Supporting Information:

Charge and Energy Transfer Processes in Ruthenium(II) Phthalocyanine Based Electron Donor-Acceptor Materials – Implications for Solar Cell Performance

Fabian Spänig,[a] Ismael López-Duarte,[b] Markus K. R. Fischer,[c] M. Victoria Martínez-Díaz,[b] Peter Bäuerle,[c] Tomás Torres* [b,d] and Dirk M. Guldi.* [a]

a Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@chemie.uni-erlangen.de

b Departamento de Química Orgánica, Universidad Autónoma de Madrid, E-28049 Cantoblanco, Spain. E-mail: tomas.torres@uam.es

c Prof. Dr. P. Bäuerle, Dr. M. K. R. Fischer, Institute of Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, D-9081 Ulm, Germany. E-mail: peter.baeuerle@uni-ulm.de

d IMDEA-Nanociencia, Facultad de Ciencias, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain.

Experimental Section

Materials: Compounds RuPcCO(Py-3T), $RuPc(Py\text{-}3T)_2$, RuPcCO(Py-9T), $RuPc(Py\text{-}9T)_2$, RuPcCO(Py-21T) and $RuPc(Py\text{-}21T)_2$ were prepared following a literature procedure.[1] All solvents employed for the electrochemical, photochemical and photophysical investigations were purchased by chemical suppliers in dry, spectroscopic grade and used without further purification.

UV/Vis Spectroscopy: Varian Cary 5000 UV-VIS-NIR Spectrophotometer; absorption maxima λ_{max} are given in [nm].

Electrochemistry: Electrochemical experiments were carried out using a BAS-CV50W electrochemical workstation with positive feedback compensation. Cyclic voltammetry, differential pulse voltammetry and square wave voltammetry was performed in a three electrode cell with a platinum wire as counter electrode, a glassy carbon disk as working electrode (Ø = 2 mm) versus a silver wire as reference electrode; ferrocene is applied as an internal standard and a 0.1 M solution of $(t\text{-Bu})_4NBF_4$ as the supporting electrolyte. All experiments were performed under inert gas atmosphere and a compound concentration of 0.2 mM.

Spectroelectrochemistry: Spectroelectrochemical experiments were carried out using a BAS-CV50W electrochemical workstation - with positive feedback compensation - and a SPECORD S600 Analytic Jena Spectrophotometer. The measurements were performed in a especially designed three electrode cuvette (~ 0.5 cm) with a platinum mesh as working electrode, a platinum wire as counter electrode versus a silver wire under Argon atmosphere. Tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6 - 0.2 M) was used as supporting electrolyte.

Steady State Fluorescence Spectroscopy: Horiba-Jobin Yvon Fluoromax 3 spectrophotometer; in deaerated solution at room temperature (298 K) in a 1 to 1 cm quartz cuvette. All spectra were corrected for the instrument response. The monitoring wavelength was corresponding to the maximum of the emission band. For excitation wavelength below 450 nm a cut off filter (450 nm) was inserted.

Time Resolved Fluorescence: The fluorescence lifetime measurements were performed with a SPEX Fluorolog-3 (Horiba-Jobin Yvon) supplied with an integrated TCSPC software. 403 nm was selected as the excitation wavelength for the lifetime measurements (nano-LED-403 L; pulse width <100 ps). Fluorescence lifetimes were measured at the emission maximum at room temperature in deaerated solution in a 1 to 1 cm quartz cuvette.

fs-Transient Absorption Spectroscopy: Femtosecond transient absorption studies were performed with 387 nm laser pulses (1 kHz, 150 fs pulse width, 200 nJ) from an amplified Ti/sapphire laser system (Model CPA 2010, Clark-MXR Inc. – output 775 nm). For excitation wavelength of 650 nm a non linear optical parametric converter (NOPA) was used to generate ultra short tunable visible pulses out of the pump pulses. The transient absorption pump probe spectrometer (TAPPS) is referred to as a two-beam setup, where the pump pulse is used as excitation source for transient species and the delay of the probe pulse is exactly controlled by an optical delay rail. As probe (white light continuum), a small fraction of pulses stemming from the CPA laser system was focused by a 50 mm lens into a 5-mm thick sapphire disc. The transient spectra were recorded using fresh oxygen free solutions in each laser excitation. All experiments were performed at 298 K in a 2 mm quartz cuvette.

Pulse Radiolysis: Pulse radiolysis experiments were performed using 50 ns pulses of 15 MeV electrons from a linear electron accelerator (LINAC). Dosimetry was based on the oxidation of SCN^- to $(SCN)^{2\bullet-}$ which in aqueous, N_2O-saturated solution takes place with G ≈ 6 (G denotes the number of species per 100 eV, or the approximate μM concentration per 10 J absorbed energy). The radical concentration generated per pulse was varied between (1-3) × 10^{-6} M.

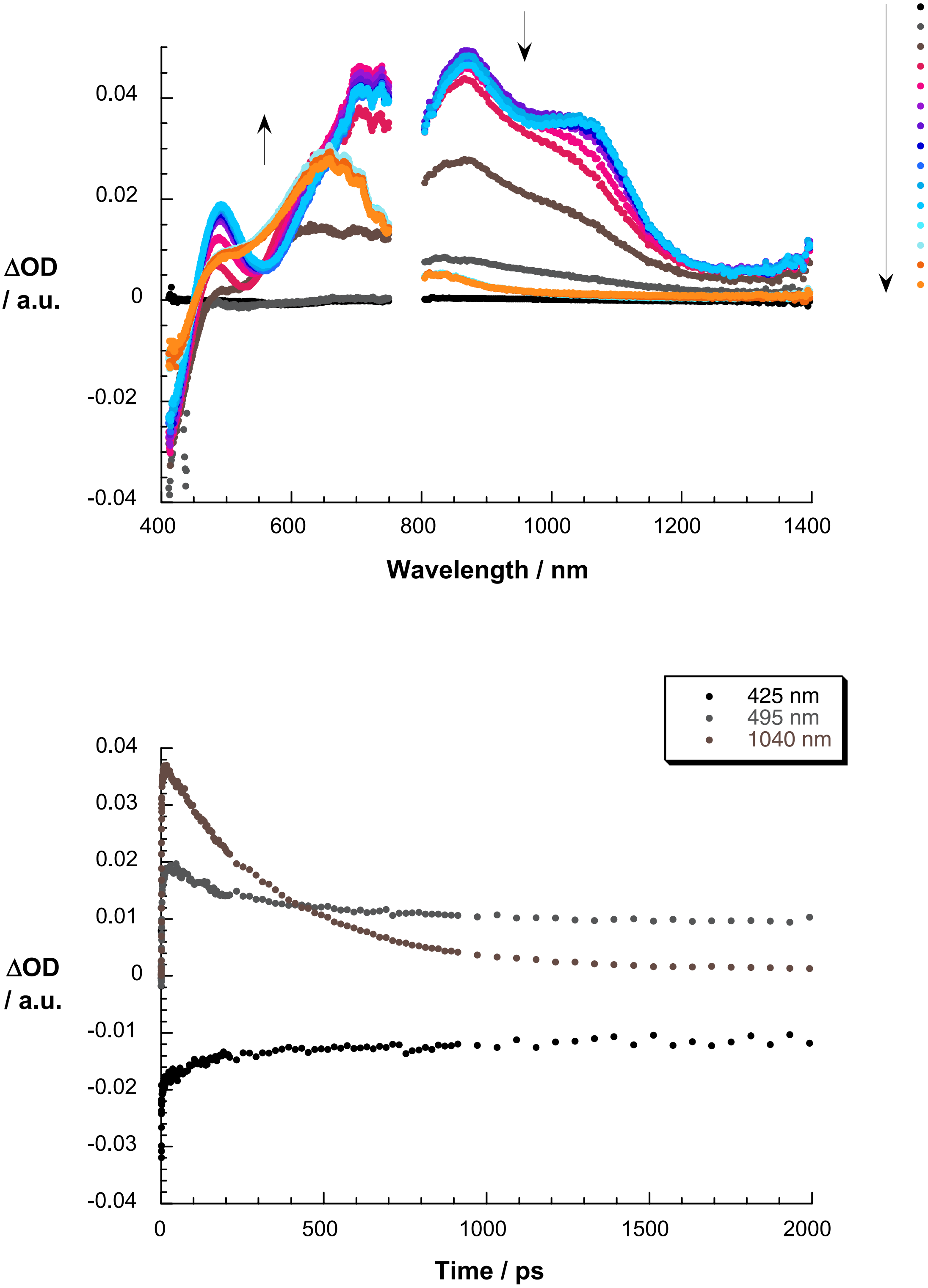
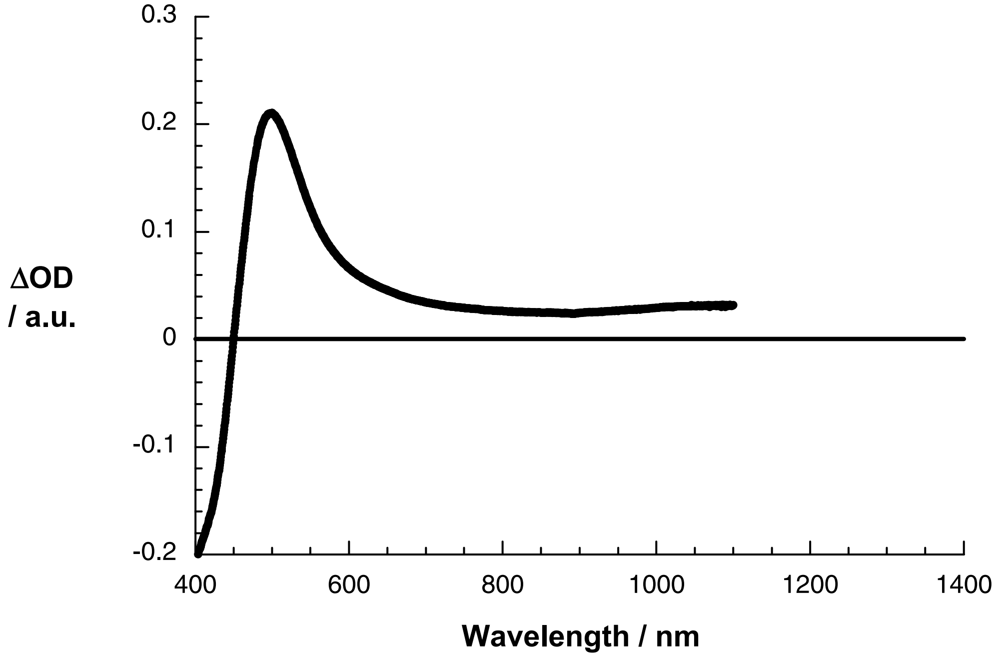


Fig. S1 Upper part: differential absorption spectra (near-infrared) obtained upon femtosecond flash photolysis (387 nm – 150 nJ) of Py-9T in toluene with several time delays between 0 and 2000 ps at room temperature – arrows are indicating the progression of the reaction as they are reflect in the legend. Lower part: time-absorption profiles of the spectra shown in the upper part at 425, 495 and 1040 nm monitoring the intersystem crossing.



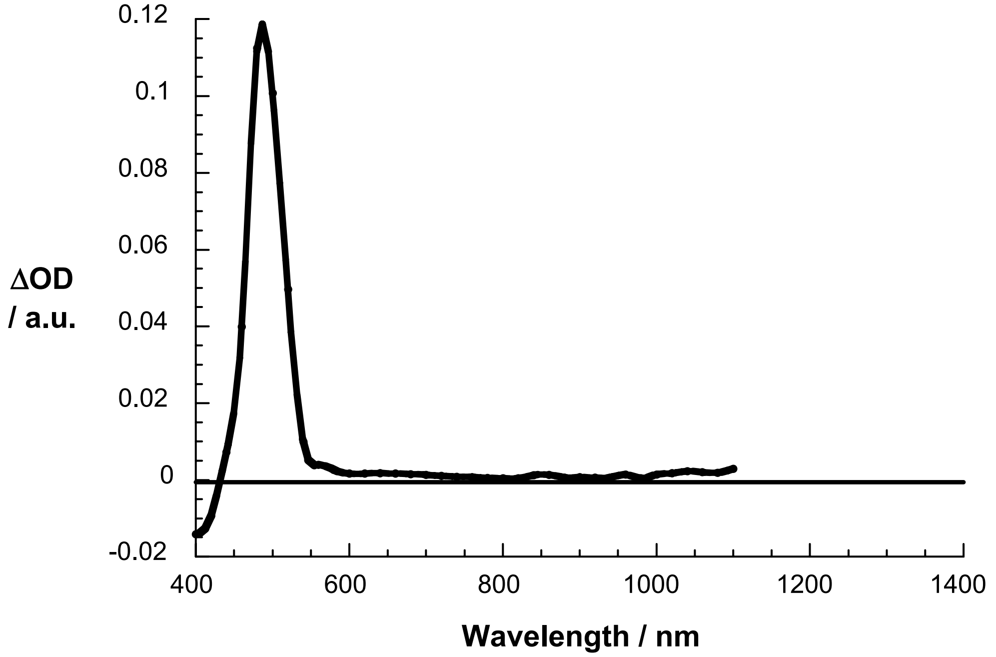


Fig. S2 Spectroelectrochemical and pulse radiolytic oxidation of Py-9T in dichloromethane at a potential of 1.8 V

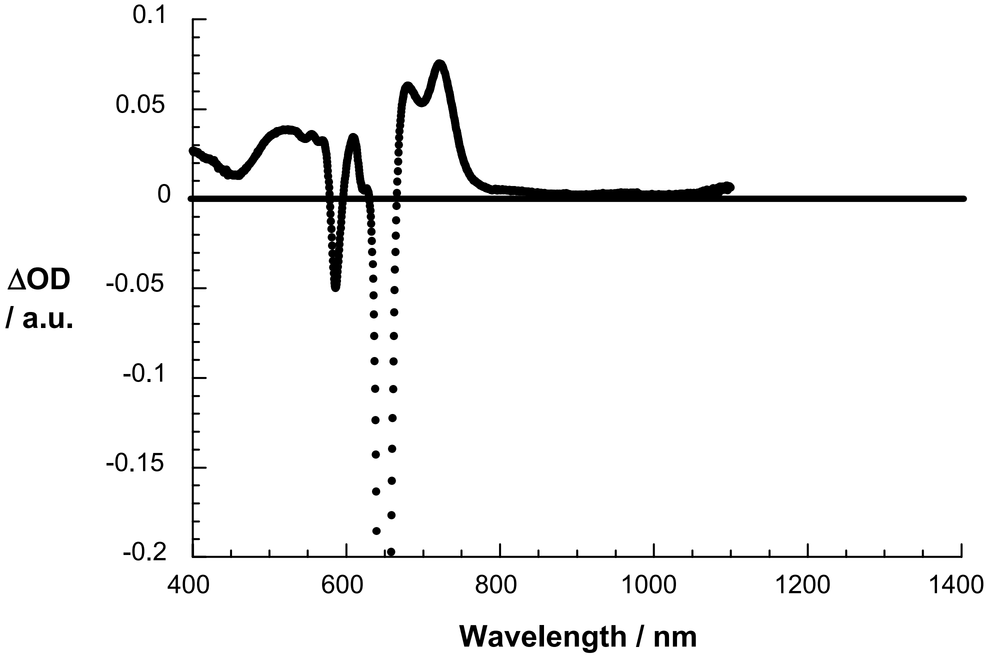


Fig. S3 Spectroelectrochemical reduction of RuPcCO(Py-9T) in dichloromethane at a potential of -1.4 V.

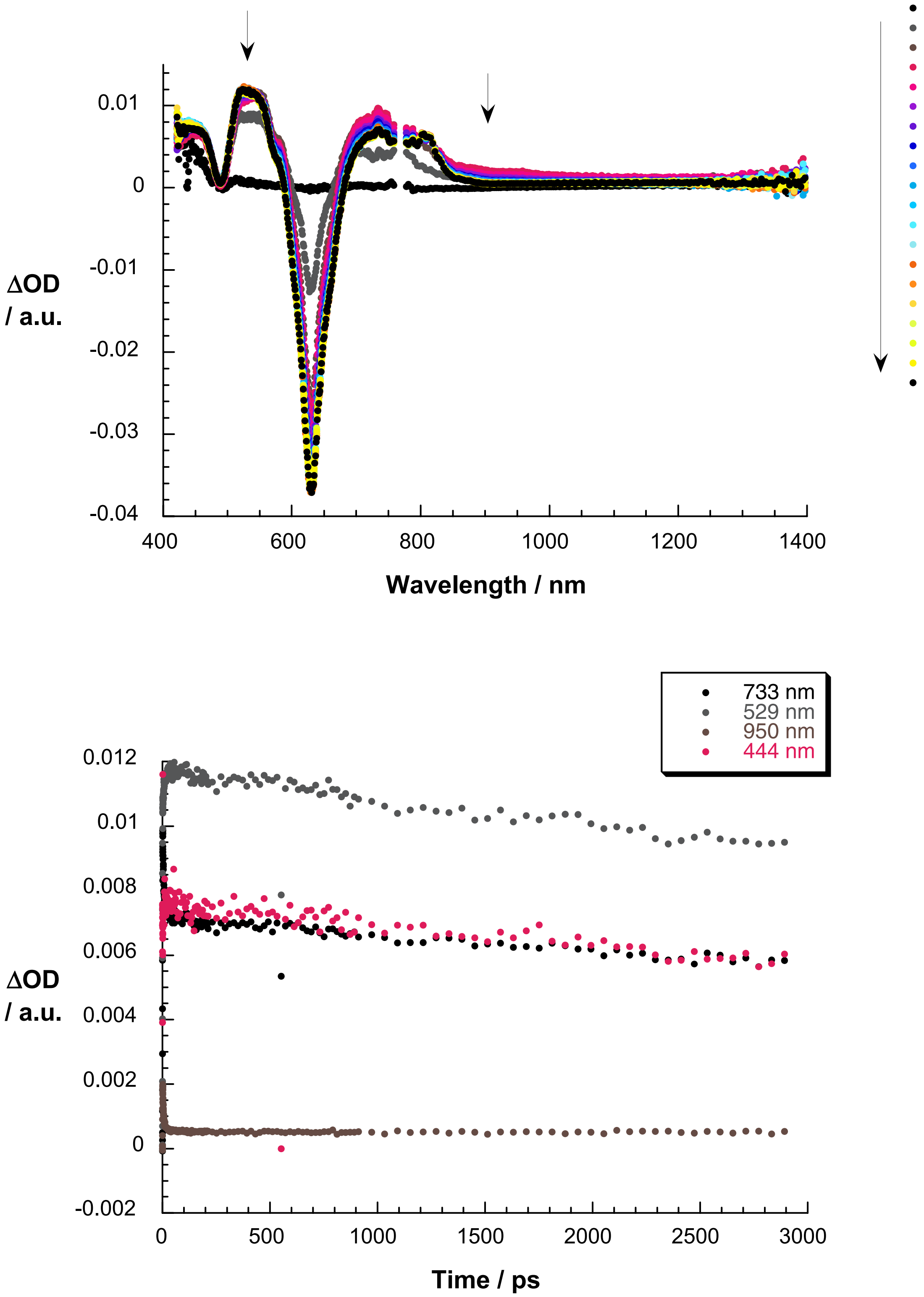


Fig. S4 Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm – 150 nJ) of RuPc(Py-9T)$_2$ in toluene with several time delays between 0 and 200 ps at room temperature – arrows are indicating the progression of the reaction as they are reflect in the legend. Lower part: time-absorption profiles of the spectra shown in the upper part at 444, 529, 733, and 950 nm monitoring the competition between energy and charge transfer.

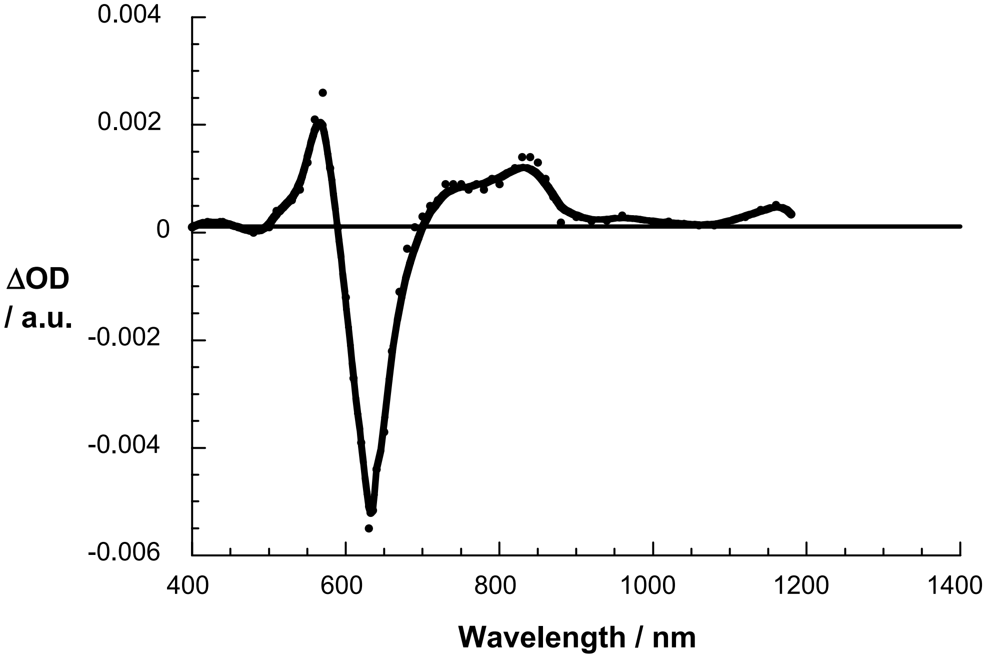


Fig. S5 Pulse radiolytic reduction of RuPc(Py)$_2$ in a solvent mixture of toluene, acetone, and iso-propanol (v/v 8:1:1).

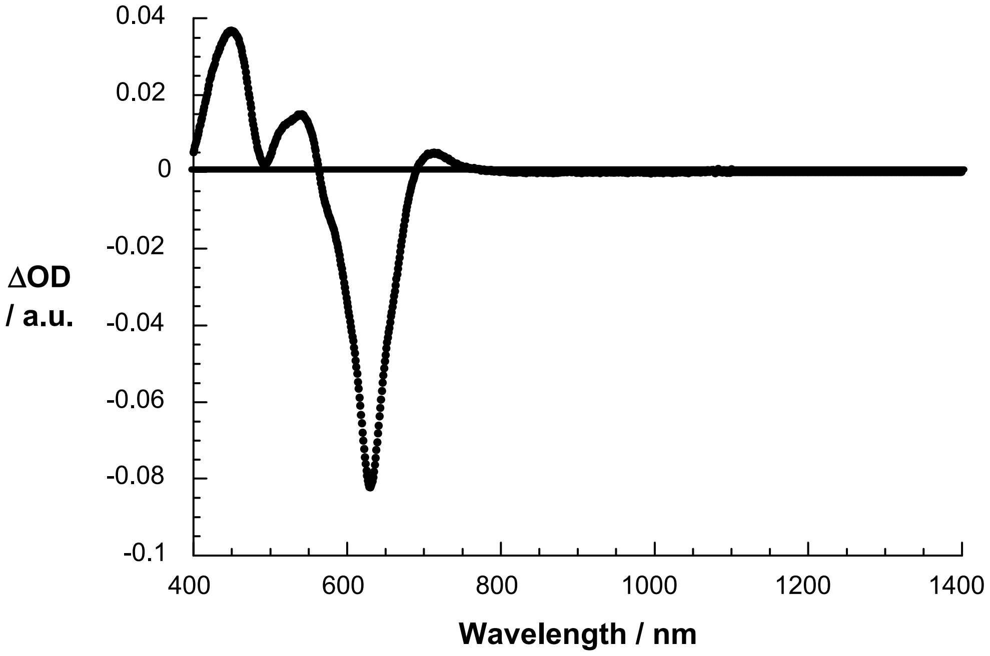


Fig. S6 Spectroelectrochemical oxidation of RuPc(Py-9T)$_2$ in dichloromethane at a potential of +1.8 V.

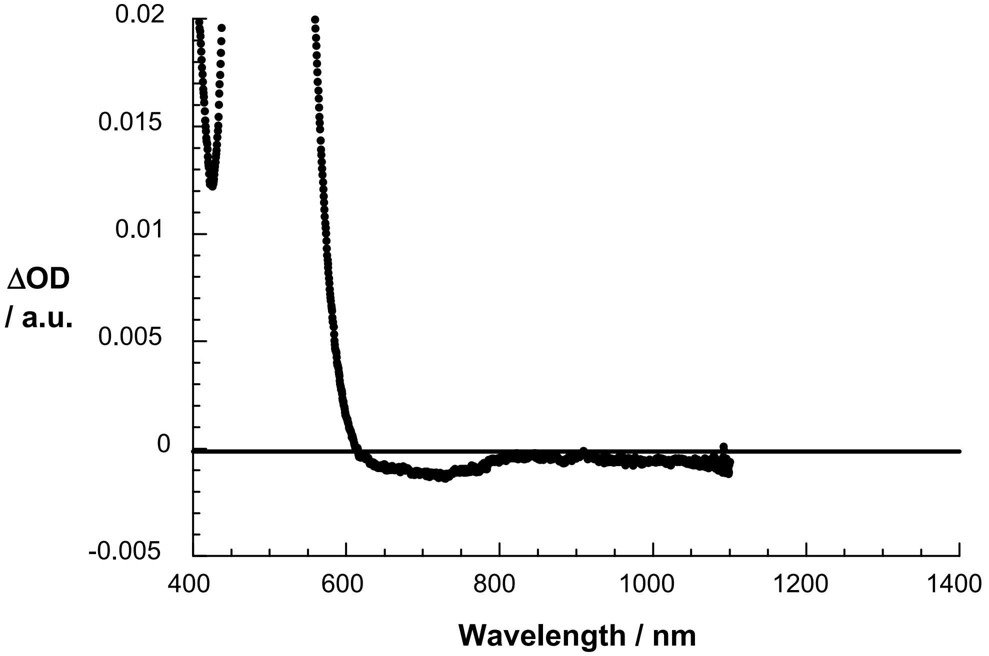


Fig. S7 Spectroelectrochemical reduction of Py-9T in dichloromethane at a potential of –2.2 V.

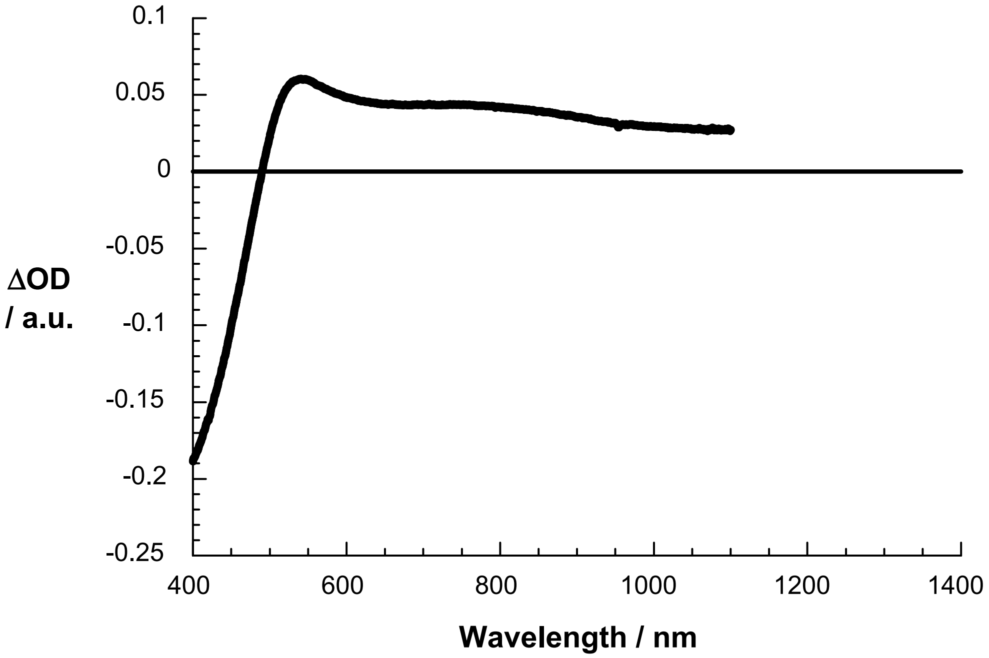


Fig. S8 Spectroelectrochemical oxidation of Py-21T in dichloromethane at a potential of +1.25 V.

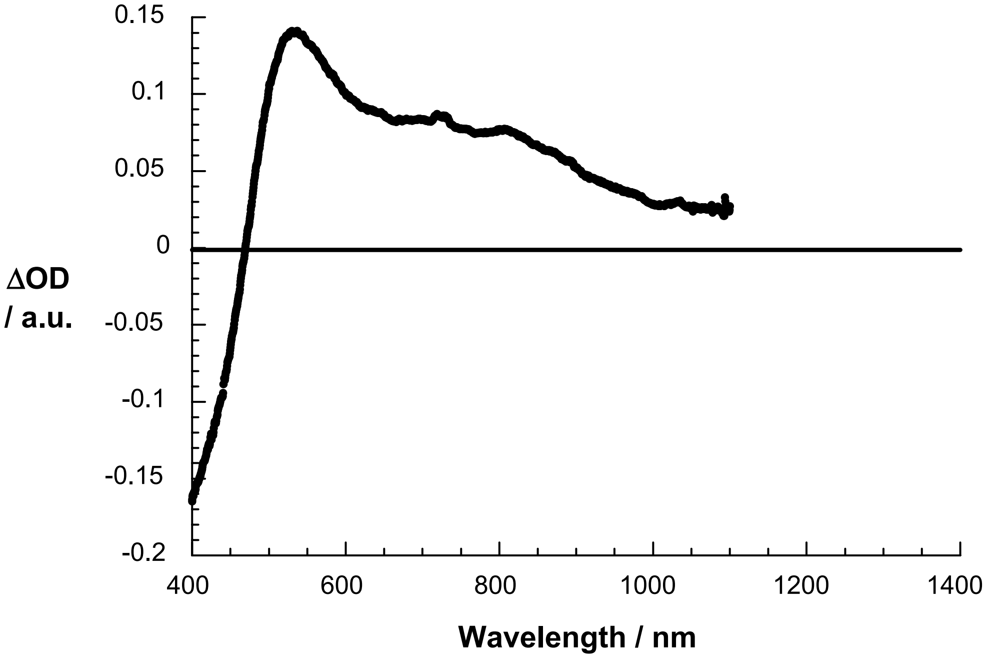


Fig. S9 Spectroelectrochemical reduction of Py-21T in dichloromethane at a potential of -1.5 V.

References

[1] M. K. R. Fischer, I. López-Duarte, M. M. Wienk, M. V. Martínez-Díaz, R. A. J. Janssen, P. Bäuerle, T. Torres, *J. Am. Chem. Soc.* 2009, **131**, 8669.