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### **Electron Transfer**

## Porphyrin Donor and Tunable Push–Pull Acceptor Conjugates – Experimental Investigation of Marcus Theory

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Dedication In memory of Günther Wilke

**Abstract:** We report on a series of electron donor–acceptor conjugates incorporating a Zn<sup>II</sup> porphyrin-based electron donor and a variety of non-conjugated rigid linkers connecting to push–pull chromophores as electron acceptors. The electron acceptors comprize multicyanobutadienes or extended tetracyanoquinodimethane analogues with first reduction potentials ranging from -1.67 to -0.23 V vs. Fc<sup>+</sup>/Fc in CH<sub>2</sub>Cl<sub>2</sub>, which are accessible through a final-step cycloaddition–retroelectrocyclization (CA–RE) reaction. Characterization of the conjugates includes electrochemistry, spectroelectrochemistry, DFT calculations, and photophysical measurements in a range of solvents. The collected

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Supporting Information (SI) available: [Synthesis and full characterization of all new compounds, as well as copies of their <sup>1</sup>H and <sup>13</sup>C NMR spectra, X-ray crystallography details and CIF files for compounds **12** and **16**, cyclic voltammetry (CV), rotating disk voltammetry (RDV) and UV/Vis spectroelectrochemical data and spectral traces, quantum chemical calculations (DFT) on the conjugates and control compounds, UV/Vis spectra of the conjugates and control compounds, detailed report on the transient absorption spectroscopic measurements, and Marcus curves.]. See DOI:

data allows for the construction of multiple Marcus curves that consider electron acceptor strength, linker length and solvent, with data points extending well into the inverted region. The enhancement of electronic-vibration couplings, resulting from the rigid spacers and, in particular, multicyano-groups in the conformationally highly fixed push-pull acceptor chromophores affects the charge-recombination kinetics in the inverted region drastically.

#### Introduction

In the quest for artificial photosynthetic model systems, a key to controlling photoinduced electron transfer in electron donoracceptor assemblies is the successful matching of chromophoric electron donors and acceptors in terms of electrochemical and photophysical properties. In particular, the efficiency of photoinduced electron transfer in covalent systems is determined by critical factors such as the separation distance between the electron donor and acceptor, the conformation of the molecular bridge, the energy gap between the excited and charge-separated states, and the nature of the solvent. Importantly, control over the ratio of the rates for charge separation and charge recombination is crucial to create longlived charge-separated states. Mastering these factors is essential when trying to achieve molecular-scale electronics, artificial photosynthesis, and photovoltaic applications. Generally, Marcus theory is used to rationalize the rates of electron transfer (ET) reactions seen in the photosynthetic reaction centers.<sup>[1]</sup> It describes the rate of electron transfer as a non-linear function of the reaction Gibbs free energy ( $\Delta G$ ). More specifically, Marcus theory implies that rates of electron transfer start to decrease for reactions with a  $-\Delta G$  higher than the reorganization energy  $\lambda$ . The latter defines the Marcus inverted region, whose confirmation remained elusive for almost 30 years until Miller, Closs and Calcaterra provided unambiguous, experimental verification of the inverted region.<sup>[2]</sup> Classic Marcus equation works remarkably well in the normal region and close to the maximum rate, but for the inverted region electron-transfer rates higher than expected have also been observed. This deviation of the classical parabolic is the

result of quantum chemical vibrational effects, in which large electron-vibration (e-v) couplings in small molecules with highly polarized functional groups open a channel of vibrationassisted electron tunneling in the inverted region. This phenomenon is not only found for electron donors, but has also recently been observed in molecular wires at room temperature. In this work, photoinduced electron transfer in Zn<sup>II</sup> porphyrin-bridge-fullerene conjugates has been studied extensively, in which π-conjugated molecular wires were used as Interestingly, bridges. carbon-bridged oligophenylenevinylene, which is both rigid and flat, leads to an 840fold increase in the ET rate compared to the equivalent flexible molecular bridges. The presence of vibrational channels decreases the activation barrier of electron transfer and, in turn, opens the inelastic-tunneling pathway, explaining the rate enhancement. Until now, experimental evidence for the inverted region from intramolecular electron transfer has been limited to examples featuring electron-accepting guinones or fullerenes.[2-4]

Lately, a new class of push-pull acceptors derived from [2+2] cycloaddition-retroelectrocyclization (CA-RE) reactions that bear great potential as unique electron acceptors in electron transfer reactions has emerged.<sup>[5]</sup> CA-RE reactions take place between electron-rich, activated alkynes and electron-poor alkenes. In the original reaction, ruthenium-acetylides<sup>[6]</sup> served as the activated alkyne, while recent examples are based on purely organic molecules featuring anilino- and arvl ethersubstituted acetylenes<sup>[7]</sup> and amides<sup>[8]</sup> for alkyne activation.<sup>[9]</sup> Most CA-RE-based products give rise to interesting physical properties, such as tunable intermolecular charge-transfer (CT) bands expanding into the near infrared (NIR).<sup>[10]</sup> large thirdorder optical nonlinearities,<sup>[5,11]</sup> high two-photon absorption cross sections,<sup>[11b]</sup> thermal and environmental stability up to 300 °C,<sup>[10]</sup> and in many cases sublimability.<sup>[12]</sup> Products from CA-RE reactions have already proven useful for the synthesis of tetracenes,<sup>[13]</sup> with applicability to singlet fission,<sup>[14]</sup> and chiral optically active buta-1,3-dienes,[15] and found application as waveguides.<sup>[16]</sup> In addition, CA-RE-derived products stand out among all electron acceptors as a unique set of photoactive molecular materials for solar cells, in general, and electrontransfer reactions, in particular.<sup>[9d,17]</sup>

Our first foray into the field of photoinduced electron transfer was the successful linking of a Zn<sup>II</sup> porphyrin electron donor to an anilino-substituted alkyne activated towards the CA–RE reaction allowing for the formation of a tetracyanobuta-1,3diene electron acceptor.<sup>[18]</sup> Notably, this system underwent photoinduced electron transfer to afford a long-lived chargeseparated state of 2.3 µs in benzonitrile. Expanding upon this work, we recently reported the synthesis of a variety of conjugates with electron-donating porphyrins, electronaccepting push–pull chromophores, and aliphatic linkers<sup>[19]</sup> with the aim of rigidifying the aliphatic linker. This was intended to reduce the flexibility between electron donor and acceptor and to allow for an accurate determination of the distance between the separate building blocks, essential for determining further

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properties of the conjugates. Two major drawbacks were, however, noted: the synthetic complexity in obtaining them and, the rather large distance between electron donor and acceptor. In the current work, we aim to circumvent these problems by utilizing the easier to synthesize piperidyls as the rigid, though not conformationally locked, linker and by varying the electron donor-acceptor separation to ensure the optimal distance for electron transfer rates.

Herein, we report the synthesis of new porphyrin-donor based compounds with an activated alkyne component of four different lengths and their CA–RE reaction products forming a variety of push–pull acceptor conjugates. The newly synthesized conjugates 1–5, in addition to relevant previously reported conjugates 6–9,<sup>[19]</sup> which are all the subject of the current investigation, are shown in Figure 1. A full-fledged photophysical investigation/analysis of conjugates 1–9, together with electrochemical and X-ray structural analysis, has led to the construction of numerous Marcus curves with observed rates extending from the normal to the Marcus inverted region.

#### **Results and Discussion**

#### Synthesis

The synthesis began with a piperidine ring formation between the previously reported diol  $10^{[20]}$  and aniline  $11^{[21]}$  via the intermediate ditriflate to give compound 12 (Scheme 1). Halogen-lithium exchange and quenching with molecular iodine provided the corresponding iodide 13. The previously reported phenylacetylene- and pinacolborane-substituted porphyrins  $14^{[22]}$  and  $15^{[23]}$  could then be coupled with aryl halides 13 or 12 to give 16 and 17, respectively. Aldehyde 18, the synthesis of which is outlined in Section S2 of the Supporting Information, could be used to form porphyrin 19, whereby the aliphatic portion of the linker is bound directly to the porphyrin. The iodoaryl moiety present on 19 allows for Sonogashira crosscoupling with phenylacetylene, or with the related diyne<sup>[7]</sup> to give 20 and 21, respectively.

Compounds 16, 17, 20, and 21 were subjected to the CA–RE reaction with electron deficient alkenes 22–26. TCNE- (22) and TCNQ- (23) bearing conjugates, 1a–3a and 1b–3b, respectively, with three different distances between the electron donors and acceptors, were obtained in excellent yields. For the F<sub>4</sub>-TCNQ- (24) based conjugates, only those with shorter spacer distances, 2c and 3c, were synthesized. <sup>1</sup>H and <sup>13</sup>C NMR spectra revealed significant line broadenings and peak losses for those signals in close proximity to the electron acceptors. We imply that stable radical species from unpaired electrons exist centered on the F<sub>4</sub>-TCNQ-based electron acceptors. We have previously shown that the push-pull chromophores with the strongest acceptors, such as those derived from F<sub>4</sub>-TCNQ, give EPR spectra in agreement with

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acceptor-based radicals.<sup>[9a,c,m]</sup> Considering the fact that much

signals were observed

porphyrin



sharper

Figure 1. Newly synthesized conjugates 1–5 and previously reported conjugates 6–9<sup>[19]</sup> for subsequent investigation. For the full structure of the Zn<sup>II</sup> porphyrin, see Scheme 1.



Scheme 1. Synthesis of conjugates 1–5. Reagents and conditions: a) (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O (2.1 equiv.), *N*,*N*-diisopropylethylamine (2.1 equiv.), MeCN, –30 °C, 1 h, then 11 (1.2 equiv.), *N*,*N*-diisopropylethylamine (2.1 equiv.), –30 to 23 °C, 18 h; 68%. b) *n*BuLi (2.2 equiv.), I<sub>2</sub> (2.3 equiv.), THF, –78 °C to 23 °C, 1.5 h; 98%. c) 13 (2.1 equiv.), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (20 mol%), Cul (50 mol%), *i*Pr<sub>2</sub>NH/THF (1:1), 24 °C, 16 h; 45%. d) 12 (1.2 equiv.), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (10 mol%), Cs<sub>2</sub>CO<sub>3</sub> (4.0 equiv.), toluene, 95 °C, 36 h; 87%. e) 1) Pyrrole (4.0 equiv.), 3,5-di-*tert*-butylbenzaldehyde (3.0 equiv.), TFA (1.8 equiv.), CHCl<sub>3</sub>, 24 °C, 16 h then chloranil (3.0 equiv.), reflux, 1.5 h; 2) Zn(OAC)<sup>2</sup>·2H<sub>2</sub>O (1.0 equiv.), CHCl<sub>3</sub>/MeOH, 24 °C, 1 h; 5%. f) Phenylacetylene (2.1 equiv.), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (10 mol%), Cul (10 mol%), *P*<sub>7</sub>/2NH/THF (1:1), 24 °C, 16 h; 89%. g) 4-(Buta-1,3-diyn-1-yl)-N,N-dimethylaniline (2.1 equiv.), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (10 mol%), Cul (10 mol%), *P*<sub>7</sub>/2NH/THF (1:1), 24 °C, 16 h; 89%. g) 4-(Buta-1,3-diyn-1-yl)-N,N-dimethylaniline (2.1 equiv.), (PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (10 mol%), Cul (10 mol%), *P*<sub>7</sub>/2NH/THF (1:1), 24 °C, 16 h; 76%. h) TCNE (22) (1.0 equiv.), (CH<sub>2</sub>Cl)<sub>2</sub>, 23 °C, 1 h; 77–97%. i) TCNQ (23) (1.0 equiv.), (CH<sub>2</sub>Cl)<sub>2</sub>, 85 °C, 1 h; 69–89%. j) F<sub>4</sub>-TCNQ (24) (1.0 equiv.), (CH<sub>2</sub>Cl)<sub>2</sub>, 23 °C, 1 h; 35–9%. j) T<sub>4</sub>-TCNQ (24) (1.0 equiv.), (CH<sub>2</sub>Cl)<sub>2</sub>, 23 °C, 1 h; 53–97%. i) TCNQ (23) (1.0 equiv.), DMF, 100 °C, 16 h; 72%. For the X-ray crystal structures of 12 and 16, see Section S3 in the Supporting Information.

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nuclei, the radical species is most likely confined to the electron acceptor rather than resulting from intramolecular single electron transfer.

Alkenes **25** and **26** could also undergo the CA–RE reaction. This was, however, only performed for conjugates **2d** and **2e** with medium spacer distance. When buta-1,3-diyne **21** was subjected to the CA–RE reaction, two regioisomers, **4** and **5**, were obtained, where the resulting tetracyanobuta-1,3-diene is located closer to the piperidyl nitrogen (20%) or the dimethylamino nitrogen (77%), respectively. All conjugates were isolated as colored solids that did not undergo decomposition in air as solids or in solution over long periods (months). Photosensitivity under ambient light was also not detected. Additionally, the majority exhibit melting points above 300 °C without any observable decomposition.

Reference compounds **27–29** were also synthesized (see Section S2 of the Supporting Information) to allow for a comparison between conjugates and properties attributable solely to the acceptor moieties, (Figure 2). Similar to conjugates **2c** and **3c**, compound **29** exists as a stable radical species.



Figure 2. Reference compunds 27-29.

#### Electrochemistry

All compounds were subjected to cyclic voltammetry (CV) and rotating disk voltammetry (RDV) to determine their redox properties. Table 1 shows the values for **ZnP-S2 17** and conjugates **2a**—e by means of CV and RDV in CH<sub>2</sub>Cl<sub>2</sub> containing  $nBu_4NPF_6$  (0.1 M) vs. the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple and are uncorrected for any ohmic drops. The data for the remaining compounds are provided in Table S1 of the Supporting Information.

**ZnP-S2 17** features two reversible one-electron oxidations at approximately +0.33 and +0.62 V, one reversible one-electron reduction at approximately –1.84 V, and one irreversible one-electron reduction at –2.28 V. The two successive reductions are porphyrin centered. The remaining irreversible one-electron oxidation at approximately +0.43 V is attributed to the oxidation of the *N*-phenylpiperidyl moiety. The oxidations and reductions associated with the Zn<sup>II</sup> porphyrin remain constant in all of the examined conjugates. We take the lack of appreciable changes in the redox behavior of the porphyrin as support for the absence of electronic communication between the electron donors and acceptors in their ground state.

The *N*-phenylpiperidyl oxidation varies between **ZnP-S2 17** and the respective conjugates without any clear trend. For the electron acceptors, which were derived from the same electrondeficient alkene, similar values for the *N*-phenylpiperidyl oxidation, regardless of the linker, were noted. The electron acceptors originating from the CA–RE reaction undergo two one-electron reductions in sound agreement with the reference compounds. Again, the absence of electronic communication between the electron-donating porphyrin and the acceptor in the ground state is confirmed. Therefore, substitution of the rigid aliphatic bicyclo[2.2.2]octane linker by the synthetically more accessible piperidyl linker did not alter the independence of the redox behavior of electron donor and acceptor.

The first reduction for each acceptor is identical in all systems. As expected, the F<sub>4</sub>-TCNQ (24) derived acceptor, represented by ZnP-S2-F<sub>4</sub>-TCNQ 2c, shows the most anodically shifted process at -0.23 V, which decreases to -0.63, -0.89, and -1.18 V for ZnP-S2-TCNQ 2b, ZnP-S2-TCBD 2a, and ZnP-S2-TriCBD 2d, respectively. The weakest acceptor - ZnP-S2-DCBD 2e – with a one-electron reduction at -1.67 V is the only case, in which the first reduction is not reversible. The low value was to be expected due to the original alkene 26 only possessing three electron-withdrawing groups.

As a complement to the CV and RDV measurements, ZnP-S2-TCBD 2a, ZnP-S2-TCNQ 2b, ZnP-S2-F4-TCNQ 2c, and ZnP-S6-TCNQ 8 (for the corresponding CV and RDV, see reference <sup>[19]</sup>) were probed in spectroelectrochemical studies (see Section S5 of the Supporting Information). Negative potentials were applied to generate the one-electron reduced anions of the TCBD, TCNQ, and F<sub>4</sub>-TCNQ derived acceptors. In our previous report, we already illustrated the changes in the absorption spectra of a ZnP reference upon the first one-electron oxidation, and for ZnP-S6-TCBD 6 upon the first one-electron reduction.<sup>[19]</sup> Noteworthy for the oxidation of the ZnP reference are the newly developing absorptions at 410 and 620 nm. Both are well-known characteristics for the one-electron oxidized ZnP radical cation.<sup>[24]</sup> In contrast, reduction of ZnP-S6-TCBD 6 leads to a decrease and vanishing of the intramolecular CT band at 468 nm - vide infra. In addition, new absorptions evolve between 300 and 440 nm as well as between 550 and 800 nm. These features stem from the reduction of the TCBD moiety. The results are in line with the one-electron reduction of ZnP-S2-TCBD 2a, indicating that the piperidyl linker in ZnP-S2-TCBD 2a and the extra electron-accepting ethynediyl unit in ZnP-S6-TCBD 6, do not alter the reduction behavior of the electron acceptor. Upon one-electron reduction of ZnP-S2-TCNQ 2b and ZnP-S6-TCNQ 8, a decrease of the characteristic intramolecular CT bands appears at 685 and 716 nm, respectively. In addition to a minimum at 480 nm, a broad maximum grows in at 1060 nm and an isosbestic point evolves at 850 nm for ZnP-S2-TCNQ 2b, while for ZnP-S6-TCNQ 8 the maximum appears at 1068 nm and the isosbestic point is seen at 893 nm. For ZnP-S2-F4-TCNQ 2c, the corresponding differential absorption spectrum features maxima at 379, 576, and 1133 nm as well as minima at 480 and 859 nm. The latter

is again a result of the CT band deactivation. In all of the investigated systems, resetting the applied potential to zero leads to a restoring of the original spectrum as the reduction signatures decrease.

#### **Quantum Chemical Calculations**

DFT gas-phase calculations using the Perdew, Burke, and Ernzerhof generalized gradient approximation functional (PBE)<sup>[25]</sup> were performed with 1-3 (containing TCBD, TCNQ, and F<sub>4</sub>-TCNQ) using DMol3<sup>[26]</sup> to obtain qualitative insights into the electronic structure of the electron donor-acceptor conjugates. The structures were first annealed with the forciteforce field to determine the most stable conformers. These were subsequently optimized using the PBE functional with a double numeric basis set including polarization functions, a dispersion correction,<sup>[27]</sup> and effective core potentials for the Zn atom.<sup>[28]</sup> The molecular orbitals (MO) involved in the electronic transitions were then visualized and analyzed. Finally, singlepoint unrestricted calculations for the radical cation and anion were performed on ground-state optimized structures and spindensity plots used to visualize the regions involved in oxidation and reduction (see Section S6 of the Supporting Information).

The MOs and energies of the TCBD-derived conjugates were compared to the corresponding reference compounds. In all cases, the frontier MOs are either located on the electron acceptors or donors, confirming that piperidine is a true insulating spacer due to the lack of conjugation. Energetically, the a<sub>1u</sub>- and a<sub>2u</sub>-porphyrin-centered molecular orbitals are HOMO (highest occupied MO) and HOMO-1 with comparable energies to zinc tetraphenylporphyrin (ZnTPP). Likewise, the electron densities of LUMO (lowest unoccupied MO) and LUMO+1 are located on the electron acceptor and significantly lowered as the reduction strength is increased from, for example, TCBD to F<sub>4</sub>-TCNQ (see Figure S23 of the Supporting Information). This is consistent with the electrochemical studies. Overall, the length of the spacer does not impact the acceptor energies. Increasing the spacer length does, however, lead to a better stabilization of the bridge MOs, as shown for ZnP-S1-TCBD 1a (LUMO+4). Because of the reduced symmetry of the conjugates, the egx- (LUMO+2) and egy-(LUMO+3) orbitals of the porphyrins split relative to the degenerate ZnTPP. Nevertheless, the energetic splitting is less than 0.04 eV in all cases. The HOMO-LUMO gaps of the porphyrin centered a<sub>1/2u</sub>- and e<sub>g</sub>- orbitals are within 0.03 eV of that of ZnTPP. Thus, the results confirm our interpretation of the role of the linker, which is that it separates the HOMO from the LUMO spatially and limits the degree of electronic communication between the porphyrin donor and the push-pull acceptors in order to achieve longer charge-separated state lifetimes.

In addition, the internal reorganization energy was calculated as the sum of the vertical reorganization energies from the neutral to the cationic ( $\lambda$ +) and anionic ( $\lambda$ -) species using the

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semiempirical AM1<sup>[29]</sup> Hamiltonian as implemented in VAMP<sup>[30]</sup> as well as the DNP/PBE level of theory. Both calculations gave internal reorganization energies of approximately 0.4 eV for TCNQ-based systems and 0.6 eV for push–pull chromophores based on TCBD.

Та	ble	e 1.	Elec	ctroche	emical	data	of 2	a–e an	d Zr	P-S2	17	by CV at a	scan	rate
of	v	=	0.1	Vs <sup>-1</sup>	and	RDV	in	CH <sub>2</sub> Cl	2 +	0.1	М	<i>n</i> Bu₄NPF <sub>6</sub> ,	with	the
ferrocenium/ferrocene (Fc <sup>+</sup> /Fc) couple used as an internal standard.														

		CV		RDV	
	<i>E</i> ° [V] <sup>a)</sup>	Δ <i>E</i> <sub>p</sub> [mV] <sup>b)</sup>	<i>E</i> <sub>P</sub> [V] <sup>c)</sup>	<i>E</i> <sub>1/2</sub> [V]	Slope [mV] <sup>d)</sup>
ZnP-S2-	+0.84	65		+0.87 (1e⁻)	60
TCBD	+0.60	100		+0.62 (1e⁻)	60
2a	+0.30	120		+0.30 (1e <sup>-</sup> )	60
	-0.89	120		–0.92 (1e⁻)	60
	-1.21	90		–1.28 (1e⁻)	120
	-1.90	125		e)	
4	-2.27	100			
ZnP-S2-	+0.63	90		+0.67	
TCNQ			+0.45	+0.44 (1e <sup>-</sup> )	60
2b	+0.32	80		+0.35 (1e⁻)	60
	-0.63	85		–0.65 (1e⁻)	60
	-0.75	80		–0.78 (1e⁻)	60
	-1.85	120		e)	
	-2.24	80			
ZnP-S2-F4-	+0.63	150		+0.68 (2e <sup>-</sup> )	120
TCNQ			+0.59		
2c	+0.27	75		+0.34 (1e <sup>-</sup> )	60
	-0.23	79		–0.30 (1e⁻)	60
	-0.51	85		–0.53 (1e⁻)	60
	-1.85	95		–1.94 (1e⁻)	110
ZnP-S2-	+0.86	80		+0.90 (1e <sup>-</sup> )	60
TriCBD	+0.63	110		+0.73 (1e⁻)	60
2d	+0.32	100		+0.35 (1e⁻)	75
	-1.18	220		–1.22 (1e⁻)	60
	-1.46	120		–1.50 (1e⁻)	130
	-1.90	120			
ZnP-S2-	+0.75	100		+0.76 (1e⁻)	65
DCBD	+0.62	100		+0.65 (1e⁻)	60
2e	+0.32	100		+0.33 (1e⁻)	70
			-1.67	–1.66 (1e⁻)	70
			-1.93	–1.94 (1e⁻)	70
			-2.20	–2.23 (1e⁻)	
			-2.31		
ZnP-S2	+0.62	85		+0.57	
17			+0.43	+0.44 (1e <sup>-</sup> )	60
	+0.33	65		+0.35 (1e⁻)	60
	-1.84	90		–1.88 (1e⁻)	60
			-2.28		

<sup>a)</sup>  $E^{\rm b} = (E_{\rm pc} + E_{\rm pa})/2$ , where  $E_{\rm pc}$  and  $E_{\rm pa}$  correspond to the cathodic and anodic peak potentials, respectively. <sup>b)</sup>  $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$ . <sup>c)</sup>  $E_{\rm p} =$  irreversible peak potential. <sup>d)</sup> Logarithmic analysis of the wave obtained by plotting *E* versus

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 $\text{Log}[\textit{II}(\textit{I_{inrr}-h})]; \textit{I_{inrr}}$  is the limiting current and I the current.  $^{e)}$  Further oxidation and reduction not observed.

#### **Photophysical Properties**

Photoactive Porphyrin Conjugates. To shed light on the electronic interactions between the photo- and redox-active components, the absorption and fluorescence features of the electron donor–acceptor conjugates were compared in toluene with those of the individual components. We focus first on conjugates **2** featuring all the different investigated acceptor types with a center-to-center distance of 18.2 Å between the electron donor and acceptors. Next, we discuss the influence of the bridge length – leading to center-to-center distances starting at 13.9 Å and reaching 25.1 Å – on the photophysical properties (Table 3). To investigate the influence of the solvent polarity on the photophysical properties, THF and benzonitrile were used as additional solvents (see the Supporting Information, Sections S7 and S8, for photophysical properties of the reference compounds).

The absorption spectra of 2a-e in toluene are displayed in Figure 3. As far as the Soret- and Q-band maxima are concerned, no notable differences relative to the reference compounds are noted. For **2a-e**, an additional broad feature is observable, which undergoes distinct redshifts as the reduction strength of the electron acceptor increases. The latter is located for ZnP-S2-DCBD 2e at 452 nm, for ZnP-S2-TriCBD 2d at 459 nm, for ZnP-S2-TCBD 2a at 466 nm, for ZnP-S2-TCNQ 2b at 630 nm, and for ZnP-S2-F4-TCNQ 2c at 783 nm. The origin of this feature is a CT transition involving the terminal electron acceptors and the N-phenylpiperidyl nitrogens. Table 2 summarizes the absorption bands for 2a-e. The CT band is even further redshifted when increasing the solvent polarity to THF and benzonitrile. The strongest shifts evolved for the TCNQ based conjugates, that is, ZnP-S2-TCNQ 2b and ZnP-S2-F4-TCNQ 2c with shifts up to 705 and 865 nm, respectively, in benzonitrile.

Noteworthy is the impact of an additional aniline substitution in addition to TCBD in **ZnP-S4-TCBD 4** and **ZnP-S5-TCBD 5**. The absorption spectra reveal a broadening and a shift of the CT features between the respective nitrogens in aniline and/or piperidine and TCBD. Independent of the additional ethynediyl unit next to piperidine as in **ZnP-S4-TCBD 4** or next to aniline as in **ZnP-S5-TCBD 5**, the CT band maximizes at 514 nm.

The absorption spectra as a function of the electron donoracceptor distances reveal no notable changes in terms of position and intensity of the porphyrin and acceptor relevant features. The bridge disrupts the electronic communication between the photo- and redox-active components in the conjugates at distances of at least 13.9 Å. Evidence for this postulate came from absorption spectra, which are best described as the simple superimpositions of the component spectra. Notably, these results back up the electrochemical data as well as the quantum chemical calculations.



Figure 3. Absorption spectra of ZnP-S2-TCBD 2a (red line), ZnP-S2-TCNQ 2b (light grey line), ZnP-S2-F4-TCNQ 2c (dark grey line), ZnP-S2-TriCBD 2d (blue line), and ZnP-S2-DCBD 2e (black line) in toluene. Inset: fluorescence spectra after excitation at 420 nm in toluene.

First insights into possible electron donor–acceptor interactions came from fluorescence assays. Table 2 summarizes the photophysical data taken from steady-state and time-resolved fluorescence measurements. We note porphyrin-centered fluorescence bands with maxima at 600 and 649 nm in all systems. As for the reference porphyrins, the fluorescence is subject to redshifts in polar solvents like benzonitrile with 611 and 664 nm maxima.

For 2a-e, the fluorescence quenching is in line with the reduction strength of the different acceptors. In particular, the strongest fluorescence quenching is derived for the F<sub>4</sub>-TCNQ containing conjugate **ZnP-S2-F<sub>4</sub>-TCNQ 2c** ( $\Phi_{fl} = 1.5 \times 10^{-4}$ ). The fluorescence quenching weakens from ZnP-S2-TCNQ 2b  $(\Phi_{\rm fl} = 2.5 \times 10^{-4})$  to ZnP-S2-TCBD 2a  $(\Phi_{\rm fl} = 1 \times 10^{-3})$ , to ZnP-**S2-TriCBD 2d** ( $\Phi_{fl} = 1.6 \times 10^{-2}$ ), and to **ZnP-S2-DCBD 2e** ( $\Phi_{fl} =$ 5 x 10<sup>-2</sup>). ZnP-S2-DCBD 2e, endowed with only two withdrawing CN-groups, lacks any affinity for energy- or electron transfer. The distance between the porphyrin donors and acceptors plays a crucial role with regard to the fluorescence quenching. A comparison between the TCBD based conjugates in toluene shows that the weakest quenching is observed for ZnP-S1-TCBD 1a ( $\Phi_{fl} = 1 \times 10^{-2}$ ) with a distance between electron donor and acceptor ( $R_{DA}$ ) of 25.1 Å. The quenching intensifies towards **ZnP-S3-TCBD 3a** ( $\Phi_{fl}$  =  $6 \times 10^{-4}$ ) with an  $R_{DA}$  of 13.9 Å. Taking the aforementioned trends into concert, ZnP-S3-F4-TCNQ 3c reveals strongest quenching with a fluorescence quantum yield of  $9 \times 10^{-5}$ . In THF and benzonitrile (PhCN), the fluorescence quenching further intensifies. Overall, the fluorescence lifetimes match the trend seen for the fluorescence quantum yields (Table 2). In most cases, an exact determination of the fluorescence lifetimes is, however, hampered by the time resolution of 200 ps for our instrumentation.

Thermodynamics and Driving Forces of Electron Transfer. Taking the aforementioned steady-state and time-resolved measurements into concert, we infer – next to the intrinsic

deactivation channels of the photoexcited porphyrins additional decay pathways in the electron donor-acceptor conjugates, especially for the multicomponent arrays featuring F4-TCNQ, TCNQ, and TCBD electron acceptors. Still, for ZnP-S2-TriCBD 2d and ZnP-S2-DCBD 2e minor and/or almost no fluorescence quenching was noted. We hypothesize that neither energy nor electron transfer - evolving from the photoexcited porphyrin - takes place. At this point we estimated the energetics of the energy and electron transfer reactions. Considering that the electron acceptors lack notable fluorescence, the energies of their lowest-lying electronic states were extrapolated from their corresponding absorption spectra. In the case of TriCBD and DCBD, the lowest energetic states with absorption onsets at 459 nm for ZnP-S2-TriCBD 2d and at 452 nm for ZnP-S2-DCBD 2e leading to singlet excited state energies of around 2.75 eV, are substantially higher than that of the porphyrins at 591 nm, which corresponds to 2.1 eV. Accordingly, a porphyrin to TriCBD and/or a porphyrin to DCBD energy transfer processes are ruled out thermodynamically. When turning to TCBD, a similar picture is noted, namely the lowest localized electronic states in the TCBD-containing porphyrin conjugates are porphyrin centered. For example, we note in the absorption spectra the presence of a TCBD

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centered transition as high as 2.7 eV. This is substantially higher than the porphyrin centered transition at 2.1 eV, rendering an energy transfer from the porphyrin to TCBD impossible. In other words, the porphyrin fluorescence quenching must relate to a porphyrin-to-TCBD electron transfer.

The situation changes for those porphyrin conjugates featuring extended TCNQs. As an example, we note for **ZnP-S2-TCNQ 2b** that the absorption onset of TCNQ coincides in toluene (1.97 eV) with that of the porphyrin. When increasing the solvent polarity, the energetically lowest-lying TCNQ excited state decreases in energy to 1.87 eV in THF and 1.76 eV in benzonitrile. Likewise, an energy transfer should be taken into consideration for **ZnP-S2-F4-TCNQ 2c**, as even in toluene the lowest electronic level is as low as 1.58 eV.

To elucidate if, in addition to an energy transfer, a thermodynamically supported electron transfer may govern the porphyrin singlet excited state deactivation in the conjugates, we determined the corresponding thermodynamic driving forces in different solvents by using the Rehm-Weller approach.<sup>[31]</sup>

Table 2. Photophysical data of porphyrin conjugates 1-9 together with porphyrin reference compounds.

						0			
	$\lambda_{\max}$ (CT-band) <sup>[a]</sup> [nm]				Φ <sub>fl</sub>		τ <sup>[b]</sup> [ns]		
	toluene	THF	PhCN	toluene	THF	PhCN	toluene	THF	PhCN
ZnP-S1 16	-	-	-	5.5·10 <sup>-2</sup>	5.5·10 <sup>-2</sup>	5.5·10 <sup>-2</sup>	2.05	1.87	1.75
ZnP-S2 17	-	-	-	5·10 <sup>-2</sup>	5·10 <sup>-2</sup>	5·10 <sup>-2</sup>	2.11	1.85	1.69
ZnP-S3 20	-	-	-	5.5·10 <sup>-2</sup>	5.5·10 <sup>-2</sup>	5.5·10 <sup>-2</sup>	2.05	1.92	1.77
ZnP-S4 21	-	-	-	5·10 <sup>-2</sup>	5·10 <sup>-2</sup>	5·10 <sup>-2</sup>	2.03	1.89	1.72
ZnP-S1-TCBD 1a	466	474	486	1.10-2	9·10 <sup>-3</sup>	6·10 <sup>-3</sup>	0.423	0.324	0.298
ZnP-S2-TCBD 2a	466	474	486	1.10-3	6·10 <sup>-4</sup>	5·10 <sup>-4</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S3-TCBD 3a	466	474	486	6.10-4	2·10 <sup>-4</sup>	1.10-4	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S1-TCNQ 1b	630	662	705	2·10 <sup>−3</sup>	1.6·10 <sup>-3</sup>	1.4·10 <sup>-3</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S2-TCNQ 2b	630	662	705	2.5.10-4	8·10 <sup>-5</sup>	5·10 <sup>-5</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S3-TCNQ 3b	630	662	705	1.5·10 <sup>-4</sup>	9·10 <sup>-5</sup>	5·10 <sup>-5</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S2-F4-TCNQ 2c	783	860	865	1.5·10 <sup>-4</sup>	9·10 <sup>-5</sup>	9·10 <sup>-5</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S3-F4-TCNQ 3c	783	860	865	9·10 <sup>-5</sup>	9·10 <sup>-5</sup>	1.10-4	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S2-TriCBD 2d	459	465	476	1.6·10 <sup>-2</sup>	1.10-2	8·10 <sup>-3</sup>	0.57	0.33	0.34
ZnP-S2-DCBD 2e	452	456	462	5·10 <sup>-2</sup>	3·10 <sup>-2</sup>	3·10 <sup>-2</sup>	1.82	1.71	1.59
ZnP-S4-TCBD 4	514	517	527	3.10-4	2·10 <sup>-4</sup>	1.8·10 <sup>-4</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S5-TCBD 5	514	517	527	4.5·10 <sup>-4</sup>	3.5.10-4	3.10-4	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S6-TCBD 6	461	468	476	1.2·10 <sup>-5</sup>	1.4·10 <sup>-5</sup>	1.4·10 <sup>-5</sup>	0.43	0.39	0.41
ZnP-S7-TCNQ 7	588	618	657	3·10 <sup>-3</sup>	2·10 <sup>-3</sup>	2·10 <sup>-3</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S6-TCNQ 8	648	678	717	5·10 <sup>-3</sup>	7·10 <sup>-3</sup>	1.10-2	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>	< 0.2 <sup>[c]</sup>
ZnP-S8-TCBD (±)-9	466	474	486	1.5·10 <sup>-2</sup>	1.2·10 <sup>-2</sup>	1.1·10 <sup>-2</sup>	0.80	0.52	0.40

[a] Charge-transfer band of the respective push-pull chromophore in conjugates 1–9; [b]  $\lambda_{exc}$  = 403 nm, TCSPC laser diode; [c] under the limit of instrumental resolution.

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The latter is used as an estimation of the Gibbs energy for radical ion pair formation in solvents of different dielectric constants  $\epsilon_{\rm s}{}^{\rm [32]}$ 

$$\Delta G_{CS}^0 = \left[ e \left( E_{D,ox}^\circ - E_{A,red}^\circ \right) - E_{00^*}(ZnP) \right] - E_C$$

where *e* is the elementary charge,  $E^{\circ}_{D,ox}$  and  $E^{\circ}_{A,red}$  are the first oxidation and reduction of the electron donor and acceptor, respectively, measured in a solvent with  $\varepsilon_{ref}$  (CH<sub>2</sub>Cl<sub>2</sub>: 8.93),  $E_{00}$  is the zero-zero transition energy of the first singlet excited state of the porphyrin (2.1 eV), and  $E_C$  is a correction factor based on the Born dielectric continuum model accounting for Coulombic interactions in the radical ion pair state in a solvent of dielectric constant  $\varepsilon_s$ :

$$E_{\rm C} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\rm s}}\frac{1}{R_{\rm DA}} + \frac{e^2}{4\pi\varepsilon_0} \left[ \left(\frac{1}{2r_{\rm D^+}} + \frac{1}{2r_{\rm A^-}}\right) \left(\frac{1}{\varepsilon_{\rm ref}} - \frac{1}{\varepsilon_{\rm s}}\right) \right]$$

where  $\varepsilon_0$  is the permittivity of vacuum (8.854 Fm<sup>-1</sup>),  $R_{DA}$  is the electron donor–acceptor separation, and  $r_{D+}$  and  $r_{A-}$  are the ionic radii of the electron donor and acceptor, respectively. To describe the separation more accurately, the center-to-center distances rather than the corresponding edge-to-edge distances were taken. The values are collected in Table 3.

In toluene, the data suggests that for the five different electron acceptors the radical ion pair state formation is thermodynamically unlikely in those porphyrin conjugates containing DCBD or TriCBD, namely **ZnP-S2-DCBD 2e** ( $\Delta G_{CS}^0 = +0.54 \text{ eV}$ ) and **ZnP-S2-TriCBD 2d** ( $\Delta G_{CS}^0 = +0.04 \text{ eV}$ ). This is in line with the fluorescence quantum yields, which disclosed no appreciable quenching for **ZnP-S2-DCBD 2e**. For **ZnP-S2-TCBD 2a**, the presence of the stronger electron accepting TCBD evokes a significant driving force for the radical ion pair

state formation ( $\Delta G_{CS}^0 = -0.15$  eV). Thermodynamically, the most favored radical ion pair state formation is estimated for **ZnP-S2-F4-TCNQ 2c** with a driving force of -0.96 eV in toluene.

The driving force for an electron transfer depends on the distance between the electron donors and acceptors according to the Rehm-Weller equation. To this end, shortening the spacer exemplary from **ZnP-S1-TCBD 1a** to **ZnP-S3-TCBD 3a** increases the driving force from -0.03 up to -0.29 eV.

Overall, increasing the solvent polarity to, for example, benzonitrile increases the driving force for electron transfer in all of the conjugates due to the lower energy of the polar charge-separated state. Table 3 summarizes the driving forces in the different solvents.

Excited State Processes. Deeper insights into the nature of the intramolecular deactivation processes came from ultrafast transient absorption spectroscopy, which was recorded after 420 nm excitation in toluene, THF, and benzonitrile (see Section 8 of the Supporting Information). The transient features were analyzed by multiwavelength as well as global and target analyses. The ZnP-centered second singlet excited state excitation of ZnP-S2-DCBD 2e results within 2 ps in the formation of the first singlet excited state due to internal conversion. Most notable are minima at 555 and 602 nm as well as maxima at 464, 581, and 627 nm. This is followed by intersystem crossing to the corresponding triplet excited state of ZnP. The ZnP singlet excited state features are short lived since they decay with a lifetime of 2.1 ns in toluene. The corresponding times in THF and benzonitrile were determined to be 1.9 and 1.8 ns, respectively, which match those of the reference compounds 16, 17, 20 and 21.

	E <sup>°</sup> ox <sup>[b]</sup>	E <sup>o</sup> red <sup>[b]</sup>	/D+ <sup>[C]</sup>	r <sub>A-</sub> [d]	R <sub>cc</sub> <sup>[e]</sup>		$\Delta G_{CS}^0$ [eV]			$\Delta G_{CR}^0$ [eV]	
	[V]	[V]	[A]	[A]	[A]	toluene	THF	PhCN	toluene	THF	PhCN
ZnP-S1-TCBD 1a	+0.36	-0.86	4.7	3.6	25.1	-0.03	-0.88	-1.16	-2.07	-1.22	-0.94
ZnP-S2-TCBD 2a	+0.30	-0.89	4.7	3.6	18.2	-0.15	-0.94	-1.20	-1.95	-1.16	-0.90
ZnP-S3-TCBD 3a	+0.31	-0.85	4.7	3.6	13.9	-0.29	-1.00	-1.24	-1.81	-1.10	-0.86
ZnP-S1-TCNQ 1b	+0.35	-0.64	4.7	4.3	25.1	-0.36	-1.12	-1.37	-1.74	-0.98	-0.73
ZnP-S2-TCNQ 2b	+0.32	-0.63	4.7	4.3	18.2	-0.49	-1.19	-1.42	-1.61	-0.91	-0.68
ZnP-S3-TCNQ 3b	+0.30	-0.66	4.7	4.3	13.9	-0.59	-1.21	-1.42	-1.51	-0.89	-0.68
ZnP-S2-F4-TCNQ 2c	+0.27	-0.23	4.7	4.4	18.2	-0.96	-1.64	-1.86	-1.14	-0.46	-0.24
ZnP-S3-F4-TCNQ 3c	+0.30	-0.29	4.7	4.4	13.9	-0.97	-1.58	-1.78	-1.13	-0.52	-0.32
ZnP-S2-TriCBD 2d	+0.32	-1.18	4.7	4.4	18.2	+0.04	-0.64	-0.86	-2.14	-1.46	-1.24
ZnP-S2-DCBD 2e	+0.32	-1.66	4.7	4.3	18.2	+0.54	-0.16	-0.39	-2.64	-1.94	-1.71
ZnP-S4-TCBD 4	+0.33	-0.85	4.7	3.8	14.5	-0.28	-0.98	-1.21	-1.82	-1.12	-0.89
ZnP-S5-TCBD 5	+0.33	-0.81	4.7	3.8	16.0	-0.28	-1.01	-1.25	-1.82	-1.09	-0.85
ZnP-S6-TCBD 6	+0.36	-0.79	4.7	3.8	22.9	-0.16	-0.96	-1.23	-1.94	-1.14	-0.87
ZnP-S7-TCNQ 7	+0.35	-0.89	4.7	4.4	20.6	-0.17	-0.89	-1.12	-1.93	-1.21	-0.98
ZnP-S6-TCNQ 8	+0.35	-0.58	4.7	4.4	22.9	-0.46	-1.19	-1.43	-1.64	-0.91	-0.67
ZnP-S8-TCBD (±)-9	+0.35	-1.03	4.7	3.6	25.1	+0.13	-0.72	-1.00	-2.23	-1.38	-1.04

Table 3. Gibbs free energies of charge separation and recombination, and the parameters used for the calculations according to the Weller equation.<sup>[a]</sup>

[a] Values for all physical constants are taken from <sup>[32]</sup>; [b] measured in CH<sub>2</sub>Cl<sub>2</sub>, see Table 1 and Supporting Information; [c] estimated from X-ray structure data and molecular volume calculations; [d] estimated from the molecular volume of the acceptor molety;<sup>[33]</sup> [e] center-to-center distance of the donor and acceptor  $\pi$ -systems; see the Supporting Information for more details.

Spectroscopic evidence for the triplet excited state population comes from the characteristic 476 and 844 nm maxima. Importantly, the same features were seen in 420 nm photoexcitation experiments with **ZnP-S2 17**. This, in turn, attests to the exclusive ZnP excitation and deactivation in **ZnP-S2-DCBD 2e**, as our aforementioned experiments and calculations already suggested neither an energy transfer nor an electron transfer from the porphyrin to the acceptor are likely to happen (Figure 4c).

Different is the transient behavior in conjugate ZnP-S2-TriCBD 2d (Figure 4b). Analysis of the differential absorption changes recorded after 2 ps, attributes, which are in accordance with the formation of the ZnP singlet excited state - like in ZnP-S2 17 are seen. Intersystem crossing to the triplet excited state of ZnP is evidenced by the transients at 475 and 844 nm. A closer look reveals the formation within 2 ns to a minor extent. In doing so, a second transformation out of the ZnP singlet excited state sets in to generate a bleaching between 468 and 511 nm. The latter resembles the spectroelectrochemical analysis, where the reduction of the electron acceptor leads to a bleaching of the respective CT band. In addition, a distinct evolution of the one electron oxidized ZnP radical cation fingerprint at around 620 nm is observable. As such, the newly formed transients relates to the ZnP"+-S2-TriCBD"- radical ion pair state. Multiwavelength analyses gave charge separation dynamics of 200 ± 20 ps. The slow dynamics are in line with the thermodynamics according to the Weller approach, where we estimated that the charge-separated state in the rigid structure is nearly isoenergetic to the porphyrin singlet excited state in toluene ( $\Delta G_{CS}^0 = +0.04 \text{ eV}$ ). The radical ion pair state is, however, metastable and decays within 1200 ± 50 ps. Increasing the solvent polarity increases the driving force for the charge separation. As a consequence, formation and decay of ZnP+-S2-TriCBD- radical ion-pair state takes place within 29 ± 2 and 122 ± 5 ps in THF ( $\Delta G_{CS}^0 = -0.64 \text{ eV}$ ), respectively. In benzonitrile ( $\Delta G_{CS}^0 = -0.86 \text{ eV}$ ), the values are 32 ± 7 and 107 ± 5 ps.

A similar picture unfolds for ZnP-S2-TCBD 2a (Figure 4a). which upon photoexcitation is subject to a charge-transfer from the singlet-excited state of ZnP to the electron accepting TCBD. With time delays of 2 ps, only spectral characteristics of the ZnP singlet excited state are detectable. In particular, ground state bleaching of the Soret- and Q-bands is seen in the 400 to 450 and 500 to 650 nm regions, respectively. These singlet excited state features decay with dynamics of 90 ± 10 ps in toluene to afford a new product with a transient minimum at 470 nm and a transient maximum at 625 nm. These transients are in perfect agreement with those established for the oneelectron reduced TCBD radical anion and the one-electron oxidized ZnP radical cation. The ZnP"+-S2-TCBD"- is short lived with 510 ± 20 ps and decays to the ground state. Kinetic analysis in THF and benzonitrile leads to charge separation/recombination dynamics of 57 ± 5 / 5 ± 1.5 ps and 18 ± 3 / 70 ± 5 ps, respectively. Interestingly, electron transfer from the ZnP singlet excited state competes strongly in THF

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with an intersystem crossing to the ZnP triplet excited state as evidenced by the spectroscopic markers at 473 and 844 nm. However, in line with thermodynamics, the ZnP triplet excited state formation is only enabled via intersystem crossing. In the case of the shorter-linked TCBD-based ZnP-S3-TCBD 3a (see Section S8 in the Supporting Information), we also noticed photoinduced charge separation followed by charge recombination, upon excitation of the porphyrin in the three different solvents. A minimum at 469 nm and a maximum at 625 nm document the ZnP"+-S3-TCBD - generation. In line with the increased driving force for charge separation and the stronger fluorescence quenching, the charge separation is facilitated from 19 ± 3 ps in toluene up to 6 ± 1.5 ps in benzonitrile, while charge recombination to reinstate the ground state takes place with 147  $\pm$  5 ps in toluene and 31  $\pm$  3 ps in benzonitrile. Finally, ZnP-S1-TCBD 1a with an R<sub>DA</sub> of 25.1 Å shows the singlet excited state features of ZnP. These decay with triexponential and solvent dependent dynamics. For example, from multiple wavelength analysis in benzonitrile we derived lifetimes of 2.1  $\pm$  0.1 ns, 232  $\pm$  7 ps, and 16  $\pm$  3 ps. The former is attributed to the singlet excited state decay via intersystem crossing leading to the corresponding triplet excited state as shown by the characteristic fingerprints at 481 and 850 nm. Interestingly, no spectroscopic proof for the formation of any appreciable photoproduct is observable at first glance. However, we noticed that in benzonitrile, the porphyrin fluorescence quantum yield of 6 x 10<sup>-3</sup> and the singlet excited lifetime of 298 ps are quenched in ZnP-S1-TCBD 1a relative to ZnP-S1 16, while a porphyrin to TCBD energy transfer is thermodynamically not allowed. Thus, a reasonable interpretation is an electron transfer from ZnP to TCBD, with a slow charge separation (232  $\pm$  7 ps) and a much faster charge recombination.

Similarly, excitation of the TCNQ based ZnP-S1/S2/S3-TCNQ 1-3b at 420 nm results in the generation of a charge-separated state. In ZnP-S2-TCNQ 2b we see a fast transformation of the ZnP singlet excited state into the charge-separated ZnP"+-S2-TCNQ<sup>-</sup>. With time delays of 2 ps, features in the visible and in the near infrared regions develop that are in perfect agreement with the spectroelectrochemically generated spectra of the oneelectron reduced TCNQ radical anion and the one-electron oxidized ZnP radical cation. To this end, the bleaching in the differential absorption spectra at around 600 nm in toluene and/or 700 nm in benzonitrile are clear fingerprints of the TCNQ centered reduction, whereas the maximum at 640 nm is due to the oxidation of ZnP. Kinetically,  $8 \pm 1$  and  $140 \pm 10$  ps were determined to be the charge separation and charge recombination dynamics in toluene, respectively. Charge recombination from ZnP"+-S2-TCNQ"- 2b leads to the population of the ground state. This is compared to the values of 4  $\pm$  1 ps (THF) / 3  $\pm$  0.5 ps (benzonitrile) for charge separation and 31 ± 5 ps (THF) / 20 ± 2 ps (benzonitrile) for charge recombination. Here, similar to ZnP-S2-TCBD 2a in THF and benzonitrile, intersystem crossing to the triplet excited state of ZnP results.

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Figure 4. Species-associated spectra and (inset) associated time dependent amplitudes and fits of the femtosecond flash photolysis (420 nm, 200 nJ) of a) ZnP-S2-TCBD 2a; b) ZnP-S2-TriCBD 2d; c) ZnP-S2-DCBD 2e in argon-saturated toluene (optical density, OD = 0.5) monitoring the charge separation and charge recombination processes (2a, 2d) and intersystem crossing (2e), respectively.

Comparing the results with the longer spaced **ZnP-S1-TCNQ 1b** ( $R_{DA}$ = 25.1 Å) and the shorter spaced **ZnP-S3-TCNQ 3b** ( $R_{DA}$ = 13.9 Å) show a clear trend for the charge separation dynamics that follow the results based on the Rehm-Weller approach and the fluorescence quantum yields. As a matter of fact, **ZnP-S3-TCNQ 3b** with a more exogenous  $\Delta G_{CS}^0$  of -0.59 eV reveals a faster charge separation with 5 ± 1 ps in toluene, while the electron transfer from ZnP to TCNQ in **ZnP-S1-TCNQ 1b** occurs within 21 ± 2 ps as a consequence of the smaller  $\Delta G_{CS}^0$  of -0.36 eV and greater distance between electron donor and acceptor. However, the spatial separation in **ZnP-S1-TCNQ 1b** leads to charge recombination dynamics of 279 ± 20 ps, which are slower than for **ZnP-S2-TCNQ 2b** and **ZnP-S3-TCNQ 3b** (71 ± 6 ps).

Finally, the ZnP singlet excited state was generated and probed in **ZnP-S2-F4-TCNQ 2c** and **ZnP-S3-F4-TCNQ 3c** (see Section S8 in the Supporting Information). Immediately after 420 nm excitation, a strong broad bleaching around 780 nm in toluene develops. This transient bleaching is accompanied by a broad absorption in the near infrared region. The features are a perfect spectral resemblance to the spectroelectrochemical studies, verifying the presence of the one electron reduced F4-TCNQ radical anion after an electron transfer from ZnP. The lifetime of the radical ion pair state was gauged at  $35 \pm 5 / 21 \pm$  $2 / 15 \pm 2$  ps for **ZnP-S2-F4-TCNQ 2c** and  $12 \pm 2 / 63 \pm 5 / 19 \pm$ 3 ps for **ZnP-S3-F4-TCNQ 3c** in toluene / THF / benzonitrile. In competition with electron transfer is intersystem crossing to the triplet excited state of ZnP, which shows the highest quantum yields in THF compared to toluene and benzonitrile.

Table 4 summarizes the results for the electron donor-acceptor conjugates in toluene, including the electron transfer dynamics for conjugates **4–9**. The respective spectra are gathered in Section 8 of the Supporting Information. Comparing the results for **ZnP-S4-TCBD 4** with **ZnP-S5-TCBD 5** shows that the additional ethynediyl – connected to piperidyl or next to aniline – has almost no influence on the electron transfer kinetics. This observation supports the assumption that the electron-accepting LUMO of the electron acceptor is spread out over the whole push-pull chromophore structure, which is in conjugation despite the twisted structure. In terms of charge recombination,

conjugates **6–9** show the longest lifetimes in toluene overall. For example, multiwavelength analysis afforded chargeseparated state lifetimes of around 13  $\pm$  0.5 ns in the TCBDderived **ZnP-S6-TCBD 6** and of around 5.6  $\pm$  0.4 ns in the TCNQ-derived **ZnP-S6-TCNQ 8**. In summary, the aliphatic, not fully conjugated linkage seems to slow down, on one hand, the charge separation and, on the other hand, the charge recombination dynamics. As a matter of fact, slow charge separation in THF and benzonitrile is followed by even faster charge recombination, thereby preventing a reasonable analysis of the charge recombination kinetics (see Section S9 of the Supporting Information for further explanations).

Table 4. Lifetimes for charge separation and recombination in the electron donor–acceptor conjugates  $1\!-\!9$  in toluene.

	Toluene					
_	<i>τ</i> <sub>CS</sub> [ps]	<i>т</i> <sub>СR</sub> [ps]				
ZnP-S1-TCBD 1a	460 ± 20	680 ± 20				
ZnP-S2-TCBD 2a	90 ± 10	510 ± 20				
ZnP-S3-TCBD 3a	19 ± 3	147 ± 5				
ZnP-S1-TCNQ 1b	21 ± 2	279 ± 20				
ZnP-S2-TCNQ 2b	8 ± 1	140 ± 10				
ZnP-S3-TCNQ 3b	5 ± 1	71 ± 6				
ZnP-S2-F4-TCNQ 2c	6 ± 1	35 ± 5				
ZnP-S3-F4-TCNQ 3c	$3 \pm 0.5$	12 ± 2				
ZnP-S2-TriCBD 2d	200 ± 20	1200 ± 50				
ZnP-S4-TCBD 4	15 ± 1	118 ± 5				
ZnP-S5-TCBD 5	13 ± 1	115 ± 5				
ZnP-S6-TCBD 6	$300 \pm 30$	13000 ± 500				
ZnP-S7-TCNQ 7	115 ± 10	$24000 \pm 500$				
ZnP-S6-TCNQ 8	135 ± 15	$5600 \pm 400$				
ZnP-S8-TCBD (±)-9	931 ± 30	$23000 \pm 500$				

#### Analysis according to the Marcus theory

In the final step of our investigations, we analyzed the charge transfer dynamics in the different conjugates by correlating them with the free energy changes of the underlying electron transfer. The rate constant ( $k_{\text{ET}}$ ) for nonadiabatic electron transfer reactions, in which electronic coupling between the reactant and product potential is weak, can be described by:

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$$k_{ET} = \sqrt{\frac{\pi}{\hbar^2 \lambda_R k_B T}} |V|^2 exp \left[ \frac{-(\lambda_R + \Delta G^0)^2}{4 \lambda_R k_B T} \right]$$

The preexponential term consists of the Planck constant  $\hbar$ , the Boltzmann constant  $k_{\rm B}$ , the absolute temperature *T*, the total reorganization energy  $\lambda_{\rm R}$ , and the electronic matrix element *V*. The latter describes the coupling of the reactant state with that of the product and dictates the rate of electron transfer. Hereby, *V* depends on the spatial overlap of the electron donor and acceptor orbitals. Finally, the driving forces for electron transfer are expressed by  $\Delta G^0$ . Going a step further, the semiclassical approach of the Marcus theory includes nuclear factors, especially electron-vibrational couplings, giving the deviation of the Marcus plot from the classical parabolic shape:

$$k_{ET} = \sqrt{\frac{\pi}{\hbar^2 \lambda_S k_B T}} |V|^2 \sum_{\nu}^{\infty} \frac{e^{-S} S^{\nu}}{\nu!} exp\left[\frac{-(\nu \hbar \omega + \lambda_S + \Delta G^0)^2}{4 \lambda_S k_B T}\right]$$

The total reorganization energy  $\lambda_R$  is split into the solvent ( $\lambda_S$ ) and internal/vibrational reorganization energy ( $\lambda_v$ ). *S* is the Huang-Rhys factor, which characterizes the strength of electron-vibrational (e-v) coupling and  $\omega$  relates to the averaged frequency of the coupled quantum mechanical vibration modes:

$$S = \frac{\lambda_V}{\hbar\omega}$$

The semiclassical approach enables the explanation for quantum chemical vibrational effects and explains the occurrence of electron tunneling effects.<sup>[34]</sup>

We constructed the Marcus curves by plotting the electron transfer rates of the conjugates with nearly the same  $R_{DA}$ versus the corresponding thermodynamic driving forces neglecting minor differences in the internal reorganization energies of the respective push-pull acceptors and assuming almost similar electronic couplings V for CS and CR. Figure 6 top, for example, displays all electron donor-acceptor conjugates with R<sub>DA</sub> between 13.9 and 16 Å in toluene. The influence of the push-pull chromophores on the charge-transfer dynamics is clearly discernable. On one hand, increasing the reduction strength of the latter expedites the charge separation as in ZnP-S3-F4-TCNQ 3c and moves the underlying kinetics to the top of the Marcus curve. On the other hand, the slowest charge recombination is realized for TCBD based ZnP-S3-TCBD 3a featuring the weakest electron accepting part. Detailed analyses reveal that the rate of charge recombination decreases much more slowly than that of the charge separation, which leads to a leveling off of the Marcus inverted region. Here, the semiclassical Marcus approach rather than the classical Marcus approach (for comparison see Section S9 of the Supporting Information) is necessary to obtain reasonable fits, from which we derive sizeable electronvibration couplings. It is fair to conclude that those push-pull based electron acceptors, which are endowed with highly polarized CN bonds, favor vibrational interactions with electrons. These open a channel of vibration-assisted electron

tunneling in the Marcus inverted region and explain the acceleration of charge recombination processes.<sup>[35]</sup> Please note that the vibrational quantum  $\hbar\omega$  is taken as 2200 cm<sup>-1</sup> corresponding to CN stretching vibrations.<sup>[36]</sup>

In the same way, the characteristic dependence known from the semiclassical Marcus approach on electron transfer was established for conjugates 2 (constant  $R_{DA}$  =18.2 Å) as well as conjugates 1 and 6-9 ( $R_{DA}$  = 20.6-25.1 Å). A closer look at electron donor-acceptor conjugates 2 in toluene reveals that the dynamics for charge separation are located in the normal / top region, whereas for charge recombination the dynamics are in the inverted region of the Marcus parabola (Figure 6 middle). On the one hand, by changing the acceptor TriCBD in 2d to F4-TCNQ in 2c and, thus, increasing the driving force from +0.04 to -0.96 eV the charge separation is accelerated nearly 50 fold. On the other hand, the charge recombination decelerates in the electron donor-acceptor conjugates with the weakest acceptor, that is, in **ZnP-S2-TriCBD 2d**, while the charge recombination in ZnP-S2-F4-TCNQ 2c is located near to the top region of the Marcus parabola. Similar is the behavior for conjugates 1 and 6–9 (Figure 6 bottom).





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**Figure 6.** Driving-force  $(-\Delta G^{0}_{\text{ET}})$  dependence of  $k_{\text{CS}}$  (filled symbols) and  $k_{\text{CR}}$  (open symbols) with the semiclassical Marcus approach. Top: **ZnP-S3-TCBD 3a** (blue), **ZnP-S4-TCBD 4** (grey), **ZnP-S5-TCBD 5** (orange), **ZnP-S3-TCNQ 3b** (green), **ZnP-S3-F\_4-TCNQ 3c** (dark green) with  $R_{\text{DA}} = 13.9-16$  Å in toluene. The fitting parameters are  $\lambda_{\text{S}} = 0.30$  eV,  $\lambda_{\text{V}} = 0.49$  eV and V = 30.9 cm<sup>-1</sup>.

Middle: ZnP-S2-TriCBD 2d (blue), ZnP-S2-TCBD 2a (grey), ZnP-S2-TCNQ 2b (orange), ZnP-S2-F<sub>4</sub>-TCNQ 2c (dark green) with  $R_{DA} = 18.2$  Å in toluene. The fitting parameters are  $\lambda_S = 0.31$  eV,  $\lambda_V = 0.45$  eV and V = 28.4 cm<sup>-1</sup>. Bottom: ZnP-S8-TCBD 9 (green), ZnP-S1-TCBD 1a (blue), ZnP-S7-TCNQ 7 (orange), ZnP-S6-TCBD 6 (grey), ZnP-S1-TCNQ 1b (violet), and ZnP-S6-TCNQ 8 (dark green) with  $R_{DA} = 20.6-25.1$  Å in toluene. The fitting parameters are  $\lambda_S = 0.31$  eV,  $\lambda_V = 0.34$  eV and V = 13.9 cm<sup>-1</sup>.

In general, the derived electronic couplings with values between 13.9 and 30.9 cm<sup>-1</sup> reflect the overall distance dependence. At the shortest distance in, for example, conjugates **3**, the largest value of  $30.9 \text{ cm}^{-1}$  evolves, while for the longest distance in conjugates **1** and **9** the value is as low as  $13.9 \text{ cm}^{-1}$ .

Notably, the internal reorganization  $\lambda_v$  energy with 0.45-0.49 eV is in sound agreement with our calculations for TCNQ and TCBD-based systems (vide supra). For conjugates with  $R_{DA}$  between 20.6 and 25.1 Å, the internal reorganization energy is reduced to 0.34 eV, which points to the role of more rigid linkers in, for example, conjugates 6-9. Please note that the parameters for reorganization energy and electronic coupling are averaged values and might slightly differ from conjugate to conjugate. The access to the inverted region of the Marcus curve and the derived total reorganization energies  $\lambda_{R}$ (0.66-0.79 eV) for photoinduced electron transfer are of great value, since for the first time these are established for acetylene-derived non-planar push-pull chromophores as electron acceptors in D–A conjugates. The values for  $\lambda_R$  are remarkably small compared to other artificial model acceptors (0.8-1.4 eV)<sup>[3a,3d,37]</sup> and compete with those seen for fullerenebased systems.<sup>[3f,38]</sup> Taking the aforementioned into account, smaller  $\lambda_{\rm R}$  combine faster charge separation and slower charge recombination for our push-pull derived systems.

Solvent polarity impacts the electron donor-acceptor conjugates not only in the ground state but also in the excited state. In fact, it increases the reorganization energy. Noteworthy, in THF and benzonitrile the solvent rearrangement is affected during an electron transfer. Based on larger  $\lambda_{R}$ , the

charge recombination is now placed in the normal/activationless regions of the Marcus parabola rather than in the inverted region (see Section S9 of the Supporting Information).

#### Summary and Conclusions

We have successfully shown that our multicyanobuta-1,3dienes and tetracyanoquinodimethane analogues offer synthetically viable alternatives to established electron acceptors (e.g. fullerenes, perylenediimides, quinones) for the preparation of multicomponent arrays featuring photoinduced electron transfer. Notably, data from the latter as well as X-ray crystal structures show that the conjugates are geometrically well-defined systems, with the electron donors and acceptors held at fixed center-to-center distances of approximately 13.9 Å up to 25.1 Å. Therefore, we can conclude that any intramolecular interactions, such as electron transfer must result from through-bond effects. Förster resonance energy transfer is unlikely due to a lack of spectral overlap between the porphyrin and acceptor moieties.

Based on the optoelectronic results, we are able to fine-tune the photophysical properties of the electron donor-acceptor systems by changing the spacer, the absorption properties, and the strength of the electron acceptor. For the latter, we synthesized different acceptors with first reduction potentials between -0.23 and -1.67 V (vs. Fc+/Fc). To the best of our knowledge, the reduction potential of F<sub>4</sub>-TCNQ-based pushpull acceptors is the lowest incorporated in electron donoracceptor systems so far. In terms of electron transfer, we derived the typical Marcus curves from the semiclassical approach, indicating longest lifetimes (up to 23 ns) for the charge-separated state in nonpolar solvents such as toluene, as the charge recombination dynamics are placed in the Marcus inverted region. The overall rate enhancement for charge recombination is explained by large e-v couplings of the push-pull acceptors. Analysis of the electron transfer dynamics using Marcus theory gives reorganization energies for these systems between 0.66 and 0.79 eV and electronic coupling matrix elements between 13.9 and 30.9 cm<sup>-1</sup>. The values encourage the development of further push-pull derived electron donor-acceptor systems as future platform for photosynthetic mimics and organic photovoltaic applications. As such, the rich redox chemistry, broad absorption in the visible and near infrared region, and excellent thermal as well as chemical stability may exert a noteworthy impact on the improvement of photoinduced charge-transfer processes in organic photovoltaics.

#### **Experimental Section**

All experimental methods, synthesis, and characterization are provided in the Supporting Information (Sections S1, S2 and S10).

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### Entry for the Table of Contents

## FULL PAPER

A series of electron donor–acceptor conjugates incorporating a Zn<sup>II</sup> porphyrin based electron donor and push–pull chromophores as electron acceptors has been prepared. The electron acceptors comprize multicyanobutadienes or extended tetracyanoquinodimethane analogues with first reduction potentials ranging from –1.67 to –0.23 V vs. Fc<sup>+</sup>/Fc. As such, the rich redox chemistry, broad absorption in the visible and near infrared region, and electron transfer behavior upon photoexcitation with charge recombination kinetics in the inverted region render these systems promising materials for applications in the field of molecular photovoltaics.



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Porphyrin Donor and Tunable Push– Pull Acceptor Conjugates – Experimental Investigation of Marcus Theory