Efficient Low Driving Force Charge Separation in an Electron Deficient Zn-Porphyrin-Fullerene Donor-Acceptor Conjugate

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Synthesis and characterization

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Experimental section
Synthesis and characterization

The ZnTF₅PP–C₆₀ conjugate 1 was synthesized by the following synthetic route:

\[
\begin{align*}
\text{TF₅PP} &\quad + \quad \text{CHO} \\
&\xrightarrow{K₂CO₃, \text{DMSO}} \quad \text{MeNHCH₂CO₂H, C₆₀, toluene, N₂, reflux} \\
&\quad \xrightarrow{\text{50 °C, N₂, 7 h}} \quad \text{2 (53% yield)} \\
&\quad \xrightarrow{\text{Zn(OAc)}₂, \text{CHCl₃/MeOH}} \quad \text{3 (63% yield)} \\
\end{align*}
\]

**Synthesis of the 4-(porphyrinyloxy)benzaldehyde 2**

To a solution of TF₅PP (100.0 mg, 0.103 mmol, 1.5 equiv.) and 4-hydroxybenzaldehyde (8.4 mg, 68.4 μmol) in dry DMSO (3 mL) was added potassium carbonate (47.3 mg, 0.342 mmol, 5 equiv.). The reaction mixture was stirred at 50 °C for 7 h under a nitrogen atmosphere. After cooling to room temperature, an aqueous solution of citric acid was added to the reaction mixture and the porphyrinic material was precipitated. After filtration, the solid was dissolved in dichloromethane and washed with water. The organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated to dryness on the rotary evaporator. The residue was dissolved in dichloromethane and purified by silica gel column chromatography using dichloromethane/hexane (2:1) as the eluent. The first fraction was the unreacted TF₅PP (45 mg recovered) and then the mono-substituted porphyrin 2 (39 mg, 53% yield) was collected, which was further crystallized from dichloromethane/hexane. Two minor fractions were also isolated and identified as the 5,15- and 5,10-di-substituted porphyrins (3 mg (4% yield) and 8 mg (11% yield), respectively.

\[^1H \text{NMR} (300 MHz, CDCl}_3 \delta: -2.90 \text{ (s, 2H, NH), 7.45 \ (d, J = 8.6 Hz, 2H, H-3), 8.09 \ (d, J = 8.6 Hz, 2H, H-2), 8.93-9.01 \ (m, 8H, H-B), 10.08 \ (s, 1H, CHO) ppm.} \]

\[^{19}F \text{NMR} (282\text{MHz}) \delta: -170.8 \text{ ppm.} \]
MHz, CDCl₃ δ: -162.03 to -161.84 (m, 6F, C₆F₅-m-F), -153.88 (dd, J = 23.4 and 9.8 Hz, 2F, C₆F₅-m-F), -151.9 to -151.71 (m, 3F, C₆F₅-p-F), -137.2 (dd, J = 23.3 and 7.8 Hz, 6F, C₆F₅-o-F), -136.92 (dd, J = 23.4 and 9.8 Hz, 2F, C₆F₅-o-F) ppm. ¹³C NMR (75 MHz, CDCl₃) δ: 103.5, 116.2, 132.3, 132.8, 161.3, 190.5 (CHO) ppm.

UV-vis (CHCl₃) λmax (log ε): 412 (5.2), 505 (4.3), 539 (sh), 583 (4.1), 634 (3.9) nm. MS (MALDI) m/z: 1076.1 [M]⁺. HRMS (ESI) m/z: calculated for C₅₁H₁₅F₁₉N₄O₂ [M+H]⁺ 1077.0964, obtained 1077.0957.

Synthesis of the porphyrin–C₆₀ conjugate 1

A mixture of porphyrin 2 (30.0 mg, 27.9 µmol), N-methylglycine (14.9 mg, 0.167 mmol, 6 equiv.) and C₆₀ (40.1 mg, 55.7 µmol, 2 equiv.) in dry toluene (40 mL) was refluxed under nitrogen for 28 h. The reaction mixture was concentrated on the rotary evaporator and purified by silica gel column chromatography using toluene/hexane (1:1) as the eluent. The first fraction was the unreacted C₆₀ (14 mg recovered); then conjugate 3 was collected and crystallized from toluene/hexane (32 mg, 63% yield). Metallation with zinc acetate in CHCl₃/MeOH at 50 ºC, afforded the conjugate 1 in quantitative yield.

Data for the conjugate 3: ¹H NMR (300 MHz, CDCl₃) δ: -2.93 (s, 2H, NH), 2.88 (s, 3H, CH₃), 4.29 (d, J = 9.6 Hz, 1H, H-5), 5.00-5.03 (m, 2H, H-2 and H-5), 7.38 (d, J = 8.5 Hz, 2H, H-3'), 7.88-8.01 (br s, 2H, H-2'), 8.92 (s, 6H, H-β), 8.98 (d, J = 4.1 Hz, 2H, H-β) ppm. ¹⁹F NMR (282 MHz, CDCl₃) δ: -162.03 to -161.85 (m, 6F, C₆F₅-m-F), -154.1 (dd, J = 23.1 and 9.1 Hz, 2F, C₆F₅-m-F), -151.97 to -151.78 (m, 3F, C₆F₅-p-F), -137.66 (dd, J = 23.1 and 9.1 Hz, 2F, C₆F₅-o-F), -137.1 (dd, J = 23.7 and 7.8 Hz, 6F, C₆F₅-o-F) ppm. UV-vis (toluene) λmax (log ε): 416 (5.5), 508 (4.6), 545 (sh), 586 (4.4), 640 (4.2) nm.
Characterization of conjugate 1

NMR

Note: A $^{13}$C NMR spectrum has been recorded, but the multitude of couplings between $^{13}$C and $^{19}$F nuclei prohibit meaningful analysis of the spectrum. $^1$H and $^{19}$F spectra are presented in the following.

Figure S 1: β-pyrrolic region of the $^1$H-NMR spectrum recorded in CDCl$_3$.

Figure S 2: aromatic region of the $^1$H-NMR spectrum recorded in CDCl$_3$.

Note: due to coupling with the diastereotopic, readily flipping proton (f) the signals of the protons (c) coalesce to one broad signal. Due to the high resolution of the instrument, impurities stemming from solvents used in the synthesis are visible in the range of 7.4 to 7.7 ppm.
Figure S 3: aliphatic region of the ¹H-NMR spectrum recorded in CDCl₃.

Note: the signal near 5 ppm is a pseudo-triplet composed of one part of the doublet of doublets of the protons (e) and the singlet of the proton (f). A measurement at 350K leading to independent shifts of the signals in the pseudo-triplet confirmed this assignment.

Figure S 4: ¹⁹F-NMR spectrum recorded in CDCl₃.
Figure S 5: Top: ESI mass spectrum of 1 displaying the measured isotope distribution of the corresponding radical anion. Bottom: simulated isotope pattern of the radical anion of 1.
Figure S 6: MS/MS spectrum of $1^-$ with the blue diamond indicating the mass-selected precursor ion. Insets show the measured isotope pattern of the fragment ions with the respective simulated pattern below. The fragment ions can be assigned to the radical anion of $C_{60}$ at m/z 720.0 and the radical anion of ZnTF$_5$PP at m/z 1165.1. The intensity ratio of the fragment ions clearly indicates that the negative charge is preferably located at the fullerene.
Figure S 7: decay of ZnTF$_5$PP main emission peak at 640 nm in Toluene as obtained by TCSPC. Excitation at 420 nm.
Figure S 8: Transient absorption results of ZnTF$_2$PP on the sub-ps to ns time scale in Toluene upon excitation at 430 nm; detector change and probe fundamental at 775 nm. Top left: raw data (vis and NIR) with time delays from -0.5 to 5000 ps after excitation. Top right: time profiles of important features and the corresponding fits / residuals obtained from global target analysis. Bottom left: Species associated spectra (SAS) obtained from global target analysis (vis and NIR). Bottom right: time-concentration profiles of the species obtained from global target analysis.
Figure S9: Transient absorption results of ZnTF$_2$PP on the ns to µs time scale in Toluene upon excitation at 430 nm. Top left: raw data (vis to NIR) with time delays from 0.001 to 350 µs after excitation. Top right: time profiles of important features and the corresponding fits / residuals obtained from global target analysis. Bottom left: Species associated spectra (SAS) obtained from global target analysis (vis to NIR). Bottom right: time-concentration profiles of the species obtained from global target analysis. Note: the S2 state cannot be resolved here due to the time resolution of ~1ns.
Figure S 10: energy diagram and reaction rates of the excited state deactivation of ZnTF₅PP, combining results from the sub-ps to ns, on one hand, and ns to µs timescale measurements, on the other hand.
Figure S 8: spectroelectrochemical oxidation of ZnTF$_2$PP in o-DCB with 0.2 M of TBA ClO$_4$. *peak likely enhanced by coordination of ClO$_4^-$ to ZnTF$_2$PP$^+$. 
Figure S 9: Transient absorption results of ZnTF₅PP-C₆₀ on the sub-ps to ns time scale in Toluene upon excitation at 430 nm. Top left: raw data (vis and NIR) with time delays from 2 to 5000 ps after excitation; detector change and probe fundamental at 775 nm. Top right: time profiles of important features and the corresponding fits / residuals obtained from global target analysis. Bottom left: Species associated spectra (SAS) obtained from global target analysis (vis and NIR). Bottom right: time-concentration profiles of the species obtained from global target analysis. Note: T₁₆₀ and T₁₆₀ cannot be deconvoluted on this time scale since their decay times are orders of magnitude outside the measurement time window.
Figure S10: Transient absorption results of ZnTF₆PP-C₆₀ on the ns to µs time scale in Toluene upon excitation at 430 nm. Top left: raw data (vis and NIR) with time delays from 0.0001 to 400 µs after excitation; detector change at 914 nm, probe fundamental at 1064 nm. Top right: time profiles of important features and the corresponding fits / residuals obtained from global target analysis. Bottom left: Species associated spectra (SAS) obtained from global target analysis (vis and NIR). Bottom right: time-concentration profiles of the species obtained from global target analysis. Note: S2p cannot be resolved here due to the time resolution of ~1 ns; deconvolution of S1p and P⁺-C₆₀ is partially hampered by limited separability for species with lifetimes close to the time resolution limit.
Figure S 11: Comparison of species associated spectra for the ZnTF₅PP triplet excited state (as depicted in Figure S9 bottom left) and the porphyrin triplet excited state in 1 (as depicted in Figure S13 bottom left), resulting from global target analysis with parameters as given in Figure S11 and Figure 5.
Experimental section

NMR. $^1$H NMR spectra were taken at 600 MHz on a Bruker Avance NEO spectrometer equipped with a DCH cryo probe. Chemical shifts were referenced by residual CHCl$_3$ (7.24 ppm). $^{19}$F NMR spectra were taken at 500 MHz on a Bruker Avance NEO spectrometer equipped with a PA TBO probe. Chemical shifts referenced to C$_6$F$_6$ (-164.9 ppm).

MS. A concentration of 10$^{-5}$ mol L$^{-1}$ of 1 in a mixture of dichloromethane:acetonitrile (1:2, V:V) was used as the sample solution for the electrospray ionization (ESI) experiments. The solvents were of HPLC grade purity and used as provided. Mass spectra were recorded with a microTOF Q-II (Bruker, Bremen, Germany) equipped with an electrospray ion source using nitrogen as nebulizing gas and a collision cell also utilizing nitrogen as collision gas. The instrument was operated in the negative-ion mode and the capillary voltage was set to 4 kV to obtain sufficient electrochemical reduction of the analyte. For the fragmentation experiment (MS/MS spectrum) the radical anion of the analyte was mass selected and subsequently accelerated with a potential of 35 V before entering the collision cell.

Electrochemistry. 1 and ZnTF$_5$PP reference were dissolved in ortho-dichlorobenzene (o-DCB) with addition of 0.2 M of electrolyte tetrabutylammonium perchlorate (TBAClO$_4$). Potentials were measured against an Ag$|$AgNO$_3$ reference electrode, while ferrocene was used as external standard. Prior to any measurements, the Solutions (2-5 ml) were flushed with Argon for at least 20 minutes. Both were investigated by Squarewave Voltammetry within a window of approximately 3.5 V (-2 V to 1.5 V vs Ag$|$AgNO$_3$) and without showing any signs of solvent electrolysis.

Time-resolved transient absorption spectroscopy. Time resolved transient absorption spectra with 150 fs resolution and time delays from 0 to 7500 ps were acquired using Ultrafast Systems HELIOS Femtosecond Transient Absorption Spectrometer. The laser source was a Clark MXR CPA2110 Ti:Sapphire amplifier with a pulsed output of 775 nm at 1 kHz and pulse width of 150 fs. Visible white light (~400-770 nm) was generated by focusing a fraction of the fundamental 775 nm output onto a 2 mm sapphire disk; for the (near) IR (780-1500 nm), a 1 cm sapphire was used. Excitation pulses of 430 nm wavelength were generated by a NOPA with subsequent frequency doubling; a bandpass filter with ±5 nm was used to ensure low spectral width and to exclude 775 and 387 nm photons.

Ultrafast Systems EOS Sub-Nanosecond Transient Absorption Spectrometer was employed to measure transient absorption spectra with time delays of ~1 ns to 400 µs with 1 ns time resolution. The laser source for excitation was a Clark MXR CPA2101 Ti:Sapphire amplifier with a pulsed output of 775 nm at 1050 Hz and pulse width of 150 fs. Excitation pulses of 430 nm wavelength were generated by a NOPA with subsequent frequency doubling; a bandpass filter with ±5 nm was used to ensure low spectral width and to exclude 775 and 387 nm photons. White light (~370 to >1600 nm) was generated by a built-in photonic crystal fiber supercontinuum laser source with a fundamental of 1064 nm at 2 kHz output frequency and pulse width of approximately 1 ns.

ZnTF$_5$PP and 1 were probed by transient absorption experiments on the sub-ps to ns and ns to µs time scales upon excitation into the Soret-band absorption at 430 nm with pulse lengths of about 200 fs. Toluene was used as solvent in all experiments. Solutions were flushed with Ar for 15-20 min prior to measurements.