Energy and Electron Transfer in β -Alkynyl-Linked Porphyrin–[60]Fullerene Dyads

Sean A. Vail,^{†,⊥} David I. Schuster,^{*,†} Dirk M. Guldi,[‡] Marja Isosomppi,[§] Nikolai Tkachenko,[§] Helge Lemmetyinen,[§] Amit Palkar,^{||} Luis Echegoyen,^{||} Xihua Chen,[†] and John Z. H. Zhang[†]

Department of Chemistry, New York University, New York, New York 10003, Institute for Physical and Theoretical Chemistry, University of Erlangen, 91058 Erlangen, Germany, Institute of Materials Chemistry, Tampere University of Technology, 33101 Tampere, Finland, and Department of Chemistry, Clemson University, Clemson, South Carolina 29634

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Three porphyrin–fullerene dyads, in which a divide bridge links C_{60} with a β -position on a tetraaryl porphyrin, have been synthesized. The free-base dyad was prepared, as well as the corresponding Zn(II) and Ni(II) materials. These represent the first examples of a new class of conjugatively linked electron donor-acceptor systems in which π -conjugation extends from the porphyrin ring system directly to the fullerene surface. The processes that occur following photoexcitation of these dyads were examined using fluorescence and transient absorption techniques on the femtosecond, picosecond, and nanosecond time scales. In sharp contrast to the photodynamics associated with singlet excited-state decay of reference tetraphenylporphyrins (ZnTPP, NiTPP, and H_2 TPP), the divided dyads undergo ultrafast (<10 ps) singlet excited-state deactivation in toluene, tetrahydrofuran (THF), and benzonitrile (PhCN). Transient absorption techniques with the $ZnP-C_{60}$ dyad clearly show that in toluene intramolecular energy transfer (EnT) to ultimately generate C_{60} triplet excited states is the dominant singlet decay mechanism, while intramolecular electron transfer (ET) dominates in THF and PhCN to give the $ZnP^{\bullet+}/C_{60}^{\bullet-}$ charge-separated radical ion pair (CSRP). Electrochemical studies indicate that there is no significant charge transfer in the ground states of these systems. The lifetime of $ZnP^{\bullet+}/C_{60}^{\bullet-}$ in PhCN was ~40 ps, determined by two different types of transient absorption measurement in two different laboratories. Thus, in this system, the ratio of the rates for charge separation (k_{CS}) to rates for charge recombination (k_{CR}), k_{CS}/k_{CR} , is quite small, \sim 7. The fact that charge separation (CS) rates increase with increasing solvent polarity is consistent with this process occurring in the *normal* region of the Marcus curve, while the slower charge recombination (CR) rates in less polar solvents indicate that the CR process occurs in the Marcus inverted region. While photoinduced ET occurs on a similar time scale in a related dyad 15 in which a diethynyl bridge connects C₆₀ to the para position of a meso phenyl moiety of a tetrarylporphyrin, CR occurs much more slowly; i.e., $k_{CS}/k_{CR} \approx 7400$. Thus, the position at which the conjugative linker is attached to the porphyrin moiety has a dramatic influence on k_{CR} but not on k_{CS} . On the basis of electron density calculations, we tentatively conclude that unfavorable orbital symmetries inhibit charge recombination in 15 vis a vis the β -linked dyads.

Introduction

A major consideration in the design of molecular photonic devices involves the factors that mediate electronic communication between photoactive moieties. Some of these include the intrinsic properties of the individual chromophores, system energetics, and overall molecular topology, including interchromophoric distances and spatial orientation. Lindsey et al. showed that energy transfer (EnT) and electron transfer (ET) processes, which were operative in a series of covalent donor–acceptor systems consisting of zinc and free-base porphyrins, were strongly dependent on the location of the diarylethyne linker (meso vs β linkages) and were significantly influenced by the

§ Tampere University of Technology.

presence of electron-*releasing* or electron-*withdrawing* aryl rings at the meso positions.¹ These results indicate that the intrinsic properties of the linking element, as well as the site of connectivity between the porphyrin chromophores in covalently linked porphyrin arrays, play a crucial role in the system's overall molecular electronics.

The synthesis and study of a series of polyalkynyl zinc porphyrin– C_{60} dyads covalently linked to the para position of a phenyl ring on a zinc tetraaryl porphyrin have previously been reported.² These systems exhibited values for the ratio of charge separation to charge recombination, k_{CS}/k_{CR} , on the order of 3900–6100 and 4100–7400 in tetrahydrofuran (THF) and benzonitrile (PhCN), respectively. To further investigate EnT and ET processes in highly conjugated donor–acceptor systems involving porphyrins and fullerenes, a new series of porphyrin– C_{60} dyads has been synthesized. These dyads, in which the ligand at the porphyrin core is either Ni, Zn, or H₂, exhibit homoconjugation through the butadiynyl bridge that links the β -position of the porphyrin donor to the surface of the fullerene.

^{*} Author to whom correspondence should be addressed. E-mail: david.schuster@nyu.edu.

[†] New York University.

[‡] University of Erlangen.

Clemson University.

 $^{^\}perp$ Present Address: Department of Chemistry and Biochemistry, Arizona State University Tempe, AZ 85287.



Figure 1. Molecular structures of porphyrin– C_{60} dyads 1–3 and reference compounds 4, 5, and 12.

Results and Discussion

Synthesis. Tetraphenylporphyrin (H₂TPP) was quantitatively metalated with $Zn(OAc)_2 \cdot 2H_2O$ in refluxing chloroform/ methanol (2:1) for 1 h, according to thin-layer chromatography (TLC). Similarly, treatment of H₂TPP with Ni(OAc)₂ \cdot 4H₂O in refluxing chloroform/methanol (2:1) for 16 h showed quantitative conversion to nickel tetraphenylporphyrin (NiTPP) by TLC.

The synthesis of 1-ethynyl-2-methyl[60]fullerene 4 was carried out according to a procedure previously reported by us.³ In this procedure, nucleophilic addition of lithium (trimethylsilyl, TMS)acetylide to C₆₀, followed by quenching with excess iodomethane, furnished a TMS-protected compound that was subsequently deprotected with potassium carbonate in refluxing THF/CH₃OH (5:1), affording fullerene derivative 4 in 23% overall yield. Zinc porphyrin 5 was prepared using a modified procedure for oxidative heterocoupling of terminal alkynes as previously reported in the literature (see Experimental Section for details).² β -Butadiyne-linked porphyrin-C₆₀ dyads **1**-**3** were synthesized according to the pathway outlined in Scheme 1. β -Bromotetraphenylporphyrin **6** was prepared using a procedure previously reported for β -bromination of free-base porphyrins.⁴ Commercial H₂TPP was treated with N-bromosuccinimide in refluxing CHCl₃, and the reaction progress was carefully monitored by TLC. Due to similar R_f values for $\beta(2)$ -bromo-H₂TPP 6 and 2,12(13)-dibromo-H₂TPP, the reaction was terminated when an increase in the formation of the dibromoporphyrin was demonstrated by TLC. The low yield of the undesired dibromo product facilitated isolation of pure monobromoporphyrin 6, which was isolated in 64% yield by column chromatography on silica gel using toluene/cyclohexane (1:1) as the eluent. The order of elution was: dibromo-TPP, monobromo-TPP, followed by unreacted H₂TPP. Bromoporphyrin 6 was metalated by treatment with Zn(OAc)2+2H2O in refluxing chloroform/methanol (2:1) for 1 h, quantitatively affording zinc porphyrin 7. Analogously, nickel porphyrin 8 was prepared in near quantitative yield by treating 6 with Ni(OAc)₂·4H₂O in refluxing chloroform/methanol (2:1) for 16 h.

 β -(Trimethylsilyl)ethynyl porphyrins **9** and **11** were prepared from **7** and **8** via a modified palladium-catalyzed Heck coupling reaction, as previously reported in the literature.^{4–6} Zinc porphyrin **9** was isolated in 63% yield from a long silica gel column using cyclohexane/methylene chloride (1:1) as the eluent. Free-base porphyrin **10** was obtained by demetalation of porphyrin **9** using trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature. A pure sample of nickel alkynylporphyrin **11** could not be isolated due to a nearly identical R_f value to that of nickel bromoporphyrin **8** in a variety of solvent systems.

 β -Ethynylporphyrins **12** and **14** were obtained in 98% and 97% yields, respectively, by deprotection of porphyrins **9** and **11** with tetrabutylammonium fluoride (TBAF) in THF at room temperature. The corresponding free-base porphyrin **13** was isolated in nearly quantitative yield by treatment of zinc porphyrin **12** with TFA in CH₂Cl₂ at room temperature.

Dyads 1 and 3 were synthesized via oxidative heterocoupling reactions between ethynyl fullerene derivative 4 (1 equiv) and an excess of nickel and zinc porphyrins 12 and 14 (3 equiv). This procedure, which involves in situ generation of the Hay catalyst CuCl/tetramethylethylenediamine (TMEDA)/O₂)⁷ in chlorobenzene under a dry oxygen atmosphere, afforded nonfluorescent dyads 1 and 3 in 27% and 31% yields, along with homodimers (β - β -butadiynyl-linked NiTPP–NiTPP, ZnTPP– ZnTPP, and C₆₀–C₆₀) formed under the reaction conditions. Dyads 1 and 3 were effectively isolated via preparative TLC on silica gel using CS₂ as the eluent. Finally, treatment of 1 with TFA in CH₂Cl₂ furnished H₂P–C₆₀ dyad 2, which was further purified by preparative TLC on silica gel using CS₂ as the eluent.

Electrochemistry. The potentials obtained by cyclic voltammetry (CV) for both NiTPP and ZnTPP exhibit two reduction and two oxidation peaks, respectively. Both oxidation peaks appear to be reversible while the second reduction is irreversible. A comparison of these data with those previously reported for H_2TPP^8 leads to the following trend in the order of first reduction potentials: ZnTPP > NiTPP > H_2TPP. However, an opposite trend is observed for the corresponding first and second oxidation potentials along the series, namely, H_2TPP > NiTPP > ZnTPP.

As shown by potentials obtained from CV measurements for bromoporphyrins **6**, **7**, and **8**, incorporation of the electronegative bromine atom on the porphyrin periphery caused a pronounced effect on the voltammetric response. The electron-withdrawing bromine atom lowers electron density on the porphyrin, making porphyrins **6**, **7**, and **8** easier to reduce and more difficult to oxidize.

In the cyclic voltammograms for porphyrins **5**, **9**, and **10**, two oxidations and two reductions are observed, the second reduction being reversible. Extension of the alkyne chain of porphyrin **9** by one acetylene unit, which affords TMS-terminal porphyrin **5**, has no significant effect on the reduction potentials. The respective oxidation and reduction potentials for TMS-terminal porphyrins **9** and **10** are shifted anodically with respect to porphyrins **12** and **13**, which possess an H terminus, and can be rationalized in terms of the electropositive character of the trimethysilyl group.

The consequences of β -alkynyl substitution become apparent from the reduction potentials of porphyrins **12**, **13**, and **14**. The 50 mV anodic shifts observed for the first reduction potentials of porphyrins **12–14**, relative to ZnTPP, H₂TPP, and NiTPP, can be attributed to conjugation between the porphyrin and the acetylene moieties, which enhances the electron accepting ability of the porphyrin, thereby facilitating reduction. Porphyrins **12**, **13**, and **14**, all of which contain an H terminus, exhibit no additional peaks as compared to ZnTPP, H₂TPP, and NiTPP. Therefore, it can be concluded that both oxidation and reduction of the acetylene moiety are beyond the operative potential window.

SCHEME 1: Synthetic Route to Porphyrin-C₆₀ Dyads 1-3



The CV measurements for β -alkynyl-linked porphyrin $-C_{60}$ dyads 1-3 show overlapping potentials for both the porphyrin and the fullerene moieties, with each dyad exhibiting a total of four reduction waves and two oxidation waves. The corresponding oxidation potential for ZnP-C₆₀ 1 could not be determined accurately due to limited sample availability. Since ethynylfullerene derivative 4 does not show any oxidation within this potential window,² the two peaks are attributed to the oxidation of the porphyrin moieties. Anodic shifts of approximately 30 and 10 mV, respectively, are observed in the potentials obtained from CV measurements for dyads 2 and 3 as compared to precursor alkynyl porphyrins 13 and 14. With regard to the cathodic region of the scan, the cyclic voltammograms show four reduction processes, which were confirmed by differential pulse voltammetry (DPV) experiments. Since no reductions were observed in the earlier cyclic voltammograms for the porphyrin derivatives below -1.5 V, the first two reductions can be attributed to fullerene derivative 4, while the remaining peaks appear to be overlaps between porphyrin and fullerene reduction peaks.

The first reduction peak potential obtained from DPV for ethynylfullerene **4** is almost the same as that for $ZnP-C_{60}$ dyad **1**; H_2P-C_{60} dyad **2** and NiP-C₆₀ dyad **3** behave in a similar manner. Therefore, data obtained from DPV measurements support the notion that the porphyrin and fullerene moieties do not exhibit any significant ground-state electronic communication in dyads **1**–**3**. Table 1contains a summary of electrochemical potentials obtained from CV and DPV experiments.

Steady-State Absorption Studies. The steady-state absorption spectra of ZnTPP, H₂TPP, and NiTPP references were

TABLE 1: Oxidation and Reduction Potentials Obtained by Cyclic Voltammetry and Differential Pulse Voltammetry for ZnTPP, NiTPP, Compounds 1–10 and 12–14 in CH_2Cl_2 (V versus $F_c/F_c^{+})^a$

| compound | oxd1 | oxd 2 | red 1 | red 2 | red 3 | red 4 |
|----------|----------|----------|-------------|-------------|-------------|-------------|
| ZnTPP | 0.39 | 0.67 | | | -1.77 | -2.20^{b} |
| NiTPP | 0.59 | 0.88 | | | -1.67 | -2.07^{b} |
| 1 | ND^{c} | ND^{c} | -1.03^{d} | -1.44^{d} | -1.68^{d} | -1.95^{d} |
| 2 | 0.6 | 0.84 | -1.05 | -1.45 | -1.59^{d} | -1.83^{d} |
| 3 | 0.63 | 0.90 | -1.04^{d} | -1.46^{d} | -1.66^{d} | -1.96^{d} |
| 4 | | | -1.04 | -1.42 | | -1.94 |
| 5 | 0.43 | 0.68 | | | -1.69 | -2.01 |
| 6 | 0.59 | 0.80 | | | -1.55 | -1.85^{b} |
| 7 | 0.44 | 0.68 | | | -1.69 | -2.07^{b} |
| 8 | 0.63 | 0.88 | | | -1.62 | -2.14^{b} |
| 9 | 0.43 | 0.67 | | | -1.68 | -2.04 |
| 10 | 0.57 | 0.81 | | | -1.55 | -1.85 |
| 12 | 0.44 | 0.69 | | | -1.70 | -2.06^{b} |
| 13 | 0.57 | 0.83 | | | -1.58 | -1.87^{b} |
| 14 | 0.62 | 0.89 | | | -1.62 | -2.07^{b} |
| | | | | | | |

^{*a*} All processes are reversible unless otherwise noted. ^{*b*} Irreversible. ^{*c*} Not determined due to lack of sample availability. ^{*d*} Obtained from DPV.

consistent with previously reported data.^{9,10} For comparison purposes, the concentrations of all samples were normalized to optical densities of 1.45 at the Soret band of ZnTPP (422 nm). The data for ZnTPP, H₂TPP, NiTPP, β -alkynyl-linked porphyrin–C₆₀ dyads 1–3, and porphyrins 5–10 and 12–14 in CHCl₃ are summarized in Table 2.

As indicated in Table 2, a small bathochromic shift (3-4 nm) is observed in the absorption spectra of the free-base and zinc bromoporphyrins **6** and **7** relative to H₂TPP and ZnTPP.

TABLE 2: Ground-State Absorption Maxima for ZnTPP, H₂TPP, NiTPP, Porphyrin $-C_{60}$ Dyads 1–3, and Porphyrins 5–10 and 12–14 in CHCl₃

| compound | λ_{max} (nm) (Soret band) | absorbance λ_{max} (nm) |
|----------|-----------------------------------|--------------------------------------------|
| ZnTPP | 422 | 551, 593 |
| H_2TPP | 418 | 515, 551, 589, 647 |
| NiTPP | 422 | 535 |
| 1 | 437 | 257 (C ₆₀), 563, 603 |
| 2 | 432 | 256 (C ₆₀), 526, 563, 603, 659 |
| 3 | 430 | 257 (C ₆₀), 541, 579 |
| 5 | 435 | 562, 603 |
| 6 | 421 | 518, 552, 594, 649 |
| 7 | 426 | 555, 595 |
| 8 | 419 | 533 |
| 9 | 431 | 559, 597 |
| 10 | 427 | 522, 558, 598, 655 |
| 12 | 429 | 558, 598 |
| 13 | 425 | 521, 556, 598, 654 |
| 14 | 423 | 536 |

Conversely, the spectrum of nickel bromoporphyrin 8 shows a small hypsochromic shift (3 nm) relative to that of NiTPP.

A more significant change is apparent in the absorption spectra of TMS-terminal alkynylporphyrins 9 and 10. The bathchromic shifts (9 nm) for the porphyrin Soret bands of 9 and 10, relative to those of ZnTPP and H₂TPP, respectively, are consistent with previous observations for other β -alkynylporphyrin derivatives.⁴

The absorption spectra of porphyrins 12 and 13, with an H terminus, exhibit a slightly smaller red shift in the Soret band (7 nm) than corresponding TMS-terminal porphyrins 9 and 10, relative to the bands in ZnTPP and H_2 TPP, respectively.

The absorption spectra of porphyrin– C_{60} dyads **1–3** all show a significant bathochromic shift, accompanied by substantial broadening of the porphyrin Soret band. In all cases, the spectra show characteristic absorptions for both the porphyrin and the fullerene moieties.

A considerable bathochromic shift of 7 nm is observed for the porphyrin Soret band of NiP–C₆₀ dyad **3** relative to its porphyrin counterpart **14**. The most significant red shift in porphyrin Soret band absorption among these dyads is observed in the case of ZnP–C₆₀ dyad **1**, which exhibits bathochromic shifts of approximately 8 and 15 nm relative to zinc alkynylporphyrin **12** and ZnTPP, respectively. A similar trend is evident in the absorption spectrum of H_2P-C_{60} dyad **2**, which exhibits bathochromic shifts of 7 and 14 nm relative to free-base porphyrin **13** and H_2 TPP, respectively.

The significant bathochromic shifts for the porphyrin Soret bands in porphryin–C₆₀ dyads 1–3, relative to H-terminal alkynylporphyrin precursors 12–14, are similarly observed in the absorption spectrum of β -butadiynylporphyrin 5. Thus, lengthening the β -alkyne chain on the porphyrin periphery causes both an increased bathochromic shift and substantial broadening of the porphyrin Soret band, arising from extension of the porphyrin π -system. Indeed, this phenomenon has been observed in other porphyrins with extended conjugation originating from the β -position.⁴

Since significant red-shifted and broadened absorption for the porphyrin Soret band is observed for zinc porphyrin **5**, which lacks C_{60} , as well as for ZnP- C_{60} dyad **1**, the spectral changes for dyads **1**-**3** cannot reasonably be attributed to significant electronic interactions between the porphyrin and C_{60} moieties in the ground state (Figure 2).

Steady-State Fluorescence Studies. Steady-state fluorescence studies on $ZnP-C_{60}$ **1** were carried out using identical optical densities at the 426 nm excitation wavelength. After



Figure 2. UV/visible absorption spectra of zinc porphyrins 5 and 9 and $\text{ZnP-}C_{60}$ dyad 1 in chloroform.



Figure 3. Normalized room-temperature fluorescence spectra of ZnP 12 and ZnP– C_{60} dyad 1, using identical optical densities at the 426 nm excitation wavelength (360 nm for C_{60}) in toluene. The spectra of ZnP 12 and C_{60} are scaled to fit the dyad emissions at 650 and 710 nm.

photoexcitation, efficient quenching of ZnP fluorescence by the attached C_{60} moiety is observed in toluene. In addition to ZnP emissions at 600 and 650 nm, a new band corresponding to C_{60} fluorescence develops at 710 nm,^{11,12} which evolves with quantum yields of 5×10^{-4} , and is indicative of rapid intramolecular transduction of singlet excitation energy from the porphyrin to the fullerene (Figure 3).

Since measurements were performed using excitation wavelengths corresponding to the absorption maximum (λ_{max}) for the ZnP component, at wavelengths where absorption by the C₆₀ moiety composes less than 5% of the total ZnP-C₆₀ absorption, these observations are consistent with the occurrence of intramolecular transduction of singlet excitation.¹² Further support is derived from the excitation spectrum of the fullerene emission above 700 nm, which exhibits features resembling the ZnP ground state, with maxima at 430, 555, and 595 nm, respectively.¹³ Although it can be assumed that photoexcited H₂P-C₆₀ dyad **2** behaves similarly to dyad **1**, overlapping H₂P (Φ_f 0.11) and C₆₀ fluorescence prevented a quantitative determination of the fullerene fluorescence yield, typically ~6.0 × 10⁻⁴,^{11,12}

In THF, the steady-state fluorescence spectra of porphyrin– C₆₀ dyads **1–3** were measured using normalized optical densities of 0.5 at the 425 nm excitation wavelength. Quantum yields of porphyrin fluorescence in THF of 6.0×10^{-4} for **1**, 1.5×10^{-3} for **2**, and <1.0 × 10⁻⁵ for **3** are indicative of *ultrafast* deactivation of the porphyrin singlet excited states.

As shown in Figure 4, the fluorescence spectrum of ZnP– C_{60} dyad 1 in PhCN exhibits the characteristic ZnP emissions at 600 and 650 nm but lacks C_{60} fluorescence at 710 nm (compare with Figure 3), suggesting that EnT processes



Figure 4. Room-temperature fluorescence spectrum of $ZnP-C_{60}$ dyad 1 following excitation at 433 nm in PhCN.

observed for 1 in toluene are not operative in PhCN. The same observation was made for dyad 1 in THF; i.e., no C_{60} fluorescence at ~710 nm was detected.

In the more polar solvent PhCN, the fluorescence quantum yields decrease to 4.4×10^{-4} for **1** and 9.0×10^{-4} for **2**. Acceleration of porphyrin fluorescence quenching rates with increasing solvent polarity is consistent with *intramolecular* ET directly from ¹P* to C₆₀ to afford P*+/C₆₀*-.¹²⁻¹⁹ This observation can be rationalized in terms of the ability of polar solvents (i.e, THF or PhCN) to stabilize the charge-separated radical pair (CSRP) state through effective solvation of ions, thereby lowering its energy relative to the ground state, or viewed alternatively by increasing the energy gap between excited and CSRP states. Similar conclusions could not be made in the case of NiP-C₆₀ dyad **3** due to the characteristically low fluorescence quantum yields (10⁻⁵) of nickel porphyrins.²⁰

The alternative mechanism for the formation of the CSRP state in THF and PhCN, namely, rapid intramolecular EnT followed by ET evolving from the fullerene singlet excited state, seems much less likely based on a comparison of rate constants (see below) and consideration of the energy levels of the various states. Furthermore, we have no spectroscopic evidence to support such a sequence of intramolecular events.

From the fluorescence quantum yields (Φ_f) and lifetimes (τ) of photoexcited **1**, **2**, and **3** and ZnTPP and H₂TPP (X),^{21,22} the rate constants (k) for intramolecular EnT (k_{EnT} in toluene) and ET (k_{ET} in THF and PhCN) for porphyrin–C₆₀ dyads (Y) can be calculated according to the following equation

 $k(\mathbf{Y}) = [\Phi(\mathbf{X}) - \Phi(\mathbf{1}, \mathbf{2}, \mathbf{3})] / [\tau(\mathbf{X})\Phi(\mathbf{1}, \mathbf{2}, \mathbf{3})]$

in which $\Phi(X)$ and $\tau(X)$ represent the literature values for the fluorescence quantum yields and fluorescence lifetimes of ZnTPP ($\Phi = 0.04$, $\tau = 2.1 \pm 0.2$ ns) and H₂TPP ($\Phi = 0.15$, $\tau = 10.1 \pm 0.5$ ns).²¹ The corresponding rate constants obtained from the fluorescence experiments are included in Table 3. Interestingly, the rates for deactivation of the porphyrin S₁ excited state are greater for ZnP-C₆₀ (1) than those for H₂P-C₆₀ (2). At least in toluene, where there is a weaker overlap between the porphyrin fluorescence and the fullerene absorption, singlet—singlet energy transfer dominates.

Time-Resolved Fluorescence Up-Conversion. Femtosecond time-resolved up-conversion fluorescence experiments on ZnP– C_{60} **1** were carried out to elucidate the processes occurring on extremely short time scales in this system. In the up-conversion studies, excitation at 410 nm using 50 fs pulses was performed, and emission was monitored at 600 or 610 nm, corresponding to the first emission maximum of ZnP in toluene and PhCN, respectively. The 410 nm excitation promotes ZnP to the S₂ excited state, which rapidly decays via internal conversion to the S₁ state, whose decay is monitored in these experiments.

TABLE 3: Fluorescence Quantum Yields (Φ_f), Rate Constants for Charge Separation (k_{CS}), Rate Constants for Charge Recombination (k_{CR}), and CSRP State Lifetimes (τ_{CS}) for ZnP-C₆₀ 1, H₂P-C₆₀ 2, and NiP-C₆₀ 3

| | solvent | Φ _f (porpyrin) | $k_{\rm CS}^a$ (s ⁻¹) | k_{CS}^{b} (s ⁻¹) | $k_{\rm CR}$ (s ⁻¹) | τ_{CS} (ps) |
|-----------------------------------|---------|------------------------------|--------------------------------------|------------------------------------|------------------------------------|------------------|
| 1 ZnPC ₆₀ | toluene | 9.0×10^{-4} | $2.2 \times 10^{10} c$ | | | |
| | THF | 6.0×10^{-4} | 3.3×10^{10} | 9.0×10^{10} | 9.8×10^{9} | 100 |
| | PhCN | 4.4×10^{-4} | 4.5×10^{10} | 1.1×10^{11} | 1.6×10^{10} | 60 |
| 2 H ₂ PC ₆₀ | toluene | 2.1×10^{-3} | $7.0 \times 10^{9} c$ | | | |
| | THF | 1.5×10^{-3} | 9.9×10^{9} | 6.6×10^{10} | 2.8×10^9 | 360 |
| | PhCN | 9.0×10^{-4} | 1.7×10^{10} | 7.6×10^{10} | 6.2×10^{9} | 160 |
| 3 NiPC ₆₀ | toluene | $< 1.0 \times 10^{-5}$ | | | | |
| | THF | $< 1.0 \times 10^{-5}$ | | 5.2×10^{10} | | |
| | PhCN | $\leq 1.0 \times 10^{-5}$ | | 6.2×10^{10} | 4.7×10^{9} | 210 |

^{*a*} Extrapolated from fluorescence experiments. ^{*b*} Determined from femtosecond/picosecond transient absorption measurements. ^{*c*} Energy transfer.



Figure 5. Room-temperature emission decay of $\text{ZnP}-\text{C}_{60}$ dyad 1 at 600 nm following femtosecond excitation at 410 nm in toluene. The lifetimes (and amplitudes) of the decay components are indicated in the figure.



Figure 6. Room-temperature emission decay of $\text{ZnP}-\text{C}_{60}$ dyad **1** at 610 nm following femtosecond excitation at 410 nm in PhCN. The lifetimes (and amplitudes) of the decay components are indicated in the figure.

As seen in Figures 5 and 6, the major decay components in toluene and PhCN have lifetimes of 5.3 and 3.2 ps, while the longer-lived minor components have lifetimes of 25 and 41 ps. In toluene, the second decay component is attributed to an equilibrium between porphyrin and fullerene singlet excited states (${}^{1}ZnP^{*}-C_{60} \leftrightarrow ZnP-{}^{1}C_{60}^{*}$). In PhCN, the presence of a second decay component can be rationalized in terms of equilibrium between ${}^{1}ZnP^{*}$ and the CSRP state. It is also possible that the biexponential decay arises from two competing processes from ${}^{1}ZnP^{*}$, namely, direct ET to give the CSRP state, and singlet-singlet energy transfer to give ${}^{1}C_{60}^{*}$ followed by ET. Since the direct ET process in PhCN is very rapid and no evidence for C₆₀ emission in PhCN was obtained in this study, we favor equilibration between ZnP* and the CSRP state.

Time-Resolved Transient Absorption Spectra. Transient absorption spectroscopy was used to investigate the fate of porphyrin excited states in dyads 1-3 and porphyrin reference compounds ZnTPP, H₂TPP, and NiTPP. The course of the



Figure 7. Room-temperature differential absorption spectrum obtained following femtosecond flash excitation (387 nm) of ZnTPP in nitrogensaturated PhCN with a time delay of 5 ps.

excited-state processes was monitored through differential absorption changes following irradiation (387 nm) of dilute solutions ($\sim 10^{-5}$ M) with femtosecond laser pulses.

The singlet–singlet features for photoexcited ZnTPP include transient bleaching of the porphyrin Soret and Q-band transitions, which is accompanied by a new, albeit weak, transition in the region above 600 nm (Figure 7).^{13,23} The intrinsic decays for ZnTPP and H₂TPP, 2.1 \pm 0.2 and 10.1 \pm 0.5 ns, respectively, were found to be independent of solvent (toluene, THF, or PhCN).

In contrast to ZnTPP and H₂TPP, the kinetics for NiTPP suggest that formation of excited states proceeds through a twostep mechanism. Initially, a short-lived singlet excited state, which kinetically resembles those of ZnTPP and H₂TPP, is observed. A transient decay (0.89 ps), which involves transformation to the d-d excited state,²⁴ is observed prior to the completion of singlet excited-state formation. This observation is consistent with the rapid deactivation (<1 ps) of nickel porphyrin singlet excited states.²⁴ Both of these intermediates can be differentiated spectroscopically (Figure S1).

The initial intermediate formed from NiTPP has a spectral resemblance to the nickel porphyrin singlet excited state ($^{1}NiP^{*}$), including a maximum at 500 nm, while the features of the d-d photoexcited state, which has a measured lifetime of 220 ps, lack the maximum at ~500 nm. These findings are consistent with previous observations associated with the decay of $^{1}NiP^{*}$ and d-d excited states.²⁴

Time-resolved transient absorption studies confirmed formation of ¹P* upon photoexcitation of the porphyrin chromophores in **1**, **2**, and **3**. In the case of NiP–C₆₀ **3**, an additional pathway followed, leading to the d–d photoexcited state. Instead of the slow decay dynamics typical of porphyrin excited states, a rapid deactivation of singlet excited energy was observed for **1** and **2** ($\sim 10^{10}$ s⁻¹) and of the d–d state in the case of **3**. Figures 8 and S2 show the typical decay dynamics for ZnP–C₆₀ **1**, measured in PhCN at room temperature after the 387 nm femtosecond laser pulse, with time delays between 0 and 20 ps and between 5 and 50 ps, respectively.

The differential absorption changes that accompany the decay of ZnP singlet excited states in ZnP–C₆₀ **1** in THF and PhCN, for H₂P in H₂P–C₆₀ **2**, and NiP in NiP–C₆₀ **3**, all display the spectral features associated with one-electron-oxidized π -radical cations, as shown by strong and broad absorptions in the 600–800 nm range.^{13,23} In contrast, fullerene singlet–singlet absorption at 880 nm evolves in toluene, which on a longer time scale (ns) leads to population of the triplet manifold through efficient



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Figure 8. Room-temperature differential absorption spectra obtained following femtosecond flash excitation (387 nm) of $ZnP-C_{60}$ **1** in nitrogen-saturated PhCN with time delays between 0 and 20 ps. Up arrows indicate regions of increasing absorption with time, and down arrows decreasing absorption.



Figure 9. Time absorption profiles for the spectrum depicted in Figure 8 at 440 nm (black circles) and 640 nm (red circles), monitoring the formation and subsequent decay of ZnP^{+}/C_{60}^{-} in PhCN.

intersystem crossing, as shown by growth of the characteristic C_{60} triplet-triplet absorption maximum at 700 nm (data not shown).^{11,12} These observations support the conclusion that intramolecular ET from the porphyrin to C_{60} in **1**, **2**, and **3**, which leads to the formation of P^{•+}/C₆₀^{•-}, is the dominant pathway for deactivation of porphyrin excited states in **1**-**3** in both THF and PhCN, while singlet-singlet EnT is the dominant if not exclusive decay pathway in toluene.

The corresponding time absorption profiles at 440 and 640 nm for ZnP-C_{60} **1** in PhCN are depicted in Figure 9. As shown, $\text{ZnP}^{\bullet+}/\text{C}_{60}^{\bullet-}$ begins to decay on the picosecond time scale. Singlet ground states for dyads **1–3** evolve as a product of charge recombination processes in all cases.

As shown in Table 3, the lifetimes of the CSRP states for 1 and 2 were longer in THF than in the more polar PhCN: 1, 100 ps in THF, 60 ps in PhCN; 2, 360 ps in THF, 160 in PhCN. In PhCN, the CSRP state lifetime for 3 was determined to be 210 ps. This trend in rates as a function of solvent polarity indicates charge recombination is occurring in the Marcus inverted region.

Pump–Probe Transient Absorption Measurements on ZnP–C₆₀ 1. Femtosecond pump–probe transient absorption experiments were performed to elucidate the processes occurring on shorter time scales in $ZnP-C_{60}$ **1**. These studies confirmed



Figure 10. Room-temperature transient absorption spectra (decay components) of $ZnP-C_{60}$ dyad **1** (460–760 nm) following femtosecond excitation at 413 nm in toluene.



Figure 11. Room-temperature transient absorption spectra (decay components) of $ZnP-C_{60}$ dyad 1 (850–1070 nm) following femto-second excitation at 413 nm in toluene.

previous results obtained for photoexcited 1, namely, the occurrence of intramolecular EnT (toluene) and ultrafast intramolecular ET (PhCN) producing $\text{ZnP}^{\bullet+}/\text{C}_{60}^{\bullet-}$ within approximately 10 ps.

Time-resolved absorption experiments were performed using 413 nm excitation, which is located at the blue shoulder of the porphyrin Soret band. The measurements were carried out in three wavelength ranges: 460-680, 540-760, and 850-1070 nm. The data in the visible region of the spectrum (460-680 and 540-760 nm) were combined for global fitting, while those in the near-infrared (NIR) were fitted separately. The decay component spectra for $ZnP-C_{60}$ 1 in toluene (visible and NIR) are presented in Figures 10 and 11. The corresponding calculated time-resolved spectra derived from Figures 10 and 11, at selected delay times, are shown in Figures S3 and S4.

As seen in Figure 10, strong bleaching of the zinc porphyrin Q-band (~550 nm) and the appearance of broad absorption between 580 and 750 nm, following photoexcitation in toluene at 413 nm, attests to the formation of ¹ZnP*.¹³ The decay component spectra show no evidence of ZnP*⁺ formation, which is normally detected by its absorption around 650 nm.^{13,23} In addition, the absence of spectral features in the NIR region characteristic of C₆₀⁻⁻, which would lead to absorption around 1000 nm, corresponding to a negative amplitude of the decay-associated spectra in this region, indicates that CS does not take place in toluene (Figure 11).^{12–19,23,25–39} Rather, the strong quenching of ZnP fluorescence in toluene is attributed to rapid *intramolecular* EnT from ¹ZnP* to C₆₀.

The decay component spectra and calculated time-resolved spectra for ZnP–C₆₀ dyad **1** in PhCN are shown in Figures S5–S8, respectively. The spectra in Figure S5 possess characteristic features of ZnP^{•+}, as shown by an absorption band at 650 nm for the 39 ps component.^{13,23} In Figure S7, the absorption band at 1020 nm observed for the 31 ps component is attributed to $C_{60}^{\bullet-12-19,23,25-39}$ and is consistent with intramolecular ET from ¹ZnP* to C_{60} to afford ZnP^{•+}/C₆₀^{•-} in PhCN.

The decay component spectrum of $ZnP-C_{60}$ **1**, as determined from pump-probe measurements, indicates that the CSRP state is formed in ~10 ps in PhCN. The formation of ZnP^{++} and C_{60}^{--} is demonstrated by the negative amplitudes at 650 and 1020 nm; the formation lifetimes are 11 and 6 ps, respectively (Figures S5 and S7). Noteworthy is the fact that the lifetimes in the two wavelength ranges are in good agreement. However, up-conversion (fluorescence) measurements yielded a lifetime of 3.2 ps for the decay for ¹ZnP*. Since the solvent gives rise to its own signal in the pump-probe measurements, the lifetime obtained from the fluorescence measurements is probably more reliable. All the data point to formation of the CSRP state in less than 10 ps.

The lifetime of $ZnP^{\bullet+}/C_{60}^{\bullet-}$ in PhCN was determined to be \sim 40 ps from pump-probe transient absorption measurements. The longest-lived component (680 ps) resolved in the measurements does not exhibit spectral features associated with a CSRP state and is reasonably attributed to solvent relaxation, with lifetimes of 8 and 600 ps, respectively. The broad band observed at 650 nm for the 39 ps component, which has a mirror image corresponding to an 11 ps component, is attributed to ZnP^{•+}.^{13,23} The time profile for the 650 nm signal shows that at least 90% of the molecules in the CSRP state $(ZnP^{\bullet+}/C_{60}^{\bullet-})$ decay in less than 1 ns. The lifetime of the main component is 48 ps, which is consistent with the global fitting (39 ps). Noteworthy is the fact that rates for charge separation and charge recombination, which were determined independently through two entirely different experimental methods for ZnP-C₆₀ dyad 1 in PhCN, are entirely consistent. Due to a lack of sample availability, analogous femtosecond experiments could not be performed on dyads 2 and 3.

Molecular Structure Calculations. Theoretical calculations on $ZnP-C_{60}$ dyad **1** were carried out with the Gaussian 03 package⁴⁰ using a fully optimized ground-state structure. Results are shown in Figure 12.

As shown in Figure 12, the phenyl rings at positions 5, 10, and 15 are staggered by approximately 65° with respect to the plane of the porphyrin. Due to its proximity to the butadiynyl linker at position 2, the phenyl ring at meso position 20 shows increased staggering, from 65° to 82° . The butadiyne group is covalently bonded to one of the two pyrrole units coordinated to the cental zinc atom. The zinc porphyrin core shows little elasticity, due to the presence of the dialkynyl group, which essentially "pulls" on the pyrrole nitrogen ring, increasing the N–Zn bond length by about 0.01 Å.

The calculated interchromophoric center-to-center distance (R_{cc}) in the optimized structure was determined to be 14.75 Å. With respect to the porphyrin, the bond angle between the β -carbon and the first two carbon atoms of the alkyne moiety $(\beta$ -C $-C\equiv$ C) is slightly bent due to the influence of the phenyl ring on the adjacent meso position. The methyl group adjacent to C1 on the fullerene exerts a similar effect, causing a slight bending of the C₁–C \equiv C bond angle. Therefore, it can be concluded that the butadiyne bridging element is both rigid and planar, although not completely linear.

The two sp³ carbon atoms on the fullerene, designated C1 and C2 in Figure 12, constitute a bridge that disrupts electronic conjugation within the dyad. The C₁-C₂ bond (1.638 Å) is considerably longer than the other C-C bonds between hexagons on C₆₀ (~1.41 Å). In addition, the two C₁-C (1.561 Å) and two C₂-C bonds (1.550 Å) on C₆₀ are longer than the C-C bonds between other hexagons and pentagons of C₆₀ (~1.46 Å).

Although Kohn-Sham density functional orbitals are of little



Figure 12. Optimized structure of zinc porphyrin– C_{60} dyad 1 showing selected bond lengths (in Å). The angles (in deg) between each of the four phenyl groups and the porphyrin plane are indicated by numbers in boxes. The arrows leading to the number of 81.9° illustrate how dihedral angles were measured.

physical significance, they are consistent with the ground-state electron density and can be qualitatively analyzed.⁴¹ An examination of the molecular orbitals (MOs) reveals that the two highest occupied MOs (HOMO + 1 and HOMO) are centered on the dialkynyl zinc porphyrin while the three lowest unoccupied MOs (LUMO, LUMO + 1 and LUMO + 2) are centered almost exclusively on the fullerene, as illustrated in Figure 13. This suggests a strong propensity for intramolecular charge transfer from the zinc porphyrin to the fullerene following photoexcitation. The properties of the frontier orbitals and the HOMO–LUMO energy gap (calculated by B3LYP) have previously been shown to be in good agreement with experimental data.⁴²

In ZnP–C₆₀ dyad **1**, the HOMO–LUMO energy gap was determined to be \sim 1.6 eV, corresponding to a wavelength of \sim 770 nm. However, more extensive computational analysis of the ground- and excited-state electronic structures are required to elucidate the detailed optical transition features.

Conclusion

A series of P–C₆₀ dyads with covalent linkages originating from the β -position of a nickel, zinc, or free-base porphyrin to C₆₀ was synthesized to assess photophysical and electrochemical properties of such dyads as a function of molecular structure. Dyads **1–3** represent a new class of conjugatively linked electron donor–acceptor systems in which the π conjugation extends from the porphyrin to the surface of the fullerene through a butadiynyl bridge.

Significant bathochromic shifts for the porphyrin Soret bands in the ground-state absorption spectra of $P-C_{60}$ dyads 1-3 can be attributed to extended conjugation of the porphyrin π system and not to ground-state interactions between the chromophores. Cyclic voltammetry and differential pulse voltammetry measurements confirm that the porphyrin and fullerene moieties in dyads 1-3 are not electronically coupled to any detectable extent in the dyad ground states.

In nonpolar solvents, these systems exhibit singlet–singlet EnT from the photoexcited porphyrin to C_{60} , as shown by the formation of ${}^{3}C_{60}$ *. In polar solvents, rapid formation of a CSRP



Figure 13. The two highest occupied MOs (HOMO + 1 and HOMO) and three lowest unoccupied MOs (LUMO, LUMO + 1 and LUMO + 2) of zinc porphyrin– C_{60} dyad 1, accompanied by the corresponding calculated orbital energies. Computations were performed with B3LYP/LANL2DZ using an optimized geometrical structure.

state is followed by somewhat slower charge recombination dynamics leading back to the singlet ground state. Deactivation of porphyrin excited states via EnT (in nonpolar solvents) and ET (in polar solvents) is similar to the behavior observed in a number of other photoexcited porphyrin– C_{60} systems.^{13,38,39,43–47} An increase in ET rates with increasing solvent polarity is consistent with charge separation occurring in the *normal* region of the Marcus parabola. Slower charge recombination rates in less polar solvents, namely, THF as compared with PhCN, are indicative of charge recombination events operating in the Marcus *inverted* region.

Finally, it is interesting to compare the photophysical behaviors of β -alkynyl ZnP–C₆₀ dyad **1** and *para*-phenylalkynyl ZnP–C₆₀ dyad **15**, which has been previously described.²



In toluene, fast intramolecular EnT from ${}^{1}\text{ZnP*}$ to C₆₀ is observed for both ZnP–C₆₀ dyads **1** and **15**, as shown by high quantum yields for the formation of ${}^{3}\text{C}_{60}*$. In THF and PhCN, both dyads **1** and **15** exhibit rapid and efficient intramolecular ET leading to a CSRP state. Increasingly fast deactivation of porphyrin fluorescence for both **1** and **15** with increasing solvent polarity is consistent with intramolecular ET operating in the Marcus *normal* region. However, increasingly faster rates for charge recombination with a decrease in thermodynamic driving force, resulting in shorter CSRP state lifetimes in more polar solvents, proves that charge recombination processes for both **1** and **15** are occurring in the Marcus *inverted* region.

In THF and PhCN, photoinduced electron transfer from ZnP to C₆₀ affords a CSRP state (ZnP^{•+}/C₆₀^{•-}) with $k_{\rm CS}$ on the order of 10¹¹ s⁻¹ for **1** and 10¹⁰ s⁻¹ for **15**. For dyad **1**, CSRP state lifetimes were 100 and 60 ps in THF and PhCN, respectively. In contrast, substantially longer CSRP state lifetimes were found in the case of **15**, namely, 550 ns in THF and 320 ns in PhCN. It is particularly interesting that the $k_{\rm CS}/k_{\rm CR}$ ratios derived from charge separation and charge recombination data in PhCN were more than 3 orders of magnitude greater for **15** ($k_{\rm CS}/k_{\rm CR} \approx 7400$) than those for **1** ($k_{\rm CS}/k_{\rm CR} \approx 7$).

It has been shown that porphyrins containing electronreleasing aryl groups at the nonlinking meso positions have an a_{2u} HOMO,¹ as is the case for both **1** and **15**. Despite an electronic distribution favoring through-bond communication via a linking element extending from the meso position of the porphyrin to C₆₀, k_{ET} values are similar for **1** and **15**. Since dyads **1** and **15** exhibit CS rates of approximately the same order of magnitude, the significantly higher k_{CS}/k_{CR} values for **15** are obviously a consequence of much slower charge recombination rates in this dyad. A possible explanation for these results is significantly greater stabilization of the CSRP state in the case of **15**, which would retard charge recombination to produce the ground state. Alternatively, the longer CSRP lifetime for **15** may be due, at least in part, to unfavorable orbital interactions between the ZnP and the C_{60} moieties, which could inhibit charge recombination processes from the CSRP state.³¹

Experimental Section

Electrochemistry (Clemson University). The electrochemical measurements for ZnTPP, NiTPP, ethynylfullerene 4, and porphyrins 5-10 and 12-14 were performed using a CHI 440 electrochemical workstation (CH Instruments, Inc., Austin, TX). Tetrabutylammonium hexafluorophosphate (Fluka) in redistilled CH₂Cl₂ (0.1 M) was used as the supporting electrolyte (degassed with argon and saturated with CH₂Cl₂ vapors). A platinum wire was employed as the counter electrode, and a nonaqueous Ag/ AgCl electrode was used as the reference. Ferrocene (Fc) was added as an internal reference, and all the potentials were referenced relative to the Fc/Fc⁺ couple. A glassy carbon electrode (CHI, 1.5 mm in diameter), polished with 0.3 μ m aluminum paste and ultrasonicated in a deionized water and CH₂Cl₂ bath, was used as the working electrode. The scan rates for cyclic voltammetry were 100 mV while the pulse rate was set at 0.05 s at increments of 4 mV and an amplitude of 50 mV for differential pulse voltammetry measurements. All experiments were performed at room temperature (20 ± 2 °C).

Dyads 1–3 were studied in a special cell similar to one described earlier.^{48,49} This assembly consists of a glass tube (1.5 mm diameter) fitted with a Vycor tip (working volume of 100 μ L) and contains the test solution (compound + TBAPF₆ in CH₂Cl₂). This cell was immersed in a glass vial containing the electrolyte solution. A platinum wire was employed as the counter electrode, and a nonaqueous Ag/AgCl electrode was used as the reference. This electrode was similarly immersed in the electrolyte contained in the outside glass vial.

Photophysical Measurements (University of Erlangen). Picosecond laser flash excitation experiments were performed using 355 or 532 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (18 ps pulse width, 2-3 mJ/pulse). Nanosecond laser flash excitation experiments were performed with 355 or 532 nm laser pulses from a Quanta-Ray CDR Nd:YAG system (6 ns pulse width) in a front-face excitation geometry. The photomultiplier output was digitized with a Tektronix 7912 AD programmable digitizer. A typical experiment consisted of 5-10 replicate pulses per measurement. The averaged signal was processed with a LSI-11 microprocessor interfaced with a VAX-370 computer. The details of the experimental setups and their operation can be found elsewhere.⁵⁰

Fluorescence lifetimes were measured with a laser strobe fluorescence lifetime spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fiber coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the systems are described on the manufacturer's Web site, http://www.pti-nj.com.

Emission spectra, all measured at room temperature, were recorded on a SLM 8100 spectrofluorometer. Each spectrum represents an average of at least five individual scans, with appropriate corrections when necessary. Quantum yields were measured as before relative to that of H₂TPP (0.11).³⁸

Photophysical Measurements (Tampere University of Technology). Steady-state fluorescence spectra were measured on a Fluorolog 3 spectrofluorimeter (ISA, Inc.) equipped with a cooled IR-sensitive photomultiplier (R2658, Hamamatsu, Inc.). The excitation wavelength was at the maximum of the Soret

band (426 nm). The emission spectra were recorded in the wavelength range from 600 to 1000 nm.

Ultrafast fluorescence decays were measured by an upconversion method as described previously.³⁴ The instrument (FOG100, CDP, Moscow, Russia) utilizes the second harmonic (420 nm) of a 50 fs pulsed Ti:sapphire laser (TiF50, CDP, Moscow, Russia) pumped by an Ar ion laser (Innova 316P, Coherent). The samples were placed into rotating disk-shaped 1 mm cuvettes. Typical time resolution for the instrument was 150 fs (fwhm). Subnanosecond emission decays were studied using a time-correlated single-photon-counting instrument described elsewhere.⁵¹ Femtosecond to picosecond time-resolved absorption spectra were collected using a pump-probe technique as described elsewhere.34 The femtosecond pulses of the Ti:sapphire generator were amplified by using a multipass amplifier (CDP-Avesta, Moscow, Russia) pumped by a second harmonic of the Nd:YAG Q-switched laser (model LF114, Solar TII, Minsk, Belarus). The amplified pulses were used to generate the second harmonic (420 nm) for sample excitation (pump beam) and white continuum for time-resolved spectrum detection (probe beam).

Molecular Modeling Calculations. (X.C. and J.Z.H.Z.) All computations were performed with the Gaussian 03 package,⁴⁰ using Becke's three-parameter hybrid exchange functional with the Lee–Yang–Parr correlation functional (B3LYP)^{52–55} and a LANL2DZ basis set. LANL2DZ, with effective core potentials (ECPs), is a double- ζ basis set containing ECP presentations of near-nuclei electrons.^{56–59}

Synthesis. General Information. All commercially available reagents were used as received unless otherwise noted. Anhydrous toluene (containing <0.001% water) was purchased from Aldrich and was used as received. Tetrahydrofuran was freshly distilled over potassium, with benzophenone as an indicator, prior to use. Methylene chloride was dried by distillation over sodium metal and was used immediately following distillation. All moisture-sensitive reagents were transferred via syringe or double-tipped cannulae through rubber septa under an argon atmosphere. Oxidative coupling reactions were performed in one-neck round-bottom flasks equipped with a calcium sulfate drying tube, protected from light. Whenever possible, the progress of the reactions was monitored by TLC using precoated glass plates (Silica gel 60, 0.25 mm thickness) with a fluorescent indicator (254 nm). All spots were visualized using a shortwave ultraviolet lamp ($\lambda = 254$ nm). Column chromatography was performed using Silica 60 from Sorbent Technology, Inc. Preparative thin-layer chromatography was performed using TLC standard grade silica gel (Aldrich), with gypsum binder (particle size $2-25 \mu m$, Brunauer–Emmett–Teller surface area \sim 500 m²/g, pore volume 0.75 cm³/g, average pore diameter 60 Å).

¹H NMR spectra for **4** were acquired using a 200 MHz Varian NMR spectrometer. ¹H NMR spectra for ZnTPP, NiTPP, and compounds **1**–**3**, **5**–**10**, and **12–14** were obtained using a 400 MHz Bruker-AV spectrometer. All spectra were measured in CDCl₃ and reported relative to a trimethylsilane internal standard (0.1% v/v).

Mass spectra for all samples were obtained using a Bruker Daltronics matrix-assisted laser desorption ionization time-of flight (MALDI-TOF) mass spectrometer without a matrix. Mass spectra for compounds 1-4 were obtained using pristine C_{60} as standard. Mass calibrations for ZnTPP, NiTPP, and compounds 5-10 and 12-14 were performed using commercial H₂TPP. All absorption spectra were measured on a Hewlett-Packard 8453 UV/vis spectrophotometer. *Zn*(*II*)–*Tetraphenylporphyrin*. H₂–Tetraphenylporphyrin (300 mg) and Zn(OAc)₂·2H₂O (800 mg) were heated at reflux in 300 mL of chloroform/methanol (2:1) for 1 h. The mixture was cooled, and the solvent was removed under reduced pressure. The product was redissolved in chloroform and eluted through a short silica column with chloroform to furnish ZnTPP in near quantitative yield. UV/vis (CHCl₃): λ_{max} 422, 551, 593 nm. ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, 12H), 8.23 (d, 8H), 8.94 (s, 8 β-H) ppm. MALDI-TOF: *m/z* 678.38 [M⁺].

Ni(*II*)–*Tetraphenylporphyrin*. H₂–Tetraphenylporphyrin (300 mg) and Ni(OAc)₂·4H₂O (1 g) were heated at reflux in 300 mL of chloroform/methanol (2:1) for 16 h. The mixture was cooled, and the solvent was removed under reduced pressure. The product was redissolved in chloroform and eluted through a short silica column with chloroform to furnish NiTPP in near quantitative yield. UV/vis (CHCl₃): λ_{max} 422, 535 nm. ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, 12H), 8.02 (d, 8H), 8.74 (s, 8 β -H) ppm. MALDI-TOF: *m/z* 671.71 [M⁺].

1-Ethynyl-2-methyl[60]fullerene **4**. Ethynylfullerene **4** was synthesized according to the procedure previously reported for the preparation of the same compound.³ ¹H NMR (200 MHz, CDCl₃): δ 0.44 (s, 9H, TMS), 3.43 (s, 3H, CH₃). MALDI-TOF: *m/z* 832.99 [M⁺], 817.92 [M⁺ – CH₃], 720.64 [C₆₀].

 $Zn(II) - \beta$ -(Trimethylsilyl)butadiynyltetraphenylporphyrin 5. To a solution of $Zn(II) - \beta$ -ethynyltetraphenylporphyrin 12 (25 mg, 35.6 µmol) in dry CH₂Cl₂ (25 mL) were added (trimethylsilyl)acetylene (35 mg, 0.36 mmol) and CuCl (75 mg). The mixture was stirred vigorously under a dry oxygen atmosphere for 2 h followed by dropwise addition of TMEDA (0.8 mL). The reaction mixture was vigorously stirred for 2 h under dry oxygen and was filtered through a silica funnel to remove any insoluble residue. The solvent was removed under reduced pressure, and the crude porphyrin was redissolved in chloroform and transferred onto a silica funnel. The porphyrin was washed thoroughly on the funnel with hexanes and then eluted with chloroform. The solvent was removed under reduced pressure to afford 5 as a purple crystalline solid (26 mg, 92%). UV/vis (CHCl₃): λ_{max} 435, 562, 603 nm. ¹H NMR (400 MHz, CDCl₃): δ 1.30 (s, 9H Si-CH₃), 7.68–7.72 (m, 12H), 8.11 (d, 2H), 8.18 (m, 6H), 8.84–8.97 (m, 6 β -H), 9.22 (s, 1 β -H) ppm. MALDI-TOF: *m*/*z* 798.85 [M⁺].

 $H_2-\beta$ -Bromotetraphenylporphyrin **6**. To a solution of TPP (425 mg, 0.69 mmol) in chloroform (350 mL) at reflux was added *N*-bromosuccinimide (135 mg, 0.76 mmol). The course of the reaction was monitored by TLC and was terminated when the quantity of undesired 2,12(13)-dibromo-TPP began to increase. The mixture was cooled and washed with a saturated sodium bicarbonate solution until the wash water was slightly basic. The crude product was dried with sodium sulfate, concentrated, and chromatographed on a long silica column using toluene/cyclohexane (1:1) as the eluent, affording $H_2-\beta$ -bromoTPP **6** (306 mg, 64%). UV/vis (CHCl₃): λ_{max} 421, 518, 552, 594, 649 nm. ¹H NMR (400 MHz, CDCl₃): δ -2.81 (s, 2H), 7.7–7.82 (m, 12H), 8.10 (m, 2H), 8.21 (m, 6H), 8.78 (m, 2 β-H), 8.8–8.92 (m, 5 β-H) ppm. MALDI-TOF: *m/z* 694.17 [M⁺].

Zn(*II*)–β-*Bromotetraphenylporphyrin* **7**. A solution of **6** (240 mg) and Zn(OAc)₂•4H₂O (750 mg) in 2:1 chloroform/methanol (240 mL) was heated at reflux for 1 h. The mixture was cooled, and the solvent was removed under reduced pressure. The product was redissolved in chloroform and eluted through a short silica column with chloroform to furnish Zn(II)–β-bromoTPP **7** in quantitative yield. UV/vis (CHCl₃): λ_{max} 426, 555, 595 nm. ¹H NMR (400 MHz, CDCl₃): δ 7.66–7.84 (m, 12H), 8.02–

8.11 (m, 2H), 8.13–8.28 (m, 6H), 8.83–8.98 (m, 7 β -H) ppm. MALDI-TOF: 757.59 [M⁺].

Ni(*II*)–2-*Bromotetraphenylporphyrin* **8**. A solution of **6** (240 mg) and Ni(OAc)₂·4H₂O (800 mg) in 2:1 chloroform/methanol (240 mL) was heated at reflux for 16 h. The mixture was cooled, and the solvent was removed under reduced pressure. The product was redissolved in chloroform and eluted through a short silica column with chloroform to furnish Ni(II)– β -bromoTPP **8** in near quantitative yield. UV/vis (CHCl₃): λ_{max} 419, 533 nm. ¹H NMR (400 MHz, CDCl₃): δ 7.58–7.71 (m, 12H), 7.86 (m, 2H), 7.98 (m, 6H), 8.63–8.76 (m, 6 β -H), 8.83 (s, 1 β -H) ppm. MALDI-TOF: *m/z* 750.76 [M⁺].

Zn(*II*)-β-(*Trimethylsilylethynyl*)*tetraphenylporphyrin* **9**. To a deoxygenated solution of **7** (200 mg, 0.26 mmol) in dry triethylamine (300 mL) and dimethylformamide (DMF, 30 mL) were added bis(triphenylphosphine) palladium(II) chloride (150 mg), cuprous iodide (75 mg), and (trimethylsilyl)acetylene (128 mg, 1.3 mmol). The reaction mixture was heated at reflux for 16 h, cooled, and filtered through a short silica column using chloroform as the eluent. The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel using cyclohexane/CH₂Cl₂ (1:1) as theeluent, affording **9** (126 mg, 63%). UV/vis (CHCl₃): λ_{max} 431, 559, 597 nm. ¹H NMR (400 MHz, CDCl₃): δ 1.29 (s, 9H Si–CH₃), 7.67 (d, 2H), 7.70–7.82 (m, 10H), 8.12 (d, 2H), 8.21 (m, 6H), 8.78 (s, 1 β-H), 8.88 (m, 1 β-H), 8.91 (m, 4 β-H), 9.21 (s, 1 β-H) ppm. MALDI-TOF: *m/z* 774.70 [M⁺].

 $H_2-\beta$ -(*Trimethylsilyl*)*ethynyltetraphenylporphyrin* **10**. To a solution of **9** (25 mg) in CH₂Cl₂ (15 mL) was added TFA (0.5 mL). The reaction mixture was stirred vigorously at room temperature for 15 min, washed with water and saturated sodium hydrogen carbonate, and dried with sodium sulfate. The solvent was removed under reduced pressure to furnish **10** in near quantitative yield. UV/vis (CHCl₃): λ_{max} 427, 522, 558, 598, 655 nm. ¹H NMR (400 MHz, CDCl₃): δ -2.70 (s, 2H), 1.29 (s, 9H Si-CH₃), 7.68 (d, 2H), 7.71-7.84 (m, 10H), 8.13 (d, 2H), 8.18-8.22 (m, 6H), 8.74 (m, 3 β-H), 8.82 (m, 1 β-H), 8.86 (m, 2 β-H), 9.06 (s, 1 β-H) ppm. MALDI-TOF: *m/z* 711.54 [M⁺].

 $Ni(II)-\beta$ -(*Trimethylsilylethynyl*)*tetraphenylporphyrin* **11**. To a deoxygenated solution of **8** (200 mg, 0.27 mmol) in dry triethylamine (300 mL) and DMF (30 mL) were added bis-(triphenylphosphine) palladium(II) chloride (150 mg), cuprous iodide (75 mg), and (trimethylsilyl)acetylene (132 mg, 1.35 mmol). The reaction mixture was heated at reflux for 12 h, cooled, and filtered through a short silica column using chloroform as the eluent. The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel using cyclohexane/CH₂Cl₂ (2:1) as the eluent, affording impure **11**, which was deprotected prior to further purification.

Zn(*II*)-β-*Ethynyltetraphenylporphyrin* **12**. To a solution of **9** (100 mg, 0.13 mmol) in THF (20 mL) was added TBAF (410 mg, 1.56 mmol) with vigorous stirring. After 15 min, glacial acetic acid (1 mL) was added, and the reaction mixture was filtered through a silica funnel using CH₂Cl₂ as the eluent to afford **12** (89 mg, 98%) as a purple crystalline solid. UV/vis (CHCl₃): λ_{max} 429, 558, 598 nm. ¹H NMR (400 MHz, CDCl₃): δ 3.28 (s, 1H CC-H), 7.64 (d, 2H), 7.68–7.83 (m, 10H), 8.09 (d, 2H), 8.18 (m, 6H), 8.88 (m, 2 β-H), 8.91 (m, 4 β-H), 9.22 (s, 1 β-H) ppm. MALDI-TOF: *m/z* 702.65 [M⁺].

 $H_2-\beta$ -Ethynyltetraphenylporphyrin 13. To a solution of 12 (25 mg) in CH₂Cl₂ (15 mL) was added TFA (0.5 mL). The reaction mixture was stirred vigorously at room temperature for 15 min, washed with water and saturated sodium hydrogen

carbonate, and dried with sodium sulfate. The solvent was removed under reduced pressure to furnish **13** in near quantitative yield. UV/vis (CHCl₃): λ_{max} 425, 521, 556, 598, 654 nm. ¹H NMR (400 MHz, CDCl₃): δ –2.82 (s, 2H), 3.28 (s, 1H CC–H), 7.64 (d, 2H), 7.68–7.83 (m, 10H), 8.09 (d, 2H), 8.18 (m, 6H), 8.88 (m, 2 β -H), 8.91 (m, 4 β -H), 9.22 (s, 1 β -H) ppm. MALDI-TOF: m/z 639.39 [M⁺].

Ni(*II*)-β-*Ethynyltetraphenylporphyrin* **14**. To a solution of **11** (100 mg, 0.13 mmol) in THF (20 mL) was added TBAF (410 mg, 1.56 mmol) with vigorous stirring. After 15 min, glacial acetic acid (1 mL) was added, and the reaction mixture was filtered through a silica funnel using CH₂Cl₂ as the eluent to afford **34** (88 mg, 97%) as a purple crystalline solid. UV/vis (CHCl₃): λ_{max} 423, 536 nm. ¹H NMR (400 MHz, CDCl₃): δ 3.20 (s, 1H CC-H), 7.58 (d, 2H), 7.64-7.72 (m, 10H), 7.89 (d, 2H), 7.98 (m, 6H), 8.68 (m, 1 β-H), 8.71 (m, 4 β-H), 8.80 (m, 1 β-H), 8.98 (s, 1 β-H) ppm. MALDI-TOF: *m*/*z* 695.94 [M⁺].

 $Zn(II) - \beta$ -Butadiynylporphyrin - C_{60} Dyad 1. To a solution of 4 (20 mg, 26.2 μ mol) and 12 (55 mg, 78.3 μ mol) in chlorobenzene (70 mL) at room temperature were added CuCl (250 mg, 2.5 mmol) and TMEDA (0.4 mL) under a dry oxygen atmosphere. The reaction mixture was stirred at room temperature for 2 h and filtered through a silica funnel using CS₂ the as eluent. The solvent was removed under reduced pressure, and the crude product was dissolved in CS2 and transferred onto a silica funnel. Separation of the zinc porphyrin $-C_{60}$ dyad from the zinc porphyrin homodimer was accomplished by eluting the silica funnel with CS₂. The dyad was further purified by preparative TLC on silica gel using CS₂ the as eluent to furnish dyad 1 (10.3 mg, 27%). UV/vis (CHCl₃): λ_{max} 257, 437, 563, 603 nm. ¹H NMR (400 MHz, CDCl₃): δ 3.42 (s, 3H, C₆₀-CH₃), 7.67–7.88 (m, 12H), 7.98–8.24 (m, 8H), 8.81–8.97 (m, 6β -H), 9.33 (s, 1 β -H) ppm.MALDI-TOF: m/z 1461.13 [M⁺].

 $H_2-\beta$ -Butadiynylporphyrin-C₆₀ Dyad **2**. To a solution of **1** (6 mg) in CH₂Cl₂ (10 mL) was added TFA (0.2 mL). The reaction mixture was stirred vigorously at room temperature for 10 min, washed with water, and dried with sodium sulfate. The solvent was removed under reduced pressure, and the dyad was further purified by preparative TLC on silica gel using CS₂, affording **2** (4.4 mg). UV/vis (CHCl₃): λ_{max} 256, 432, 526, 563, 603, 659 nm. ¹H NMR (400 MHz, CDCl₃): δ -2.62 (s, 2H), 3.51 (s, 3H, C₆₀-CH₃), 7.64-7.86 (m, 12H), 8.08-8.29 (m, 8H), 8.72-8.98 (m, 6 β-H), 9.21 (m, 1 β-H) ppm.MALDI-TOF: *m/z* 1397.98 [M⁺].

 $Ni(II) - \beta$ -Butadiynylporphyrin - C₆₀ Dyad 3. To a dry, oxygenated solution of 4 (15 mg, 19.7 μ m) and 14 (41 mg, 59 μ m) in chlorobenzene (50 mL) were added CuCl (200 mg, 2 mmol) and TMEDA (0.3 mL) at room temperature. The reaction mixture was stirred at room temperature for 90 min and filtered through a silica funnel using CS₂ as the eluent. The solvent was removed under reduced pressure, and the crude product was dissolved in CS_2 and transferred onto a silica funnel. Separation of the nickel porphyrin $-C_{60}$ dyad from the nickel porphyrin homodimer was accomplished by eluting the silica funnel with CS₂. The dyad was further purified by preparative TLC on silica gel using CS₂ as the eluent to furnish dyad 3 (9 mg, 31%). UV/vis (CHCl₃): λ_{max} 257, 430, 541, 579 nm. ¹H NMR (400 MHz, CDCl₃): δ 3.48 (s, 3H, C₆₀-CH₃), 7.63-7.81 (m, 12H), 7.96–8.08 (m, 8H), 8.68–8.74 (m, 5 β -H), 8.82 (m, 1 β -H), 9.13(s, 1 β -H) ppm. MALDI-TOF: m/z 1454.56 $[M^+].$

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Supporting Information Available: UV/vis absorption spectra for ZnTPP, zinc porphyrin 5, and zinc porphyrin 9, differential absorption spectra for NiTPP and ZnP-C₆₀ dyad 1, pump-probe decay component and time-resolved transient absorption spectra for $ZnP-C_{60}$ **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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