Supplementary Material (ESI) for Dalton Transactions
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Supporting information for

Extension of the charge separated-state lifetime by supramolecular association of a tetrathiafulvalene electron donor to a zinc/gold bisporphyrin

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-1- Materials and methods:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 MHz. Chemical shifts for ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent ($CDCl_3$ δ = 7.26 ppm). High resolution electro-spray mass spectra (HR- ESMS) were collected in positive mode on a MS/MS ZABSpec TOF of Micromass equipped with a geometry EBE TOF. The samples were injected in mixture of $CHCl_3$/MeOH: 9/1. Electron-impact mass spectrometry (EI-MS) were recorded on a HP 5989A spectrometer. Matrix assisted laser desorption mass spectrometry analyses were performed on Brucker biflex III MALDI-TOF spectrometer using cyano 4-hydroxycinnamic acid (CHCA) or dithranol as matrix. The instrument is equipped with a nitrogen laser emitting at 337 nm, a 2-GHz sampling rate digitizer, a pulsed ion extraction source and a reflectron.

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel $60F_{254}$. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh) or with SDS neutral alumina (0.05-0.2 mm mesh). Air sensitive reactions were carried out under argon in dry solvents and glassware. 4-bromo-pyridine was purchased from Acros and used as received and (tetrabutylstannyl)tetrathiafulvalene was prepared according to literature method.

Electrochemistry and spectroelectrochemistry

The electrochemical measurements were performed with a potentiostat-galvanostat MacLab model ML160 controlled by resident software (Echem v1.5.2 for Windows) using a conventional single-compartment three-electrode cell. The working electrode was a platinum

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disk of 4 mm^2 area, the auxiliary was a Pt wire and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supported electrolyte was 0.15 N Bu_4NPF_6 in dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s for the cyclic voltammetry and 15 Hz for pulse voltammetry. Spectroelectrochemical spectra were recorded in a thin quartz UV-Visible cell (0.5 mm) surmounted with a reference electrode (SCE) and a platinum wire as counter electrode. The working electrode was a platinum grid inserted within the quartz cell and the other conditions are the same as those for the cyclic voltammetry.

Spectroscopy

UV-Visible absorption spectra were recorded on a CARY 5 spectrophotometer.

The laser pulses generated for the transient absorption pump-probe experiments have been previously described.[7] The 800 nm output was converted to 640 nm, with a temporal width of ~100 fs, in an optical parametric amplifier (TOPAS, Light Conversion Ltp, Vilnius, Lithuania). A mechanical chopper blocked every second pump beam. The 800 nm probe light was passed through a movable delay line allowing the delay between pump and probe to vary with as much as 6 ns without changing the spatial overlap at the sample. A vertically moving CaF_2 crystal in the probe beam produced a continuous white light and a λ/2-plate adjusted the polarization of the light so that the difference in polarization between pump and probe was fixed at magic angle conditions. The pump and probe beam was then focused in a vertically moving 1×10 mm optical quarts cell. The pump energy at the sample was ≈600 nJ/pulse. The transmitted probe light was divided spatially on an optical diffraction grating and further detected on a diode array. The transient absorption was calculated as $\Delta A = -\log[(I_{probe,\ pump\ on} / I_{reference,\ pump\ on}) / (I_{probe,\ pump\ off} / I_{reference,\ pump\ off})]$. The reported values are averages of 5000-10000 individual measurements.

-2- Synthesis of 4'-pyridyl-2-tetrathiafulvalene (π-TTF)

To a solution of 4-bromopyridine hydrochloride (85 mg, 0.44 mmol) in toluene (10 mL) was added sodium hydrogen carbonate (saturated aqueous solution) until carbon dioxide evolution ceased. The mixture was washed with water (2 x 20 mL). The organic phase was dried over $MgSO_4$ and the mixture concentrated to ca. 2 mL. This solution was added to (tetrabutylstannyl)tetrathiafulvalene (150 mg, 0.29 mmol in 10 mL of dry toluene) and the resulting mixture was purged with argon through 3 freeze-pump-thaw cycles.

Tetrakis(triphenylphosphine)palladium(0) (32 mg, 10 mol-%) was added and the mixture stirred at reflux overnight. After evaporation of the solvent the crude was chromatographed over silica gel (petroleum ether/CH_2Cl_2: 2/8) to afford **π-TTF** as an orange solid (123 mg, 39 %). ^{1}H NMR δ: (300MHz, $CDCl_3$, 25°C): 8.60 (2H, d, J_1 = 6 Hz), 7.24 (2H, d, J_1 = 6 Hz), 6.84 (1H, s), 6.35 (1H, s). HR-MS (CI) m/z: calcd for $C_{11}H_8NS_4$ [MH^+] 281.9540, found 281.9541. E.A.: calcd for $C_{11}H_4NS_4$.toluene: C, 57.87; H, 4.05; N, 3.75, found: C, 58.02; H, 4.36; N, 4.21.

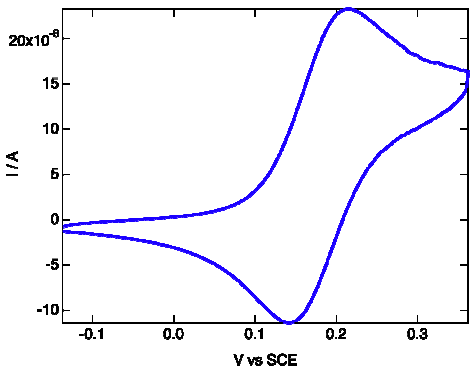

Figure 1 SI. Cyclic voltammetry of **π-TTF** recorded in dichloromethane with Bu_4NPF_6 (0.15 M) with scan rate 100 mV/s.

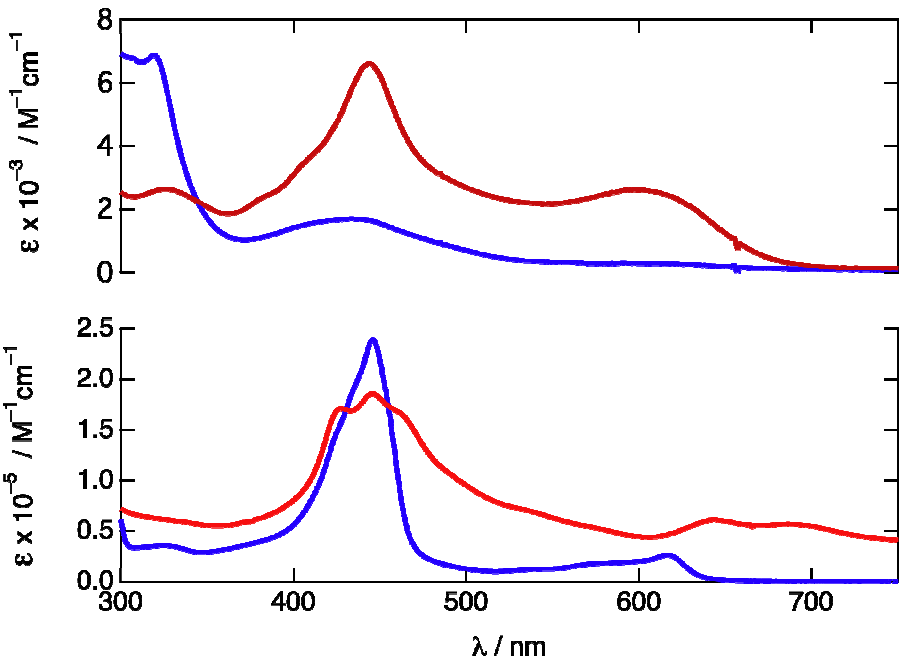

Figure 2 SI. UV-Vis absorption spectra of (top) π-TTF (blue) and one electron oxidized of π-TTF^+ (red) recorded in dichloromethane with Bu_4NPF_6 (0.15 M) by spectroelectrochemistry upon electrolysis at 0.25 V vs SCE, and (bottom) ZnP–OPE–AuP (blue), and ZnP-quater-AuP (red).

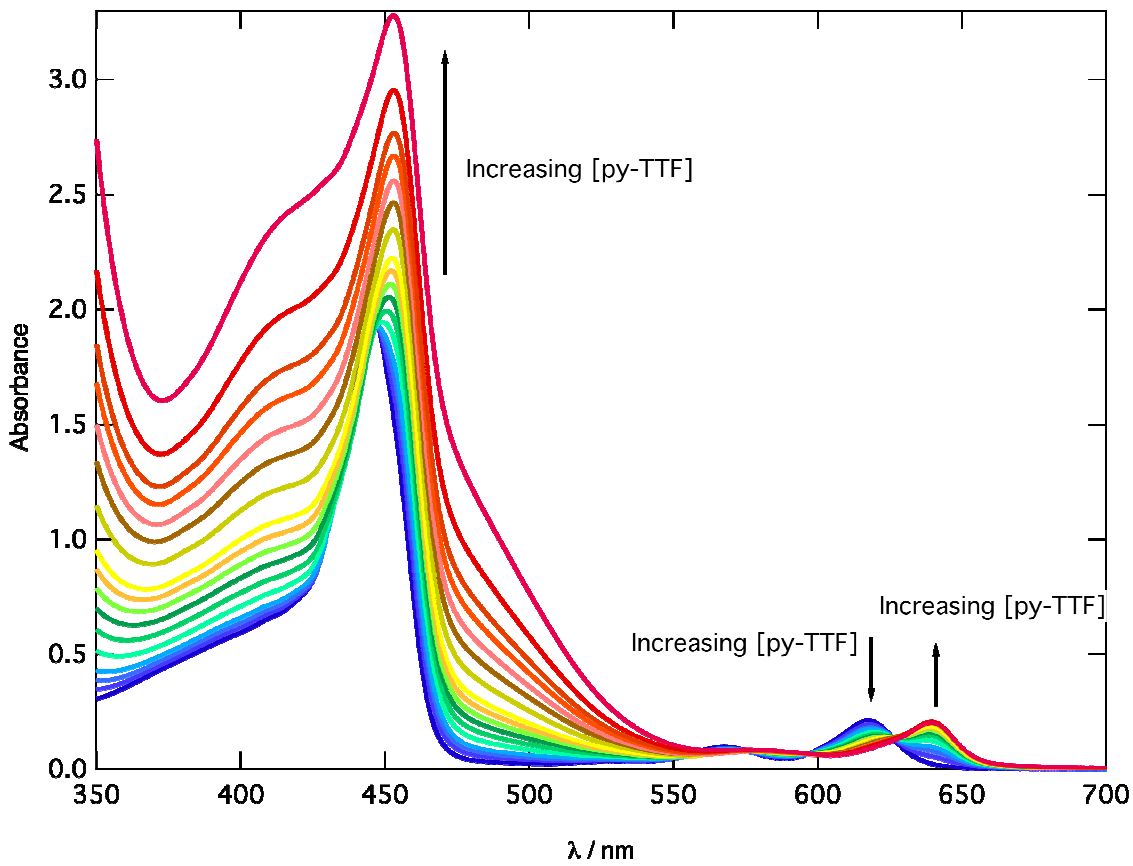

Figure 3 SI. UV-Vis absorption spectra upon titration of a solution of **ZnP-OPE-TIPS** with increasing amount of **π-TTF**. Concentrations in the titrations were typically 5–10 μM porphyrin, and 0–1 mM π-TTF.

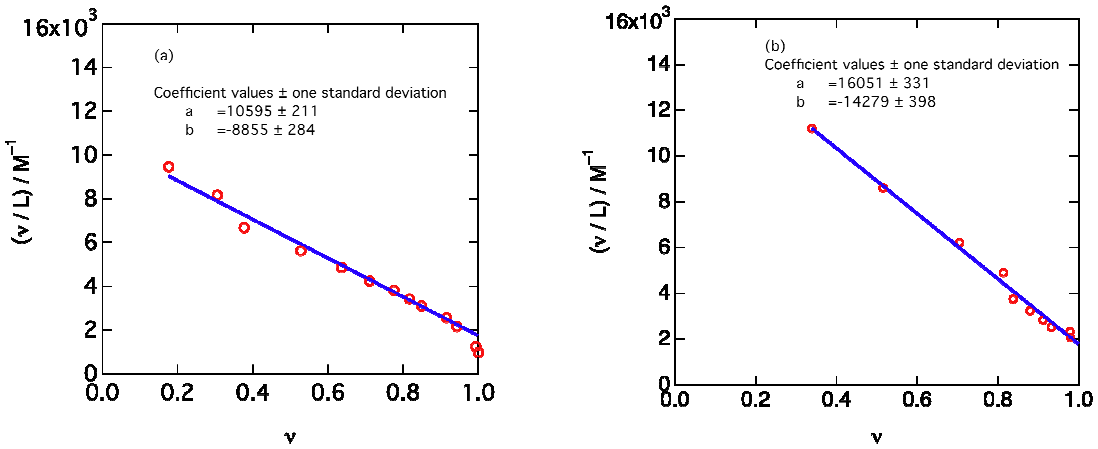

Figure 4 SI. Scatchard plots for the binding of π-TTF to (a) **ZnP-OPE-TIPS** in dichloromethane, and (b) **ZnP-quater-TIPS** in toluene. ν is the number of bound py-TTF molecules per total available ZnP, and *L* is the concentration of free (uncomplexed) py-TTF.

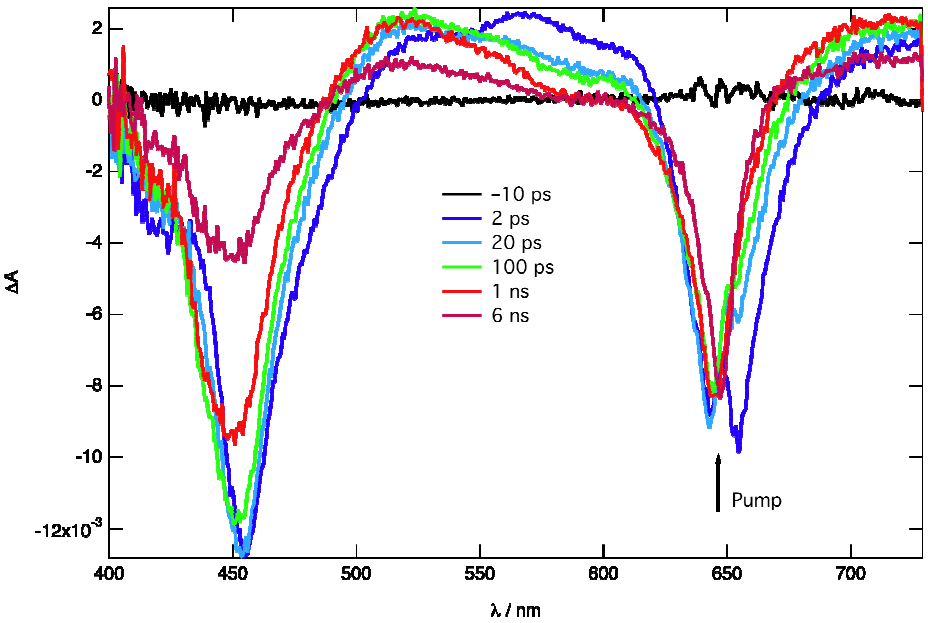

Figure 5 SI. Femtosecond transient absorption spectra for TTF-π···ZnP–quaterthiophene–AuP^+ in toluene, excited at 650 nm (ZnP Q band). Black: –10 ps, blue: 10 ps, light blue: 90 ps, green: 180 ps, orange: 500 ps, red: 6000 ns.

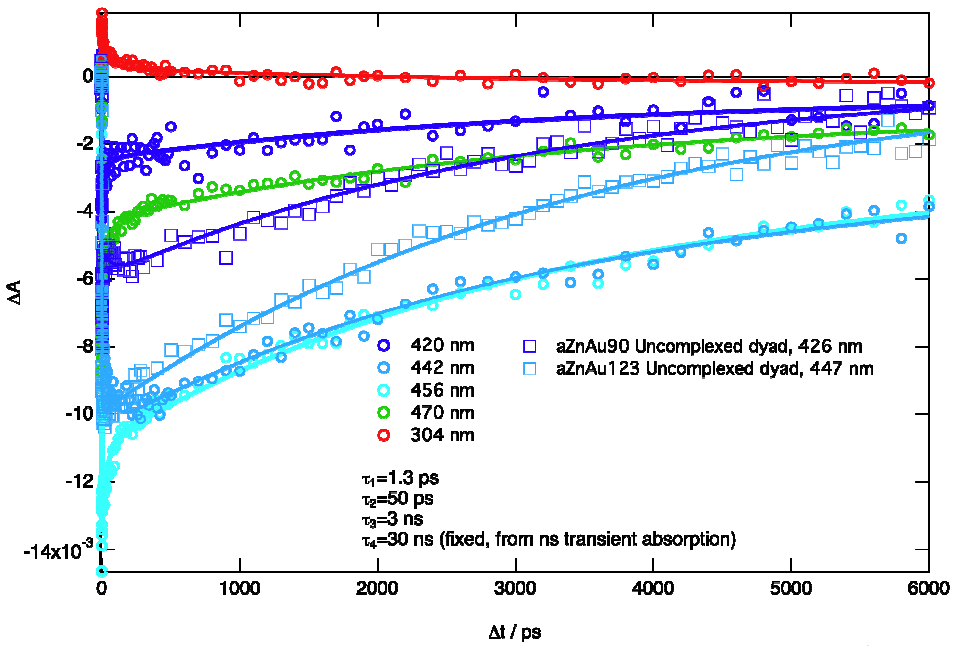

Figure 6 SI. Femtosecond kinetic traces for TTF-π···ZnP–quater–AuP^+ (circles) in toluene, excited at 650 nm (ZnP Q band). Solid lines are best fits to four time-constants. A slightly worse fit can be made using three time-constants, but the long time-scale is not as well described as in the fit above. Included are also corresponding kinetic traces for the uncomplexed dyad (squares). Note the slower recombination kinetics when the π-TTF is present.