ARTICLE

Wiley

Is it common for charge recombination to be faster than charge separation?

Eli M. Espinoza¹ Duoduo Bao² Maciej Krzeszewski^{2,3} D Aniel T. Gryko³ Valentine I. Vullev^{1,2,4,5,6}

¹Department of Chemistry, University of California, Riverside, California

²Department of Bioengineering, University of California, Riverside, California

³Instytut Chemii Organicznej, Polskiej Akademii Nauk, Warsaw, Poland

⁴Department of Biochemistry, University of California, Riverside, California

⁵Materials Science and Engineering Program, University of California, Riverside, California

⁶Instituto de Química, Universidade de São Paulo, Cidade Universitária, São Paulo, Brazil

Correspondence

Daniel T. Gryko, Instytut Chemii Organicznej, Polskiej Academii Nauk, Kasprzaka 44-52, 01-224 Warsaw, Poland. Email: dtgryko@icho.edu.pl Valentine I. Vullev, Department of Chemistry, University of California, Riverside, CA 92521. Email: vullev@ucr.edu

Funding information

Fulbright Commission Brazil; Division of Chemical, Bioengineering, Environmental, and Transport Systems, Grant/Award Number: CBET 0923408; Narodowe Centrum Badań i Rozwoju, Grant/Award Number: PL-TWIII/17/2016; Division of Chemistry, Grant/Award Numbers: CHE 1465284, CHE 1800602

Present address

Eli M. Espinoza, Department of Bioengineering, University of California, Berkeley, CA 94720.

Duoduo Bao, PrimusLabs, Santa Maria, CA 93455.

Maciej Krzeszewski, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan.

Abstract

Attaining long-lived charge-transfer (CT) states is of the utmost importance for energy science, photocatalysis, and materials engineering. When charge separation (CS) is slower than consequent charge recombination (CR), formation of a CT state is not apparent, yet the CT process provides parallel pathways for deactivation of electronically excited systems. The nuclear, or Franck-Condon (FC), contributions to the CT kinetics, as implemented by various formalisms based on the Marcus transition-state theory, provide an excellent platform for designing systems that produce long-lived CT states. Such approaches, however, tend to underestimate the complexity of alternative parameters that govern CT kinetics. Here we show a comparative analysis of two systems that have quite similar FC CT characteristics but manifest distinctly different CT kinetics. A decrease in the donor-acceptor electronic coupling during the charge-separation step provides an alternative route for slowing down undesired charge recombination. These examples suggest that, while infrequently reported and discussed, cases where CR is faster than CS are not necessarily rare occurrences.

KEYWORDS

charge recombination, charge separation, charge transfer, electrets, electronic coupling, singlet-triplet mixing

1 | INTRODUCTION

-WILEY

This work shows how electronic coupling and singlet-triplet mixing affect the ratio between the rate of photoinduced charge separation (CS) and consecutive charge recombination (CR). We focus on two donor-acceptor dyads (Scheme 1) that show different charge-transfer (CT) behavior. In one of the dyads, CS occurs faster than CR and, therefore, we observe the formation of a CT state. In the other dyad, CR is faster than CS, which prevents the accumulation of a CT state. Evidence for triplet formation provides a plausible rationale for the retardation of CR rates. Concurrently, molecular-orbital (MO) analysis reveals changes in donor-acceptor electronic coupling that encompass additional underlying reasons for the differences in CT behavior and provides a broadly applicable implication of how to attain CR that is slower than the preceding CS.

As one of the most fundamental processes in natural and manmade systems, CT ensures energy flow and conversion, as well as the operation of electronic and photonic materials and devices.^{1–6} Photoinduced CT, a principle process in photosynthesis, has sustained life on Earth for billions of years.^{7–9} Indirectly, sunlight remains the main energy source for our modern lives via the burning of photosynthetically generated fossil fuels,¹⁰ although photovoltaic, photothermal, and other solar-driven technologies present a highly promising and environmentally benign alternative.^{11–13} After all, the energy flux of solar light that hits the Earth's surface surpasses the current and projected global energy-consumption rates by orders of magnitude.^{14–16}

Inefficient means of energy conversion and storage, along with the prohibitive cost frequently needed for improving the efficacy, currently prevents solar from becoming a large-scale energy technology worldwide.^{17,18} In nature, photosynthetic reaction centers mediate the initial CS, which is followed by a cascade of electron-transfer (ET) steps, in 100% quantum efficiency, that is, CR involving back ET to the special pair does not occur in photosynthesis.¹⁹ Conversely, undesired CR in photovoltaic and other engineered devices is a source of losses. Increasing the CS driving force $(-\Delta G_{CS}^{(0)})$ can ensure high quantum efficiencies, but it also compromises the magnitude of the voltage that PV devices can possibly produce, decreasing the overall power-conversion efficiencies. Therefore, the paradigms that biology displays provide incomparable learning grounds not only for the basic sciences but also for applied engineering. While components of natural systems may not be the best choices for incorporating in manmade devices, utilizing ideas from biology provides an important path for progress, as reflected by the evolution from biomimetics to biological inspiration.¹⁵

The achievement of long-lived photogenerated CT states, where CR is considerably slower than CS, is of paramount importance for energy science and engineering. A large CS rate ensures a high quantum efficiency of CT by making the contribution of other pathways of nonradiative and radiative deactivation of the photoexcited sensitizer negligible. Concurrently, small rates of CR ensure that the CT states live long enough to do useful work, for example, generate electricity, or induce chemical conversions. Therefore, the ratio between the rates of CS and CR provides a good guideline for the potential utility of light-driven CT systems.

Frequently, CR is the most likely outcome for Coulombically trapped CT states at donor-acceptor interfaces, especially in nonpolar organic media.²⁰ Taking advantage of electric forces, which can involve the movement of protons along with electrons, that is, proton-coupled electron transfer,^{21–25} hole transfer (HT) to polarize interfaces for aiding ET,²⁶ or permanent electric dipoles, that is, from electrets,^{27–30} to guide the different CT steps,^{4,31–33} can improve the chance of obtaining long-lived CT states by altering the driving forces of CS and CR.³⁴

In general, Marcus transition-state theory offers a promising paradigm for ensuring long-lived CT states.^{35,36} Small driving forces of CS usually place it in the normal region and even close to the tip of the Marcus curve, depending on how $-\Delta G_{CS}^{(0)}$ compares with the reorganization energy (λ). Concurrently, a small $-\Delta G_{CS}^{(0)}$ leads to a large driving forces for CR, placing it in the Marcus inverted region that ensures slow CR rates. As attractive as this way of thinking is, it assumes that λ and the donor-acceptor electronic coupling for CS and CR are similar which may not always be the case. It is incorrect, indeed, to place CS and CR on the same Marcus curve: CS represents a transition from the locally excited (LE) to the CT state and CR from the CT state to the ground state (GS).

The above arguments for attaining long-lived CT states focus on the driving forces of CS and CR, as well as on the reorganization energy, that is, on the Franck-Condon (FC), or nuclear, component of the CT kinetics.⁴ Donor-acceptor electronic coupling provides another major contribution to the CT kinetics. Its evaluation, however, is not as easy as that of $\Delta G^{(0)}$ and λ , which are commonly used for estimating the FC term for nonadiabatic CT.⁴ Furthermore, rational designs for achieving strong electronic coupling for CS, while weakening it for the undesired CR steps, appears prohibitively challenging especially when the forward and back CT involve the same pathways.

Meanwhile, much of the analysis of CT in organic systems focuses on singlet manifolds and does not accommodate for spin transitions. Singlet-triplet mixing in biradical CT states, for example, provides alternative routes, such as CR leading to low-lying triplet states (TSs).^{37–40}

Herein, we present two donor-acceptor dyads (Scheme 1) that have similar $-\Delta G_{\rm CS}^{(0)}$. Both of them mediate subnanosecond photoinduced CS with rate constants ($k_{\rm CS}$) of 13 $\times 10^9$ s⁻¹ and 2.5 $\times 10^9$ s⁻¹, that is, differing by a factor of five. The CR rate constants ($k_{\rm CR}$) for the two dyads are, **SCHEME 1** Donor-acceptor dyads composed of electret residues, 5Pip and Aaa, as electron donors, and pyrene (Py) and diketopyrrolopyrrole (DPP) as acceptors. 5Pip and DPP are the photosensitizers in the dyads



659

however, drastically different. For one of the dyads, the CR rate is more than 40 times slower than the rate of CS. The other has a faster CR rate than CS, that is, $k_{CS} \le k_{CR}$, leading to quenching of the LE state without accumulation of the radical ions comprising the CT state. By itself the FC analysis of the CT kinetics cannot explain the observed trends. Considering the evidence for triplet formation and examining the donor-acceptor electronic coupling prove instrumental in elucidating the multifaceted requirements for attaining long-lived CT states.

2 | EXPERIMENTAL

2.1 | Materials

The spectroscopy-grade solvents were purchased from Fisher Scientific, and the synthesis and characterization of the conjugates used for this study, 5-piperidinylanthranilamide (5Pip), diketopyrrolopyrrole (DPP), 2-hexanamido-5-(piperidin-*N*-yl)-*N*-(pyren-1-ylmethyl)benzamide (5Pip-Py), and *N*-(heptan-4-yl)-5-(2-(5-octyl-1,4-dioxo-3,6-bis(4-(trifluoro-methyl)phenyl)-4,5-dihydropyrrolo[3,4-c]pyrrol-2(1H)-yl)-acetamido)-2-(2-propylpentanamido)benzamide (Aaa(DPP)) (Scheme 1) have been previously described.^{31,34}

2.2 | Methods

The transient-absorption (TA) spectra were recorded using a Helios pump-probe system (Ultrafast Systems, Sarasota, FL, USA) with a laser source comprising a SpitFire Pro 35F regenerative amplifier (Spectra-Physics, Santa Clara, CA, U.S.A.) and OPA-800CU (Newport Corporation, Newport, CA, USA).⁴¹ Global fit analysis was performed using Surface Xplorer (Ultrafast Systems, Sarasota, FL, USA).⁴² Steady-state optical spectroscopy provided a means for estimating the excitation energies and testing for solvatochromic behavior of the chromophores.^{43–45} Cyclic voltammetry and spectroelec-trochemistry allowed for determining the reduction potentials (needed for estimating the driving forces), and the absorption spectra of the radical ions (needed for the assignments of the TA features of the CT states).^{34,46,47}

The *N*-acylated anthranilic residues (5Pip and Aaa), DPP and 1-methylpyrene (Figure 3) were modeled using density functional theory (DFT). For saving computational time, the aliphatic chains of 5Pip, Aaa, and DPP were truncated to two carbons. The DFT calculations were performed at the B3LYP/6-311+G(d,p) level of theory for the gas phase using Gaussian 09.³⁴ We used spin-unrestricted calculations for modeling the doublet states, that is, the radical cations and the radical anion.⁴⁸ For 5Pip, in addition to the optimized ground state, S₀, we calculated the FC excited state, S₁, for the gas phase and dichloromethane (DCM) as implemented by the polarizable continuum model for that solvent. The total electron density was mapped with the electrostatic potential.

3 | RESULTS AND DISCUSSION

3.1 | Kinetic models

This study focuses on two electron donor-acceptor dyads that have similar structural and thermodynamic features (Scheme 1) but manifest distinctly different CT kinetics. (1) The donors in both dyads are electron-rich anthranilamide residues, that is, 5Pip^{34,49,50} or Aaa,^{31,51} with permanent electric dipoles. Pyrene (Py) and an electron-deficient diketopyrrolopyrrole (DPP) serve as acceptors. (2) A methylene linker connects the donor and the acceptor in each dyad providing a CT pathway through two σ -bonds that results in nonadiabaticity. (3) In both dyads, a relatively small driving force, that is, $\Delta G_{\rm CS}^{(0)} \approx -0.1$ eV, guides the initial photoinduced CS. With excitation energy, E_{00} , corresponding to the violet and bluegreen spectral regions, such a small CS driving force results in a large $-\Delta G^{(0)}$ of CR. Thus, relatively nonpolar media, such as DCM, ensure the reorganization energy is small enough to place the CS kinetics in the Marcus normal region while pushing CR into the inverted region.^{31,34,52} These considerations from the Marcus transition-state theory, therefore, suggest that, for similar donor-acceptor electronic coupling in the LE and the CT states, such $-\Delta G_{CS}^{(0)}$ and $-\Delta G_{CR}^{(0)}$ should ensure CR is slower than CS. For Aaa(DPP), however, this is not the case.

In both dyads, the permanent electric dipoles of the donors point toward the acceptors.^{31,34} In 5Pip, the dipole is oriented from the N-terminal amide to position 6 of the aromatic ring next to the C-terminal carbonyl, that is, the negative pole of the residue dipole points toward its N-terminus whereas the positive pole points toward the carbon in the aromatic ring between the C-terminal amide and the piperidinyl side chain.^{34,49} In Aaa, the dipole points from the N-terminal amide to the side-chain amide at position 5.³¹ A moderately nonpolar solvent, such as DCM, allows the dipole-generated field from the donor to permeate to the acceptor, which not only favors the initial CS (involving ET along the dipole) in 5Pip-Py,³⁴ but also makes it possible in Aaa(DPP).³¹

A principal difference between the two dyads is that while in 5Pip-Py the photoinduced CS step occurs via ET, in Aaa(DPP) it is via HT. The electron donor, 5Pip, acts as the photosensitizer in the 5Pip-Py dyad. The alkylpyrene acceptor is a UV absorber, and selective excitation of 5Pip at 390 nm leads to the LE state, ¹5Pip*-Py, that induces ET from the lowest unoccupied molecular orbital (LUMO) of the donor to the LUMO of the acceptor (Scheme 2A). Conversely, the electron acceptor, DPP, is the photosensitizer in Aaa(DPP) that we selectively excite within the visible spectral region. This locally excited state, Aaa(¹DPP*), induces ET from the highest occupied molecular orbital (HOMO) of the donor to the singly occupied "HOMO" of ¹DPP*, that is, transfer of a hole from the photoexcited acceptor to the donor (Scheme 2B).⁴ For simplicity, the MO diagrams showing the fundamental differences between photoinduced ET and HT⁴ do not depict the CT dynamics involving triplet pathways. Instead, the Jablonski diagrams for the dyads clearly illustrate the excited-state dynamics involving triplet manifolds (Scheme 3).

As the electron donors are nonnative amino acid residues, adopting the nomenclature of protein chemistry allows for describing the dyads. Specifically, a moiety connected to the C-terminal amide of the residue is hyphenated, for example, 5Pip-Py, and a moiety that is connected to the side chain is placed in parenthesis, for example, Aaa(DPP) (Scheme 1).

3.2 | When charge recombination is slower than charge separation

Photoexcitation of 5Pip-Py leads to the formation of the LE state characterized by the TA features of ¹5Pip*: that is, broad bands in the violet and the red regions of the spectra (Figure 1A).³⁴ The decay of ¹5Pip* accompanies the rise of the CT state, exhibiting the overlapping absorption bands of Py^{•-} at 500 nm and 5Pip^{•+} at 580 nm (Figure 1A) as assigned from spectroelectrochemical analysis.³⁴

The TA dynamics are consistent with the initial photoinduced CS step in the 5Pip-Py dyad (Scheme 3A). The TA spectral evolution reveals two isosbestic points (Figure 1A) indicating that CS is the sole transition, that is, no other parallel processes, such as internal conversion or radiative decay of the LE to the ground state, interfere with the CS step. Global fit multiexponential analysis confirms the LE \rightarrow CT transition. For $\tau = 76$ ps, the positive amplitudes at the region where ¹5Pip* absorbs and the negative amplitudes at the TA of the radical ions (Figure 1B) reveal a simultaneous decay of the LE and growth of the CT state with $k_{CS} = 1.3 \times 10^{10}$ s⁻¹.

The lifetime of the singlet-excited state of 5Pip without an electron acceptor is 18.2 ns (Figure 1C). That is, CS is more than 200 times faster than the other processes leading to the deactivation of ¹5Pip*, indicating that the CS quantum yield of this dyad is practically quantitative.

The decay of the CT state, $5Pip^{\bullet+}-Py^{\bullet-}$, leads to the rise of a small band at about 420 nm (Figure 1A,B) that is consistent with the formation of the TS of the acceptor, ${}^{3}Py^{*}$.³⁴ Deactivation of CT states to low-lying triplets (Scheme 3A) is not unusual for pyrene-containing conjugates.³⁸ The global fit analysis reveals negative amplitudes for $\tau = 3.2$ ns in the region where the radical ions absorb and positive amplitudes at the narrow region around 420 nm (Figure 1B). This trend indicates that the decay of the CT state leads to $5Pip^{-3}Py^*$ (${}^{3}k_{CR} = 3.0 \times 10^{8} \text{ s}^{-1}$, Scheme 3A), with no evidence for CR leading directly to the ground state within the time frame of the TA measurements. The TA dynamics, leading into the nanosecond time domain, yield a mixture of CT and TS, as is evident from the shape of the $\Delta A(\lambda)$ curve (Figure 1B).

The photoinduced dynamics start with a singlet LE state, for which we have clear evidence in the TA spectra (Figure 1A). The triplet excited state of the sensitizer, ³5Pip*, has a broad TA band at about 465 nm³⁴ that we do not observe. Therefore, the singlet LE state induces CS that leads to the formation of a singlet radical-ion pair, that is, ¹CT (Scheme 3A).



SCHEME 3 Jablonski diagrams depicting the excited-state dynamics of electron donor-acceptor dyads, 5Pip-Py and Aaa(DPP)

Singlet-triplet mixing within the radical ion pair leads to ³CT that forces CR to produce the lowest lying TS, which is that of the acceptor, instead of the GS, which has a singlet character (Scheme 3A). Meanwhile, because of the relatively weak donor-acceptor electronic coupling, the ¹CT and ³CT states are almost isoenergetic (Scheme 3A).³⁹

This phenomenon is different to cases involving organic sensitizers that have a high propensity for intersystem crossing (ISC), which either leads to the formation of triplet CT states, or does not allow CS if the triplet excitation energy is below the CT energy level.^{53,54} Such triplet CT manifolds have been known for quite some time, and they can affect the performance of organic devices.^{55–57}

These findings pose an important question about what is responsible for the relatively long lifetime of the photogenerated CT state. Is it the introduction of triplet character in the CT state? Is it the large $-\Delta G_{CR}^{(0)}$, placing the CR kinetics in the Marcus inverted region? Does donor-acceptor electronic coupling have anything to do with it? After all, for the 5Pip-Py dyad, $k_{CS} / {}^{3}k_{CR} = 43$.

Because the lowest TS of pyrene is about 2.1 eV above its S₀ state,⁵⁸ $\Delta G^{(0)}$ of the CR leading the triplet is about –0.8 eV. Concurrently, the estimated reorganization energy is in the range of about 0.5-0.6 eV. Therefore, ${}^{3}k_{CR}$ in the inverted region is closer to the tip of the Marcus curve than k_{CS} is in the normal region. Contrary to the observed results, this feature should make $k_{CS} < {}^{3}k_{CR}$ if the donor-acceptor electronic coupling and the reorganization energy for CS and CR are similar. Expected differences in the reorganization energy of the LE \rightarrow CT and CT \rightarrow TS transitions would shift the tips of the Marcus curves for CS and CR away from each other. These differences, however, cannot be large enough to result in $k_{CS} \gg {}^{3}k_{CR}$. Therefore, placing CR in the Marcus inverted region cannot account for the observed trend.

661

While ISC is an inherently slow process, the transition from a triplet CT state to the TS of the acceptor does not involve ISC, that is, a spin-forbidden change in multiplicity. Hence, (1) the singlet CT state has to live long enough to undergo ISC instead of CR to the S₀ ground state and/or (2) the formed triplet CT state has to undergo slow CR to 5Pip-³Py* to concur with the observed kinetic trends. These considerations illustrate that the triplet CT pathways cannot account for the observed ³k_{CR} that is smaller than k_{CS} .



FIGURE 1 Excited-state dynamics of 5Pip-Py in DCM as revealed by time-resolved spectroscopy. (A) TA spectra of 5Pip-Py recorded at different times after photoexcitation ($\lambda_{ex} = 390$ nm, 4 µJ per pulse). (B) Wavelength dependence of the preexponential parameters, α_i , obtained from triexponential global fits of the TA data for 5Pip-Py, $\Delta A(\lambda,t) = \Delta A_{\infty}(\lambda) + \Sigma_i \alpha_i(\lambda) \exp(-t/\tau_i)$. The second component, τ_2 , depicts the CS step, that is, the concurrent decay of the LE and the growth of the CT state, with $k_{CS} = 1.3 \times 10^{10}$ s⁻¹, and the third component, τ_3 – the CR leading to the triplet-excited state, 5Pip-3Py*, with ${}^{3}k_{CR} = 3.0 \times 10^{8}$ s⁻¹ (Scheme 3A). (C) Emission decay of 5Pip in DCM obtained using time-correlated single photon counting ($\lambda_{ex} = 406$ nm, $\lambda_{em} = 460$ nm). Monoexponential data fits yield $\tau = 18.2$ ns; analysis of steady-state absorption and emission spectra produces $\Phi_f = 0.46$; hence, $k_f = \Phi_f / \tau = 2.5 \times 10^7$ s⁻¹ and $k_{nd} = (1 - \Phi_f)$ / $\tau = 3.0 \times 10^7$ s⁻¹ (Scheme 3A)

The experimental evidence and the mechanistic consideration for the excited-state dynamics of 5Pip-Py render differences in the donor-acceptor electronic coupling the most plausible reason for the observed CS that is faster than the consequent CR.

3.3 | When charge recombination is faster than charge separation

Photoexcitation of Aaa(DPP) leads to the formation of the LE state that has the characteristics of ¹DPP*, that is, overlapping broad TA bands in the red and NIR spectral region associated with $S_1 \rightarrow S_{n+1}$ transitions of DPP. The GS bleach (B) and the stimulated emission (SE) in the blue-green region accompany the ¹DPP* TA bands (Figure 2A).⁶ Global-fit analysis reveals that Aaa(¹DPP*) decays directly to its GS without any detectable intermediate state (Figure 2B). The rate of this decay is about 21 times faster than the deactivation of ¹DPP* without an electron donor, which has a lifetime of 8.3 ns (Figure 2C). Hence, the process that leads to the accelerated deactivation of Aaa(¹DPP*) has a quantum yield of about 0.95.

The characteristics of the dyads, such as the reduction potentials of the donor and the acceptor, along with the excitation energy E_{00} of DPP, indicate that CS is responsible for the observed deactivation of the LE state Aaa(¹DPP*) (Scheme 3B).³¹ Furthermore, an electron donor (attached to the N-terminal of the dyad), which oxidizes at less positive potentials than Aaa, can extract the hole from the short-lived Aaa⁺(DPP⁺) CT state faster than the CR step.³¹ This feature allows accumulation and detection of the radical anion DPP⁻ and provides additional evidence that the process, which efficiently quenches the LE state is, indeed, CS.³¹

When $k_{CS}/k_{CR} \leq 1$, the quenching of the LE state is apparent, however, the accumulation of any CT species is not observed (Figure 2A,B). It clearly shows that CS becomes the rate-limiting step for the transition LE \rightarrow CT \rightarrow GS, making it appear identical to a one-step deactivation of the LE state to the GS, that is, LE \rightarrow GS (Schemes 2B and 3B).

With $\Delta G_{CR}^{(0)} = -2.3$ eV, the CR kinetics is deep in the Marcus inverted region and yet $k_{CS} \le k_{CR}$. This consideration clearly shows that the CS and CR kinetics cannot be on the same Marcus curve. A difference in the reorganization energies for CS and CR that exceeds 1.5 eV can account for the observed $k_{CS} \le k_{CR}$. Such a large difference, however, is quite implausible. Most likely, differences in the donor-acceptor electronic coupling for the CS and CR processes provide the underlying reason for the observed trends in the excited-state dynamics of Aaa(DPP).

3.4 | Donor-acceptor electronic coupling

Designing systems that mediate CS close to the tip of the Marcus curve, that is, $-\Delta G_{\rm CS}^{(0)} \approx \lambda$, and with CR kinetics deep into the Marcus inverted region, provides some assurance that $k_{\rm CS} > k_{\rm CR}$. As the CT dynamics of Aaa(DPP) reveal, this condition is not sufficient. Concurrently, the CT dynamics of 5Pip-Py suggest that introducing triplet character to the CT state considerably slows down the CR leading directly to the



FIGURE 2 Excited-state dynamics of Aaa(DPP) in DCM as revealed by time-resolved spectroscopy. (A) TA spectra of Aaa(DPP) recorded at different times after photoexcitation ($\lambda_{ex} = 465 \text{ nm}, 4 \mu \text{J}$ per pulse, B = ground-state bleach, SE = stimulated emission). (B) Wavelength dependence of the preexponential parameters, αi , obtained from biexponential global fits of the TA data for Aaa(DPP), $\Delta A(\lambda,t) = \Delta A_{\infty}(\lambda) + \Sigma_i \alpha_i(\lambda) \exp(-t/\tau_i)$. The two components, τ_1 and τ_2 , depict the multiexponential character of the decay of 1DPP* dominated by CS with $k_{CS} = 2.5 \times 10^9 \text{ s}^{-1}$ extracted intensity-averaged lifetimes (Scheme 3B). (C) Emission decay of DPP in DCM obtained using time-correlated single photon counting ($\lambda_{ex} = 406 \text{ nm}$, $\lambda_{em} = 540 \text{ nm}$). Monoexponential data fits yield $\tau = 8.3 \text{ ns}$; analysis of steady-state absorption and emission spectra produces $\Phi_f = 0.85$; hence, $k_f = \Phi_f / \tau = 1.0 \times 10^8 \text{ s}^{-1}$ and $k_{nd} = (1 - \Phi_f) / \tau = 1.9 \times 10^7 \text{ s}^{-1}$ (Scheme 3B)

singlet GS. Conversely, many systems that exhibit $k_{\text{CS}}/k_{\text{CR}} > 1$ do not involve the formation of biradical triplet CT states.

Differences in the donor-acceptor electronic coupling for the CS and CR steps provide an alternative for attaining $k_{\rm CS} \gg k_{\rm CR}$. Even with the great advances of computational tools, estimation of electronic coupling is still a challenging and involved process. Furthermore, the rational design of systems that adjust the strength of donor-acceptor coupling in order to control the kinetics of CS and CR currently appears implausible.

One important commonality between the two dyads is the methylene that links the donor with the acceptor (Scheme 1). While the methylene linkers provides sufficient electronic coupling for nonadiabatic CT,^{31,34} the two σ -bonds ensure that the donor and the acceptor do not perturb the electronic properties of each other.⁵⁹ Therefore, studies on the donors and the acceptors by themselves can provide truly reliable information about their features in the dyads.

The dyad Aaa(DPP) undergoes photoinduced CS with 95% quantum efficiency at a relatively small $-\Delta G_{\rm CS}^{(0)}$ of about 0.1 eV, that is, ~ $4k_{\rm B}T$. The overwhelmingly fast CR, however, dampens the enthusiasm for potential utility of such systems.

The CS in Aaa(DPP) proceeds via HT involving the HOMOs of the donor and the acceptor (Scheme 2B). The methylene links the amide side chain at position 5 of Aaa with the lactam nitrogen of DPP. The HOMO of Aaa delocalizes over its side-chain amide, and the HOMO of DPP over its lactam nitrogens (Figure 3B). This delocalization of the frontier orbitals is favorable for HT through the two bonds linking the photoexcited acceptor to the ground-state donor.

Conversely, CR involves the coupling between the singly occupied MOs of the donor and the acceptor. Analysis of the radical ions reveals that the electron spin density of Aaa^{•+} extends over its side-chain amide, and DPP^{•-} over its lactams (Figure 3D). Despite the nodes on the lactam nitrogens of DPP^{•-}, and the excess spin down region localized on the amide carbonyl of the side-chain amide of Aaa^{•+}, this spin-density distribution suggests that only two linker bonds separate the positive and the negative charges in Aaa^{•+}(DPP^{•-}). While this analysis is qualitative and does not provide the exact donor-acceptor electronic-coupling matrices for Aaa(¹DPP^{*}) and Aaa^{•+}(DPP^{•-}), it suggests that both CS and CR involve electron tunneling over a distance of two covalent bonds.

These results suggest similar donor-acceptor electronic coupling in Aaa(¹DPP*) and Aaa^{•+}(DPP^{•-}), and, according the Marcus transition-state theory, CR should be in the inverted region and expectedly slower than CS (assuming similar λ for CR and CS), which is not the case. What are the possible reasons for the observed $k_{CS}/k_{CR} \leq 1$? If λ for CR is larger than λ for CS (which is possible), the CR kinetics should not be too deep into the inverted region. After all, the CS kinetics are in the normal region but not near the activationless regime at the tip of the Marcus curve, that is, $\Delta G_{CS}^{(0)} \approx -0.1$ eV and $\lambda_{CS} \approx -0.4$ eV.³¹ Therefore, CR can still operate in the inverted region, but if it is closer to the tip of the Marcus curve than CS is, k_{CR} can become larger than k_{CS} . As attractive as this explanation appears, it cannot alone account for the observed trends. Even if $\lambda_{CR} > \lambda_{CS}$, this

WILEY



FIGURE 3 Frontier MOs and electron spin-density distributions of the donors and the acceptors of the two dyads (Scheme 1) obtained from DFT calculations for the gas phase at the B3LYP/6-311+G(d,p) level of theory. The arrows indicate the points where the donors and the acceptors are linked in the dyads. (A) Frontier MOs of 5Pip and Py, that is, the donor and the acceptor of 5Pip-Py. (B) Frontier MOs of Aaa and DPP, that is, the donor and the acceptor of Aaa(DPP). (C) Electron spin density of the radical ions composing the CT state of 5Pip-Py. (D) Electron spin density of the radical ions composing the CT state of Aaa(DPP). (C,D) Black, excess spin up, that is, the radical ion; and white, excess spin down

difference between λ_{CR} and λ_{CS} has to account for the 2.2 eV difference between $\Delta G_{CS}^{(0)}$ and $\Delta G_{CR}^{(0)}$. Therefore, differences in the donor-acceptor electronic coupling in the LE and the CT state have to contribute to the observed $k_{CS}/k_{CR} \leq 1$.

The type of frontier orbitals involved encompass a principal difference between CS and CR in Aaa(DPP). While CS occurs between the HOMOs of the donor and the acceptor, CR involves the LUMO of the acceptor and the HOMO of the donor (Scheme 2B). In general, LUMOs tend to be more diffused than HOMOs and while not depicted by the orbital graphs (Figure 3), the evanescent components of the wavefunctions of LUMOs extend further than those of HOMOs. Hence, the donor-acceptor electronic coupling for CR, involving the DPP LUMO, should be larger than that for CS, involving the DPP HOMO. Furthermore, the higher energy of electrons in the LUMOs (in comparison with those in HOMOs) would increase their probability for tunneling through potential barriers as defined by the covalent bonds linking the donor with the acceptor. Indeed, despite the identical $\Delta G_{CS}^{(0)}$ for the two dyads, the CS in 5Pip-Py, which involves the LUMOs of the donor and the acceptor, is about five times faster than the CS in Aaa(DPP), which involves the HOMOs of the donor



FIGURE 4 Electron densities, along with the orientations of the permanent electric dipole moments, μ , of the ground-state, S_0 , and the lowest singlet-excited-state electronic structure, S_1 , in the optimized S_0 geometry, that is, FC S_1 , obtained from DFT calculations. For S_0 and the FC S_1 states in the gas phase, $|\mu| = 5.9$ D, and in DCM, $|\mu| = 8.2$ D

and the acceptor (Figures 1B and 2B). This illustration of how ET from LUMOs can yield faster CT kinetics than HT from HOMOs can also shed light on why in Aaa(DPP) $k_{CS} \le k_{CR}$.

The electronic-coupling features governing the CT dynamics in 5Pip-Py are quite different from those in Aaa(DPP). Considering that 5Pip-Py undergoes CS via ET (Scheme 2A), we examine the LUMOs of the donor and the acceptor. The LUMO and the HOMO of Py and the electron spin density distribution of Py^{•-} cover the four rings of this polycyclic aromatic moiety and extend a bit over the linking alkyl moiety (Figure 3A,C). These trends indicate favorable electronic coupling with Py for both CS and CR.

The frontier orbitals of 5Pip, along with the electron spin density distribution in 5Pip^{•+} reveal distinctly different trends in the electronic coupling for CS and CR. The LUMO of 5Pip extends over the C-terminal amide to which the acceptor is attached (Figure 3A), suggesting favorable electronic coupling for the photoinduced CS step. Conversely, the electron spin density of 5Pip^{•+} does not expand over its C-terminal amide, adding two extra covalent bonds to the tunneling pathway for CR (Figure 3C).⁴⁸

These results reveal a distinctly different donor-acceptor electronic coupling in the LE and CT states of the 5Pip-Py dyad. The ET tunneling distance for CR is twice as large as that for CS. Therefore, even without singlet-triplet mixing in the CT state, the CR should be slower than CS in 5Pip-Py. In addition, the increase in the lifetime of the CT state, which is induced by the decreased donor-acceptor electronic coupling, can aid the efficacy of triplet formation that further slows the CR step.

Meanwhile, the substantial difference between the delocalization of the HOMO and the LUMO of 5Pip, responsible for the changes in the donor-acceptor electronic coupling, does not significantly alter the magnitude and the direction of its electric dipole moment upon photoexcitation. While solvation increases the dipole magnitude of due to the Onsager field, ^{30,49,60} the computational analysis did not reveal differences between the dipole moments of the S₀ and the FC S₁ state of 5Pip (Figure 4). This feature of 5Pip is consistent with its relatively small molar extinction coefficient for the S₀ \rightarrow S₁ transition and the lack of detectable solvatochromism.^{34,49}

The electron spin density distribution in the radical anions, for example, DPP^{•-} and Py^{•-}, closely follows the delocalization of the LUMOs of the electroneutral species as depicted by GS computations (Figure 3). Similarly, the electron spin density distribution in the radical cations, for example, Aaa^{•+} and 5Pip^{•+}, resembles the HOMOs of Aaa and 5Pip (Figure 3). Therefore, relatively simple GS MO computations can serve as key guidelines for the design of CT systems. Comparing the findings for 5Pip-Py and Aaa(DPP) reveals that different delocalization in the HOMO and LUMO of the photosensitizer along the CT pathways can ensure electronic coupling ⁶⁶⁶ WILE

for CR that is smaller than that for CS and prove beneficial for attaining $k_{\rm CS} > k_{\rm CR}$.

4 | CONCLUSIONS

While it could be quite common for CR to occur faster than CS, the lack of direct evidence for the formation of CT states would tend to make such cases underreported. For nonadiabatic processes, formalisms based on the Marcus transitionstate theory provide an excellent predictive platform for evaluating CT kinetics. As included in the Marcus-Hush and Marcus-Levich-Jortner equations, donor-acceptor electronic coupling contributes profoundly to the CT rates. Its evaluation, however, is quite challenging and involved. Delocalization of the HOMOs and LUMOs of the donors and acceptors, obtained from straightforward computations, proves informative about changes in the electronic coupling after each CT step. Assessing how the coupling between the LE and CT states differs from the coupling between the CT and ground states is of the utmost importance for evaluating if CR can be slow enough to ensure the utility of the initial photoinduced CS. While somewhat qualitative, such MO evaluations, in combination with Marcus transition-state analysis, can provide important guidelines for the design of energy-conversion systems and electronic materials.

ACKNOWLEDGMENTS

Funding for this work was provided by the US National Science Foundation (grants CHE 1800602 and CHE 1465284, along with CBET 0923408 for the laser equipment), and by the National Centre for Research and Development (Polish-Taiwanese project PL-TWIII/17/2016). V.I.V. extends his gratitude to the Fulbright Commission Brazil for supporting his work at the University of São Paulo.

ORCID

Eli M. Espinoza https://orcid.org/0000-0002-0134-2833 *Maciej Krzeszewski* https://orcid.org/0000-0002-0940-7443 *Daniel T. Gryko* https://orcid.org/0000-0002-2146-1282 *Valentine I. Vullev* https://orcid.org/0000-0002-3416-9686

REFERENCES

- 1. Warren JJ, Winkler JR, Gray HB. Hopping maps for photosynthetic reaction centers. *Coord Chem Rev.* 2013; 257: 165-170.
- Brandt U. Structure and function of mitochondrial respiratory complex. *BIOspektrum*. 2014; 20: 267-270.
- 3. Metzger RM. Unimolecular electronics. *Chem Rev.* 2015;115:5056-5115.

- Derr JB, Tamayo J, Espinoza EM, Clark JA, Vullev VI. Dipoleinduced effects on charge transfer and charge transport. Why do molecular electrets matter. *Can J Chem.* 2018; 96: 843-858.
- Ilic S, Alherz A, Musgrave CB, Glusac KD. Thermodynamic and kinetic hydricities of metal-free hydrides. *Chem Soc Rev.* 2018; 47: 2809-2836.
- Purc A, Espinoza EM, Nazir R, et al. Gating that suppresses charge recombination–the role of mono-*N*-arylated diketopyrrolopyrrole. *J Am Chem Soc.* 2016; 138: 12826-12832.
- Kupitz C, Basu S, Grotjohann I, et al. Serial time-resolved crystallography of photosystem II using a femtosecond X-ray laser. *Nature*. 2014; 513: 261.
- Anbar AD, Duan Y, Lyons TW, et al. A whiff of oxygen before the great oxidation event. *Science*. 2007; 317: 1903-1906.
- Kopp RE, Kirschvink JL, Hilburn IA, Nash CZ. The paleoproterozoic snowball earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proc Natl Acad Sci USA*. 2005;102:11131-11136.
- Ciamician G. Photochemistry of the future. *Science*. 1912;36:385-394.
- 11. Gray HB. Powering the planet with solar fuel. *Nat Chem.* 2009;1:7.
- He Y, Hamann T, Wang D. Thin film photoelectrodes for solar water splitting. *Chem Soc Rev.* 2019;48:2182-2215.
- Swierk JR, Mendez-Hernandez DD, McCool NS, et al. Metal-free organic sensitizers for use in water-splitting dye-sensitized photoelectrochemical cells. *Proc Natl Acad Sci USA*. 2015;112:1681-1686.
- Barnham KWJ, Mazzer M, Clive B. Resolving the energy crisis: nuclear or photovoltaics. *Nat Mater*. 2006;5:161-164.
- Vullev VI. From biomimesis to bioinspiration: what's the benefit for solar energy conversion applications. J Phys Chem Lett. 2011;2:503-508.
- Ort DR, Merchant SS, Alric J, et al. Redesigning photosynthesis to sustainably meet global food and bioenergy demand. *Proc Natl Acad Sci U S A*. 2015;112:8529-8536.
- Sherman BD, Bergkamp JJ, Brown CL, Moore AL, Gust D, Moore TA. A tandem dye-sensitized photoelectrochemical cell for light driven hydrogen production. *Energy Environ Sci.* 2016;9:1812-1817.
- Sherman BD, Sheridan MV, Wee KR, et al. A dye-sensitized photoelectrochemical tandem cell for light driven hydrogen production from water. J Am Chem Soc. 2016;138:16745-16753.
- Chuang JI, Boxer SG, Holten D, Kirmaier C. High yield of Mside electron transfer in mutants of *Rhodobacter capsulatus* reaction centers lacking the L-side bacteriopheophytin. *Biochemistry*. 2006;45:3845-3851.
- Zhu XY, Yang Q, Muntwiler M. Charge-transfer excitons at organic semiconductor surfaces and interfaces. Acc Chem Res. 2009;42:1779-1787.
- Barroso M, Arnaut LG, Formosinho SJ. Proton-coupled electron transfer in natural and artificial photosynthesis. In: Formosinho S, Barroso M, eds. *Proton-Coupled Electron Transfer: A Carrefour of Chemical Reactivity Traditions*. RSC Catalysis Series No. 8. Cambridge, UK: RSC Publishing; 2012:126-151.
- Megiatto JD, Mendez-Hernandez DD, Tejeda-Ferrari ME, et al. A bioinspired redox relay that mimics radical interactions of the Tyr-His pairs of photosystem II. *Nat Chem.* 2014; 6: 423-428.

- Hammarström L, Styring S. Proton-coupled electron transfer of tyrosines in photosystem II and model systems for artificial photosynthesis: the role of a redox-active link between catalyst and photosensitizer. *Energy Environ Sci.* 2011; 4: 2379-2388.
- Gagliardi CJ, Vannucci AK, Concepcion JJ, Chen Z, Meyer TJ. The role of proton coupled electron transfer in water oxidation. *Energy Environ Sci.* 2012;5:7704-7717.
- Skonieczny K, Yoo J, Larsen JM, et al. How to reach intense luminescence for compounds capable of excited-state intramolecular proton transfer. *Chem–Eur J*. 2016;22:7485-7496.
- Guo S, Bao D, Upadhyayula S, et al. Photoinduced electron transfer between pyridine coated cadmium selenide quantum dots and single sheet graphene. *Adv Funct Mater*. 2013;23:5199-5211.
- Xia B, Bao D, Upadhyayula S, Jones G, Vullev VI. Anthranilamides as bioinspired molecular electrets: experimental evidence for a permanent ground-state electric dipole moment. *J Org Chem.* 2013;78:1994-2004.
- Ashraf MK, Pandey RR, Lake RK, et al. Theoretical design of bioinspired macromolecular electrets based on anthranilamide derivatives. *Biotechnol Prog.* 2009;25:915-922.
- Larsen JM, Espinoza EM, Vullev VI. Bioinspired molecular electrets: bottom-up approach to energy materials and applications. J Photon Energy. 2015;5:055598.
- Upadhyayula S, Bao D, Millare B, et al. Permanent electric dipole moments of carboxyamides in condensed media: what are the limitations of theory and experiment. *J Phys Chem B*. 2011;115:9473-9490.
- Krzeszewski M, Espinoza EM, Cervinka C, et al. Dipole effects on electron transfer are enormous. *Angew Chem, Int Ed.* 2018;57:12365-12369.
- Yasutomi S, Morita T, Imanishi Y, Kimura S. A molecular photodiode system that can switch photocurrent direction. *Science*. 2004;304:1944-1947.
- Galoppini E, Fox MA. Effect of the electric field generated by the helix dipole on photoinduced intramolecular electron transfer in dichromophoric alpha-helical peptides. *J Am Chem Soc.* 1996;118:2299-2300.
- Bao D, Upadhyayula S, Larsen JM, et al. Dipole-mediated rectification of intramolecular photoinduced charge separation and charge recombination. J Am Chem Soc. 2014;136:12966-12973.
- Waskasi MM, Kodis G, Moore AL, Moore TA, Gust D, Matyushov DV. Marcus bell-shaped electron transfer kinetics observed in an Arrhenius plot. J Am Chem Soc. 2016;138:9251-9257.
- Verhoeven JW, van Ramesdonk HJ, Groeneveld MM, Benniston AC, Harriman A. Long-lived charge-transfer states in compact donor-acceptor dyads. *ChemPhysChem.* 2005;6:2251-2260.
- Wiederrecht GP, Svec WA, Wasielewski MR, Galili T, Levanon H. Novel mechanism for triplet state formation in short distance covalently linked radical ion pairs. *J Am Chem Soc*. 2000;122:9715-9722.
- Jones G, II, Vullev VI. Photoinduced electron transfer between nonnative donor-acceptor moieties incorporated in synthetic polypeptide aggregates. *Org Lett.* 2002;4:4001-4004.
- Weiss EA, Ratner MA, Wasielewski MR. Direct measurement of singlet-triplet splitting within rodlike photogenerated radical ion pairs using magnetic field effects: estimation of the electronic coupling for charge recombination. *J Phys Chem A*. 2003;107:3639-3647.

- Bandi V, Gobeze HB, Lakshmi V, Ravikanth M, D'Souza F. Vectorial charge separation and selective triplet-state formation during charge recombination in a pyrrolyl-bridged BODIPY-fullerene dyad. J Phys Chem C. 2015;119:8095-8102.
- Upadhyayula S, Nunez V, Espinoza EM, et al. Photoinduced dynamics of a cyanine dye: parallel pathways of non-radiative deactivation involving multiple excited-state twisted transients. *Chem Sci.* 2015;6:2237-2251.
- Ryu HG, Mayther MF, Tamayo J, et al. Bidirectional solvatofluorochromism of a pyrrolo[3,2-b]pyrrole-diketopyrrolopyrrole hybrid. *J Phys Chem C*. 2018;122:13424-13434.
- Krzeszewski M, Kodama T, Espinoza EM, Vullev VI, Kubo T, Gryko DT. Nonplanar butterfly-shaped π-expanded pyrrolopyrroles. *Chem–Eur J*. 2016;22(46):16478-16488.
- Bahmani B, Gupta S, Upadhyayula S, Vullev VI, Anvari B. Effect of polyethylene glycol coatings on uptake of indocyanine green loaded nanocapsules by human spleen macrophages in vitro. *J Biomed Opt.* 2011; 16:051303.
- Gupta S, Chatni MR, Rao ALN, Vullev VI, Wang LV, Anvari B. Virus-mimicking nano-constructs as a contrast agent for near infrared photoacoustic imaging. *Nanoscale*. 2013;5:1772-1776.
- Espinoza EM, Clark JA, Soliman J, Derr JB, Morales M, Vullev VI. Practical aspects of cyclic voltammetry: how to estimate reduction potentials when irreversibility prevails. *J Electrochem Soc*. 2019;166:H3175-H3187.
- Bao D, Millare B, Xia W, et al. Electrochemical oxidation of ferrocene: a strong dependence on the concentration of the supporting electrolyte for nonpolar solvents. *J Phys Chem A*. 2009;113:1259-1267.
- Espinoza EM, Larsen JM, Vullev VI. What makes oxidized N-acylanthranilamides stable. J Phys Chem Lett. 2016;7:758-764.
- Larsen JM, Espinoza EM, Hartman JD, et al. Building blocks for bioinspired electrets: molecular-level approach to materials for energy and electronics. *Pure Appl Chem.* 2015;87:779-792.
- Larsen-Clinton JM, Espinoza EM, Mayther MF, et al. Fluorinated aminoanthranilamides: non-native amino acids for bringing proteomic approaches to charge-transfer systems. *Phys Chem Chem Phys.* 2017;19:7871-7876.
- Espinoza EM, Larsen-Clinton JM, Krzeszewski M, Darabedian N, Gryko DT, Vullev VI. Bioinspired approach toward molecular electrets: synthetic proteome for materials. *Pure Appl Chem.* 2017;89:1777-1797.
- Wan J, Ferreira A, Xia W, et al. Solvent dependence of the chargetransfer properties of a quaterthiophene-anthraquinone dyad. *J Photochem Photobiol*, A. 2008;197:364-374.
- Espinoza EM, Xia B, Darabedian N, et al. Nitropyrene photoprobes: making them, and what are they good for. *Eur J Org Chem*. 2016;2016:343-356.
- 54. Jones G, II, Lu LN, Vullev V, Gosztola D, Greenfield S, Wasielewski M. Photoactive peptides. 6. Photoinduced electron transfer for pyrenesulfonamide conjugates of tryptophan-containing peptides. Mitigation of fluoroprobe behavior in N-terminal labeling experiments. *Bioorg Med Chem Lett.* 1995;5:2385-2390.
- 55. Smit KJ, Warman JM. The formation of singlet and triplet charge-transfer states on photo-excitation of carbazole-(Ch2)Ntetrachlorophthalimide compounds studied by time-resolved microwave conductivity. *J Lumin*. 1988;42:149-154.

WILEY

- 56. Etzold F, Howard IA, Forler N, et al. Sub-ns triplet state formation by non-geminate recombination in PSBTBT: pC70BM and PCPDTBT:pC60BM organic solar cells. *Energy Environ Sci.* 2015;8:1511-1522.
- 57. Williams RM, Chen HC, Di Nuzzo D, Meskers SCJ, Janssen RAJ. Ultrafast charge and triplet state formation in diketopyrrolopyrrole low band gap polymer/fullerene blends: influence of nanoscale morphology of organic photovoltaic materials on charge recombination to the triplet state. *J Spectrosc.* 2017: 6867507.
- Mistelberger K, Port H. The triplet state in pyrene: optical manifestation of excitonic energy transfer in the dimeric high and low temperature crystalline phases. *Mol Cryst Liq Cryst.* 1980;57:203-276.

- Espinoza EM, Clark JA, Derr JB, et al. How do amides affect the electronic properties of pyrene. ACS Omega. 2018;3:12857-12867.
- Onsager L. Electric moments of molecules in liquids. J Am Chem Soc. 1936;58:1486-1493.

How to cite this article: Espinoza EM, Bao D, Krzeszewski M, Gryko DT, Vullev VI. Is it common for charge recombination to be faster than charge separation? *Int J Chem Kinet*. 2019;51:657–668. <u>https://doi.org/10.1002/kin.21285</u>