \) M in 10 \( \mu \)L (6.60 \( \times 10^{-4} \) M) increments to a 1 mL (4 \( \times 10^{-6} \) M) solution of AlPor-Ph, (e) AlPorF3-Ph vs BTMPA-Im: BTMPA-Im was added up to 3.0 \( \times 10^{-5} \) M in 10 \( \mu \)L (1.37 \( \times 10^{-4} \) M) increments to a 1 mL (4 \( \times 10^{-6} \) M) solution of AlPorF3-Ph, and (f) AlPorF5-Ph vs BTMPA-Im: BTMPA-Im was added up to 5.54 \( \times 10^{-6} \) M in 10 \( \mu \)L (6.7 \( \times 10^{-5} \) M) increments to a 1 mL (4 \( \times 10^{-6} \) M) solution of AlPorF5-Ph. All the titrations were performed in o-DCB.
−0.15 and 0.02−0.06 eV are obtained for BTMPA**−AlPorFn−C60 in o-DCB and toluene, respectively. For the radical ion-pairs AlPorF5**−Ph-C60**− in the dyads and BTMPA**−Im→AlPorFn−Ph-C60**− in the triads, the calculated Coulomb stabilization due to the attraction between the cation and anion of the radical pair is small because of the relatively large RDA, values. However, the calculated destabilization in toluene compared to o-DCB is unreasonably large, because of the small radius estimated for C60**−. Hence for AlPorF5**−Ph-C60**− and BTMPA**−Im→AlPorFn−Ph-C60**− we have not included the Gs term in their energies. Using the energies obtained from the optical and electrochemical data, the energy-level diagram was constructed for the dyads and triads in toluene (Figure 4) and o-DCB (Figure S21). The calculated free-energy level diagrams suggest the following electron transfer processes are energetically favorable in these triads upon excitation of AlPorFn: (i) oxidative electron transfer from the excited singlet state of AlPor (1AlPorFn) to fullerene followed by a hole shift to BTMPA or (ii) reductive electron transfer from BTMPA to 1AlPorF3* followed by a charge shift to C60. However, the rates of these processes are determined by the electronic coupling and activation energy, which depends on the reorganization energy as well as the free energy change.

**Steady-State Fluorescence Studies.** The steady-state fluorescence spectra of the dyads and triads were measured in o-DCB (Figure 5) and toluene (Figure S22). Interestingly, very similar results were observed in both solvents. This is unusual because fluorescence quenching by electron transfer is typically less efficient in nonpolar solvents such as toluene. The experiments were carried out at same concentration of porphyrin in all samples. The spectra were measured with an excitation wavelength of 555 nm, which excites the Q-band transition of the porphyrin.

*AlPorF5−Ph-C60.* Figure 5 shows the fluorescence spectra of the dyads AlPor−Ph-C60, AlPorF3−Ph-C60, and AlPorF5−Ph-C60 and their reference compounds AlPor−Ph, AlPorF3−Ph, and AlPorF5−Ph, respectively, in o-DCB, and the emission maxima are summarized in Table 1. All of the compounds exhibit two bands due to porphyrin emission. The band positions in the dyad and its reference porphyrin are very similar indicating that the electronic structure of the porphyrin is not perturbed by axial-linkage of C60 unit. However, the fluorescence of the porphyrin is quenched, 80%, 66%, and 50%, in AlPor−Ph-C60, AlPorF3−Ph-C60, and AlPorF5−Ph-C60, respectively. On the basis of the energy level diagram, the AlPor**−**−Ph-C60**, AlPorF3**−**−Ph-C60**, and AlPorF5**−**−Ph-C60**− charge separated states lie energetically below the excited singlet state of porphyrin (1AlPorF5*); therefore, the observed quenching is assigned to oxidative electron transfer from 1AlPorF5* to C60. The calculated ΔGCS for this electron transfer was found to be −0.64, −0.27, and −0.10 eV for AlPor−Ph-C60, AlPorF3−Ph-C60, and AlPorF5−Ph-C60, respectively (see Table 2). The fact that the quenching follows the same trend as the driving force for the electron transfer suggests that electron transfer lies in the normal region of the Marcus curve as would be expected.

*BTMPA−Im→AlPorFn−Ph.* In order to establish the formation of the dyads (Scheme 2) and evaluate possible photoinduced processes between BTMPA−Im and AlPorFn, steady-state fluorescence titrations were performed between BTMPA−Im and AlPorF5−Ph in o-DCB. The excitation wavelength in each of these titrations was adjusted to the isobestic point, which was obtained from the corresponding absorption titrations, so that the extinction coefficient is the same for each sample solution. As shown in Figure 5d, upon addition of BTMPA−Im to AlPor−Ph, the AlPor fluorescence peaks shift to longer wavelengths from 594 and 646 nm to 613 and 665 nm, respectively, along with a change in their relative intensities. The observed spectral changes support the formation of the dyad BTMPA−Im→AlPor−Ph in solution. To investigate the possible reductive electron transfer between the BTMPA and AlPor, a control titration of AlPorF3−Ph vs Me−Im (without BTMPA, Figure S23a) was performed. Spectral changes similar to those found in the titration of AlPor−Ph vs BTMPA−Im are observed suggesting that they are a result of the binding of the imidazole moiety and not due to the presence of BTMPA as an electron donor. Therefore, the rate of the anticipated reductive electron transfer from BTMPA to 1AlPor* is negligible compared to the fluorescence rate. This is consistent with the small free energy change of −0.01 eV calculated for this process (ΔGCS in Table 2) since in this case, the activation energy for the electron transfer is determined mostly by the reorganization energy and is expected to be fairly large.

In the case of AlPorF3−Ph vs BTMPA−Im (Figure 5e) titrations, the fluorescence bands are red-shifted which again confirms the formation of the dyad BTMPA−Im→AlPorF3−Ph. However, the fluorescence intensity decreases upon addition of BTMPA−Im. The corresponding control titrations AlPorF3−Ph vs Me−Im (Figure S23b) revealed band shifts to longer wavelengths but without a change in fluorescence intensity suggesting that the fluorescence quenching during the titrations of AlPorF3−Ph vs BTMPA−Im is indeed due to the presence of BTMPA and reductive electron transfer from BTMPA to 1AlPorF3*. This is also consistent with the much larger value of −0.22 eV for the ΔGCS. Figure 5f shows the titrations of AlPorF3−Ph vs BTMPA−Im, which establish the formation of BTMPA−Im→AlPorF3−Ph. A significant fluorescence quenching is exhibited without a spectral shift in the presence of BTMPA−Im. In contrast, the control titrations AlPorF5−Ph vs Me−Im (Figure S23c) show a shift of the bands but no quenching. This implies that essentially complete quenching occurs when BTMPA−Im binds and the fluorescence observed in the titration with BTMPA−Im arises only from the fraction of unbound porphyrin molecules. The observed substantial quenching is assigned to the reductive electron transfer from BTMPA to 1AlPorF3* and again is consistent with the larger free energy change of −0.44 eV and hence lower activation energy for this process. Overall, the observed fluorescence quenching pattern in the dyads is consistent with the expected behavior based on the Gibbs free energy values and electron transfer in the normal region of the Marcus curve.

*BTMPA−Im→AlPorFn−Ph−C60.* Figure S24 shows the fluorescence titrations of AlPorF3−Ph−C60 vs BTMPA−Im in o-DCB. The spectral trends are very similar to their corresponding AlPorF5−Ph vs BTMPA−Im titrations and confirm the formation of the triad BTMPA−Im→AlPorF3−Ph−C60 in solution. The excitation of AlPorF3−Ph in the triad results in an initial charge separation either as the oxidative electron transfer from 1AlPorF3* to C60 or the reductive electron transfer from BTMPA to 1AlPorF3*. Qualitatively, the observed spectral trends during the titrations show that degree of fluorination of the porphyrin substituents influences which of the two possible electron transfer reactions occurs. Upon addition of BTMPA−Im to AlPor−Ph−C60 (Figure S24a) the AlPor fluorescence bands shift to longer wavelengths 613 and 665 nm without any additional quenching. By comparing these...
trends with control titrations, AlPor-Ph vs BTMPA-Im (Figure 5d) and AlPor-Ph-C60 vs Me-Im (Figure S23d), it is reasonable to predict that oxidative electron transfer from \(^{1}\text{AlPor}^*\) to C\(_{60}\) is the initial process in the triad BTMPA-Im→AlPor-Ph-C\(_{60}\). In contrast, in the titrations of AlPor\(_{3}\)-Ph-C\(_{60}\) with BTMPA-Im (Figure S24b) the fluorescence bands are shifted to 609 and 657 nm with a moderate decrease in their intensities. In this case, comparison with control titrations of AlPor\(_{3}\)-Ph vs BTMPA-Im (Figure 5e) and AlPor\(_{3}\)-Ph-C\(_{60}\) vs Me-Im (Figure S23e) as well as the energy level diagram (Figure 4) suggest that the observed decrease in fluorescence intensity is due to reductive electron transfer from BTMPA to \(^{1}\text{AlPor}^*\). This implies that the rate of reductive electron transfer rate is comparable to or faster than that of the oxidative electron transfer rate from \(^{1}\text{AlPor}^*\) to C\(_{60}\). Lastly, Figure S24c shows the fluorescence spectra of the AlPor\(_{3}\)-Ph-C\(_{60}\) with increasing amounts of BTMPA-Im. In this case, addition of BTMPA-Im leads to strong quenching without any significant shift of the emission bands. Consistent with the control experiments, AlPor\(_{3}\)-Ph vs BTMPA-Im (Figure 5f) and AlPor\(_{5}\)-Ph-C\(_{60}\) vs Me-Im (Figure S23f), as well as the energy diagram (Figure 4), the observed strong quenching in BTMPA-Im→AlPor\(_{3}\)-Ph-C\(_{60}\) implies that reductive electron transfer from BTMPA to \(^{1}\text{AlPor}^*\) is the fastest process in this triad.

**Spectroelectrochemistry.** To help interpret the transient spectral data of the products formed during the process of charge injection, spectroelectrochemical studies were performed on AlPor\(_{3}\)-Ph and AlPor\(_{5}\)-Ph, and BTMPA-Im in o-DCB containing 0.2 M TBA.ClO\(_{4}\). As shown in Figure S25, the oxidation of BTMPA-Im results in a decrease in absorbance at 308 nm which is accompanied by the appearance of a new peak with a maximum around 333 nm. An isobestic point at 340 nm is also observed. The oxidation of AlPor\(_{3}\) revealed the appearance of new bands at 595 and 690 nm, whereas the reduction produced bands at 568 and 608 nm, Figure S26. In the case of AlPor\(_{5}\), the oxidation resulted in new peaks at 644 and 686 nm and reduction developed peaks at 450 and 627 nm, Figure S27. The spectroelectrochemical data of the AlPor have been reported previously\(^ {63}\) and show that peaks at 600 and 685 nm are formed when AlPor is oxidized and at 570 and 610 nm when it is reduced.

**Femtosecond Transient Absorption Spectroscopy.** Having proposed the different photochemical charge separation events in the AlPor\(_{3}\)-Ph-C\(_{60}\) dyads and BTMPA-Im→AlPor\(_{3}\)-Ph-C\(_{60}\) triads from the energy levels diagrams shown in Figure 4 and fluorescence titrations shown in Figure 5, femtosecond and nanosecond transient absorption spectral studies were performed to secure direct experimental evidence of charge separation and also to evaluate the lifetimes of the charge separated states. In the present study, we have used toluene rather than o-DCB as the solvent because of its better photochemical stability under laser irradiation.

Figure 6 shows the femtosecond transient spectra at the indicated delay times for AlPor-Ph, AlPor\(_{3}\)-Ph, and AlPor\(_{5}\)-Ph in the absence and presence of axial coordinating BTMPA-Im. The transient spectral features of AlPor-Ph, AlPor\(_{3}\)-Ph, and AlPor\(_{5}\)-Ph have a similar pattern, however, with subtle differences. In the case of AlPor-Ph, the instantaneously formed \(^{1}\text{AlPor}^*\) (see the spectrum at 1 ps in Figure 6a) has positive peaks at 448, 578, 611, and 1240 nm due to transitions originating from the \(^{1}\text{AlPor}^*\) state. Negative peaks at 550, 595, and 651 nm are also observed. By comparison with the absorption and fluorescence spectral data described above, the 550 nm peak is assigned to ground state bleaching and the latter two peaks are assigned to stimulated emission. The lifetime of the decay of positive peaks and recovery of the negative peaks is longer than the 3 ns time window accessible in the experiment, which is consistent with the 7.88 ns fluorescence lifetime of AlPor, determined from time correlated single photon counting measurements. The decay and recovery of the positive and negative peaks are accompanied by new peaks emerging in the 500 and 840 nm region due to the formation of \(^{1}\text{AlPor}^*\) by intersystem crossing. In the case of AlPor\(_{3}\)-Ph, transient positive peaks of \(^{1}\text{AlPor}^*\) are observed at 453, 595, and 1236 nm while the transient negative peak at 550 nm due to ground state bleaching and at 650 nm due to stimulated emission are also observed (Figure 6d). Slow intersystem crossing populating \(^{1}\text{AlPor}^*\) leads to peaks at 490 and 835 nm on a time scale consistent with the fluorescence lifetime of 3.74 ns. Finally, for AlPor\(_{5}\)-Ph, photoexcitation results in positive peaks at 454, 573, 610, and 1230 nm from the excited singlet state accompanied by negative peaks at 546, 589, and 645 nm due to ground state bleaching and stimulated emission (Figure 6g). The \(^{3}\text{AlPor}^*\) state formed by intersystem crossing resulted in the growth of new peaks at 450 and 832 nm on a ns time scale.

Again, this is consistent with the fluorescence lifetimes of 2.32 ns. In summary, AlPor-Ph, AlPor\(_{3}\)-Ph, and AlPor\(_{5}\)-Ph all show similar behavior with instantaneous formation of the excited singlet state, which decays with a lifetime of several nanoseconds to the ground state and excited triplet state.

Figure 6c, f, i shows the femtosecond transient absorbance spectra of dyads BTMPA-Im→AlPor-Ph, BTMPA-Im→AlPor\(_{3}\)-Ph, and BTMPA-Im→AlPor\(_{5}\)-Ph. The central panels (b, e, and h) show the time profiles of the near-IR peak located at 1240 nm due to singlet→singlet absorption of \(^{1}\text{AlPor}^*\) in the presence (red) and absence (blue) of BTMPA. Upon coordination of BTMPA-Im with AlPor-Ph, positive transient peaks originating from BTMPA-Im→\(^{1}\text{AlPor}^*\)-Ph are located at 452, 587, 627, 710, and 1248 nm; negative red-shifted transient peaks at 556 nm, due to ground state bleaching, and at 608 and 660 nm due to stimulated emission are observed. The energy level diagram shown in Figure 4 predicts BTMPA\(^*\)→AlPor\(^*\) only by 0.01 eV lower than \(^{1}\text{AlPor}^*\); thus hole transfer from the porphyrin to the donor is expected to be slow or negligible. Consistent with this, the two kinetic traces overlap in Figure 6b revealing little or no effect of BTMPA, that is, the absence of significant amounts of a hole shift leading to BTMPA\(^*\)→AlPor\(^*\)-Ph. In the cases of BTMPA-Im→\(^{1}\text{AlPor}^*\)-Ph and BTMPA-Im→\(^{3}\text{AlPor}^*\)-Ph, the hole shift leading to BTMPA\(^*\)AlPor\(_{3}\)\(^*\) and BTMPA\(^*\)AlPor\(_{5}\)\(^*\) were found to be exothermic by 0.22 and 0.44 eV, respectively. Under such conditions, new transient peaks corresponding to the charge-separated states is expected. Spectroelectrochemical studies show that BTMPA\(^*\) has a band at 333 nm (Figure S25) while AlPor\(_{5}\)\(^*\) has bands at 568 and 608 nm (Figure S26) and AlPor\(_{3}\)\(^*\) has bands at 450 and 627 nm (Figure S27). The band at 333 nm due to BTMPA\(^*\) is not accessible with the femtosecond setup used. The bands due to the porphyrin radical anion overlap with those of the excited singlet state or have weak intensity making it difficult to positively identify them in the femtosecond data. However, the kinetic time profiles of the 1240 nm near-IR peak provide some evidence for the expected charge separation. As shown in Figure 6e, h, there is an indication of a slight acceleration of the decay of both \(^{1}\text{AlPor}^*\) and \(^{3}\text{AlPor}^*\) in the presence of BTMPA,
which might be due to the hole shift in these two dyads. From the fitted decay lifetimes, the rate constants for hole shift, \( k_{\text{HS}} \), were estimated to be \( 0.80 \times 10^9 \text{ s}^{-1} \) and \( 1.83 \times 10^9 \text{ s}^{-1} \), respectively, for BTMPA-Im→AlPorF_3-Ph and BTMPA-Im→AlPorF_5-Ph.

Next, photoinduced charge separation in the covalently linked AlPor-Ph-C_{60}, AlPorF_3-Ph-C_{60}, and AlPorF_5-Ph-C_{60} and their coordination complexes with BTMPA-Im were performed. In agreement with our earlier studies, the femtosecond data reveal that photoexcitation of AlPor in the dyad AlPor-Ph-C_{60} results in charge separation from \(^1\text{AlPor}^*\) to \( \text{C}_{60}^- \) leading to the formation of \(^1\text{AlPor}^*\cdot\text{C}_{60}^-\), Figure 7a. The absorption peak at \( \sim 450 \text{ nm} \), the near-IR peak at 1240 nm, and the negative peaks due to \(^1\text{AlPor}^*\) emission at 590 and 650 nm decayed more rapidly than in AlPor-Ph (see Figure 6a). Additionally, these processes were accompanied by new signals in the range of 600–650 nm corresponding to \( ^1\text{AlPor}^* \) and near 1000 nm from \( \text{C}_{60}^- \). Since the 1000 nm peak of \( \text{C}_{60}^- \) and 1240 nm peak of \(^1\text{AlPor}^*\) were far from other transient bands they can be used to estimate the rate constant for charge separation, \( k_{\text{CS}} \). The transient spectra of BTMPA-Im→AlPor-Ph-C_{60} at different delay times (Figure 7c) show peaks characteristic of the charge-separated state and provide evidence for the charge separation from \(^1\text{AlPor}^*\) to \( \text{C}_{60}^- \).

However, the decay of the absorbance change due to \( \text{C}_{60}^- \) at 1000 nm (Figure 7b, red trace) is longer than the 3 ns time window of our instrumental setup. Thus, in this case, the rate constant for charge recombination, \( k_{\text{CR}} \), was evaluated from nanosecond transient spectral studies that will be discussed in the next section. If hole transfer from BTMPA to \( \text{AlPor}^* \) occurs, then one would expect the decay of \( \text{C}_{60}^- \) to be slower when BTMPA is bound, that is, the larger separation of the radical cation and radical anion species in BTMPA-Im→AlPorF_3-Ph and BTMPA-Im→AlPorF_5-Ph.

For the triads BTMPA-Im→AlPorF_3-Ph-C_{60} and BTMPA-Im→AlPorF_5-Ph-C_{60}, the energy level diagrams shown in Figure 4 predict that the hole transfer process is exothermic by...
0.37 and 0.54 eV, respectively, which is considerably more favorable than that in BTMPA-Im→AlPor-Ph-C_{60}. Consistent with this, the effect of hole transfer process further stabilizing the final charge separated states is clearly visible in the femtosecond transient absorbance data. Figure 7d,g shows the transient absorption spectra at selected delay time, and in both dyads, evidence for charge separation from the excited singlet state of the porphyrin leading to the formation of AlPorF_{3\cdot}Ph-C_{60}\cdot−\ and AlPorF_{5\cdot}Ph-C_{60}\cdot−\ is seen. The values of $k_{CS}$ were determined by fitting the decay of the 1230 nm peak corresponding to singlet–singlet absorption of $^{1}$AlPorF_{3\cdot} and $^{1}$AlPorF_{5\cdot} and are listed in Table 3. As shown in the middle panels of Figure 7e,h, the decay of the C_{60}\cdot−\ peak (red trace) lasted beyond 3 ns (red trace), similar to that observed for AlPor-Ph-C_{60} dyad. For BTMPA-Im→AlPorF_{3\cdot}Ph-C_{60} and BTMPA-Im→AlPorF_{5\cdot}Ph-C_{60} (Figure 7f,i) similar $k_{CS}$ values are obtained (see Table 3). The comparisons of the time profiles of the C_{60}\cdot−\ peak of the triads (blue traces) dyads (red traces) show that the decay is significantly slower in the triads and is lowest in BTMPA-Im→AlPorF_{5\cdot}Ph-C_{60}. This suggests that the decay of C_{60}\cdot−\ competes with hole transfer from BTMPA and that rate of hole transfer is faster BTMPA-Im→AlPorF_{5\cdot}Ph-C_{60} as expected from the larger driving force and lower activation energy.

### Table 3. Rate Constants for Charge Separation, $k_{CS}$, and Charge Recombination, $k_{CR}$, and Overall Lifetime of the Radical Ion-Pair, $\tau_{RI}$, Evaluated from Femto- and Nanosecond Transient Absorption Spectroscopy for the Investigated Dyads and Triads in Toluene

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{CS} \times 10^{9}$ (s$^{-1}$)</th>
<th>$k_{CR} \times 10^{6}$ (s$^{-1}$)</th>
<th>$\tau_{RI}$ (μs)</th>
<th>ref*</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTMPA-Im→AlPor-Ph</td>
<td></td>
<td></td>
<td></td>
<td>tw</td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF_{3\cdot}Ph</td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF_{5\cdot}Ph</td>
<td>1.83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlPor-Ph-C_{60}</td>
<td>6.45</td>
<td>26.3</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td>AlPorF_{3\cdot}Ph-C_{60}</td>
<td>2.52</td>
<td>1.85</td>
<td>0.54</td>
<td>tw</td>
</tr>
<tr>
<td>AlPorF_{5\cdot}Ph-C_{60}</td>
<td>4.27</td>
<td>1.51</td>
<td>0.66</td>
<td>tw</td>
</tr>
<tr>
<td>BTMPA-Im→AlPor-Ph-C_{60}</td>
<td>2.53</td>
<td>17.9</td>
<td>0.056</td>
<td>tw</td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF_{3\cdot}Ph-C_{60}</td>
<td>1.21</td>
<td>1.35</td>
<td>0.74</td>
<td>tw</td>
</tr>
<tr>
<td>BTMPA-Im→AlPorF_{5\cdot}Ph-C_{60}</td>
<td>3.44</td>
<td>0.81</td>
<td>1.24</td>
<td>tw</td>
</tr>
</tbody>
</table>

*tw = this work.

### Nanosecond Transient Absorption Spectroscopy.

Lastly, to evaluate the lifetime of the final charge-separated...
states, nanosecond transient spectral measurements were performed on all of the newly assembled systems and the data are shown in Figure 8. Although relatively weak, in all of the dyads and triads, the C\textsubscript{60}\textsuperscript{+} peak at \(\sim 1000\) nm could be observed indicating persistence of the radical ion-pair into the nanosecond to microsecond time window. In addition to peaks of C\textsubscript{60}\textsuperscript{+}, transient features in the 460 and 850 nm range corresponding to \(^3\)AlPorF\textsubscript{3}\textsuperscript{+} and in the 700 nm range corresponding to \(^3\)C\textsubscript{60}\textsuperscript{−} were also observed. These results suggest that the singlet excited AlPorF\textsubscript{3} and/or the charge-separated species could competitively populate the triplet excited states to some extent. The lifetime of the absorbance changes at 1000 nm due to C\textsubscript{60}\textsuperscript{+} was used to calculate \(k\textsubscript{CR}\) and lifetime of the radical ion-pairs.

The data listed in Table 3 reveal several features. (i) The rates of hole transfer from \(^1\)AlPorF\textsubscript{n}\textsuperscript{+} to coordinated BTMPA are lower than those of electron transfer from \(^1\)AlPorF\textsubscript{n}\textsuperscript{+} to C\textsubscript{60}. Thus, we surmise that in the triads, electron transfer from the excited singlet state of AlPorF\textsubscript{n} to C\textsubscript{60} occurs first and subsequently, a hole transfer from AlPorF\textsubscript{n}\textsuperscript{+} to BTMPA takes place. (ii) Generally, the rate constant for charge separation \(k\textsubscript{CS}\) correlates with the free-energy difference between the excited singlet state of the porphyrin and the charge-separated state AlPor\textsuperscript{−}\textsuperscript{−}-C\textsubscript{60}\textsuperscript{+}; that is, a higher rate constant is observed for AlPor-Ph-C\textsubscript{60} compared to the dyads with the fluorinated AlPorF\textsubscript{3}-Ph-C\textsubscript{60} and AlPorF\textsubscript{5}-Ph-C\textsubscript{60}. (iii) Coordination of BTMPA causes a slight increase in \(k\textsubscript{CS}\). A possible explanation for this is that coordination of BTMPA-im to AlPorF\textsubscript{n} draws the porphyrin ring slightly closer to the C\textsubscript{60} unit by pulling the Al center into the porphyrin plane as suggested by DFT studies. (iv) Finally, the \(k\textsubscript{CR}\) values decrease (\(k\textsubscript{RIP}\) values increase) with increasing flouorination of porphyrin for both the dyads and triads. This is especially intriguing considering the fact that the final charge separated state in the triads is the same and has the same energy (1.50 eV). These results suggest that the central electron deficient AlPorF\textsubscript{3} or AlPorF\textsubscript{5} plays a key role in slowing down the charge recombination process.

Recombination Mechanism and Lifetimes. The lifetimes of the charge-separated states AlPorF\textsubscript{3}\textsuperscript{+}-C\textsubscript{60}\textsuperscript{−} in the dyads can be rationalized by using the Marcus equation (3) to relate the driving force \((\Delta G\textsubscript{ET})\) to the rate constants \((k\textsubscript{CR})\) of the charge separation or charge recombination. Here, \(\lambda\) is the reorganization energy, \(V\) is the electronic coupling matrix element, \(k_B\) is the Boltzmann constant, \(h\) is the Planck constant, and \(T\) is the absolute temperature.

\[
k_{CR} = \left( \frac{4\pi}{h} \right)^{1/2} \frac{h^2 k_B T}{2 \lambda^2} \exp \left[ \frac{-(\Delta G\textsubscript{ET} + \lambda)^2}{4 \Delta k_B T} \right]
\]

The values of 38, 540, and 660 ns for \(t\textsubscript{CR}\), in the dyads AlPor-Ph-C\textsubscript{60}, AlPorF\textsubscript{3}-Ph-C\textsubscript{60}, and AlPorF\textsubscript{5}-Ph-C\textsubscript{60}, respectively, clearly show that the radical pair is stabilized by substitution of fluorine atoms on the phenyl substituents of the porphyrin ring. This is because the corresponding driving force for recombination, \((\Delta G\textsubscript{ET} = -1.50, -1.87, -2.04\) eV\), places the recombination far into the Marcus inverted region if the reorganization energy, \(\lambda\), is on the order of 0.2 eV as suggested from studies of other porphyrin fullerene dyads. Therefore, the charge recombination becomes slower as the driving force for recombination increases. It is important to compare these results with some related systems in the literature. For example, the charge separation and recombination in “axial-bonding” type high potential zinc(II) porphyrin-C\textsubscript{60} dyads have been studied as a function of driving force. However, the recombination rates did not follow the expected trend and the highly fluorinated zinc(II) porphyrin-C\textsubscript{60} dyads showed faster recombination than the nonfluorinated zinc(II) porphyrin-C\textsubscript{60} dyad. This suggests that either the electronic coupling or the recombination pathway differed in the different systems.

Figure 8. Nanosecond transient absorption spectra at the indicated delay times (\(\lambda\textsubscript{ex} = 410\) nm) of (a) BTMPA-Im→AlPor-Ph-C\textsubscript{60}, (b) AlPorF\textsubscript{3}-Ph-C\textsubscript{60}, (c) BTMPA-Im→AlPorF\textsubscript{3}-Ph-C\textsubscript{60}, (d) AlPorF\textsubscript{3}-Ph-C\textsubscript{60}, and (e) BTMPA-Im→AlPorF\textsubscript{5}-Ph-C\textsubscript{60} in toluene.
dyads. Numerous “horizontal” zinc(II) porphyrin-C₆₀ dyad compounds have also been reported in the literature. In these systems, the charge recombination sometimes occurs to the C₆₀ triplet state depending on the nature of the bridging groups and energy of the charge separated state. For those in which direct recombination to the ground state occurs, the rates are typically slower than those observed here, suggesting that the electronic coupling is larger in the vertical arrangement. Unlike the dyads, all of the investigated triads produce the same radical pair, BTMPA⁺⁺AlPorF₅-C₆₀⁻⁻, with an identical energy of 1.50 eV but with a significant difference in their lifetimes. We note, however, that the value of the energy is based on the midpoint potential of unbound BTMPA and some small variation in the energies of the final radical pairs is expected. Nonetheless, the observed lifetime differences are too large to be reasonably explained using the free energy differences (ΔG) or different reorganization energies (Δ) of the final radical pair. Instead, factors such as the electronic coupling (V) and/or a hopping/superexchange mechanism must be invoked to explain the variation in the backreaction rates. In the case of BTMPA-Im→AlPor-Ph-C₆₀, the final radical pair lifetime was found to be 56 ns and is only slightly longer than the 38 ns observed for the corresponding dyad. The DFT calculations revealed that strong electronic coupling exists between the AlPor and BTMPA units as the HOMO and HOMO-1 are delocalized significantly onto the BTMPA and AlPor, respectively. Moreover, the estimated energies of the AlPor⁺⁺→C₆₀⁻⁻ and BTMPA⁺⁺→AlPor⁻⁻ are identical. Under these conditions, it is likely that if the radical pair BTMPA⁺⁺→AlPor⁻⁻ is formed, its recombination to AlPor⁺⁺→C₆₀⁻⁻ probably has a lifetime that is similar to that of the decay of AlPor⁺⁺→C₆₀⁻⁻ to the ground state. In an incoherent hopping mechanism, this would result in a lifetime for the BTMPA⁺⁺→AlPor⁻⁻→C₆₀⁻⁻ radical pair that is similar to that of AlPor⁺⁺→C₆₀⁻⁻ in the dyad. In contrast, for BTMPA-Im→AlPorF₅-Ph-C₆₀, a hopping mechanism is unlikely because the electronic coupling between AlPorF₅ and BTMPA is weaker and the possible intermediates AlPor⁺⁺→C₆₀⁻⁻ and BTMPA⁺⁺→AlPorF₅⁺⁺ radical pairs are much higher in energy than the final radical pair BTMPA⁺⁺→AlPorF₅-C₆₀⁻⁻. Thus, the lifetime of 740 ns probably represents direct recombination to the ground state and is an order of magnitude longer than that of BTMPA⁺⁺→AlPor⁻⁻→C₆₀⁻⁻. Similarly, in the triad BTMPA-Im→AlPorF₅-Ph-C₆₀, the final radical pair also likely decays directly to the ground state because of the high energies of the possible intermediate radical pairs and weak electronic coupling. The lifetime of 1240 ns of the final radical pair BTMPA⁺⁺→AlPorF₅⁻⁻→C₆₀⁻⁻ is slightly longer than that of BTMPA⁺⁺→AlPorF₅⁻⁻ suggesting that either there is a small difference in the electronic coupling or the electron withdrawing effect of the porphyrin substituents which leads to a small stabilization of BTMPA⁺⁺→AlPorF₅⁻⁻. In the triad. Thus, the fact that the recombination lifetime is different for the triads BTMPA-Im→AlPorF₅-Ph-C₆₀ and BTMPA-Im→AlPorF₅-Ph-C₆₀ indicates that the central porphyrin (AlPorF₅ vs AlPorF₃) is important in determining the lifetime of the charge separation because it has an impact on the energies of possible recombination intermediates and therefore on the possible recombination mechanisms.

## CONCLUSION

The triads studied here are related to other axial-bonding triads we have reported previously with a general formula of "Donor-Py/Im→Al(III)Porpyrin-Acceptor". A variety of donor and acceptor units have been employed and in all of these systems, sequential electron transfer takes place resulting in stable charge separation between the donor and acceptor. By varying the components of triads, we have been able to study the sequential charge separation and recombination processes as a function of factors such as the donor—acceptor distance, reorganization energy, Gibbs free-energy, and solvent polarity. The observed charge recombination lifetimes can be rationalized using the Marcus equation, and both the superexchange mechanism and incoherent electron transfer have been invoked to explain the recombination rates. Previously, the focus has been on varying the terminal redox units or bridging groups to study their effect on the charge separation and recombination rates. Although these studies provide insight into the relationship between the components of the complexes and the rates, it is sometimes unclear which variable is responsible for observed differences in the rates. Here, by keeping the terminal redox units constant and making as small a structural change as possible to the central porphyrin to change its redox potential, it is possible to keep some of the electron transfer factors fixed, such as the distance and bridge between redox/photoactive active units, reorganization energy, free energy of the final charge separated state, etc. As a result, the observed changes in the rates can be clearly ascribed to the changes in the redox potential of the porphyrin. Similar triads but with the donor and acceptor attached in the plane of the porphyrin have also been reported by Imahori and co-workers; but in these systems, the central metal of the porphyrin was altered to change its redox potential. In contrast to the systems reported here, in which the recombination reaction is far into the Marcus inverted region, the recombination reaction was close to the top of the Marcus curve and the back reaction rate was governed primarily by the electronic coupling which was much smaller due to the different bonding arrangement. From this comparison, it is clear that these two factors must be balanced against each other to achieve long-lived charge separation. In systems, like the ones presented here in which the electronic coupling is fairly strong, it is important that the back reaction should lie far into the Marcus inverted region. This means that the midpoint potential of the central porphyrin should be chosen so that possible intermediates in a hopping mechanism of charge recombination are high enough in energy to make them inaccessible.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c01574.

Synthesis schemes and details, spectroscopic experiments, mass, IR and NMR spectra, absorption spectra, binding constants, spectroscopic titrations, phosphorescence spectra, DFT optimized structures with frontier orbitals, energy level diagram in η-DCB, and spectroelectrochemical data (PDF)
AUTHOR INFORMATION

Corresponding Authors
Prashanth K. Podduturi — Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, United States; orcid.org/0000-0001-6007-8801; Email: ppk@d.umn.edu
Francis D’Souza — Department of Chemistry, University of North Texas, Denton, Texas 76203-5017, United States; orcid.org/0000-0003-3815-8949; Email: francis.dsouza@unt.edu
Art van der Est — Department of Chemistry, Brock University, St. Catharines, ON L2S 3A1, Canada; Email: avde@brocku.ca
Victor S. Batista — Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, United States; orcid.org/0000-0002-3262-1237; Email: victor.batista@yale.edu

Authors
Niloofar Zarrabi — Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, United States
Sairaman Seetharaman — Department of Chemistry, University of North Texas, Denton, Texas 76203-5017, United States
Subhajyoti Chaudhuri — Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, United States; orcid.org/0000-0001-8297-1123
Noah Holzer — Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c01574

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by startup grants from the University of Minnesota Duluth, to PPK, and by the National Science Foundation (Grant No. f00307) to FD and by an NSERC Discovery Grant (2015-04021) to AvdE. VSB acknowledges support from the U.S. Department of Energy, Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science (Grant DEFG02-07ER15909).

REFERENCES


