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Tuning Reductive and Oxidative Photoinduced Electron Transfer in Amide-Linked Anthraguinone–Porphyrin– **Ferrocene Architectures**

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Porphyrin amino acids 3a-3h with meso substituents Ar of tunable electron-donating power (Ar = $4-C_6H_4OnBu$, 4-C₆H₄OMe, 4-C₆H₄Me, Mes, C₆H₅, 4-C₆H₄F, 4-C₆H₄CF₃, C_6F_5) have been linked at the N terminus to anthraguinone Q as electron acceptor through amide bonds to give Q-P^{Ar} dyads 4a-4h. These were conjugated to ferrocene Fc at the C terminus as electron donor to give the acceptor-chromophore-donor Q-P^{Ar}-Fc triads **6a**-**6h**. To further modify the energies of the electronically excited and charge-separated states, the triads 6a-6h were metallated with zinc(II) to give the corresponding Q-(Zn)P^{Ar}-Fc triads **Zn-6a**–**Zn-6h**. The Q-P^{Ar1} dyad (Ar¹ = C_6H_5) was further extended with a second porphyrin P^{Ar2} (Ar² = 4-C₆H₄Me) as well as appended to a

Introduction

Photoinduced electron transfer (PET) is a key step in natural photosynthesis.^[1] For a deeper understanding of photosynthetic processes such as sunlight energy collection, light-energy storage, light-to-chemical energy conversion, electron-transport pathways and finally the efficient utilisation of sunlight, a number of elegant functional artificial reaction centres have been designed and intensively investigated to gain an increasingly clear picture of the important processes.^[2-7] The rational design of reaction centres to mimic the multistep downhill electron transfer is theoretically based on the Marcus theory of electron transfer (ET)^[8] and experimentally relies on the availability of suitable building blocks that can be assembled at will. Artificial reaction centres consist of non-covalently or covalently linked donor-acceptor units with quinones (natural acceptors),^[3] porphyrins^[4] or fullerenes^[5] acting as electron acceptors and porphyrins,^[6] ferrocene^[5e-5i,7] or carotenoid polyenes^[6] acting as electron donors. A variety of quinoneferrocene to give the tetrad Q-P^{Ar1}-P^{Ar2}-Fc 9. Almost all the conjugates show strongly reduced fluorescence quantum yields and excited-state lifetimes, which has been interpreted as photoinduced electron transfer (PET) either from the excited porphyrin to the quinone (oxidative PET) or from the ferrocene to the excited porphyrin (reductive PET). Electrochemical data, absorption spectroscopy, steady-state emission, time-resolved fluorescence, transient absorption pumpprobe spectroscopy as well as DFT calculations have been used to elaborate the preferred PET pathway (reductive vs. oxidative PET) in these architectures with systematically varied electron-donating substituents at the central chromophore.

porphyrin^[3] (Q-P) and porphyrin-ferrocene (P-Fc) systems^[5e-5i,7] have been investigated with respect to PET, proving very useful for fundamental PET research and potential applications. Furthermore, several other metal complexes have been attached to porphyrins as electron-accepting units.^[9] Variation of Q has allowed the effect of exothermicity on the rates of electron transfer to be studied in considerable detail^[3c,3e] and variation of Fc substituents has shown that energy- and electron-transfer pathways depend on the oxidation potential of the ferrocene.^[10] Elaborated C₆₀-P_n-Fc architectures feature long-lived charge-separated states.^[5e-5h] In C₆₀-(Zn)P_n-Fc conjugates with C₆₀ as the electron acceptor, the first PET typically is the thermodynamically favourable oxidative quenching of the excited porphyrin by the fullerene followed by a thermal shift of charge from the ferrocene to the central porphyrin.^[5e-5h] The effect of the number of porphyrins sandwiched between C₆₀ and ferrocene has also been thoroughly investigated.^[5e-5h] In systems containing both Fc and Q, the preference of the initial photoinduced electron-transfer step is ambiguous as the free energies for both steps are of a similar magnitude.

To the best of our knowledge, systems combining the electron-accepting features of quinones, the light-absorbing properties of porphyrin chromophores and the electron-donating properties of ferrocene derivatives have not yet been studied with respect to either the preferred PET pathways

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or the tuning of PET pathways by modifying the excitedstate energies of the central chromophore in a systematic manner with Fc donor and Q acceptor levels held at a fixed energy.

Linking reaction centre components through amide bonds has considerable advantages, namely a rather rigid connectivity of the building blocks,^[11,12] a defined directional design in linear arrays (N terminus \rightarrow C terminus) and a simple orthogonal modification at the termini with electron donors and acceptors. Furthermore, oligoamide synthesis can be conveniently accomplished by using solidphase synthesis methods.^[13]

We have previously reported suitable building blocks for directional oligoporphyrin amides, namely porphyrin amino acids with a *trans*-AB₂C substitution pattern (Scheme 1).^[11,14] These porphyrin amino acids feature electron-donating mesityl, phenyl and electron-withdrawing fluorinated aryl groups at the *meso* positions (Ar = Mes, C₆H₅, 4-C₆H₄F, 4-C₆H₄CF₃, C₆F₅).^[6c,11,14] More strongly electron-donating substituents such as Ar = 4-C₆H₄OR have not been studied. The key building blocks used in this study are porphyrin amino acids P^{Ar} and their esters with a full range of Ar substituents, anthraquinone-2-carboxylic acid Q as the electron acceptor and aminoferrocene Fc-NH₂ as the electron donor.^[15]



 $Ar = 2,4,6\text{-}C_6H_2Me_3, C_6H_5, 4\text{-}C_6H_4F, 4\text{-}C_6H_4CF_3, C_6F_5$

Scheme 1. Porphyrin amino acid building blocks.

Herein we report 1) the synthesis and properties of new trans-AB₂C-substituted porphyrin amino acid esters with electron-donating *meso* substituents $Ar = 4 - C_6 H_4 O n Bu$, 4- C_6H_4OMe , 4- C_6H_4Me and $C_6H_5^{[14]}$ (3a, 3b, 3d, 3e) and their corresponding N-acetyl-protected derivatives (Ac-3a, Ac-3b, Ac-3d, Ac-3e) as building blocks and reference compounds, 2) the coupling of eight trans-AB₂C-substituted porphyrin amino acid building blocks PAr with varying electron-withdrawing power (Ar = $4 - C_6 H_4 On Bu$, $4 - C_6 H_4 OM e$, 4-C₆H₄Me, Mes, C₆H₅, 4-C₆H₄F, 4-C₆H₄CF₃, C₆F₅) to anthraquinone-2-carboxylic acid Q to give Q-PAr dyads (4a-4h), 3) the amide coupling of Fc-NH₂ to Q-P^{Ar} to give Q-P^{Ar}-Fc triads (6a-6h) and metallation with zinc(II) to give Q-(Zn)P^{Ar}-Fc triads (Zn-6a–Zn-6h), 4) the (formal) extension of the triad Q-P^{Ar1}-Fc (Ar¹ = C_6H_5) with an additional porphyrin amino acid P^{Ar2} (Ar² = 4-C₆H₄Me) to furnish the tetrad Q-PAr1-PAr2-Fc (9) and 5) the examination of initial charge separation pathway preferences in dyads 4, triads 6 and Zn-6 as well as in tetrad 9 with fixed acceptor (Q) and donor (Fc) levels, namely oxidative (P^{Ar} to Q) versus reductive (Fc to P^{Ar}) PET with respect to the substituent Ar, by electrochemical methods, absorption spectroscopy, steady-state emission, time-resolved fluorescence, transient absorption spectroscopy as well as by DFT calculations.

The results of this work will be of considerable value to the rational design of artificial photosynthetic systems that feature multistep electron transfer by well-defined efficient single-electron transfer and charge-shift steps. Through our design strategy it is easy to tune the individual energy levels of the chromophore radical ions relative to the acceptor and donor levels. This versatile modular design will allow the construction of even larger arrays with predefined sequences and excited-state energy levels.

Results and Discussion

Synthesis and Characterisation of Building Blocks 3, Dyads 4, Triads 6 and Zn-6, and Tetrad 9

In addition to the recently reported trans-AB₂C porphyrin amino acids $P^{Ar[11,14]}$ with Ar = Mes(3c), $C_6H_5(3e)$, 4-C₆H₄F (**3f**), 4-C₆H₄CF₃ (**3g**) and C₆F₅ (**3h**), substituents with a greater electron-donating power are required for a comprehensive study. Hence, three novel trans-AB2C-substituted porphyrin^[16] amino acid esters^[11,14] with electronreleasing meso substituents [Ar = $4-C_6H_4OnBu$ (3a), 4- C_6H_4OMe (**3b**), 4- C_6H_4Me (**3d**)] were synthesised following a Lindsey-type 2+2 condensation procedure^[17] employing nitro- and ester-substituted phenyldipyrromethanes.^[18] The nitro functional group was reduced to the amine by reduction with tin(II) chloride in hydrochloric acid to obtain the porphyrin amino acid esters 3a, 3b and 3d (see the Supporting Information). As the optical properties of amines are strongly pH-dependent and the oxidation of amines is often irreversible, N-acetyl-protected reference compounds Ac-3a, Ac-3b, Ac-3d and Ac-3e as well as their corresponding Zn^{II} complexes Zn-Ac-3a, Zn-Ac-3b, Zn-Ac-3d and Zn-Ac-3e were synthesised following established procedures (see the Supporting Information).^[11,19]

The eight porphyrin amino acid esters 3a-3h, with Ar exhibiting increasing electron-withdrawing power, were coupled to anthraquinone-2-carboxylic acid (as electron acceptor) after activating the latter as the acid chloride by reaction with thionyl chloride to give the Q-P^{Ar} dyads 4a-4h (Scheme 2). Cleavage of the methyl ester by using aqueous KOH in methanol/THF delivered the quinone-porphyrin acids 5a-5g, respectively (Scheme 2). The base-catalysed cleavage of dyad 4h also led to the nucleophilic aromatic substitution of fluoride in the electron-poor aryl substituents by methoxide (Ar = $C_6F_5 \rightarrow Ar = 4 - C_6F_4OMe$) to give acid 5i. Therefore to obtain 5h from 4h, an acid-catalysed hydrolysis protocol needed to be employed (Scheme 2). Quinone-porphyrin-ferrocene triads Q-PAr-Fc (6a-6i) were assembled by activation of the acid groups in 5a-5i as acid chlorides by using thionyl chloride and coupling with aminoferrocene^[15] (as electron donor). The quin-



Scheme 2. Synthesis of dyads 4a-4h and triads 6a-6i and Zn-6a-Zn-6i.

one-(Zn)porphyrin-ferrocene triads Q-(Zn)P^{Ar}-Fc (**Zn-6a**–**Zn-6i**) were obtained from the free base triads **6a–6i** by metallation with zinc(II) acetate dihydrate (Scheme 2).

The construction of the Q-P^{C6H5}-P^{C6H4Me}-Fc tetrad **9** is depicted in Scheme 3. Q-P acid **5e** was coupled to porphyrin amino acid ester **3d** (activated as the acid chloride by using thionyl chloride) to give the Q-P^{C6H5}-P^{C6H4Me} triad **7**. The ferrocene entity was attached to **7** through an amide bond after base-catalysed methyl ester cleavage (to give free acid **8**, see the Supporting Information). Subsequent formation of the acid chloride and coupling with aminoferrocene gave the target tetrad **9**. The quinone reference *N*-ethylanthraquinone-2-carboxylic acid amide **10** as well as the bis(porphyrin) reference P^{C6H5}-P^{C6H4Me} **11** were synthesised as described in the Supporting Information.

The correct formation of all monoporphyrins 3, the dyads 4, the triads 6, Zn-6 and 7, the tetrad 9, the quinone reference compound 10 and the bis(porphyrin) reference 11 was substantiated by multinuclear NMR spectroscopy (¹H, ¹³C, ¹⁹F), IR and UV/Vis spectroscopy as well as (highresolution) mass spectrometry (see the Supporting Information). In all cases the mass spectra show the signals expected for the intact porphyrin and porphyrin conjugates. In the ¹H NMR spectra, successful amide formation is clearly indicated by the disappearance of the amine proton resonances of 3a–3h at $\delta = 4.99$ ppm and the appearance of the amide resonances of dyads 4a–4h at $\delta = 10.30–$ 10.40 ppm. The covalent attachment of the ferrocene by amide coupling to the dyads 4 was confirmed by observing a second amide proton resonance at $\delta = 9.19-9.29$ ppm in the ¹H NMR spectra of **6a–6h**. The presence of three NH amide resonances at $\delta = 9.21$, 10.21 and 10.33 ppm demonstrates the successful synthesis of tetrad 9. The resonances corresponding to the quinone and ferrocene moieties in the dyads, triads and tetrads further prove the integrity of the oligoamides. Metallation of triads 6 with Zn^{II} resulted in the expected changes in the porphyrin resonances, such as the disappearance of the pyrrole NH resonances. For the Q-(Zn)P dyads featuring an azomethine linker, the quinone proton resonances are reported to be shifted to a higher field. This has been rationalised by the coordination of the quinone carbonyl oxygen atom to the Zn^{II} centre.^[3m] The Q proton resonances of the Q-Zn(P)-Fc triads Zn-6 are not shifted, and hence a Zn····O=C interaction in Zn-6 can be excluded. Possibly for the reported Q-Zn(P) dyads, a Zn…Nazomethine interaction seems to be more likely than Zn…OC_{quinone} coordination.^[3m]

Absorption and Emission of Dyads 4, Triads 6 and Zn-6, and Tetrad 9

The absorption data for the dyads, triads, tetrad and reference compounds are presented in Table 1. The absorption spectra of **4a–4h**, **6a–6h** and **Zn-6a–Zn-6h** are essentially identical to those of the corresponding reference porphyrins **Ac-3a–Ac-3h** and **Zn-Ac-3a–Zn-Ac-3h**. As a result of the low extinction coefficients of *N*-ethylanthraquinone-2-carb-





Scheme 3. Synthesis of tetrad 9.

oxylic acid amide 10 ($\lambda_{max} = 328 \text{ nm}, \epsilon = 5300 \text{ M}^{-1} \text{ cm}^{-1}$) and 1-(acetylamino)ferrocene (Fc-NHAc; $\lambda_{max} = 441$ nm, ε = $215 \text{ m}^{-1} \text{ cm}^{-1}$,^[15] no absorption bands from these chromophores are discernible in the absorption spectra of the dyads and triads. The shapes and intensities of the Soret bands relative to their Q bands remain unaffected after the linking of quinone and ferrocene to the porphyrin core (Figure 1 and the Supporting Information). A slight blue shift of the porphyrin Soret and porphyrin Q bands is observed within the Q-P series $4a \rightarrow 4h$ and Q-P-Fc series $6a \rightarrow 6h$ due to the increasing electron-withdrawing character of meso-aryl substituents Ar. Neither new charge-transfer bands^[20] nor perturbations of the porphyrin absorption bands were detected, which indicates only a weak groundstate electronic interaction between the quinone or the ferrocene with the central porphyrin. The Q-(Zn)P^{Ar}-Fc triads **Zn-6a–Zn-6h** show a small bathochromic shift (1–4 nm) of porphyrin absorbance bands in comparison with the corresponding reference porphyrins Zn-Ac-3a-Zn-Ac-3h (Figure 1 and Table 1).

Figure 2 shows the absorption spectra of triad Q-P^{C6H5}-P^{C6H4Me} (7), tetrad Q-P^{C6H5}-P^{C6H4Me}-Fc (9) and reference dyad P^{C6H5}-P^{C6H4Me} (11). Appending a quinone or a ferrocene to the bis(porphyrin) core does not alter the absorption spectrum, similarly to the monoporphyrin conjugates. Furthermore, the absorption spectra of the bis(porphyrins) 7, 9 and 11 are nearly identical to those of the constituent porphyrins Ac-3d and Ac-3e and exhibit no splitting of the Soret or Q bands.^[11] In summary, the absorption spectra are essentially a superposition of the individual unperturbed spectra of the building blocks.

The fluorescence data, quantum yields and the exitedstate lifetimes of the new porphyrin amino acid esters 3a, 3b, 3d and 3e, and the reference porphyrins Ac-3a, Ac-3b, Ac-3d, Ac-3e, Zn-Ac-3a, Zn-Ac-3b, Zn-Ac-3d, Zn-Ac-3e and bis(porphyrin) 11 are collected in Table 2. As discussed previously^[11] for related porphyrins, a small hypsochromic shift of the emission band is observed in the series Ac-3a \rightarrow Ac-3b \rightarrow Ac-3d \rightarrow Ac-3e and Zn-Ac-3a \rightarrow Zn-Ac-3b \rightarrow Zn-Ac-3d \rightarrow Zn-Ac-3e.



Table 1. Absorption data for Ac-3a-Ac-3h, Zn-Ac-3h, Za-Ac-3h, 4a-4h, 6a-6i, Zn-6a-Zn-6i, 7, 9 and 11 in CH₂Cl₂ at room temperature.

	Ar		λ [nm	h] (ε [10 ⁻⁴ M ⁻¹ cm ⁻	¹])	
		Soret	Q _y (1,0)	$Q_{y}(0,0)$	$Q_x(1,0)$	$Q_x(0,0)$
Ac-3a	C ₆ H ₄ OnBu	422 (30.03)	517 (1.14)	555 (0.73)	593 (0.63)	649 (0.65)
4a	C_6H_4OnBu	422 (32.44)	518 (1.36)	555 (0.84)	593 (0.49)	649 (0.47)
6a	C_6H_4OnBu	422 (36.31)	518 (1.35)	555 (0.89)	593 (0.36)	650 (0.39)
Zn-Ac-3a	C ₆ H ₄ OnBu	424 (40.10)	552 (1.75)	594 (0.65)	_	—
Zn-6a	C ₆ H ₄ OnBu	425 (47.78)	552 (1.33)	594 (0.78)	_	_
Ac-3b	C ₆ H ₄ OMe	421 (35.40)	517 (1.38)	554 (0.87)	593 (0.45)	648 (0.42)
4b	C ₆ H ₄ OMe	421 (39.59)	517 (1.40)	554 (0.89)	593 (0.33)	649 (0.35)
6b	C ₆ H ₄ OMe	422 (39.19)	518 (1.67)	554 (1.11)	593 (0.69)	649 (0.53)
Zn-Ac-3b	C ₆ H ₄ OMe	424 (48.62)	551 (1.90)	593 (0.63)	_	_
Zn-6b	C ₆ H ₄ OMe	424 (51.07)	552 (1.96)	594 (0.73)	_	_
Ac-3c	Mes	420 (36.29)	516 (1.24)	550 (0.37)	593 (0.28)	652 (0.55)
4c	Mes	421 (36.33)	516 (1.55)	551 (0.68)	592 (0.34)	651 (0.56)
6c	Mes	421 (36.18)	516 (1.51)	552 (0.60)	592 (0.30)	648 (0.25)
Zn-Ac-3c	Mes	423 (45.12)	551 (1.92)	592 (0.45)	_	—
Zn-6c	Mes	424 (49.71)	552 (1.88)	594 (0.18)	_	
Ac-3d	C ₆ H ₄ Me	420 (33.60)	516 (1.27)	552 (0.71)	592 (0.39)	647 (0.35)
4d	C_6H_4Me	420 (39.00)	517 (1.93)	552 (1.26)	591 (0.85)	647 (0.82)
6d	C ₆ H ₄ Me	420 (44.69)	517 (1.72)	553 (1.57)	591 (1.12)	647 (0.61)
Zn-Ac-3d	C_6H_4Me	421 (45.15)	549 (1.82)	588 (0.46)	_	
Zn-6d	C ₆ H ₄ Me	423 (47.02)	551 (2.02)	593 (0.75)	_	_
Ac-3e	C ₆ H ₅	419 (32.60)	515 (1.34)	551 (0.68)	591 (0.43)	646 (0.34)
4 e	C_6H_5	419 (32.25)	515 (1.34)	551 (0.69)	591 (0.42)	646 (0.36)
6e	C_6H_5	419 (35.06)	516 (1.56)	551 (0.84)	591 (0.49)	646 (0.42)
Zn-Ac-3e	C_6H_5	420 (36.10)	549 (1.63)	589 (0.48)	—	_
Zn-6e	C ₆ H ₅	423 (38.89)	551 (1.63)	592 (0.46)	_	
Ac-3f	C_6H_4F	419 (50.42)	515 (2.16)	551 (1.07)	591 (0.72)	647 (0.61)
4f	C_6H_4F	419 (46.25)	515 (1.96)	551 (0.98)	591 (0.59)	647 (0.45)
6f	C_6H_4F	419 (41.79)	515 (2.22)	551 (1.38)	589 (1.00)	646 (0.86)
Zn-Ac-3f	C_6H_4F	420 (41.45)	548 (1.87)	587 (0.50)	-	_
Zn-6f	C ₆ H ₄ F	422 (47.69)	551 (2.05)	593 (0.63)	_	_
Ac-3g	$C_6H_4CF_3$	419 (41.40)	515 (1.78)	550 (0.79)	590 (0.57)	646 (0.40)
4g	$C_6H_4CF_3$	419 (31.57)	515 (1.45)	549 (0.69)	591 (0.47)	649 (0.41)
6g	$C_6H_4CF_3$	419 (32.42)	515 (1.54)	551 (0.78)	590 (0.53)	646 (0.41)
Zn-Ac-3g	$C_6H_4CF_3$	420 (28.30)	548 (1.17)	588 (0.21)	-	—
Zn-6g	$C_6H_4CF_3$	423 (34.13)	552 (1.59)	593 (0.48)	_	_
Ac-3h	C_6F_5	418 (39.31)	512 (2.38)	545 (0.84)	587 (0.93)	642 (0.56)
4h	C_6F_5	418 (34.69)	512 (2.15)	546 (0.70)	588 (0.79)	642 (0.44)
6h	C_6F_5	417 (41.02)	511 (2.20)	545 (0.42)	588 (0.49)	642 (0.48)
Zn-Ac-3h	C_6F_5	422 (51.09)	552 (2.01)	593 (0.36)	_	—
Zn-6h	C_6F_5	422 (47.51)	551 (1.68)	594 (0.65)	_	_
6i	C ₆ F ₄ OMe	419 (37.03)	512 (1.87)	546 (0.45)	589 (0.48)	644 (0.11)
Zn-6i	C ₆ F ₄ OMe	423 (43.97)	552 (1.86)	592 (0.32)	-	_
11	C ₆ H ₅ /C ₆ H ₄ Me	422 (73.50)	516 (3.53)	552 (2.05)	591 (1.19)	647 (1.06)
7	C_6H_5/C_6H_4Me	422 (76.62)	516 (3.57)	552 (2.06)	591 (1.15)	647 (1.04)
9	C_6H_5/C_6H_4Me	422 (77.48)	517 (3.74)	553 (2.14)	591 (1.14)	647 (1.02)

The emission spectra of selected dyads, triads, tetrad **9** and reference porphyrins are shown in Figures 1 and 2. Linking anthraquinone to porphyrins **3** and **Zn-3** as well as to (bis)porphyrin **11** leads to a significant decrease in the fluorescence intensity of quinone conjugates **4** and **7** (see Tables 2 and 3). The quenching efficiency varies between 10 and 92%, which indicates the presence of a new non-radiative decay channel in the dyads, namely oxidative PET. The strongest decrease in fluorescence intensity is found for dyad **4a** with Ar = 4-C₆H₄OnBu (92%, Figure 1), whereas almost no quenching at all is seen for dyad **4h** with Ar = C₆F₅ (10%, Table 2 and Table 3). As anticipated, the nature

of the *meso*-aryl substituent Ar controls the efficiency of fluorescence quenching by oxidative PET. Electron-rich substituents induce stronger quenching than electron-withdrawing substituents. Only dyad **4c** with sterically demanding mesityl groups (Ar = Mes) at the *meso* positions deviates from the described trend. DFT geometry optimisations of **4c** revealed a 90° dihedral angle between the mesityl and porphyrin planes in contrast to the smaller angles observed for all other substituents (Ar = C₆F₅: 79°; all other Ar: 63–66°; see the Supporting Information). Furthermore, full rotation of a mesityl group connected to a porphyrin has an activation barrier of around 74 kJmol⁻¹ in solu-



Figure 1. Normalised absorption and emission spectra of a) Ac-3a, 4a, 6a, b) Zn-Ac-3a, Zn-6a, c) Ac-3e, 4e, 6e, d) Zn-Ac-3e, Zn-6e, e) Ac-3h, 4h, 6h and f) Zn-Ac-3h, Zn-6h in CH₂Cl₂ at room temperature.

 λ/nm

 λ/nm



Figure 2. Normalised absorption and emission spectra of the reference compound P^{C6H5} - P^{C6H4Me} (11), triad Q- P^{C6H5} - P^{C6H4Me} (7) and tetrad Q- P^{C6H5} - P^{C6H4Me} -Fc (9) in CH_2Cl_2 at room temperature.

tion,^[21] which also prevents the population of intermediate more co-planar conformations. Therefore the rather fixed orthogonal arrangement of the Mes substituent precludes the strong electronic influence expected from the trialkylated aryl group.

In quinone-bis(porphyrin) 7, the emission is quenched by only 64% due to the attached quinone. From the extinction

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Table 2. Emission data for porphyrins 3 and bisporphyrin 11 in CH_2Cl_2 at room temperature.

	Ar	λ [1	nm]	Φ	$\tau [ns]_{[a]}$
		Q(0,0)	Q(0,1)	_	
3a	C ₆ H ₄ OnBu	660	723	0.1631	n.d. ^[b]
Ac-3a	C_6H_4OnBu	657	720	0.1594	9.28
Zn-Ac-3a	C_6H_4OnBu	606	651	0.1003	1.71
3b	C ₆ H ₄ OMe	659	721	0.1448	n.d. ^[b]
Ac-3b	C ₆ H ₄ OMe	657	719	0.1348	9.49
Zn-Ac-3b	C ₆ H ₄ OMe	606	651	0.0940	1.81
3d	C ₆ H ₄ Me	657	721	0.0878	n.d. ^[b]
Ac-3d	C_6H_4Me	654	719	0.1311	9.69
Zn-Ac-3d	C ₆ H ₄ Me	600	646	0.0884	1.91
Ac-3e	C ₆ H ₅	652	717	0.1167	9.88
Zn-Ac-3e	C_6H_5	597	645	0.1037	1.99
11	C ₆ H ₅ /C ₆ H ₄ Me	654	718	0.1284	9.70

[a] All decays are monoexponential; excitation wavelength $\lambda_{\text{exc}} = 400$ or 550 nm. [b] n.d.: not determined.

coefficients of the constituent porphyrins Ac-3d and Ac-3e (Table 1), it is reasonable to assume that both porphyrins in 7 are excited with nearly equal probability $[\epsilon(Ac-3d)/\epsilon(Ac-3e) \approx 1.03:1.00]$. If energy transfer between the two porphyrins was absent, approximately 80%(4e)/2 = 40% quenching would be expected. The larger quenching observed suggests rapid energy transfer from the Ar = C_6H_4 Me-substituted porphyrin to the Ar = C_6H_5 -substituted porphyrin in 7. The latter excited porphyrin undergoes oxidative PET to the appended quinone.

The fluorescence studies of the ferrocene conjugates **6** and **Zn-6** revealed an even stronger reduction of the emission quantum yield compared with the corresponding reference compounds **Ac-3** and **Zn-Ac-3** (Figure 1, Tables 2 and 4). The quenching of triads **6a–6h** and metallated triads **Zn-6a–Zn-6h** is almost quantitative and most of them are essentially non-fluorescent. Therefore a further efficient non-radiative decay pathway is enabled, namely reductive PET with ferrocene acting as electron donor and/or triplet energy transfer to the ferrocene.^[7a,10]

To distinguish between electron and energy transfer, the emission spectra of Ac-3a, 4a and 6a (Figure 3) as well as Ac-3h, 4h and 6h were exemplarily recorded at low temperatures $(300 \rightarrow 77 \text{ K})$. Indeed, upon cooling, the integrated emission intensity of 6a (×5.0) increases much more strongly than that of Ac-3a (×1.3) or 4a (×1.7) (Figure 3). A similar trend is observed for the Ac-3h (×1.8), 4h (×1.4), 6h (×3.3) series. Even more pronounced is the gain in fluorescence intensity in the zinc triads Zn-6a (×17.5) and Zn-6h (×16.4) at low temperature. This supports the existence of PET pathways in triads 6 and Zn-6 that are impeded at low temperatures.^[3i] However, some residual quenching by energy transfer to ferrocene cannot be fully excluded on the basis of these data alone.

Tetrad 9 essentially shows similar emission behaviour to the triads 6. The quantum yield of the $Q-P^{C6H5}-P^{C6H4Me}$ -Fc conjugate 9 is decreased by 89% with respect to the



Ar		λ [nm]		Φ	$\tau \ [ns]^{[a]}$	Quenching [%]	$k_{\rm ET} [10^9 { m s}^{-1}]^{[{ m d}]}$	$\Phi_{\mathrm{ET}}^{\mathrm{[e]}}$
		Q(0,0)	Q(0,1)					
4 a	C ₆ H ₄ OnBu	657	720	0.0125	0.613	92 ^[b]	1.524	0.93
4b	C ₆ H ₄ OMe	656	720	0.0140	0.700	90 ^[b]	1.323	0.93
4c	Mes	653	719	0.0532	1.820	32 ^[b]	0.458	0.83
4d	C ₆ H ₄ Me	654	719	0.0161	0.942	78 ^[b]	0.958	0.90
4e	C_6H_5	652	717	0.0230	1.370	80 ^[b]	0.629	0.86
4f	C ₆ H ₄ F	652	717	0.0281	2.970	72 ^[b]	0.233	0.69
4g	$C_6H_4CF_3$	652	717	0.0548	4.810	49 ^[b]	0.108	0.52
4ĥ	C_6F_5	647	712	0.0628	9.550	10 ^[b]	0.003	0.03
7	C ₆ H ₅ /C ₆ H ₄ Me	653	718	0.0458	4.070	64 ^[c]	0.143	0.58

Table 3. Emission data for Q-PAr dyads 4a-4h and triad 7 in CH₂Cl₂ at room temperature.

[a] All decays are monoexponential; excitation wavelength $\lambda_{exc} = 400$ or 550 nm. [b] Relative to reference compound Ac-3. [c] Relative to reference compound 11. [d] $k_{ET} = 1/\tau - 1/\tau_{ref}$ [e] $\Phi = k_{ET}\tau$.

Table 4. Emission data for triads 6a-6i, Zn-6a-Zn-6i and tetrad 9 in CH₂Cl₂ at room temperature.

	Ar	λ [nm]		Φ	$\tau_1 \text{ [ps] } (A_1 \text{ [\%]});$	Quenching [%]	$k_{\rm ET} [10^9 { m s}^{-1}]^{[d]}$	$\Phi_{\mathrm{ET}}^{[\mathrm{e}]}$
		Q(0,0)	Q(0,1)		$\tau_2 \text{ [ps] } (A_2 \text{ [\%]})^{[a,b]}$			
6a	C ₆ H ₄ OnBu	656	720	0.0042	214.99 (100)	97	4.544	0.98
6b	C_6H_4OMe	657	720	0.0034	240.54 (100)	97	4.052	0.97
6c	Mes	652	718	0.0041	272.83 (100)	94	3.574	0.97
6d	C ₆ H ₄ Me	655	720	0.0036	229.37 (100)	97	4.247	0.98
6e	C_6H_5	651	717	0.0030	164.02 (86); 644.23 (14)	97	5.996	0.98
6f	C_6H_4F	652	718	0.0025	148.07 (94); 586.62 (6)	98	6.650	0.98
6g	$C_6H_4CF_3$	652	717	0.0063	94.96 (86); 467.65 (14)	94	10.43	0.99
6h	C_6F_5	648	712	0.0029	26.39 (96); 274.57 (4)	96	37.79	1.00
6i	C ₆ F ₄ OMe	650	714	0.0006	39.30 (93); 398.03 (7)	n.d. ^[c]	n.d. ^[c]	n.d. ^[c]
Zn-6a	C ₆ H ₄ OnBu	607	652	0.0011	23.04 (87); 139.15 (13)	99	42.82	0.99
Zn-6b	C ₆ H ₄ OMe	606	651	0.0005	33.34 (92); 182.80 (8)	99	29.39	0.98
Zn-6c	Mes	604	653	0.0014	25.92 (77); 184.51 (13)	98	38.12	0.99
Zn-6d	C ₆ H ₄ Me	607	653	0.0012	27.13 (83); 189.38 (17)	99	36.34	0.99
Zn-6e	C_6H_5	601	647	0.0009	29.53 (88); 107.63 (12)	99	33.36	0.99
Zn-6f	C_6H_4F	602	649	0.0049	133.53 (73); 281.39 (27)	99	6.948	0.93
Zn-6g	$C_6H_4CF_3$	605	653	0.0028	35.20 (75); 285.80 (25)	97	27.93	0.98
Zn-6h	C_6F_5	602	654	0.0025	20.65 (94); 215.88 (6)	96	47.91	0.99
Zn-6i	C_6F_4OMe	602	651	0.0020	15.33 (90); 142.73 (10)	n.d. ^[c]	n.d. ^[c]	n.d. ^[c]
9	C_6H_5/C_6H_4Me	654	718	0.0145	361.77 (67); 2152.55 (33)	89	2.661; 0.363	

[a] Decays are mono- or biexponential; excitation wavelength $\lambda_{exc} = 400$ or 550 nm. [b] The relative amplitudes A were calculated from fitting the data by the equations $Y = A_1 e^{-k/\tau 1} + A_2 e^{-k/\tau 2}$ and $A_1 + A_2 = 100\%$. [c] n.d.: not determined. [d] $k_{ET} = 1/\tau - 1/\tau_{ref}$. [e] $\Phi_{ET} = k_{ET}\tau$; $\tau = \tau_1$ with the largest amplitude used in the equations.

bis(porphyrin) reference 11. When we neglect interporphyrin energy transfer, approximately 50% of the decay should occur oxidatively through Q-P^{C6H5} and 50% reductively through P^{C6H4Me}-Fc. The observed intermediate quenching of 9 (89%) between that of 4e (80%) and 6d (97%) is in accord with the concept of two decay pathways. Therefore both PET pathways appear possible in 9.

Kinetics of Photoinduced Electron Transfer by Time-Resolved Fluorescence Decay

The fluorescence lifetimes τ of dyads, triads, tetrad **9** and reference compounds are presented in Tables 2–4 and the fluorescence decay curves of selected conjugates and reference porphyrins are shown in Figure 4.

The fluorescence lifetimes of the free-base reference porphyrins and P^{Ph}-P^{PhMe} (11) are $\tau \approx 10$ ns and those of the zinc(II) porphyrins are $\tau \approx 2$ ns, as expected.^[11] All the excited states of the reference porphyrins Ac-3, Zn-Ac-3, reference dyad 11 and Q-P dyads 4a-4h decay with a single rate constant. The PET from the porphyrin to the anthraquinone in the Q-P dyads 4 opens a new deactivation pathway for the excited singlet state and reduces its lifetime generating the Q⁻-P⁺ charge-separated state (CS state). Other pathways (e.g., originating from adventitiously reduced anthraquinone to the hydroquinone^[31]) are not detected in dyads 4. The fluorescence lifetimes of 4 are in the range of $\tau = 0.613$ ns (4a, Ar = 4-C₆H₄OnBu) to $\tau = 9.55$ ns (4h, Ar = C_6F_5). A clear trend (with the exception of 4c, Ar = Mes, see above) is observed with the more electron-rich porphyrins featuring shorter lifetimes (Table 3). From these data, rate constants $k_{\rm ET}$ for oxidative PET were calculated (Table 3). The rate constants of the electron-rich porphyrins **4a**, **4b** and **4d** $(1.5 \times 10^9 - 0.9 \times 10^9 \text{ s}^{-1})$ are fully compatible with those of the reported Q-P dyads consisting of electronrich porphyrins and quinones.^[3] The much lower rates of



a)

lecav

Cence

norm. fluores

c)

1.0

8.0

0.6

0.4

0.2

0

200

400

r/ps

τ/ps

600

800

Zn-Ac-3a

Zn-6a

600 800



EurllC

1.0 1.0 Ac-3e decau lecav Zn-Ac-3e 0.8 0.8 PDCP ence 0.6 0.6 norm. fluores lintes 0.4 0.4 0.2 0.2 muuc (0 200 400 600 800 Ó 200 400 600 800 τ/ps τ/ps f) e) 1.0 Ac-3 1.0 decav decav 0.8 Ac-Zn-3h 0.8 luorescence fluorescence 0.6 0.6 0.4 0.4 0.2 norm. norm. 0.2 Zn-6h 0 0 400 600 200 200 400 600 800 τ/ DS r/ps g) 1.0 norm. fluorescence decay 0.8 homen 0.6 0.4 0.2 0 500 1000 1500 2000

b) 1.0

decav

Inorescence

d)

0.8

0.6

0.4

0.2

0

200 400

τ/ps

Figure 3. Normalised emission spectra of Ac-3a, 4a and 6a in 2methyltetrahydrofuran at $T = 300 \rightarrow 77$ K.

ET observed for the electron-withdrawing porphyrin dyads **4f–4h** are related to the lower thermodynamic driving force for the ET (see Electrochemical Studies below).

Triads **6a–6d** feature a monoexponential decay whereas the decays of all other dyads have to be fitted by biexponential decay curves (Table 4). The minor component (τ_2 , A_2) could be due to additional quenching by the heavyatom effect of the ferrocene,^[7c] population of the ferrocene triplet state,^[10] the presence of ferrocene/amide conformations that are less suitable for ET or intermolecular Zn···O=C(quinone) interactions in **Zn-6**.^[3m] The latter path, however, seems to be less pronounced based on NMR spectroscopic data for **Zn-6** (see above). Rate constants were estimated from the fluorescence lifetimes with the largest amplitude (τ_1 , A_1 ; Table 4). These rate constants for **6a–6h** are larger than those of the corresponding **4a–4h** lacking ferrocene (Table 3 and Table 4). Whereas $k_{\rm ET}$ decreases for Q-P^{Ar} dyads **4** with electron-withdrawing sub-

Figure 4. Fluorescence decay profiles of a) Ac-3a, 4a, 6a, b) Zn-Ac-3a, Zn-6a, c) Ac-3e, 4e, 6e, d) Zn-Ac-3e, Zn-6e, e) Ac-3h, 4h, 6h, f) Zn-Ac-3h, Zn-6h and g) 11, 7, 9 in CH_2Cl_2 (λ_{exc} = 400 and 550 nm).

stituents (Table 3), the reverse trend is observed for Q-P^{Ar}-Fc triads 6 (Table 4). The latter observation would be expected for reductive PET from ferrocene to the excited porphyrin as the dominant pathway. Indeed, $k_{\rm ET}$ is minimal for **6b–6d**, increases slightly for electron-rich **6a** favouring PET to the quinone and increases dramatically for electron-poor **6e–6h** favouring PET from ferrocene. Hence reductive PET seems to be favourable in **6e–6h** whereas oxidative and reductive pathways are both accessible in **6a–6d**.

In the zinc(II) porphyrin triads **Zn-6**, the rate constants k_{ET} are large $(30 \times 10^9 - 40 \times 10^9 \text{ s}^{-1})$; except for **Zn-6f**, which is unexplained at the moment) and ET is basically quantitative. No clear correlation between k_{ET} and the nature of the porphyrin substituents can be discerned (Table 4). This might be explained by the larger driving force $[\Delta(\Delta G_{\text{ET}}) \approx 0.17 \text{ eV}]$ of both PET pathways in zinc(II) porphyrin donor/acceptor assemblies due to the higher energy of the singlet excited state of zinc(II) porphyrins and the lower oxidation potential of zinc(II) porphyrins relative to free-base por-



phyrins (Table 4; see Electrochemical Studies below). Other scenarios would be accelerated quenching via ³ZnP states due to the heavy-atom effect of ferrocene^[7c] or via ferrocene triplet states.^[10]

As suggested from the quantum yield data, the singlet excited states of tetrad **9** can be quenched by PET from the C₆H₅-substituted porphyrin to its adjacent quinone and/or by PET from ferrocene to its adjacent C₆H₄Me-substituted porphyrin. The two fluorescence lifetimes of **9** [τ_1 = 362 ps (67%) and τ_2 = 2153 ps (33%)] roughly correspond to the lifetimes of Q-P^{C6H4Me}-Fc **6d** (τ = 229 ps) and Q-P^{C6H5} **4e** (τ = 1370 ps). This suggests that indeed both initial PET pathways are conceivable in **9** with the reductive PET being more probable than the oxidative PET. On the basis of this interpretation, the rate constants were estimated to be 2.66 × 10⁹ s⁻¹ (reductive PET) and 0.36 × 10⁹ s⁻¹ (oxidative PET). The thermodynamic feasibility of reductive and oxidative PET will be discussed in the next sections.

Electrochemical Studies

Cyclic voltammograms of porphyrins typically show two reversible oxidation and two reversible reduction waves. Porphyrins 3a-3h with amine substituents are only quasireversibly or even irreversibly oxidised.^[11,14] As the amino porphyrins do not qualify as references, their N-acetylated analogues Ac-3a-Ac-3h were used instead. The redox potentials of the new amino porphyrins 3a, 3b, 3e and 3d and the porphyrin reference compounds Ac-3a, Ac-3b, Ac-3d and Ac-3e are presented in Table 5. As described previously, the meso-aryl substituents cause a stepwise anodic shift of porphyrin oxidation and reduction.^[11] The new N-acetylated porphyrins Ac-3a, Ac-3b, Ac-3d and Ac-3e confirm and complete the trend in the full series Ar = 4- $C_6H_4OnBu \rightarrow 4-C_6H_4OMe \rightarrow 4-C_6H_4Me \rightarrow Mes \rightarrow C_6H_5 \rightarrow$ $4-C_6H_4F \rightarrow 4-C_6H_4CF_3 \rightarrow C_6F_5$. The shifts observed amount to 0.34 V for the first oxidation and 0.25 V for the first reduction from Ac-3a (Ar = C_6H_4OnBu) to Ac-3h (Ar $= C_6 F_5^{[11]}$).

In Q-P dyads **4a–4h** an additional redox event at a rather constant potential of $E_{1/2} = -1.20$ V corresponding to the first reversible reduction of the quinone to the semiquinonate is observed. For dyad **4c** even the second reduction of anthraquinone at $E_{1/2} = -1.72$ V has been detected. The individual redox potentials of the porphyrins **Ac-3** are essentially unperturbed by the appended quinone in **4** (Table 6 and Figure 5).



Figure 5. Cyclic voltammograms of quinone reference 12, porphyrin Ac-3e, dyad 4e and triad 6e in $(nBu_4N)(PF_6)/CH_2Cl_2$.

Attachment of a ferrocene unit (**6a–6h**, **Zn-6a–Zn-6h**) yields a further oxidation process at a rather constant potential of $E_{1/2} = -0.08$ V corresponding to the oxidation of ferrocene to ferrocenium (Table 6 and Figure 5). Only minor effects of ferrocene on the porphyrin and anthraquinone redox potentials are observed. Likewise only minor effects of the Ar substituent on the Fc and Q potentials are noted, which indicates a weak interchromophore interaction in the ground state. The quinone in the zinc porphyrins **Zn-6** is slightly easier to reduce than in the free-base porphyrins **6** (Table 6).

The redox data for bis(porphyrins) **11**, **7** and **9** are presented in Table 6. The additional porphyrin superimposes its redox waves onto those of the respective partner mono-

Table 5. Redox potentials of monoporphyrins 3, Ac-3, Zn-Ac-3 and (bis)porphyrin 11 vs. Fc/Fc^+ in $(nBu_4N)(PF_6)/CH_2Cl_2$ at room temperature.

	Ar	C ₆ H ₄ –R′	$E_{1/2}(ox^1)$ [V]	$E_{1/2}(\mathrm{ox}^2)$ [V]	$E_{1/2}(\text{red}^1)$ [V]	$E_{1/2}(\text{red}^2)$ [V]
3a	$egin{array}{c} C_6H_4OnBu\\ C_6H_4OnBu\\ C_6H_4OnBu \end{array}$	NH ₂	0.420	0.590	$-1.660^{[a]}$	$-2.010^{[a]}$
Ac-3a		NHAc	0.480	0.730	-1.640	-1.980
Zn-Ac-3a		NHAc	0.300	0.720	-1.790	-2.160
3b	C ₆ H ₄ OMe	NH ₂	0.540 ^[a]	n.o. ^[b]	$-1.660 \\ -1.630 \\ -1.780$	-1.990
Ac-3b	C ₆ H ₄ OMe	NHAc	0.510	0.750		-1.970
Zn-Ac-3b	C ₆ H ₄ OMe	NHAc	0.310	0.710		n.o. ^[b]
3d	C_6H_4Me	NH ₂	0.440	0.550	$-1.640^{[a]}$	$-1.980^{[a]}$
Ac-3d	C_6H_4Me	NHAc	0.520	0.830	-1.610	-1.950
Zn-Ac-3d	C_6H_4Me	NHAc	0.361	0.800	-1.720	-2.090
Ac-3e Zn-Ac-3e	C ₆ H ₅ C ₆ H ₅	NHAc NHAc	0.550 0.360	0.840 0.780	$-1.630 \\ -1.750$	$-2.000 \\ -2.110$
11	C_6H_5/C_6H_4Me	NHAc	0.540 (2e)	0.860	-1.660 (2e)	-2.010

[a] Irreversible. [b] n.o.: not observed.



Table 6.	Redox potentials	of 4 , 6 ,	Zn-6, 11	7 and 9	in V vs.	Fc/Fc ⁺	in (nBu ₄ N	$(PF_6)/C$	H_2Cl_2 at	room	temperature.
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	Ar	$E(P)_{1/2}(ox^1)$ [V]	$E(P)_{1/2}(ox^2)$ [V]	$E(Fc)_{1/2}(ox) [V]$	$E(Q)_{1/2}(red) [V]$	$E(P/Q)_{1/2}(red^1)$ [V]	$E(P)_{1/2}(red^2)$ [V]
4a	C ₆ H ₄ OnBu	0.500	0.750	_	-1.230	-1.640	-2.000
4b	C ₆ H ₄ OMe	0.500	0.760	-	-1.230	-1.660	-1.990
4c	Mes	0.560	0.960	-	-1.230	-1.720 (2e)	-2.070
4d	C ₆ H ₄ Me	0.540	0.840	_	-1.210	-1.600	-1.980
4 e	C_6H_5	0.580	0.870	_	-1.190	-1.560	-1.940
4f	C_6H_4F	0.600	0.880	_	-1.210	-1.580	-1.930
4g	$C_6H_4CF_3$	0.670	0.960	_	-1.200	-1.530	-1.870
4h	C ₆ F ₅	0.830	1.050	_	-1.240	-1.420	-1.850
6a	C ₆ H ₄ OnBu	0.510	0.770	-0.070	-1.210	-1.650	$-2.010^{[a]}$
6b	C ₆ H ₄ OMe	0.500	0.770	-0.079	-1.220	-1.650	-2.010 ^[a]
6c	Mes	0.560	0.990	-0.070	-1.230	-1.710 (2e)	-2.070
6d	C ₆ H ₄ Me	0.550	0.855	-0.075	-1.190	-1.605	-1.965
6e	C_6H_5	0.560	0.925	-0.090	-1.260	-1.670	-2.060
6f	C_6H_4F	0.585	0.945 ^[a]	-0.085	-1.235	-1.625	-2.015 ^[a]
6g	$C_6H_4CF_3$	0.640	0.990	-0.080	-1.230	-1.570	-1.930
6h	C_6F_5	0.800	1.040	-0.100	-1.270	-1.430	-1.900
<u>6i</u>	C ₆ F ₄ OMe	0.770	1.075	-0.050	-1.240	-1.420	-1.890
Zn-6a	C ₆ H ₄ OnBu	0.370	0.670	-0.070	-1.170	-1.620	$-2.200^{[a]}$
Zn-6b	C ₆ H ₄ OMe	0.360	0.670	-0.080	-1.150	-1.590 ^[a]	n.o. ^[b]
Zn-6c	Mes	0.410	0.750	-0.060	$-1.180^{[c]}$	$-1.620^{[a]}$	-2.220 ^[a]
Zn-6d	C ₆ H ₄ Me	0.390	0.710	-0.089	$-1.190^{[c]}$	$-1.630^{[a]}$	-2.230 ^[a]
Zn-6e	C_6H_5	0.430	0.740	-0.080	-1.120	$-1.580^{[a]}$	-2.190 ^[a]
Zn-6f	C_6H_4F	0.440	0.750	-0.080	-1.120	-1.590	-2.180 ^[a]
Zn-6g	$C_6H_4CF_3$	0.480	0.770	-0.100	$-1.240^{[a]}$	$-1.610^{[a]}$	n.o. ^[b]
Zn-6h	C_6F_5	0.630	0.910	-0.090	-1.180	n.o. ^[b]	-2.000 ^[a]
Zn-6i	C ₆ F ₄ OMe	0.600	0.880	-0.090	-1.160	-1.610 ^[a]	$-2.040^{[a]}$
11	C ₆ H ₅ /C ₆ H ₄ Me	0.540 (2e)	0.860 (2e)	_	_	-1.650 (2e)	-2.010 (2e)
7	C ₆ H ₅ /C ₆ H ₄ Me	0.570 (2e)	0.890	-	-1.200	-1.600 (2e)	-1.970
9	C ₆ H ₅ /C ₆ H ₄ Me	0.590 (2e)	0.870	-0.060	-1.190	-1.600 (2e)	-1.980

[a] Irreversible, E_p given. [b] n.o.: not observed. [c] Quasi-reversible.

porphyrin, and two-electron reversible redox waves for the first oxidation and first reduction of both porphyrins at around -0.59 and -1.60 V are detected. Tetrad **9** additionally shows the one-electron reduction of the quinone at $E_{1/2} = -1.190$ V and the one-electron oxidation of the ferrocene at $E_{1/2} = -0.060$ V.

Thermodynamic Driving Force for Photoinduced Electron Transfer

The energies of the porphyrin first excited singlet states $E(S_0 \rightarrow S_1)$ of 4a–4h were obtained from the average values of the $Q_x(0,0)$ absorption and Q(0,0) emission bands (Tables 1–4). The energies of the CS states $Q^{-}-P^{+}$ were evaluated from the first oxidation potential of the porphyrin $E_{1/2}(\mathbf{P}/\mathbf{P}^{+})$, the first reduction potential of the quinone $E_{1/2}(Q/Q^{-})$ and the Coulomb term $e_0^2/[4\pi\varepsilon_0\varepsilon_{-}$ $(CH_2Cl_2)r_{AD}$] (Table 6). From these data the thermodynamic driving forces for PET were calculated according to the Rehm-Weller equation:^[22] $\Delta G_{\rm ET} = E_{1/2}({\rm D}/{\rm D}^{+})$ – $E_{1/2}(A/A^{-}) - e_0^2/[4\pi\varepsilon_0\varepsilon(CH_2Cl_2)r_{AD}] - E(S_0 \rightarrow S_1)$ with $\varepsilon_0 =$ $8.85519 \times 10^{-12} \text{ Fm}^{-1}$, $\varepsilon(\text{CH}_2\text{Cl}_2) = 8.93$ and $r_{\text{AD}} = 15.5 \text{ Å}$, as determined by DFT models (see below), to give a Coulomb term of 0.104 eV in CH₂Cl₂. The data are presented in Table 7. Figure 6 shows the energy level diagram for all Q-P dyads 4a–4h. This series of compounds displays a $k_{\rm ET}$ / $\Delta G_{\rm ET}$ correlation in the normal Marcus region (Table 3 and Table 7) with $k_{\rm ET}$ increasing the more negative $\Delta G_{\rm ET}$ is (except for the mesityl derivative **4c**, see above). For **4h**, the ET is even calculated to be slightly endergonic, which accounts for the observed weak fluorescence quenching.

Table 7. Energies of the porphyrin S_1 and CS states for dyads 4a-4h and the driving forces ΔG_{ET} .

	Ar	$E(\mathbf{S}_0 \rightarrow \mathbf{S}_1)$	$E(\mathbf{Q}^{\cdot-}\mathbf{P}^{\cdot+})^{[a]}$	$\Delta G_{\rm ET} [{\rm eV}]$
		[eV]	[eV]	
4a	C ₆ H ₄ OnBu	1.89	1.63	-0.26
4b	C ₆ H ₄ OMe	1.89	1.63	-0.26
4c	Mes	1.90	1.69	-0.21
4d	C ₆ H ₄ Me	1.90	1.65	-0.25
4e	C_6H_5	1.91	1.67	-0.24
4f	C_6H_4F	1.91	1.71	-0.20
4g	$C_6H_4CF_3$	1.91	1.77	-0.14
4h	C_6F_5	1.93	1.97	+0.04

[a] Including Coulomb term of 0.104 eV.

As suggested above, two different PET pathways exist in triads **6a–6h** and **Zn-6a–Zn-6h**. The first one is the oxidative pathway, as is also found in Q-P dyads **4**, leading to the Q⁻⁻P⁺⁺-Fc and Q⁻⁻(Zn)P⁺⁺-Fc CS states, respectively (Table 8, Figures 7 and 8). The second one is the reductive pathway leading to the Q-P⁻⁻Fc⁺⁺ and Q-(Zn)P⁺⁻-Fc⁺⁺ CS states, respectively (Table 8, Figures 7 and 8). The final CS states are described by Q⁻⁻P-Fc⁺⁺ and Q⁻⁻(Zn)P⁻⁻Fc⁺⁺, respectively. The free energies of the initial and final CS states were estimated from the Rehm–Weller equation^[22] and are





Figure 6. Energy level diagram for Q-P dyads **4a**–**4h** (IC = internal conversion; the porphyrin triplet state T_1 is estimated to be 1.43 eV^[3f]).

given in Table 8 (quinone-porphyrin centre-to-centre distance $r_{AD} = 15.5$ Å; Coulomb term for Q⁻-P⁺-Fc 0.104 eV; porphyrin centre to iron distance $r_{AD} = 13.0$ Å; Coulomb term for Q-P⁻-Fc⁺ 0.124 eV; quinone-centre to iron distance $r_{AD} = 28.3$ Å; Coulomb term for Q⁻-P-Fc⁺ 0.057 eV).

In the free-base porphyrin triads **6a–6i**, the reductive PET to give Q-P⁻⁻Fc⁺⁺ as the initial CS state is clearly favoured over the oxidative PET that gives the Q⁻⁻-P⁺⁺-Fc initial CS state (Figure 7). This is especially pronounced in **6g–6i** with strongly electron-withdrawing substituents. In the zinc(II) porphyrin triads **Zn-6**, oxidative PET becomes competitive with reductive PET with respect to the driving force $\Delta G_{\rm ET}$ (Table 8 and Figure 8). The final Q⁻⁻-(Zn)P-Fc⁺⁺ CS states of **Zn-6** are slightly lower than the final Q⁻⁻-P-Fc⁺⁺ CS states of **6** due to the slightly preferred reduction of Q in the zinc porphyrins **Zn-6** (see above, Table 6).

In bis(porphyrin) **11**, the conceivable $P_1^{\cdot +}-P_2^{\cdot -}$ and $P_1^{\cdot -}-P_2^{\cdot +}$ CS states are located 0.15 and 0.16 eV (including the Coulomb term of 0.08 eV; porphyrin-porphyrin centre-to-



Figure 7. Energy level diagram for Q-P-Fc triads **6a–6i** (the porphyrin triplet state T_1 is estimated to be 1.43 eV^[3f]).



Figure 8. Energy level diagram for Q-(Zn)P-Fc triads **Zn-6a**–**Zn-6i** (the zinc porphyrin triplet state T_1 is estimated to be 1.53 eV.^[5b]).

centre distance 19.3 Å) above the excited singlet state S₁ and are thus less relevant for excited-state decay (Figure 9 and Table 9). This is also reflected in the unchanged lifetime of 11 ($\tau = 9.70$ ns) with respect to reference porphyrins Ac-3d ($\tau = 9.69$ ns) and Ac-3e ($\tau = 9.88$ ns). The thermodynamic driving forces for ET in tetrad 9 were again calculated from the Rehm–Weller equation^[22] (see above) and are given in

Table 8. Energies of porphyrin S₁ and CS states for 6 and Zn-6 and driving forces ΔG_{ET} .

	Ar	$\begin{array}{c} E(\mathbf{S}_0 \rightarrow \mathbf{S}_1) \\ [eV] \end{array}$	$\begin{array}{c} E(\mathbf{Q}^{\cdot-}\mathbf{P}^{\cdot+}\mathbf{F}\mathbf{c})^{[a]}\\ [eV] \end{array}$	$\begin{array}{c} E(Q-P^{-}-Fc^{+})^{[b]}\\ [eV] \end{array}$	$\begin{array}{c} E(Q^{\cdot-}P-Fc^{\cdot+})^{[c]}\\ [eV] \end{array}$	$\begin{array}{c} \Delta G_{\rm ET}({\rm Q}^{\cdot -} {\rm P}^{\cdot +} {\rm -Fc}) \\ [{\rm eV}] \end{array}$	$\begin{array}{c} \Delta G_{\rm ET}({\rm Q}\mbox{-}{\rm P}\mbox{-}\mbox{-}{\rm F}\mbox{c}\mbox{+}) \\ [\rm eV] \end{array}$	$\Delta G_{\rm ET}({\rm Q}^{-}-{\rm P}-{\rm Fc}^{+})$ [eV]
6a	C ₆ H ₄ OnBu	1.90	1.62	1.46	1.08	-0.28	-0.44	-0.82
6b	C ₆ H ₄ OMe	1.90	1.62	1.45	1.08	-0.28	-0.45	-0.82
6c	Mes	1.91	1.69	1.39	1.10	-0.22	-0.52	-0.81
6d	C ₆ H ₄ Me	1.91	1.64	1.41	1.06	-0.27	-0.50	-0.84
6e	C_6H_5	1.91	1.72	1.46	1.11	-0.19	-0.45	-0.79
6f	C_6H_4F	1.91	1.72	1.42	1.09	-0.19	-0.49	-0.82
6g	$C_6H_4CF_3$	1.91	1.77	1.37	1.09	-0.04	-0.54	-0.82
6h	C_6F_5	1.92	1.97	1.21	1.11	+0.05	-0.71	-0.81
6i	C ₆ F ₄ OMe	1.92	1.91	1.25	1.13	-0.01	-0.67	-0.79
Zn-6a	C ₆ H ₄ OnBu	2.07	1.44	1.43	1.04	-0.63	-0.64	-1.03
Zn-6b	C ₆ H ₄ OMe	2.07	1.41	1.39	1.01	-0.66	-0.66	-1.06
Zn-6c	Mes	2.07	1.49	1.44	1.06	-0.58	-0.63	-1.01
Zn-6d	C ₆ H ₄ Me	2.07	1.48	1.42	1.04	-0.59	-0.65	-1.03
Zn-6e	C_6H_5	2.08	1.45	1.38	0.98	-0.63	-0.70	-1.10
Zn-6f	C_6H_4F	2.08	1.46	1.39	0.98	-0.62	-0.69	-1.10
Zn-6g	$C_6H_4CF_3$	2.07	1.62	1.39	1.08	-0.45	-0.68	-0.99
Zn-6h	C_6F_5	2.07	1.71	1.37 ^[d]	1.03	-0.36	-0.70	-1.04
Zn-6i	C ₆ F ₄ OMe	2.08	1.66	1.40	1.01	-0.42	-0.68	-1.07

[a] Including Coulomb term of 0.104 eV. [b] Including Coulomb term of 0.124 eV. [c] Including Coulomb term of 0.057 eV. [d] Calculated with $E(P)_{1/2}(\text{red}^1) = -1.58 \text{ eV}$ from reference porphyrin Ac-3h, see ref.^[10].



Table 9. Reductive PET ($\Delta G_{\rm ET} = -0.48 \text{ eV}$) to give Q–P₁– P₂⁻⁻-Fc⁺ is thermodynamically favoured in 9 over oxidative PET ($\Delta G_{\rm ET} = -0.26 \text{ eV}$) similarly to 6d and 6e (Tables 8, 9 and Figure 9). This excellently supports the kinetic analysis of ET in 9 (see above). The shift of charge from P₂ to P₁ to give Q-P₁⁻⁻-P₂-Fc⁺ is slightly endergonic (0.09 eV) whereas the following thermal ET to give Q⁻⁻-P₁-P₂-Fc⁺ is again exergonic by 0.42 eV (Figure 9).



Figure 9. Energy level diagram for Q-P₁-P₂-Fc tetrad 9.

Table 9. Energies of porphyrin S_1 and CS states for **9** and driving forces ΔG_{ET} .

State	<i>E</i> [eV] ^[a]	r_{AD} [Å]	Coulomb term [eV]
$\overline{E_{P1}(S_0 \rightarrow S_1)}$	1.91	_	_
$E_{P2}(S_0 \rightarrow S_1)$	1.91	_	_
$E(Q-P_1^{+}-P_2^{-}-Fc)$ or	2.07/2.08	19.3	0.084
$E(Q-P_1 - P_2 + Fc)^{[b,c,d,e]}$			
$E(Q^{-}-P_1^{+}-P_2-Fc)^{[b]}$	1.65	15.5	0.104
$E(Q^{-}-P_1-P_2^{+}-F_c)^{[c]}$	1.67	34.8	0.046
$E(Q-P_1-P_2-Fc^{+})^{[d]}$	1.43	13.0	0.124
$E(Q-P_1 - P_2 - Fc^{+})^{[e]}$	1.52	32.3	0.050
$E(\mathbf{Q}^{\cdot}-\mathbf{P}_1-\mathbf{P}_2-\mathbf{F}\mathbf{c}^{\cdot+})$	1.10	47.8	0.033
Driving force	$\Delta G_{\rm ET}$ [eV]		
$\Delta G_{\rm ET}({\rm Q}^{\cdot-}-{\rm P}_1^{\cdot+}-{\rm P}_2-{\rm Fc})$	-0.26		
$\Delta G_{\rm ET}({\rm Q}^{-}-{\rm P}_1-{\rm P}_2^{+}-{\rm Fc})$	-0.24		
$\Delta G_{\rm ET}(\rm Q-P_1-P_2^{-}-Fc^{+})$	-0.48		
$\Delta G_{\rm ET}(\rm Q-P_1^{-}-P_2^{-}Fc^{+})$	-0.39		
$\Delta G_{\rm ET}({\rm Q}^{-}-{\rm P}_1-{\rm P}_2-{\rm Fc}^{+})$	-0.81		

[a] Including Coulomb terms. [b] Calculated with $E(P_1)_{1/2}(ox^1) = 0.550 \text{ V}$ from reference porphyrin **Ac-3e**. [c] Calculated with $E(P_2)_{1/2}(ox^1) = 0.520 \text{ V}$ from reference porphyrin **Ac-3d**. [d] Calculated with $E(P_1)_{1/2}(\text{red}^1) = -1.630 \text{ V}$ from reference porphyrin **Ac-3e**. [e] Calculated with $E(P_2)_{1/2}(\text{red}^1) = -1.610 \text{ V}$ from reference porphyrin **Ac-3e**.

Densitiy Functional Calculations on Ground and CS States

To estimate distances between redox sites (Q–P centreto-centre; P centre to Fe, Q centre to Fe, P–P centre-tocentre) and to visualise frontier molecular orbitals, the ground states of dyads and triads with electron-donating and -withdrawing substituents were optimised by DFT (B3LYP/LANL2DZ, PCM, $CH_2Cl_2)^{[23]}$ methods (see the Supporting Information). Figure 10 exemplarily depicts the frontier molecular orbitals of dyads **4b** and **4h** showing the typical Gouterman four orbital scheme for porphyrins (nomenclature adopted from D_{4h} local point symmetry to describe the node structure of the orbitals^[24]) and the lowest π^* orbital of the quinone located between the HOMOs and LUMOs of the porphyrin. Two points are immediately evident: 1) electron-withdrawing Ar substituents reduce the energy gap between the LUMO of the porphyrin and the π^* orbital of the quinone (Figure 11), which disfavours oxidative PET, and 2) the symmetry of the local porphyrin LUMO in **4h** (Figure 10, b; LUMO+1; Ar = C₆F₅) is different to that in all the other dyads and features a node at the *meso* carbon atoms in the amide direction. This orbital inversion is typically observed in porphyrins with strongly electron-withdrawing substituents.^[11,25] Naturally, small orbital coefficients at the bridging unit between redox centres



Figure 10. B3LYP/LANL2DZ, PCM-calculated frontier orbitals for a) **4b** and b) **4h** (isosurface value 0.05 a.u.).

1995



disfavours ET. Hence, PET in **4h** is not only thermodynamically slightly uphill (Figure 6), but probably also kinetically hindered due to the unfavourable orbital symmetry.



Figure 11. B3LYP/LANL2DZ, PCM-calculated molecular orbital energy diagram for dyads **4**.

A similar picture with respect to the quinone π^* orbital arises for the triads 6 (Figure 12) and **Zn-6**. The porphyrin LUMO inversion is also observed for 6g (Figure 13) and **6h**. In addition, the occupied ferrocene-based δ orbitals $(d_{xy}, d_{x^2-y^2})$ are close in energy to the local porphyrin HOMOs (Figure 12). For electron-rich 6a-6f, the $\delta(Fc)$ orbitals are below the porphyrin a_{2u} orbital, in 6g the a_{2u} orbital is lowered in energy and mixes with a $\delta(Fc)$ orbital (Figure 13, HOMO) and in **6h** the porphyrin $a_{2\mu}$ orbital is located even below the $\delta(Fc)$ orbitals. Naturally, this simple orbital picture cannot account for quantitative relationships, but it clearly demonstrates the lowering of the porphyrin HOMOs relative to the essentially constant ferrocene HOMOs (Figure 12), which should favour reductive PET in triads with electron-withdrawing substituents (see Tables 4 and 8). The near degeneracy of porphyrin and ferrocene HOMOs in terms of energy also allows for orbital mixing (Figure 13) and mixing of states, which should also allow energy-transfer processes between porphyrin and ferrocene. These energy-transfer processes might be assigned to the second decay (τ_2, A_2) in **6e–6i** and **Zn-6a–Zn-6i**



Figure 12. B3LYP/LANL2DZ, PCM-calculated molecular orbital energy diagram for triads **6**.



Figure 13. B3LYP/LANL2DZ, PCM-calculated frontier orbitals

Tetrad **9** features a double nearly degenerate set of Gouterman orbitals as well as the quinone π^* and the occupied ferrocene d orbitals, as expected from the constituent building blocks (see the Supporting Information). The porphyrin HOMOs are of local a_{2u} symmetry with large coefficients at the connecting *meso* carbon atoms. This should allow for energy and electron transfer between the two porphyrins^[11] based on orbital symmetry arguments, as suggested in Fig-

for triad **6g** (isosurface value 0.05 a.u.).

ure 9. For dyad **4b** (Ar = 4-C₆H₄OMe) we succeeded in optimising the Q⁻-P⁺ CS triplet state by DFT methods (Figure 14, a). The calculated spin density is clearly distributed over the porphyrin radical cation and quinone radical anion, as expected from the molecular orbital scheme (Figure 10). The quinone CO bond lengths were calculated to be 1.26 Å in the ground state and 1.30 Å in the CS state, clearly reflecting the semiquinone character. The analogous DFT optimisation of **4d** (Ar = 4-C₆H₄Me) resulted in the porphyrin triplet state T₁ (Figures 6 and 14, b), which suggests a close proximity of the CS (1.65 eV, Table 7) and local triplet states in terms of energy. Indeed, the porphyrin triplet state of H₂TPP has been reported to have an energy of 1.43 eV.^[31]

To gain an impression of the spin density and charge distribution in the final $Q^{-}-P-Fc^{+}$ and $Q^{-}-(Zn)P-Fc^{+}$ CS



Figure 14. DFT-calculated spin density of a) the $Q^{-}-P^{+}$ CS triplet state of **4b** and b) the porphyrin triplet state of **4d** (isosurface value 0.01 a.u.).

states of the triads we tried to optimise this (triplet) state, but all attempts yielded only the optimised ferrocene triplet state with a Mulliken spin density of 2.03 at the iron centre (Figure 15, a). The calculated Fe···Cp(centroid) distances



Figure 15. DFT-calculated spin densities of a) the ferrocene triplet state of **6e**, b) the Q⁻⁻P-Fc⁺ triplet CS state of **6e**(\cdot 2BF₃) and c) the Q⁻⁻(Zn)P-Fc⁺ triplet CS state of **Zn-6e**(\cdot 2BF₃) (isosurface value 0.01 a.u.).

are increased significantly from 1.73 to 1.91 Å. The energy of the triplet state of unsubstituted ferrocene has been reported to be 1.16 eV,^[10] which is clearly close to the energies of the Q⁻-P-Fc⁺ and Q⁻-(Zn)P-Fc⁺ CS states (cf. Table 8). To artificially stabilise the Q⁻-P-Fc⁺ and Q⁻-(Zn)P-Fc⁺ CS states relative to the ferrocene triplet we placed two Lewis acidic^[26] BF₃ molecules at the quinone oxygen atoms, which allowed optimisation of the CS states of **6e**(•2BF₃) and **Zn-6e**(•2BF₃) as the lowest-energy triplet states (Figure 15, b,c). The calculated spin densities are clearly at both the ferrocenium and semiquinonato radicals. Again, the quinone CO bond lengths are elongated from 1.26 to 1.30 Å. Furthermore, the Fe^{...}Cp(centroid) distances are elongated from 1.73 to 1.80 Å, which indicates the ferrocenium state.

Transient Absorption Spectroscopy of Selected Compounds

Compared with the porphyrin bands, the absorptions of the semiguinone radical anion Q⁻ and ferrocenium cation Fc⁺⁺ are rather weak. Chemical reduction of the reference N-ethylanthraquinone-2-carboxylic acid amide with decamethylcobaltocene [CoCp*2]^[27] (see the Supporting Information) generated the semiquinone radical anion Q⁻ with an absorption maximum at 618 nm and $\varepsilon_{618} = 750 \text{ M}^{-1} \text{ cm}^{-1}$ (THF). The ferrocenium reference [Fc-NHAc]⁺ absorbs at 759 nm with $\varepsilon_{759} = 350 \text{ m}^{-1} \text{ cm}^{-1} (\text{CH}_2\text{Cl}_2).^{[28]}$ Owing to the low extinction coefficients, that is, small absorption crosssections, these bands are difficult to detect in transient absorption (TA) pump-probe experiments as they are overwhelmed by the excited-state absorptions of the strongly absorbing porphyrin excited states. Hence all transient absorption spectra are largely dominated by features of the porphyrin radical(s) and porphyrin triplet states.

The pico- to nanosecond TA spectra of compounds **4a** and **6a** in THF are presented in Figure 16. The spectra show multiple peaked features that correspond to ground-



Figure 16. ps–ns transient absorption spectra of a) **4a** and b) **6a** in THF after excitation at $\lambda_{exc} = 420$ nm. Note the significantly faster decay of the TA signal for compound **6a**.



state bleaching and stimulated emission overlapped by the excited-state absorption of the porphyrin. The spectra do not change much during the observed period of time, except for compound **4a**, for which there is an increase in the intensity of the photoinduced absorption in the spectral region between 750–900 nm. This spectral evolution may be related to electron transfer from the porphyrin to the quinone, but a clear assignment is difficult.

As a consequence of the superposition of several bands corresponding to porphyrin radical ions, namely the excited-state absorption, the ground-state bleaching and stimulated emission bands, and the low extinction coefficients of the Q⁻ and Fc⁺ radicals, the transient spectra of intermediate CS states are not observed for dyad 4a and triad 6a. However, very clearly a much more rapid decay of the entire TA spectrum is observed for the ferrocenyl derivative 6a. The decay is well fitted by a single exponential with an inverse rate of 220 ps, which is essentially the same as the 215 ps determined for the fluorescence lifetime of 6a. This fast decay is likely due to the fast reductive quenching of the porphyrin excited state by the ferrocene, parallel oxidative quenching by the quinone (Figure 7) and/or heavy atom quenching by the ferrocene to give the porphyrin triplet state. For the two PET pathways, porphyrin radical anions and radical cations could be simultaneously present and would create superimposed excited-state absorption spectra that are difficult to analyse. After charge transfer from P^{-} to Q or from Fc to P^{+} , the final CS state should show no features arising from porphyrin, but only weak bands corresponding to Q⁻ and Fc⁺ radicals. These latter would be difficult to detect, especially if the final CS state is only formed in low yields. However, the significant decrease in the TA signal intensity on the nanosecond timescale observed for **6a** in comparison with **4a** indicates that in the former a large fraction of the porphyrin excited states are rapidly quenched and that the ground state of the porphyrin in 6a is quickly recovered after photoexcitation. This is in line with the experimentally observed faster photoluminescence decay of 6a, the much lower fluorescence quantum yield and the predicted higher driving force for photoinduced electron transfer from the ferrocene to the porphyrin in comparison with electron transfer from the porphyrin to the quinone moiety, all of which indicate that the charge-transfer process from ferrocenium to the porphyrin is efficient.

As the pico- to nanosecond TA spectra are rather difficult to interpret due to the multitude of features and potentially parallel photophysical processes, we had a closer look at the nano- to microsecond spectra and dynamics. On the nanosecond timescale, the shapes of the transient absorption spectra of **Ac-3a**, **4a** and **6a** are rather similar (see the Supporting Information). The decay of the TA signals on this timescale should largely reflect the recombination dynamics of the triplet and CS states in these compounds. In fact, the dynamics of the TA signals of all three compounds **Ac-3a**, **4a** and **6a** can be well described by the sum of two exponentials with a nano- and microsecond component indicating two processes, as shown in Figure 17. In the case of the reference porphyrin Ac-3a, we obtained inverse rate constants of 12 ns and 7 μ s.



Figure 17. ns– μ s transient absorption dynamics of a) Ac-3a, b) 4a, c) 4a plus 100 equiv. B(C₆F₅)₃ and d) 6a in THF solution after excitation at $\lambda_{exc} = 532$ nm. The dynamics were monitored in the spectral region 550–620 nm. The solid red lines represent exponential fits to the data and the inverse decay rates are also shown. Note the significantly slower TA signal decay for compound 4a plus additive indicating the stabilisation of the CS state by the Lewis acid.

The nanosecond lifetime τ_1 corresponds approximately to the measured fluorescence lifetime of around 10 ns within the error that can be expected between the two different experimental techniques. The microsecond lifetime τ_2 can be assigned to the decay of the porphyrin triplet T_1 state generated by intersystem crossing from the porphyrin singlet S_1 state due to its significantly longer lifetime in the range typical for the decay of triplets. Fitting the signal dynamics of 4a yields inverse rate constants of 5.7 ns and $1.7 \,\mu s$. The former is shorter than the lifetime observed for the reference porphyrin Ac-3a, indicating additional decay channels, but longer than the observed fluorescence lifetime of compound 4a (in CH_2Cl_2), which might be a solvent effect. However, in this case we most probably approached the temporal resolution of our ns-µs TA set-up, which is about several nanoseconds. The second longer-lived component has a considerably shorter lifetime than the porphyrin triplet-state lifetime observed for compound Ac-3a and thus appears to originate from a state other than the T_1 triplet. Given that the efficiency of ET obtained by analysis of the fluorescence quenching is $\Phi_{\rm ET} = 0.93$, we assign this component to the decay of the Q⁻-P⁺ CS state, which is formed in high yield in the case of compound 4a. The dynamics of the TA signals of compound 6a can be fitted with inverse rates of $\tau_1 = 3$ ns and $\tau_2 = 6.8 \,\mu$ s. Although the former is

1998



certainly limited by the temporal resolution of our set-up and represents the sub-nanosecond dynamics of the PET processes, the latter component is close to the triplet lifetime observed for compound **Ac-3a**. This appears reasonable as in this compound no features of porphyrin radicals should be observed from the final Q⁻-P-Fc⁺ CS state after electron transfer to Q and from Fc are complete. Therefore we observe the decay of a fraction of porphyrin triplet states created either by ISC from the porphyrin singlet state directly after photoexcitation or, which is more likely, by a transition of the initial Q-P⁻-Fc⁺ CS state (1.46 eV, Table 8 and Figure 7) into the T₁ state of the porphyrin (1.43 eV^[3f]).

As suggested by the DFT calculations, a CS state involving the quinone can be stabilised by coordinating a Lewis acid to the quinone carbonyl groups. Excess tris(pentafluorophenyl)boron was added to 4a and 6a in THF and the ps-ns as well as ns-us transient absorption spectra and dynamics were studied (see Figure 17 and the Supporting Information). Some spectral but mostly temporal differences were observed with respect to the spectra and dynamics of 4a and 6a in the absence of the Lewis acid. The most striking observation is a pronounced decrease in the decay rate, in other words, increase in the lifetime of the Q⁻-P⁺ CS state observed for compound 4a. In fact, the ns-µs TA experiments showed that the lifetime of the CS state is significantly increased from $\tau_2 = 1.7 \,\mu s$ to $\tau_2 = 80 \,\mu s$ upon addition of $B(C_6F_5)_3$ (cf. Figure 17, b,c). This suggests that the Q⁻⁻-P⁻⁺ CS state is significantly stabilised by the Lewis acid, as suggested by the DFT calculations, and further supports our assignment of the dynamics to the recombination of the charge-separated state. Although the effect is pronounced for 4a, it is much less obvious for 6a. This appears reasonable as we assigned the dynamics in the latter to the recombination of the porphyrin triplet state, which should not be affected by the presence of the Lewis acid.

Conclusions

Anthraquinone-porphyrin dyads (Q-P, 4), anthraquinone-porphyrin-ferrocene triads (Q-P-Fc, 6) and zincated triads [Q-(Zn)P-Fc, Zn-6] with meso substituents Ar of increasing electron-withdrawing character in the porphyrin component have been designed and synthesised by amide coupling (Ar = $4-C_6H_4OnBu$, $4-C_6H_4OMe$, Mes, 4- C_6H_4Me , C_6H_5 , 4- C_6H_4F , 4- $C_6H_4CF_3$ and C_6F_5). Based on this modular amide-coupling approach, a Q-PC6H5- P^{C6H4Me} -Fc tetrad (9) was constructed. In the ground states of 4, 6, Zn-6 and 9, only marginal interactions between the individual building blocks Q, P and Fc are observed, and energy transfer between the two porphyrins in 9 is possible. The fluorescence of dyads 4 is quenched by oxidative photoinduced electron transfer (PET). The rate of ET increases by several orders of magnitude with increasing electron-donating power of the *meso* substituent Ar ($k_{\rm ET} = 0.003 \times 10^9$ to 1.5×10^9 s⁻¹) due to the increased driving force $\Delta(\Delta G_{\rm ET})$ = -0.3 eV. In triads 6 an additional reductive PET pathway is thermodynamically feasible. This ET pathway is favoured by electron-withdrawing *meso* substituents Ar $[k_{\rm ET} =$ 4×10^9 to 38×10^9 s⁻¹; $\Delta(\Delta G_{\rm ET}) = -0.2$ eV]. Comparable rates and driving forces for reductive and oxidative quenching are found for $Ar = 4 - C_6 H_4 O n Bu$, $4 - C_6 H_4 O Me$ and $4 - C_6 H_4 O Me$ C_6H_4Me in triads 6. The zinc porphyrins **Zn-6** are basically non-fluorescent. If the major deactivation in zinc conjugates indeed occurs by PET, both pathways feature similar driving forces for Ar = $4 - C_6 H_4 O n B u$, $4 - C_6 H_4 O M e$, Mes, 4-C₆H₄Me and C₆H₅. In tetrad 9, both pathways are also feasible, although reductive PET ($\Delta G_{\rm ET} = -0.48 \text{ eV}$; $k_{\rm ET} =$ $2.66 \times 10^9 \text{ s}^{-1}$) is preferred over oxidative PET (ΔG_{ET} = -0.26 eV; $k_{\text{ET}} = 0.363 \times 10^9 \text{ s}^{-1}$). With these preparative, spectroscopic, electrochemical and theoretical results in hand, more complex architectures with well-defined excited-state energies in a structurally precisely organised manner can be envisaged.

Supporting Information (see footnote on the first page of this article): Experimental and analytical details, normalised absorption and emission spectra of selected Q-P dyads, Q-P-Fc triads and reference porphyrins in CH₂Cl₂n DFT (B3LYP/LANL2DZ, PCM) calculated frontier orbitals of Zn-6b, Zn-6g, Zn-6h and 9, absorption spectra of *N*-ethylanthraquinone-2-carboxamide treated with CoCp*₂ in THF; ns to μ s transient absorption spectra of Ac-3a, 4a, 4a + B(C₆F₅)₃, 6a and 6a + B(C₆F₅)₃ in THF; after excitation at $\lambda_{exc} = 532$ nm, energies (eV) of relevant frontier molecular orbitals of the Q-P dyads 4a-4h determined by DFT (B3LYP/LANL2DZ, PCM), energies (eV) of relevant frontier molecular orbitals of the Q-P-Fc triads 6a-6i and Q-P-Fc triads Zn-6a-Zn-6i determined by DFT (B3LYP/LANL2DZ, PCM), Cartesian coordinates of DFT-optimised geometries.

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