

Supporting information - The Janus-Faced Chromophore: Donor-Acceptor Dyad with Dual Performance in Photon Up-conversion Process

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Experimental part:

Palladium(II) tetra(4-fluorophenyl)tetrabenzoporphyrin was prepared according to the literature procedure.¹ 1,3,5,7-Tetramethyl-8-(10-methylanthracen-9-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BAD) was prepared following a modified literature procedure. 10-Methylanthracene-9-carbaldehyde (1 g, 4.5 mmol) and 2,4-dimethylpyrrole (0.95 g, 10 mmol) were dissolved in 100 mL of freshly distilled dichloromethane and the solution was degassed by bubbling with argon for 10 min. Trifluoroacetic acid (10 μ L, 0.00013 mmol) was added and the reaction mixture was stirred for 4 h under argon. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.02 g, 4.5 mmol) was added and the mixture was stirred for another 15 min. Then, the reaction mixture was transferred into a separation funnel and washed with 5% solution of NaHCO₃ (1 \times 50 mL) and brine (1 \times 50 mL). The organic phase was dried over Na₂SO₄, filtered and evaporated in vacuum. The resulting solid material was dissolved in 100 mL of dichloromethane, N,N-diisopropylethylamine (2.3 mL, 13.5 mmol) was added and the mixture was stirred for another 5 min under argon. Then, boron trifluoride diethyl etherate (1.66 mL, 13.5 mmol) was added and the reaction mixture was stirred for 2 h in the dark under argon. The reaction mixture was then transferred into a separation funnel and washed with water (1 \times 50 mL) and brine (1 \times 50 mL). The organic phase was dried over Na₂SO₄, filtered and evaporated in vacuum. The crude product was purified by silica gel column chromatography using DCM-hexane mixture (1:1 v/v) to give analytically pure product. 1.28 g (65 %), orange powder, analytical data are in correspondence to those described previously.¹ In the course of synthetic procedures and purification of BAD an attention was paid to protect the product from the light as sensitization of singlet oxygen and its subsequent cycloaddition to the anthracene moiety was noted in the recent work. However, in the course of experiments, no reasonable decomposition or impurities formation derived from photooxidation was observed upon protecting the working solutions of BAD with aluminium foil.

UV-Vis absorption spectra were recorded using a Specord 250 spectrophotometer from Analytic Jena (1 cm path length quartz cell). Emission spectra were measured using a Cary Eclipse G9800A fluorescence spectrophotometer and Horiba Jobin Yvon Fluorolog 4 instruments.

Transient absorption (TA) spectra were recorded by using a home-made pump-probe setup with a resolution of \sim 500ps. Pump pulses (355 nm, 500 Hz) were provided by the third harmonic of an actively Q-switched Nd:YVO laser (Innolas picolo-AOT MOPA). White light continuum pulses (450-1000 nm) were generated by pumping a 2 mm thick sapphire crystal, using the output of a commercial Ti:Sa amplifier (Spectra Physics Spitfire Pro XP, 800 nm, 3.5 mJ, 1 kHz, 100 fs). The white light pulses were dispersed onto a linear CCD image sensor and read out at 1 kHz. Adjacent spectra correspond to the transmission of the sample with and without pump pulse and were used to calculate $\Delta T/T$. The delay between pump and white light pulses was controlled by an electronic delay generator (Stanford Research Systems DG535).

The UC spectra and lifetimes of the emissive levels were measured in a home-built optical system. As the excitation sources a 525 nm and 638 nm laser diodes (Roithner) mounted in a temperature stabilized mount (TCLDM9, Thorlabs) and driven by a laser diode controller (ITC4001, Thorlabs) were used. The power of the laser beam was adjusted by the use of the controlled rotatable neutral density filter (Thorlabs).

For the photoluminescence lifetime measurements, time-correlated single photon counting TCSPC and a multichannel scaling (MCS) card (Timeharp 260, PicoQuant) were used. The modulation of the diode laser was performed via a built-in function generator in the laser diode driver. In order to detect rise and fall times of the UC emission, the TTL signal from the laser diode controller was delayed by the use of a delay generator (DG645, Stanford Research Systems). The spectral

separation of the photoluminescence was achieved via a double monochromator (DTMS300, Bentham) and the emission at specific wavelength was detected via a photomultiplier tube (R928P, Hamamatsu), mounted in temperature-cooled housing (CoolOne, Horiba).

For the UC PLQY measurements, the laser beam was focused by a lens (focal length 75 cm) and directed into an integrating sphere (Labsphere) with a diameter of 15 cm. The beam size on the sample was measured with a scanning slit optical beam profiler (Thorlabs), to be equal 0.9×1.3 mm (4-sigma). An optical fiber with a diameter of 1 mm (FP1000URT, Thorlabs) was used for collection of the emission from the integrating sphere and transferring this to the spectrometer (C200, Thorlabs). During the absorption measurement (measurement of the laser at the direct and indirect excitation of the sample and empty sphere), short integration times, usually 20-50 times shorter than for UC detection, were utilized. All raw detected spectra were recalculated to give power spectra using an integration time value. The linearity of the signal versus integration time of CCD was proven experimentally. The spectral response of the whole detection system was calibrated using a calibration lamp (HL-3plus-INT-CAL, Ocean Optics) and the correction was further applied to the power spectra.

UC solutions were prepared by mixing the stock solutions of the dyes and additional solvent. The solutions were placed in the glass tubes (0.4×4.0 mm, Vitrotubes Inc.). The glass tubes were sealed by using transparent in visible range two-component epoxy-glue (stable against organic solvents). All operations were performed inside glove box (GS Glovebox) with oxygen concentration less than 1 ppm.

Equations:

$$\phi_{TTET} = 1 - \tau^T / \tau_{BAD}^T, \quad (\text{Eq. S1})$$

where τ_{BAD}^T is the lifetime of the triplet state of BAD in absence of the quencher and τ^T is triplet state lifetime of BAD mixed with perylene.

$$I_{UC}(t) \propto I_{UC}(0) \left(\frac{1 - \beta}{\exp(k_{EM}t) - \beta} \right)^2 \quad (\text{Eq. S2})$$

$$\phi_{TTA} = 1 - \frac{\beta - 1}{\beta} \ln(1 - \beta), \quad (\text{Eq. S3})$$

where $I_{UC}(t)$ is decaying intensity of UC, whereas $I_{UC}(0)$ is UC intensity at time = 0 (Fig. S2 and S4), k_{EM} is decay rate of the emitter triplet state and β is the initial fraction of decay that occurs through the TTA.

$$I_{UC} \propto A \left(\sqrt{1 + 4 \frac{1}{I_{th}} P_{exc} - 1} \right)^2 + C, \quad (\text{Eq. S4})$$

where A and C are constants.

$$I_{UC} \propto (P_{exc})^n. \quad (\text{Eq. S5})$$

$$I_{th} = \frac{1}{\alpha} \frac{k_S + k_{TTET} k_{EM}^2}{k_{TTET} \gamma}, \quad (\text{Eq. S6})$$

where α is the number of absorbed photons; k_S is the sensitizer triplet decay rate, k_{TTET} is the rate of TTET, k_{EM} is the emitter triplet decay rate, γ is the second-order decay rate of TTA.

$$\phi_{TET} = 1 - \frac{\tau_1}{\tau_{PdTBTFP}}$$

(Eq. S7)

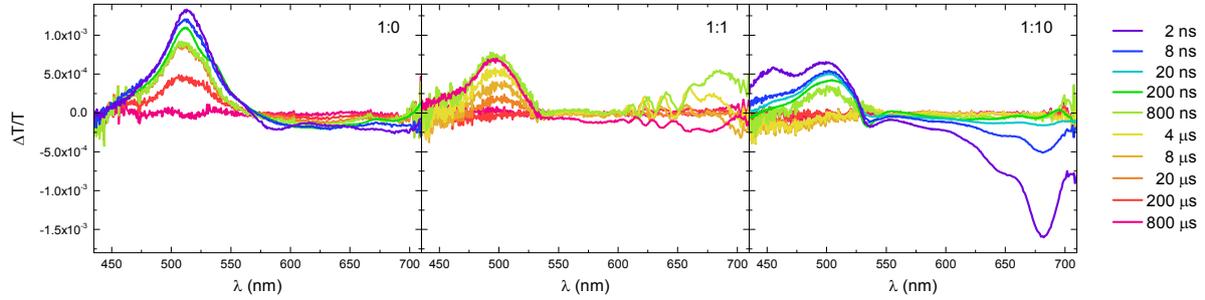


Figure S1. BAD ground state bleach in the time-resolved transient absorption experiment for different ratios BAD:perylene after excitation at 355 nm at a fluence of 0.5mJ/cm² per pulse .

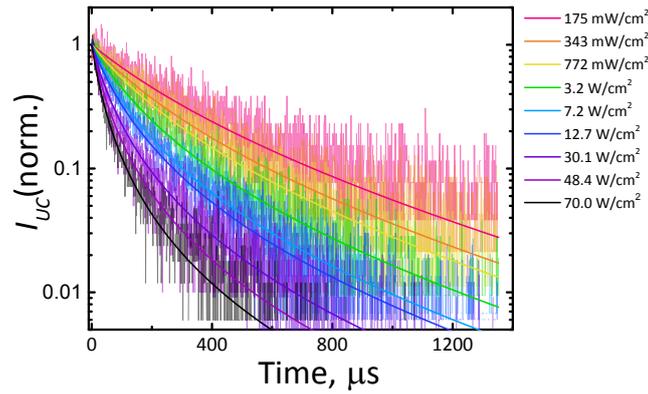


Figure S2. Normalized decays of UC luminescence of perylene in DCM at different excitation power density ($\lambda_{exc}=525$ nm).

Ratio BAD:perylene is 1:100. $C_{BAD} = 1 \times 10^{-5}$ mol/L. The decay were fitted with equation $I_{UC}(t) \propto I_{UC}(0) \left(\frac{1 - \beta}{\exp(k_{EM}t) - \beta} \right)^2$ in order to estimate parameters k_{ET}^I and β .

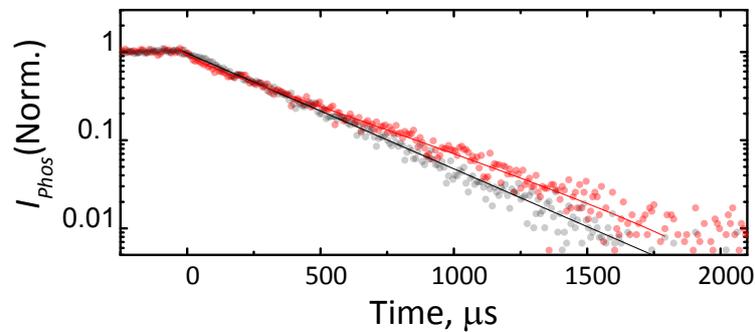


Figure S3. Normalized decays of phosphorescence (measured at 805 nm) of PdTBTFP (black points and line) and mixture PdTBTFP:BAD (1:100) (red points and line) dissolved in toluene.

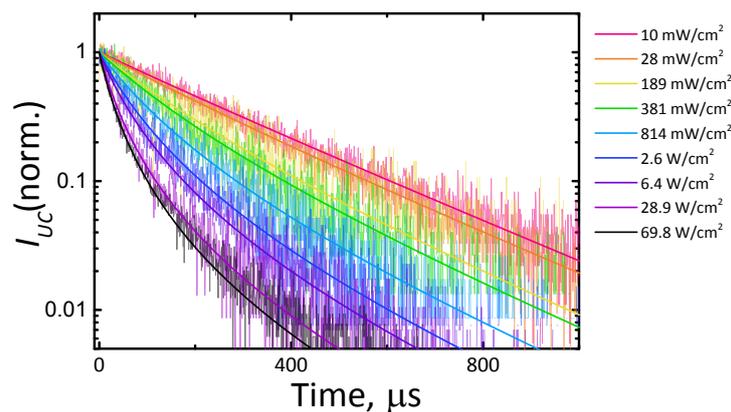


Figure S4. Normalized decays of UC luminescence of BAD in toluene at different excitation power density ($\lambda_{\text{exc}}=638$ nm).

Ratio PdBTBTFP:BAD is 1:100. $C_{\text{PdBTBTFP}} = 1 \times 10^{-5}$ mol/L. The decay were fitted with equation in order to estimate parameters k_{ET}^{-1} and β .

$$I_{UC}(t) \propto I_{UC}(0) \left(\frac{1 - \beta}{\exp(k_{EM}t) - \beta} \right)^2$$

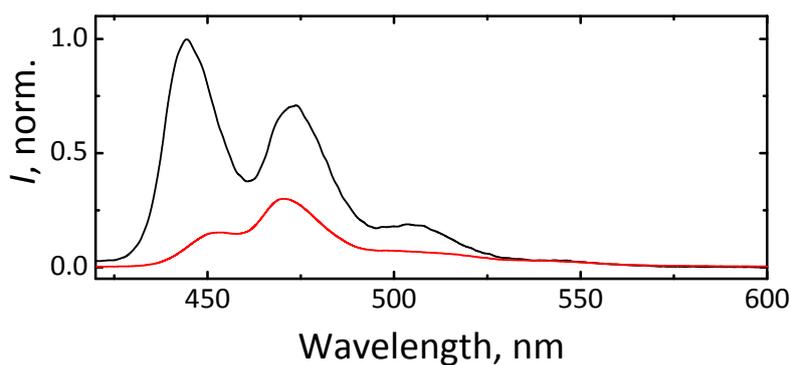


Figure S5. Fluorescence of perylene ($\lambda_{\text{exc}}=375$ nm): diluted solution of perylene in DCM (black line) and UC mixture BAD:perylene (1:100) in the integrating sphere (red line). The results indicate strong reabsorption for measurement performed in the integrating sphere.

References

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2. H. Sunahara, Y. Urano, H. Kojima and T. Nagano, J. Am. Chem. Soc., 2007, **129**, 5597-5604.