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# Gating that Suppresses Charge Recombination – the Role of Mono-*N*-Arylated Diketopyrrolopyrrole

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**ABSTRACT:** Suppressing the charge recombination (CR) that follows an efficient charge separation (CS) is of key importance for energy, electronics and photonics applications. We focus on the role of dynamic gating for impeding CR in a molecular rotor, comprising an electron donor and acceptor directly linked via a single bond. The media viscosity has an unusual dual effect on the dynamics of CS and CR in this dyad. For solvents with intermediate viscosity, CR is 1.5 to 3 times slower than CS. Lowering the viscosity below ~0.5 mPa s or increasing it above ~10 mPa s makes CR 10 to 30 times slower than CS. Ring rotation around the donor-acceptor bond can account only for the trends observed for non-viscous solvents. Media viscosity, however, affects not only torsional, but also vibrational modes. Suppressing predominantly slow vibrational modes by viscous solvents can impact the rates of CS and CR to a different extent. That is, an increase in the viscosity can plausibly suppress modes that are involved in the transition from the charge-transfer (CT) to the ground state, i.e., CR, but at the same time, are not important for the transition from the locally excited to the CT state, i.e., CS. These results provide a unique example of synergy between torsional and vibronic modes and their drastic effects on charge-transfer dynamics, thus, setting paradigms for controlling CS and CR.

## INTRODUCTION

Controlling electron transfer (ET) at a molecular and nanoscale level is paramount for improving the performance of energy-conversion materials and devices. Suppressing charge recombination (CR) that follows photoinduced charge separation (CS) renders solar energy conversion efficient. Local fields originating from molecular electric dipoles, anisotropic covalency, cascade ET events, bypassing localized charge-transfer (CT) states, and changes in multiplicity, provide an invaluable means for suppressing undesired CR.<sup>1-6</sup>

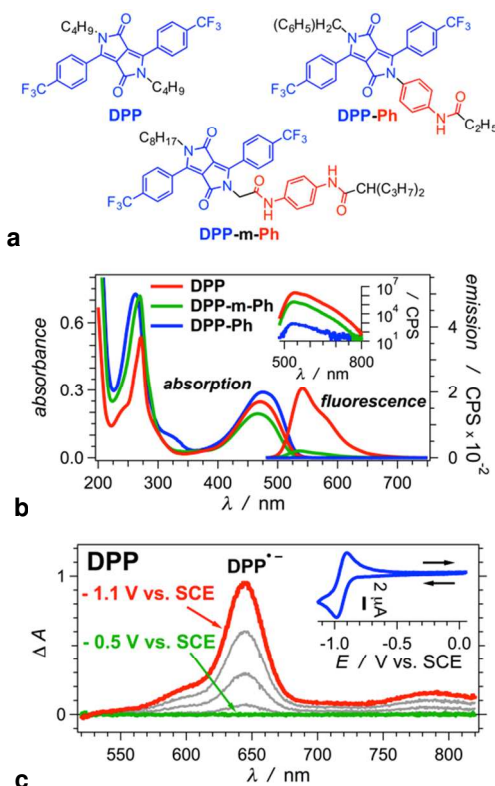
Optimizing CS driving force,  $-\Delta G_{CS}^{(0)}$ , and reorganization energy,  $\lambda$ , to attain activationless CS ( $-\Delta G_{CS}^{(0)} \approx \lambda$ ) can impede CR by placing it in the Marcus inverted region ( $-\Delta G_{CS}^{(0)} > \lambda$ ).<sup>7-9</sup> This non-adiabatic semi-classical view focuses on the Franck-Condon aspects of ET.

Conformational gating, which is important for biology, presents another approach for controlling ET.<sup>10</sup> By impacting the electronic coupling along the ET pathways, non-Condon effects from torsional dynamics can define the CT properties of molecular systems.<sup>11,12</sup> The utility of such effects for energy materials and organic electronics cannot be overstated.

With structural features resembling those of indigo, and with superior thermal stability and light-fastness, diketopyrrolopyrrole (DPP) derivatives are organic dyes with promising properties for optoelectronics.<sup>13</sup> Due to their strong light absorption, high fluorescence quantum yields and reduction potentials making them relatively good electron donors and

acceptors, DPPs have undergone significant repositioning from high-quality pigments,<sup>14</sup> through organic electronic materials<sup>15,16</sup> toward dyes for fluorescence-based applications.<sup>17-21</sup>

To explore the effects of gating on single-step CS and CR processes, herein, we focus on the ET properties of an electron deficient diketopyrrolopyrrole (**DPP**, Figure 1a) that we derivatize with moderately good electron donors. While **DPP** is strongly fluorescent, the emission of **DPP-Ph** with the donor, 4-acylamino phenyl, directly linked to one of the lactam nitrogens (Figure 1a), is considerably quenched (Figure 1b). It is due to highly efficient intramolecular CS, which the photoexcited **DPP-Ph** undergoes to produce a non-fluorescent CT state. As expected, the rate constants of CS and CR,  $k_{CS}$  and  $k_{CR}$ , respectively, manifest correlations with the media polarity. An important characteristic for efficient conversion of the harvested light energy is  $k_{CS}/k_{CR}$ , representing how much slower CR in comparison with CS. The polarity and proticity of the solvent do not correlate strongly with  $k_{CS}/k_{CR}$ . Conversely,  $k_{CS}/k_{CR}$  exhibits a defined bimodal correlation with the media viscosity. That is,  $k_{CS}/k_{CR}$  is largest for the most and the least viscous solvents, regardless their polarity or proticity.



**Figure 1.** Basic characteristics of DPP, DPP-Ph and DPP-m-Ph. (a) Structures. (b) UV/visible absorption and fluorescence spectra (10  $\mu$ M in acetonitrile, MeCN). Inset: fluorescence spectra plotted against logarithmic ordinate ( $\lambda_{ex}$  = 470 nm, fluorescence quantum yields:  $\phi_f^{(DPP)} = 0.75$ ,  $\phi_f^{(DPP-m-Ph)} = 0.073$ ,  $\phi_f^{(DPP-Ph)} = 3.6 \times 10^{-4}$ ). (c) Differential absorption spectra recorded during electrochemical reduction of DPP (for MeCN with 100 mM NBu<sub>4</sub>PF<sub>6</sub>). Inset: cyclic voltammogram of DPP (scan rate = 50 mV s<sup>-1</sup>).

## RESULTS AND DISCUSSION

**Synthetic strategies.** The synthesis of the CT conjugates requires the preparation of asymmetrically substituted DPP derivatives. While the synthesis and double *N*-alkylation of these pigments is easy and well established,<sup>13</sup> the *N*-arylation is extremely challenging and currently we know of only two reported cases that utilize strongly activated aryl fluorides.<sup>22</sup>

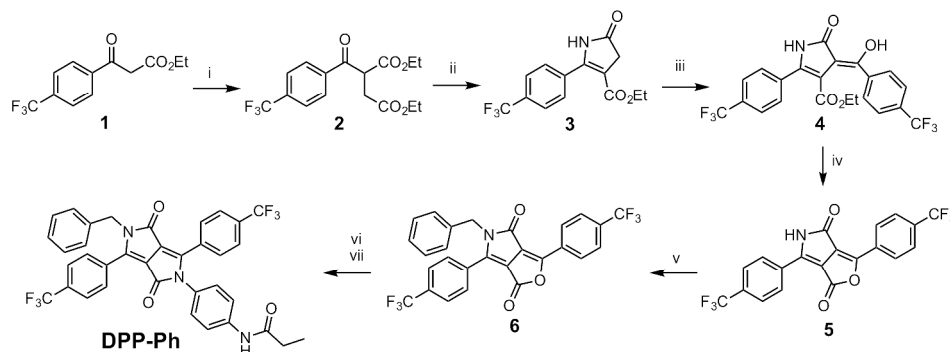
Our design requires a full control over the pattern of substituents. Therefore, we adopted a general strategy reported by Morton *et al.*<sup>23-25</sup>

The selected route is based on the synthesis of the targeted furo[3,4-*c*]pyrrole, **5**, followed by a sequence of alkylation and amidation steps (Scheme 1). Initial alkylation of  $\beta$ -keto ester, **1**, with ethyl bromoacetate in the presence of a strong base affords **2** in a good yield. Ammonia-induced ring closure results in the dihydropyrrolone, **3**, with one of the electron-deficient aryl substituent attached to it. A somewhat challenging alkenylation of the methylene carbon, followed by microwave-induced ring closure yields **5**. Alkyl bromides, regardless the use of different bases (K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, *t*-BuOK, NaH), solvents (DMF, NMP, THF), catalysts (TBAHS, KI, crown ethers) and ultrasonication, manifest limited reactivity with **5**. Therefore, we resort to benzyl bromide as a more active alkylation agent, affording *N*-benzylfuro[3,4-*c*]pyrrole **6** in 27% yield. Asymmetrically *N,N*-Disubstituted DPP, obtained via amidation from **6**, is readily acylated to the final compound, DPP-Ph, with an excellent yield (Scheme 1).

The other CT conjugate, DPP-m-Ph, possesses the same electron-deficient chromophore but a methylene links it with the donor (Figure 1a). For the synthesis of this asymmetric conjugate, we use statistical *N,N*-dialkylation of a symmetric DPP derivative, **7** (Scheme 2).

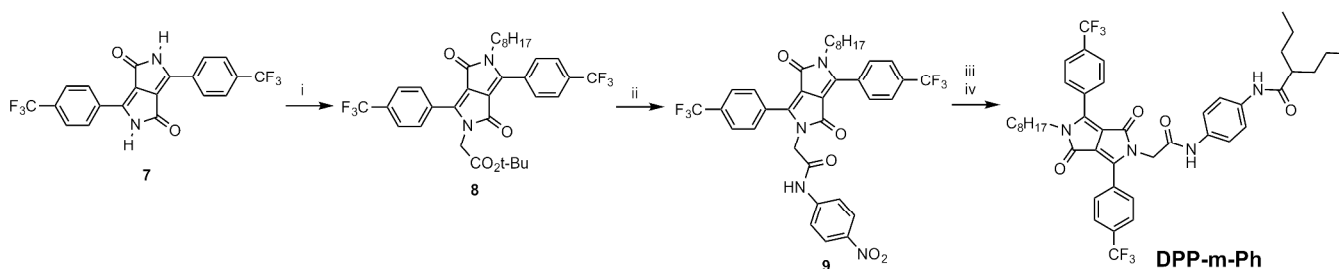
**Basic photophysical properties.** DPP exhibits visible absorption and fluorescence, with zero-to-zero energy,  $\mathcal{E}_{00}$ , of about 2.4 eV. Addition of the electron donors does not cause substantial wavelength shifts in the absorption and emission spectra, but considerably quench the fluorescence (Figure 1b). The absorption maxima for DPP, DPP-Ph and DPP-m-Ph are at 470 nm, 476 nm, and 467 nm. Because  $\Delta G_{CS}^{(0)}$  for DPP-Ph and DPP-m-Ph is around -0.2 eV for acetonitrile media (Table 1), the 6-nm bathochromic shift in the absorption of DPP-Ph (corresponding to 33 meV) cannot be unequivocally ascribed to a CT band. These results suggest that while the DPP-donor dyads undergo highly efficient CS, the donor-acceptor electronic coupling in these conjugates is not strong enough to considerably perturb the DPP absorption.

### Scheme 1. Synthesis of asymmetrically arylated diketopyrrolopyrrole, DPP-Ph.



i) BrCH<sub>2</sub>CO<sub>2</sub>Et, EtONa, EtOH, 0 °C → rt, 89%; ii) NH<sub>4</sub>OAc, AcOH, reflux, 63%; iii) 1-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Et, *t*-AmONa, *t*-AmOH, 60 °C, 23%; iv) microwave, 230 °C, 10 min, 74%; v) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, K<sub>2</sub>CO<sub>3</sub>, DMF, 40 °C, 29%; vi) 1,4-(NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, EDC, TFA, DCM, rt, 59%; vii) (CH<sub>3</sub>CH<sub>2</sub>CO)<sub>2</sub>O, NEt<sub>3</sub>, DCM, 0 °C → rt, 99%.

## Scheme 2. Synthesis of asymmetrically alkylated diketopyrrolopyrrole, DPP-m-Ph.



i)  $\text{ClCH}_2\text{CO}_2-t\text{-Bu}$ ,  $\text{C}_8\text{H}_{17}\text{I}$ ,  $\text{K}_2\text{CO}_3$ , NMP, 120 °C, 19%; ii) 1. TFA, DCM, 0 °C  $\rightarrow$  rt; 2.  $(\text{COCl})_2$ , DCM, rt, 1 h, 3.  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$ , pyridine, DCM, rt, 1 h, overall 84%; iii)  $\text{Co}_2(\text{CO})_8$ ,  $\text{H}_2\text{O}$ , DME, reflux, 1 h, 67%; iv)  $(\text{H}_7\text{C}_3)_2\text{CHCOCl}$ , pyridine, rt, 1 h, 89%.

Table 1. Estimates for CS driving forces,  $-\Delta G_{\text{CS}}^{(0)}$ .

		$\mathcal{E}_{00}$ /eV <sup>a</sup>	$E^{(1/2)}$ /V vs. SCE <sup>b</sup>		$\Delta G_{\text{CS}}^{(0)}$ /eV <sup>c</sup>
			$\text{D}^{+/0}$	$\text{A}/\text{A}^-$	
DPP-Ph	MeCN	2.42	1.39	-0.89	-0.21
	DCM	2.39	1.54	-0.87	-0.29
DPP-m-Ph	MeCN	2.43	1.32	-0.90	-0.25
	DCM	2.42	1.55	-0.84	-0.23

<sup>a</sup> The values of the zero-to-zero energy,  $\mathcal{E}_{00}$ , were obtained from the wavelengths,  $\lambda_{00}$ , of the crossing points of the normalized absorption and fluorescence spectra: i.e.,  $\mathcal{E}_{00} = hc / \lambda_{00}$ .<sup>26,27</sup>

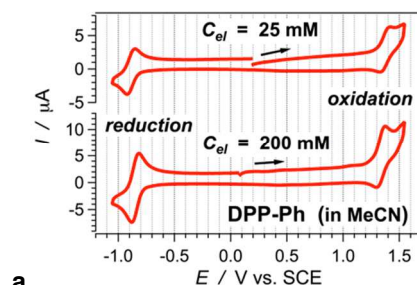
<sup>b</sup> Values of half-wave potentials,  $E^{(1/2)}$ , extrapolated to zero electrolyte concentration, representing the reduction potentials for neat solvents.<sup>28-32</sup>  $E^{(1/2)}$  for  $\text{D}^{+/0}$  was obtained from the first oxidation waves of the cyclic voltammograms of the dyads; and for  $\text{A}/\text{A}^-$  – from the first reduction waves. <sup>c</sup> Calculated from eq. 1, where  $\Delta G_{\text{S}} = 0$  and  $W = e^2/4\pi\epsilon_0\epsilon R_{\text{DA}}$ .<sup>33</sup>  $e$  – electron charge,  $\epsilon$  – static dielectric constant of the solvent (Table 2),  $\epsilon_0 = 5.526 \times 10^{-3} \text{ e V}^{-1} \text{ \AA}^{-1}$ , the donor-acceptor center-to-center distances,  $R_{\text{DA}} \approx 5.2 \text{ \AA}$  for DPP-Ph and  $7.2 \text{ \AA}$  for DPP-m-Ph.

While this finding is not surprising for methylene-linked donor-acceptor systems,<sup>1,34</sup> such as DPP-m-Ph, it is unusual for DPP-Ph. CT conjugates, in which the donor and the acceptor are linked with a single bond, tend to exhibit defined bathochromic CT absorption.<sup>35,36</sup> In DPP-Ph, however, the link is via a lactam nitrogen, which is spatially near the nodes of the frontier orbitals.<sup>37,38</sup> Indeed, the C-C bonds anchoring the trifluoromethylphenyl moieties to the principal DPP ring system at positions 3 and 6 provide strong  $\pi$ -electronic coupling. Therefore, the trifluoromethyl groups affect the whole chromophore making it electron deficient. Conversely, groups attached to the lactam nitrogens do not truly perturb the DPP electronic properties as evident from the spectroscopic and electrochemical results.

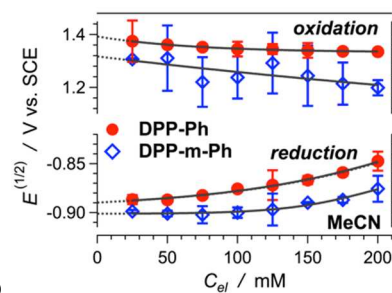
**Thermodynamics of charge separation.** The Rehm-Weller equation provides a means for estimating the driving force,  $-\Delta G_{\text{CS}}^{(0)}$ , of photoinduced CS (Table 1):<sup>28,39</sup>

$$\Delta G_{\text{CS}}^{(0)} = F \left( E_{\text{D}^{+/0}}^{(0)} - E_{\text{A}/\text{A}^-}^{(0)} \right) - \mathcal{E}_{00} + \Delta G_{\text{S}} + W \quad (1)$$

Electrochemically estimated half-wave reduction potentials,  $E^{(1/2)}$ , provide a good approximation for  $E^{(0)}$  of the oxidation of the donor, D, and the reduction of the acceptor, A.<sup>28</sup> For



a



b

**Figure 2.** Electrochemical oxidation and reduction of DPP-Ph and DPP-m-Ph. (a) Cyclic voltammograms of DPP-Ph for MeCN at different concentrations,  $C_{\text{el}}$ , of supporting electrolyte,  $\text{NBu}_4\text{PF}_6$ . (b) Dependence of the half-wave reduction potentials on electrolyte concentration for MeCN. The solid lines are the data fits and the dotted lines show the extrapolations to zero electrolyte concentration.

solvents in which  $\mathcal{E}_{00}$  is estimated from spectral data, we extrapolate  $E^{(1/2)}$  to zero electrolyte concentration.<sup>30,31,40</sup> Thus, we eliminate the Born solvation term,  $\Delta G_{\text{S}}$ , which corrects for the interactions of the formed radical ions with the solvent environment.<sup>1,28</sup> The Coulomb work term,  $W$ , accounts for the interactions between the generated radical ions.

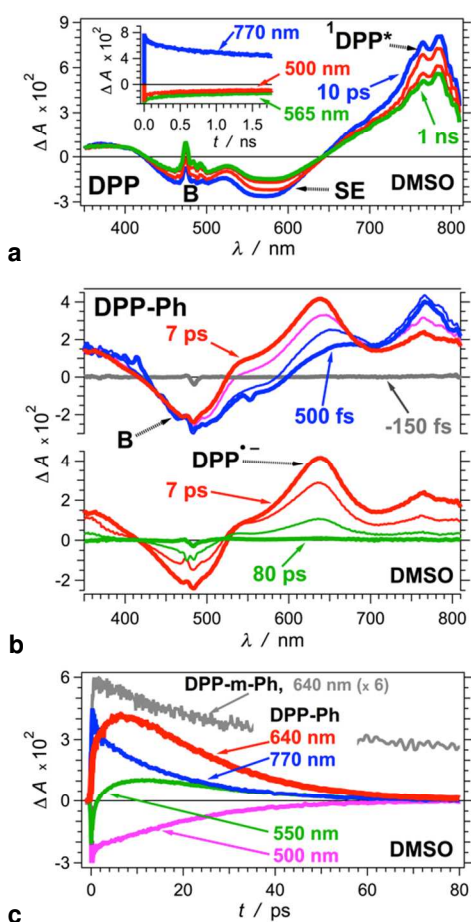
We obtain  $E_{\text{D}^{+/0}}^{(1/2)}$ , and  $E_{\text{A}/\text{A}^-}^{(1/2)}$  from the first oxidation and the first reduction waves, respectively, in the cyclic voltammograms of DPP-Ph and DPP-m-Ph (Figure 2a). Extrapolation of the half-wave potentials to zero salt concentration allows for eliminating the effect of the supporting electrolyte (Figure 2b).<sup>30-32</sup> The close similarity between the reduction potentials of DPP-Ph and DPP-m-Ph (Table 1) suggests that the electron donors in the two dyads have: (1) the same susceptibility to oxidation, and (2) no effect on the reduction of DPP.

Employing these estimates for  $E^{(1/2)}$  in eq. 1, and factoring  $W$ , yields similar CS driving forces for the two dyads (Table

**Table 2. Kinetics of CS and CR of DPP-Ph for solvents with different polarities and viscosities.<sup>a</sup>**

solvent <sup>b</sup>	$\epsilon$ <sup>c</sup>	$f_0$ <sup>d</sup>	$\mu$ / mPa s <sup>e</sup>	$k_{CS} \times 10^{-10} / s^{-1}$	$k_{CR} \times 10^{-10} / s^{-1}$	$k_{CS} / k_{CR}$
1. DMSO	47.0	0.968	1.996	17.2 ± 1.1	5.09 ± 0.21	3.38 ± 0.35
2. EG	41.4	0.965	16.1	15.1 ± 3.9	1.44 ± 0.37	10.5 ± 5.4
3. MeCN	37.5	0.961	0.347	34.4 ± 1.2	4.63 ± 0.04	7.42 ± 0.33
4. MeOH	32.7	0.955	0.544	15.1 ± 3.0	6.48 ± 0.78	2.33 ± 0.75
5. EtOH	24.5	0.940	1.074	6.60 ± 1.74	4.05 ± 0.66	1.63 ± 0.70
6. <i>n</i> -BuOH	17.8	0.918	1.399	5.91 ± 0.48	1.18 ± 0.03	4.99 ± 0.55
7. OctOH	10.3	0.861	7.36	5.23 ± 1.39	0.741 ± 0.054	7.06 ± 2.40
8. DCM	8.93	0.841	0.410	16.9 ± 1.2	0.515 ± 0.006	32.7 ± 2.7
9. THF	7.58	0.814	0.481	20.9 ± 6.6	7.93 ± 1.28	2.63 ± 1.26
10. CHCl <sub>3</sub>	4.81	0.718	0536	8.12 ± 0.22	0.894 ± 0.010	9.08 ± 0.35

<sup>a</sup> The CS and CR rate constants,  $k_{CS}$  and  $k_{CR}$ , are obtained from global fits of **DPP-Ph** TA kinetics (see Supporting Information). <sup>b</sup> Solvents: dimethyl sulfoxide (DMSO), ethylene glycol (EG), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), 1-butanol (BuOH), 1-octanol (OctOH), dichloromethane (DCM), tetrahydrofuran (THF), and chloroform (CHCl<sub>3</sub>). <sup>c</sup> Static dielectric constant, i.e., relative permittivity. <sup>d</sup> Onsager function for solvent polarity,  $f_0(\epsilon) = 2(\epsilon - 1) / (2\epsilon + 1)$ . <sup>e</sup> Dynamic viscosity.



**Figure 3.** Transient absorption (TA) dynamics of **DPP** and **DPP-Ph** for DMSO ( $\lambda_{ex} = 480$  nm, 6  $\mu$ J per pulse,  $FWHM_{(for\ 800\ nm)} = 50$  fs). (a,b) TA spectra (SE = stimulated emission, B = ground-state bleach). (c) TA dynamics monitored at different wavelengths: 770 nm for <sup>1</sup>DPP\*, 640 nm for DPP<sup>•-</sup>, 550 nm for SE, and 500 nm for B. For comparison, the top gray line is for **DPP-m-Ph** monitored at 640 nm (Figure 5b). The rest of the kinetic curves are for **DPP-Ph**.

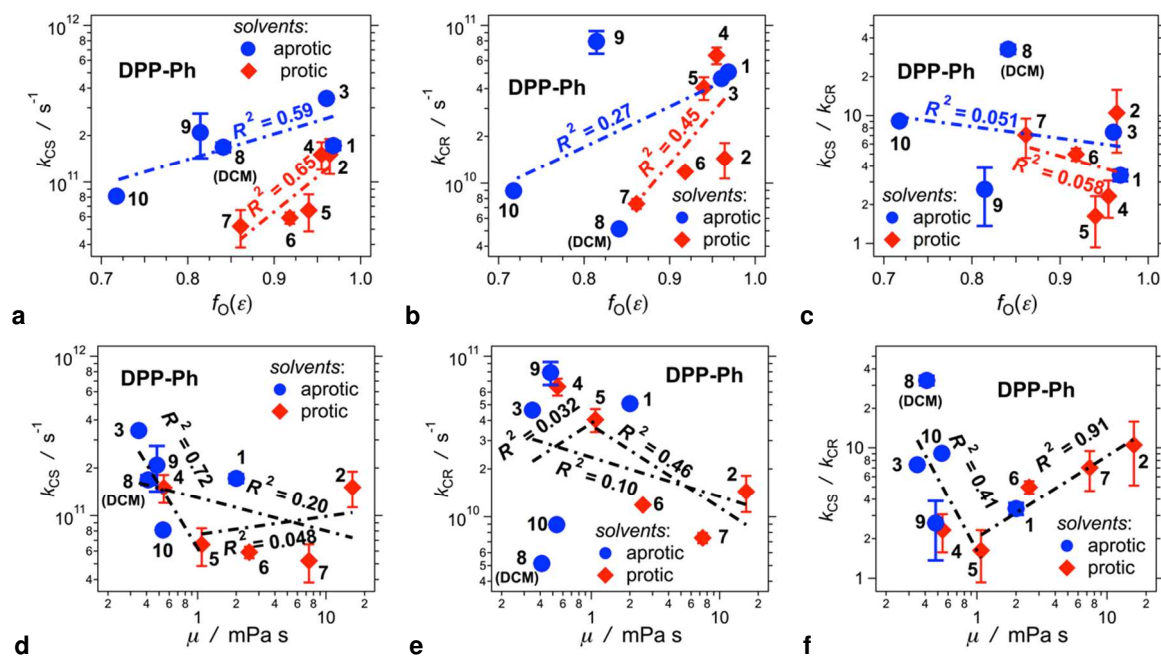
1). In addition, the CS driving forces for the relatively polar acetonitrile (MeCN) appear slightly less favorable (with 50 – 80 meV) than those for the relatively non-polar dichloromethane (DCM). Because the values of  $-\Delta G_{CS}^{(0)}$  are relatively small, the Coulomb term,  $W$  (eq. 1), has a major contribution to the estimates. The values of  $W$ , however, could be underestimates, especially for polar solvents. Typically, the calculations of  $W$  assume spherical radical ions of the oxidized donor and the reduced acceptor separated by a continuum media characterized with the dielectric constant,  $\epsilon$ , of the bulk solvent. For linked donor-acceptor systems, the donor and the acceptor are in the same solvation cavity and the space between them cannot be necessarily characterized with  $\epsilon$  of the bulk media.<sup>41</sup> Therefore, the small differences between the calculated values for the CS driving forces are within the uncertainty of the  $W$  estimates, and  $-\Delta G_{CS}^{(0)}$  should be larger, especially for MeCN.

**Kinetics of electron transfer.** Upon illumination, **DPP-Ph** forms a locally excited state, <sup>1</sup>DPP\*-Ph, manifesting a broad transient absorption (Figure 3a,b). The picosecond decay of <sup>1</sup>DPP\* is concurrent with the rise of a band at 640 nm, which corresponds to the reduced chromophore, DPP<sup>•-</sup> (Figure 1c, 3b). DPP<sup>•-</sup> decays simultaneously with the recovery of the ground state, as monitored at the bleach (Figure 3c). Therefore, we determine  $k_{CS}$  from the rise of the 640-nm band, and  $k_{CR}$  – from its decay, as quantified using global analysis.

A decrease in the media polarity tends to slow down both, CS and CR, which can be expected (Table 2).<sup>1,33</sup> This polarity dependence of  $k_{CS}$  and  $k_{CR}$ , appears more pronounced for protic than for aprotic solvents; and the correlations are stronger for CS than for CR (Figure 4a,b). These observations underline the effects of discrete solvent-solute interactions, such as hydrogen bonding, on the ET properties of **DPP-Ph**, and especially on the initial photoinduced CS.

Conversely, the ratio,  $k_{CS}/k_{CR}$ , shows no apparent correlation with the solvent polarity. For protic and aprotic media, the correlations between  $k_{CS}/k_{CR}$  and the different representations of polarity are negligibly weak, i.e.,  $R^2 < 0.1$  (Figure 4c). A





**Figure 4.** Solvent dependence of the rate constants of the photoinduced intramolecular charge separation,  $k_{CS}$ , and charge recombination,  $k_{CR}$ , of **DPP-Ph** (Table 2). (Solvents: 1 = DMSO, 2 = EG, 3 = MeCN, 4 = MeOH, 5 = EtOH, 6 = BuOH, 7 = OctOH, 8 = DCM, 9 = THF, and 10 =  $\text{CHCl}_3$ ). The values of the rate constants are from global-fit analysis (see Supporting Information). (a-c) Dependence of  $k_{CS}$ ,  $k_{CR}$  and the ratio,  $k_{CS}/k_{CR}$ , on the media polarity, represented by the Onsager function for solvent polarity,  $f_0(\epsilon)$  (Table 2), with results from correlation analyses for protic (2, 4, 5, 6, 7) and aprotic (1, 3, 8, 9, 10) solvents. (d-f) Dependence of  $k_{CS}$ ,  $k_{CR}$  and the ratio,  $k_{CS}/k_{CR}$ , on the media viscosity, represented by the solvent dynamic viscosity,  $\mu$  (Table 2), with results from correlation analyses: (d) for all solvents ( $R^2 = 0.20$ ), for low-viscosity solvents with  $\mu \leq 1$  mPa s ( $R^2 = 0.72$ ), and for viscous solvents with  $\mu \geq 1$  mPa s ( $R^2 = 0.048$ ); (e) for all solvents ( $R^2 = 0.10$ ), for low-viscosity solvents with  $\mu \leq 1$  mPa s ( $R^2 = 0.032$ ), and for viscous solvents with  $\mu \geq 1$  mPa s ( $R^2 = 0.46$ ); and (f) for low-viscosity solvents with  $\mu \leq 1$  mPa s ( $R^2 = 0.41$ ), and for viscous solvents with  $\mu \geq 1$  mPa s ( $R^2 = 0.91$ )

close examination of the  $k_{CS}/k_{CR}$ -vs.- $f_0$  plots, however, reveals two separate trends (Figure 4c): (1) for solvents more polar than EtOH,  $k_{CS}/k_{CR}$  tends to increase with polarity ( $R^2(\lg(k_{CS}/k_{CR}) \text{ vs. } f_0(\epsilon)) = 0.47$ ); and (2) for solvent less polar than EtOH,  $k_{CS}/k_{CR}$  tends to slightly decrease with polarity ( $R^2(\lg(k_{CS}/k_{CR}) \text{ vs. } f_0(\epsilon)) = 0.16$ ). The media polarity, indeed, affects the Franck-Condon components of ET kinetics via the outer reorganization energy and via the driving force (eq. 1), i.e., via the polarity dependence of reduction potentials, of  $W$ , and sometime of  $\xi_{00}$  (for light sensitizers exhibiting solvatochromism). The scattered nature of the plots showing the polarity dependence of the CT kinetics and the moderate to weak correlations, however, indicate that other characteristics of the solvent media also govern the rates of CS and CR, and especially the ratio between them,  $k_{CS}/k_{CR}$ .

Considering the solvent viscosity,  $\mu$ , reveals additional trends. Both,  $k_{CS}$  and  $k_{CR}$ , tend to decrease with an increase in media viscosity (Figure 4d,e, Table 2). For CS, the media viscosity causes a distinct decrease in the rates only for relatively non-viscous solvents, i.e., for  $\mu \leq 1$  mPa s (Figure 4d). An increase in media viscosity beyond 1 mPa s does not have a strong effect on  $k_{CS}$ , i.e.,  $R^2 \approx 0.05$  (Figure 4d). In addition to this weak correlation for media with  $\mu \geq 1$  mPa, predominantly the polarity, rather than the viscosity, appears to affect CS. For the relatively viscous solvents, the polar ones (EG and DMSO) manifest noticeably higher  $k_{CS}$  than those of the relatively non-polar ones (OctOH, BuOH, and EtOH) (Figure 4d).

Conversely, an increase in media viscosity impedes CR only for relatively viscous solvents, i.e., with  $\mu \geq 1$  mPa s (Figure 4e). For non-viscous media, i.e., with  $\mu \leq 1$  mPa s, the correlation between  $k_{CR}$  and  $\mu$  is practically negligible (Figure 4e). This difference in the dependence of CS and CR on the media viscosity results in a bimodal effect of  $\mu$  on  $k_{CS}/k_{CR}$  (Figure 4f). Indeed, the ratio  $k_{CS}/k_{CR}$  shows a well-defined dual dependence on the viscosity. The smallest  $k_{CS}/k_{CR}$  is for ethanol ( $\mu = 1.1$  mPa s). Both, a decrease and an increase in the solvent viscosity cause an increase in  $k_{CS}/k_{CR}$  (Figure 4f).

Rigidity of the environment, governed by the solvent viscosity, affects the frequency of molecular motions. Stretching, bending and rotation around the N-C bond, linking the donor with the acceptor, are modes that can influence the kinetics of ET in **DPP-Ph**. While an increase in solvent viscosity may damp mostly low-frequency molecular vibrations, it also slows down the rotations around the N-C bond.

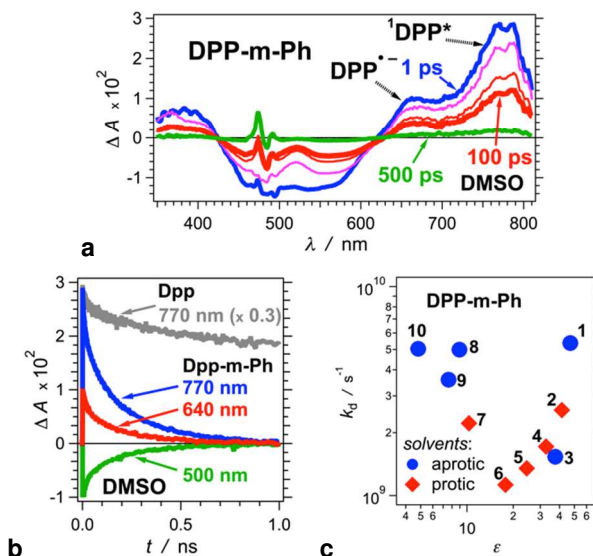
For systems such as **DPP-Ph**, in which a single covalent bond directly links a planar donor and acceptor, usually non-Condon (i.e., torsional) modes dominate the suppression of CR for non-viscous media. As observed for molecular rotors and particularly for those with propensity to form twisted intramolecular charge-transfer (TICT) states,<sup>42</sup> photoexcitation induces CS in states with a certain level of planarity and good electronic coupling between the  $\pi$ -conjugated systems of the donor and the acceptor. The formed CT states exhibit a preference for conformers with orthogonality between the rings of the donor and the acceptor. Fast torsional modes produce these

TICT states with decreased donor-acceptor electronic coupling and suppressed CR. As expected for molecular rotors, an increase in solvent viscosity impedes the fast torsional modes<sup>43</sup> that can compete with CR.

The excited-state behavior of **DPP-Ph** deviates from what would be expected for donor-acceptor dyads with propensity to form TICT excited states. Similar to TICT-forming conjugates,  $k_{CS}/k_{CR}$  for **DPP-Ph** decreases with an increase in media viscosity (for  $\mu \leq 1$  mPa s, Figure 4f). While for TICT-forming conjugates a decrease in media viscosity leads to suppression of CR due to fast torsional modes, we cannot quite claim the same for **DPP-Ph**. Indeed, for solvents with  $\mu \leq 1$  mPa s, an increase in  $\mu$  tends to cause an increase in  $k_{CR}$  (Figure 4e), which appears consistent with the formation of a TICT excited state. The weak correlation between  $k_{CR}$  and  $\mu$ , i.e.,  $R^2 < 0.05$  (Figure 4e), however, places a question on the significance of this trend for **DPP-Ph**. Conversely, the strong correlation ( $R^2 = 0.72$ ) between  $k_{CS}$  and  $\mu$  for **DPP-Ph** in relatively non-viscous solvents (Figure 4d) suggests that it is CS, rather than CR, that the media viscosity predominantly affects for  $\mu \leq 1$  mPa s. That is, the distinct decrease in  $k_{CS}$  with an increase in viscosity (for  $\mu \leq 1$  mPa s, Figure 4d) is the dominating effect responsible for the observed  $k_{CS}/k_{CR}$  vs.  $\mu$  trends (Figure 4f). This viscosity-induced suppression of CS suggests for solvent-coupled structural alterations of the locally excited state,  $^1\text{DPP}^*\text{-Ph}$ , that are essential for attaining fast ET rates. While faster than CR, the dynamics of non-viscous solvents is comparable with the picosecond time scales of CS (Table 2).

What appears quite unusual for **DPP-Ph**, however, is the suppression of CR and the increase in  $k_{CS}/k_{CR}$  by further increase in solvent viscosity, i.e., beyond 1 mPa s (Figure 4e,f). This trend is contrary to the expected behavior of TICT-forming donor-acceptor conjugates. While non-Condon modes can be behind the low-viscosity trends, they cannot account for the correlations observed for viscous media (Figure 4e,f). Furthermore, for all solvents, except EG, the TA decays of the CT state, representing CR, are mono-exponential, indicating that the time constants of CR significantly exceed the time scales of the involved structural dynamic modes.

A potential reason for this viscosity-induced decrease in  $k_{CR}$  and increase in  $k_{CS}/k_{CR}$  (for  $\mu > 1$  mPa s) can be a suppression of vibrational and bending modes that are more important for CR than for CS. For example, fast vibrational modes that are not significantly affected by the solvent viscosity could dominate the Franck-Condon contribution to the rate constant of the transition from the locally excited to the CT state, i.e., CS:  $^1\text{DPP}^*\text{-Ph} \rightarrow \text{DPP}^-\text{-Ph}^+$ . Conversely, for the transition from the CT to the ground state, i.e., CR:  $\text{DPP}^-\text{-Ph}^+ \rightarrow \text{DPP-Ph}$ , may involve relatively slow vibrational modes that are susceptible to suppression by increased media viscosity.<sup>44,45</sup> The driving forces for CS are much smaller than those for CR. Hence, similar Frank-Codon effects on the ET kinetics most likely would affect CS more significantly than CR, which is opposite to the observed trends (Figure 4d,e). Therefore, the modes that govern CS should be quite different from those that are responsible for CR in order to attain the observed kinetic trends.



**Figure 5.** Transient absorption (TA) dynamics of **DPP-m-Ph**. (a) TA spectra for DMSO ( $\lambda_{ex} = 480$  nm, 6  $\mu\text{J}$  per pulse,  $\text{FWHM}_{(for\ 800\ \text{nm})} = 50$  fs). (b) TA dynamics monitored at different wavelengths: 770 nm for  $^1\text{DPP}^*$ , 640 nm for  $\text{DPP}^-$ , 500 nm for ground-state bleach recovery. For comparison, the top gray line is for **DPP** monitored at 770 nm (Figure 3a). The rest of the kinetic curves are for **DPP-m-Ph**. (c) Dependence of the decay rate constant,  $k_d$ , recorded at 770 nm, on the solvent polarity represented by the solvent static relative dielectric constant,  $\epsilon$ . The solvent numeration is the same as in Table 2 and Figure 4.

The dynamics of solvent reorganization may present another plausible contribution to the observed viscosity-dependence trends (Figure 4d-f).<sup>46-48</sup> Despite the favorable thermodynamics, an increase in the viscosity slows down the dynamics of solvent response that can make it rate limiting for ET. This behavior would be expected for viscous polar solvents, such as EG. It appears, however, that the viscosity affects CS only for media with  $\mu \leq 1$  mPa (Figure 4d). In addition, the similar values of  $k_{CS}$  for the two most polar alcohols, EG and MeOH that have drastically different viscosities (Figure 4d, Table 2), place a question about the contribution of viscosity-limiting reorganization dynamics to the observed CS kinetics. Furthermore, the increase in  $k_{CS}/k_{CR}$  with the increase in solvent viscosity beyond 1 mPa s suggests that if such solvent reorganization dynamics plays a role in the observed kinetics, it should affect the CR more than the CS processes. Such a discriminative impact on the CR, rather than CS, kinetics requires a significant difference between the polarity of the ground and the locally excited states. The solvent reorganization dynamics, hence, cannot provide a solid rationale for the observed suppression of CR as the viscosity increases beyond 1 mPa s.

When two saturated covalent bonds link the donor and the acceptor, as in **DPP-m-Ph**, the singlet-excited state of DPP is still significantly quenched (Figure 1b, 5a,b). The lifetime of  $^1\text{DPP}^*\text{-m-Ph}$  is between 0.2 to 1 ns for the different solvents, i.e., 10 to 40 times smaller than that of  $^1\text{DPP}^*$ . While the fluorescence lifetime of **DPP** shows no solvent dependence, the

1 rates of decay of  ${}^1\text{DPP}^*\text{-m-Ph}$  increase with an increase in the  
 2 media polarity for solvents with  $\epsilon > 15$  (Figure 5c), which is  
 3 consistent with photoinduced CS.

4 A transient absorption band at 640 nm, corresponding to  
 5  $\text{DPP}^{\cdot-}$ , appears along with the band of  ${}^1\text{DPP}^*$  upon the excita-  
 6 tion of **DPP-m-Ph**. We, however, do not observe growth of  
 7  $\text{DPP}^{\cdot-}$  as  ${}^1\text{DPP}^*$  decays (Figure 3c, 5c). In addition, the 640-  
 8 nm transient absorption is less pronounced for less polar sol-  
 9 vents, appearing mostly as a shoulder.

10 The flexibility of the methylene linker promotes heteroge-  
 11 neous CT kinetics representative of the multiple possible con-  
 12 formations of **DPP-m-Ph** with different donor-acceptor cou-  
 13 pling. As a result, we observe CS and formation of  $\text{DPP}^{\cdot-}$   
 14 within the excitation of **DPP-m-Ph**, as well as bi-exponential  
 15 decays for some of the solvent media.

16 These findings suggest that while  ${}^1\text{DPP}^*\text{-m-Ph}$  undergoes  
 17 efficient CS, the consecutive CR occurs with comparable or  
 18 faster rates. That is, CS is the rate-limiting step and the com-  
 19 peting CR is fast enough to prevent accumulation of the CT  
 20 state, except when CS occurs within the duration of the femto-  
 21 second excitation pulse. Indeed, the appearance of both  $\text{DPP}^{\cdot-}$   
 22 and  ${}^1\text{DPP}^*$  transients within the femtosecond excitation pulse,  
 23 while  ${}^1\text{DPP}^*$  lives 100s of ps, suggests for multiple CS path-  
 24 ways. The flexible methylene linker provides access to con-  
 25 former where the donor contacts directly one of the trifluoro-  
 26 methylphenyl moieties, providing pathways for ultrafast CS.  
 27 Folded conformers with improved donor-acceptor coupling  
 28 dominating the locally excited states in non-polar media can  
 29 explain the relatively large decay constants for solvents with  $\epsilon$   
 30  $< 15$  (Figure 5c).

31 Along with the conformational heterogeneity, in comparison  
 32 with **DPP-Ph**, an increase in the inner reorganizational energy  
 33 for **DPP-m-Ph** can push the tips of the Marcus curves closer  
 34 to the CR and away from the CS rates, making  $k_{\text{CS}} < k_{\text{CR}}$ .  
 35 Overall the findings for the excited-state dynamics of **DPP-m-**  
 36 **Ph** reveal a key advantage in the molecular-rotor design of  
 37 **DPP-Ph** for suppressing the undesired CR.

## 38 CONCLUSIONS

39 While  $\Delta G_{\text{CS}}^{(0)}$  and  $\Delta G_{\text{CR}}^{(0)}$  are similar for both dyads,  $k_{\text{CS}} >$   
 40  $k_{\text{CR}}$  for **DPP-Ph**, whereas  $k_{\text{CS}} \leq k_{\text{CR}}$  for **DPP-m-Ph**. This fea-  
 41 ture reiterates the importance of the molecular-rotor design of  
 42 the **DPP-Ph** dyad for impeding CR while attaining efficient  
 43 CS. Suppressing CR and boosting CS in non-viscous solvents  
 44 can, indeed, be in accordance with expected non-Condon ef-  
 45 fects. The viscosity-induced increase in the difference between  
 46 the rates of CS and CR, however, suggests for dominating  
 47 synergy with vibronic modes and perhaps, solvent reorganiza-  
 48 tional dynamics. Impeding CR, while conserving the efficien-  
 49 cy of CS, is key for organic electronic materials and devices  
 50 where molecular confinement can govern their properties. The  
 51 findings for viscous media provide a potential platform for  
 52 translation of molecular design to solid-state applications.

## 53 ASSOCIATED CONTENT

### 54 Supporting Information

The Supporting Information is available free of charge on the  
 ACS Publications website.

Experimental details for the synthesis and characterization of the  
 final compounds and the key intermediates, and for the electro-  
 chemical and spectroscopic experiments (PDF)

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### 59 Notes

The authors declare no competing financial interest.

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Gating that Suppresses Charge Recombination – the Role of Mono-*N*-Arylated Diketopyrrolopyrrole

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