Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material for

Multichromophoric hybrid species made of perylene bisimide derivatives and Ru(II) and Os(II) polypyridine subunits.

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Materials and methods

All solvents used were of reagent quality and purchased commercially. All purchased starting materials were used without further purification. Microwave-assisted synthesis of perylene derivatives was developed using a CEM Discover® S. The pressure-resistant, tightly-sealed quartz tubes were 3 mm thick with a volume of 10 mL and designed for microwave reactor.

Nuclear Magnetic Resonance (NMR) ^{1}H spectra were recorded at 500 MHz on a Varian VNMRS - 500 MHz. All spectra were registered at 298 K.

Electrospray Ionization-Mass Spectrometry (ESI-MS) measurements were performed on a Perkin-Elmer APII at 5600 eV. Matrix-Assisted Laser Desorption/Ionization - Mass Spectrometry (MALDI-MS) spectra were recorded on a AB SCIEX 4800 MALDI TOF/TOF™ Reflector instrument, using reflector mirror and positive ion detection. A dual microchannel plate reflector detector was used. Samples for ToF-SIMS measurements were prepared as a (sub)monolayer on etched silver substrates following a well-established procedure.[1] Measurements were carried out in static mode in a TOFSIMS IV instrument (ION−TOF GmbH, Münster, Germany), using Bi^+ primary ions (25 keV, 0.5 pA).

UV/Vis absorption spectra were taken on a Jasco V-560 spectrophotometer. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax 2 spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier. The spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. For the luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used. As excitation sources, a Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and/or the nitrogen discharge (pulse width 2 ns at 337 nm) were employed.

Time-resolved transient absorption experiments were performed using a pump-probe setup based on the Spectra-Physics MAI-TAI Ti:sapphire system as the laser source and the Ultrafast Systems Helios spectrometer as the detector. The output of laser beam was split to generate pump and probe beam pulses with a beam splitter (85 and 15%). The pump pulse (400 nm, 1-2 μJ) was generated with a Spectra-Physics 800 FP OPA and was focused onto the sample cuvette. The probe beam was delayed with a computer controlled motion controller and then focused into a 2-mm sapphire plate to generate a white light continuum (spectral range 450–800 nm). The white light is then overlapped with the pump beam in a 2-mm quartz cuvette containing the sample. The effective time resolution was ca. 200 fs, and the temporal chirp over the white-light 450–750 nm range ca. 150 fs; the temporal window of the optical delay stage was 0–3200 ps. Please note that all the transient spectra shown in the present paper are chirp corrected. The chirp correction was done by using the pump-induced absorption signals themselves in the same conditions (same cuvette, solvent, temperature, stirring frequency…) used for each single experiment. The time-resolved data were analyzed with the Ultrafast Systems Surface Explorer Pro software.

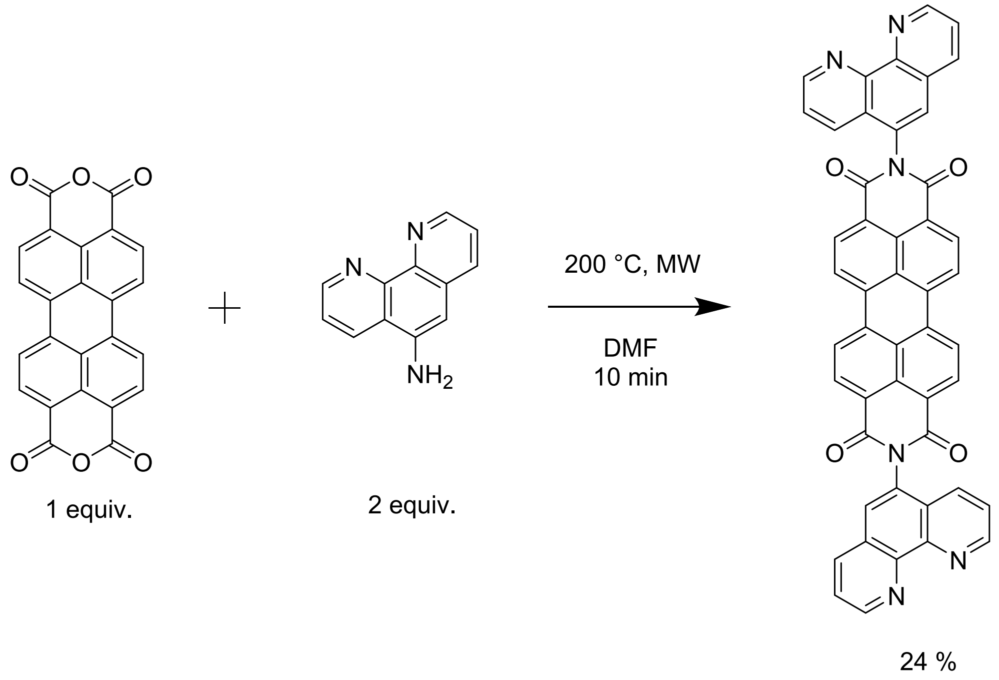
Electrochemical measurements were carried out in the dry and argon-purged stated acetonitrile, at r.t. with a Autolab multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using the redox couple ferrocene/ferrocinium as internal reference (395 mV *vs* SCE in acetonitrile). The concentration in analyte was about 0.5 mM, unless otherwise stated. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates between 50 and 500 mV/s and were stated in each case. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons reported in the main text was established using the areas of the peaks in differential pulse voltammetry (DPV).

UV−vis−NIR spectroelectrochemical measurements were obtained in acetonitrile with a SPECAC Omni Cell System: an optically transparent thin-layer electrode (OTTLE) cell with the working Pt-mesh, twinned Ag-wire reference and Pt-mesh auxiliary electrodes melt-sealed into a polyethylene spacer –CaF_2 windows and 0.25 mm path length. The UV−vis−NIR spectra were registered with a JASCO V570 spectrophotometer, applying a potential by using an Autolab multipurpose equipment interfaced to a PC. $TBAPF_6$, (+99%) supporting electrolyte and acetonitrile solvent (anhydrous, 99.8%) were supplied by Aldrich.

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 15%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; transient absorption decay and rise rates, 10%; redox potentials, 20 mV.

Synthesis and characterization

Synthesis of L



Compound **L** was synthesized with the following synthetic protocol.[1] 100 mg of perylene-3,4,9,10-tetracarboxylic bis-anhydride were suspended in dry DMF (5 mL) with 4 equiv. of 1,10-Phenanthrolin-5-amine and 50 υL of Et_3N in a pressure tight microwave tube. The suspension was sonicated for few minutes before heating under microwave irradiation at 80 W for 10 min, 10 cycles. Maximum temperature was set at 200 °C. After cooling, the color turned to dark red and the mixture appeared more homogenous. To the mixture, 50 mL of a KOH 10% aq. solution was added and the solution was stirred for 2h. The precipitate was filtered and washed abundantly with water until pH neutralization and dried using a vacuum pump (yield= 24%).

^{1}H NMR (TFA*d*, 500 MHz) - δ_H (ppm): 10.41 (s, 6H), 9.52 (s, 10H), 8.58 (s, 6H), 2.30 (H_2O). FT-IR (powder; cm^{-1}): 1704, 1666, 1590, 1357. UV-VIS: λabs. (TFA) = 530 nm; λem. (TFA) = 558 nm. ESI-MS (TFA/H_2O 1:20)(m/z) – calculated for $C_{44}H_{22}N_6O_4$: 746 ; found: 623 $[Na_2(M\text{-}TFA_4)]^{2+}$.

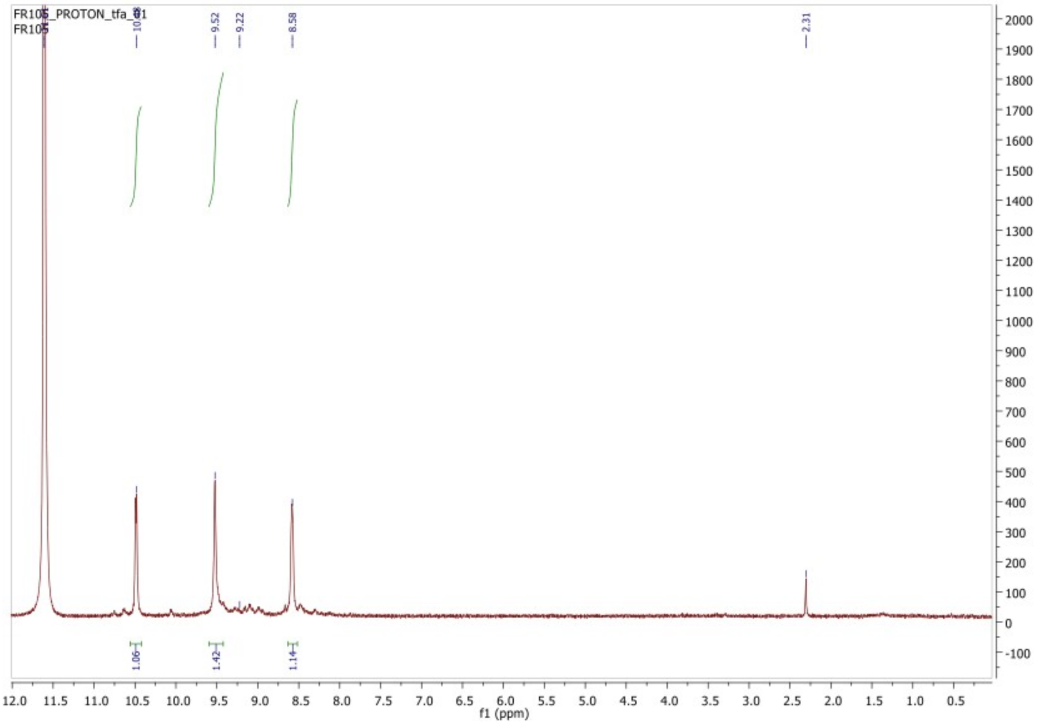


Figure S1. Proton NMR spectrum of **L** in TFA*d*.

Synthesis of Ru2*(PF_6)$_4$

20 mg of **L** (0.03 mmol) and 41 mg of [*cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O (0.09 mmol) were dissolved in 8 mL of ethanol and the mixture was refluxed under nitrogen atmosphere for 48 hours in dark conditions. After cooling, 5 ml of saturated aqueous solution of ammonium hexafluorophosphate were added to the crude reaction. The dark red solid, separated by filtration, was purified by chromatography on neutral alumina by using a mixture CH_2Cl_2/CH_3OH 9:1 (V/V) as eluent. The second fraction, containing the target product, was further purified by size exclusion chromatography (Sephadex G10; eluant: acetonitrile). The acetonitrile solution was added drop wise to 40 mL of diethyl ether under stirring for precipitation. A red solid was filtered off and dried by vacuum. (35 g, 60 % yield). TOF-SIMS: [M(PF$_6$)$_4$]$^+$ = 2010 (theoretical = 2010.51); Elemental analysis Calc. for $C_{88}H_{56}F_{24}N_{14}O_4P_4Ru_2$: C, 49.04; H, 2.62; N, 9.10; Elemental analysis Found: C, 49.12; H, 2.66; N, 9.14.

Synthesis of Os2*(PF_6)$_4$

11.2 mg of **L** (0.015 mmol) and 35 mg of [Os(Me$_2$-bpy)$_2$Cl$_2$]·2H$_2$O (0.05 mmol) were dissolved in 8 mL of ethanol/methanol (1/1, v/v) solution and the mixture was refluxed under nitrogen atmosphere for 90 hours. After cooling, 5 ml of saturated aqueous solution of ammonium hexafluorophosphate were added to the crude reaction. The dark brown solid, separated by filtration, was purified by chromatography on neutral alumina by using a mixture CH_2Cl_2/CH_3OH 9:1 (V/V) as eluent. The first fraction, containing the target product, was further purified by size exclusion chromatography (Sephadex G10; eluent: acetonitrile). The acetonitrile solution was added drop wise to 40 mL of diethyl ether under stirring for precipitation. A dark red solid was filtered off and dried by vacuum. (18.5 mg, 53 % yield). TOF-SIMS: $[M(PF_6)_4]^+$ = 2301 (theoretical = 2301.04); Elemental analysis Calc. for $C_{96}H_{72}F_{24}N_{14}O_4P_4Os_2$: C, 47.14; H, 2.97; N, 8.02; Elemental analysis Found: C, 47.20; H, 3.03; N, 8.06.

Additional information on the transient absorption spectroscopy of Ru2

As mentioned in the main text, the transient spectrum of **Ru2** shown in the bottom panel of **Figure 7** is roughly stable for some time, before starting to decay to the ground state. This time range spectral change is shown here in **Figure S2**.

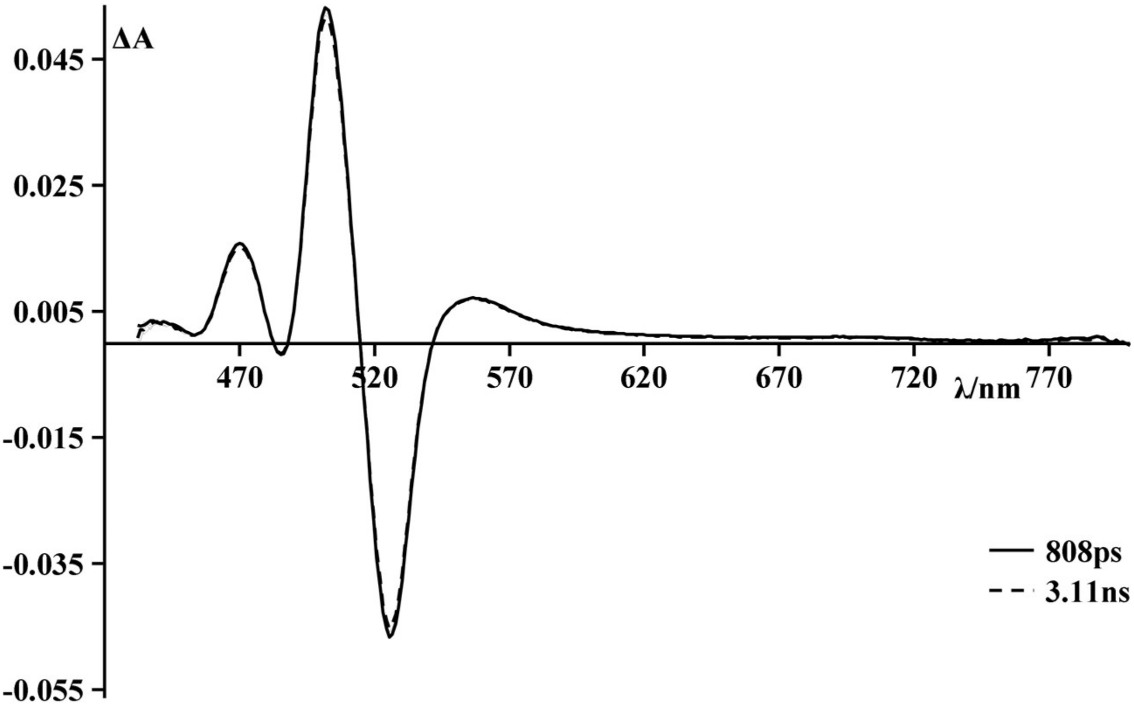


Figure S2. Final transient absorption spectra of **Ru2** in acetonitrile. The transient absorption spectrum is roughly constant within this time range. This figure should be added to the last panel of **Figure 7**, main text.

References to SI

1 F. Rigodanza, E. Tenori, A. Bonasera, Z. Syrgiannis and M. Prato, *Eur. J. Org. Chem.* 2015, 5060.