

Supporting Information

Carbon Nanohorn – Porphyrin Dimer Hybrid Material for Enhancing Light- Energy Conversion

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Experimental Section

General Information. Column flash chromatography was performed on silica gel (SDS 60A, 0.070-0.200 mm). HR-TEM measurements were carried out using a JEOL HR-TEM JEM-2100 microscope operated at an accelerating voltage of 80 kV for imaging. Mid-infrared spectra in the region 550–4000 cm^{-1} were obtained on a Fourier Transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). Steady state UV-Vis electronic absorption spectra were recorded on a Perkin Elmer (Lambda 19) UV–VIS–NIR spectrophotometer. Fluorescence measurements were carried out on a Fluorolog-3 Jobin Yvon-Spex spectrofluorometre (model GL3-21). ^1H and ^{13}C NMR spectra were recorded on Bruker DPX-500 MHz 300 MHz spectrometer and referenced to the residual protonated solvent. High-resolution mass spectra were obtained on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer. Solvents (ACS for analysis) and chemicals were purchased from Aldrich. All measurements were performed at room temperature. The thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27 instrument by TA in an inert atmosphere of nitrogen. In a typical experiment 1 mg of the material was placed in the sample pan -and the temperature was equilibrated at 40 °C. Subsequently, the temperature was increased to 800 °C with a rate of 10 °C/min and the weight changes were recorded as a function of temperature.

Preparation of CNH-based material 4.

Pristine CNHs (12 mg), aniline derivative tert-butyl 2-(2-(2-(4-aminobenzamido)ethoxy)ethoxy) ethylcarbamate (250 mg, 0.68 mmol) and o-DCB (0.5 mL) were added in a glass vial under Ar and sonicated for 10 min. Then, CH_3CN (100 μL) was added, followed by quick addition of isoamyl nitrite (0.537 mL, 4.0 mmol). The vial was sealed with a septum cap and the reaction mixture was irradiated with 10 Watt for 10 sec. (4 times) at 160 °C. After cooling down to room temperature, the reaction mixture was diluted with DMF, filtered over a PTFE membrane filter (pore size 0.2 μm) and washed with a large amount of DMF and CHCl_3 to remove completely organic impurities as well as any organic matter not associated with CNHs.

Preparation of CNH-based material 5.

CNH-based material 4 (18 mg) in dry dichloromethane (30mL) was treated with gaseous HCl. Evaporation under reduced pressure of the highly acidic solution, followed by addition of fresh dichloromethane with sonication, filtration through PTFE membrane filter (pore size 0.2 μm) and eventually washing of the solid material collected on top of the filter with methanol, furnished CNH-based material 5 as black powder (14 mg).

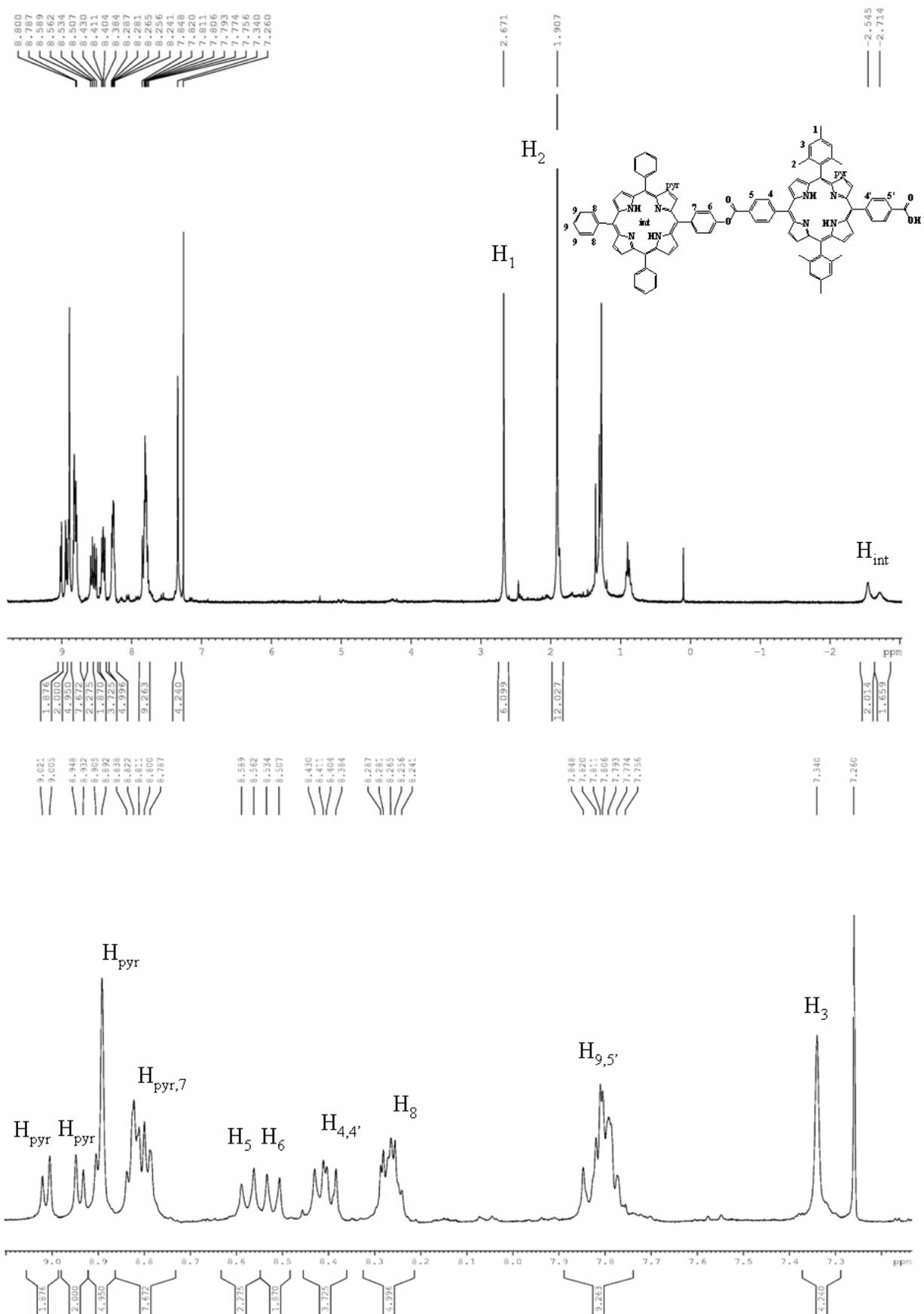


Figure S1. ^1H NMR spectrum of $(\text{H}_2\text{P})_2 \mathbf{3}$.

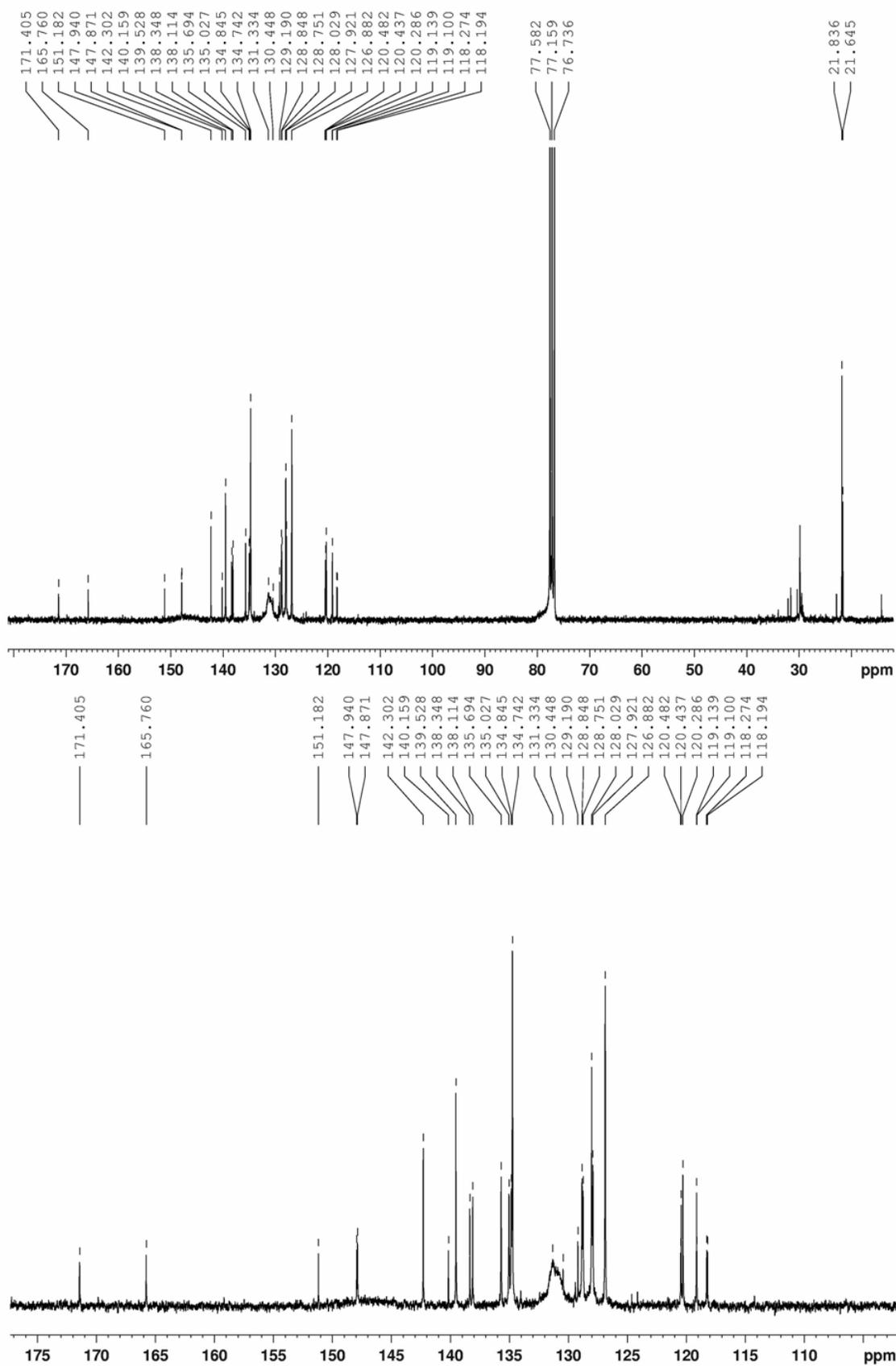


Figure S2. ^{13}C NMR spectrum of $(\text{H}_2\text{P})_2 \mathbf{3}$.

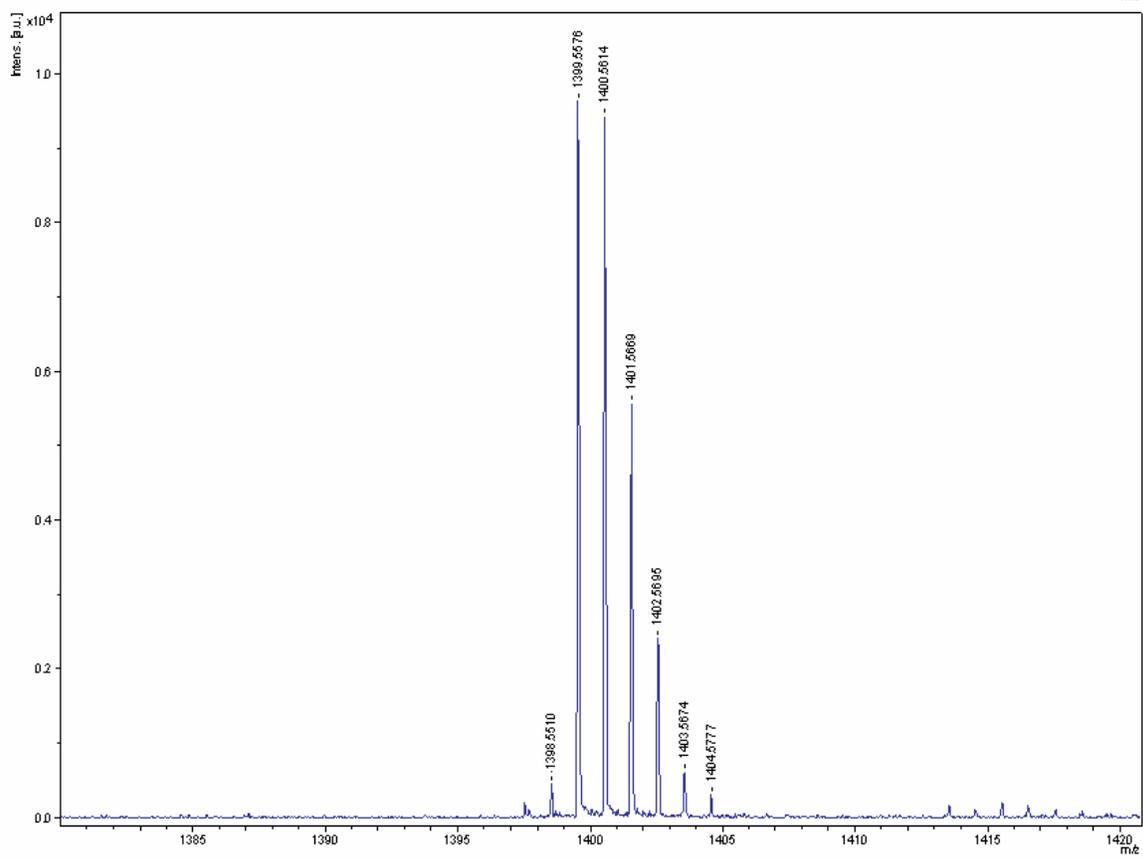
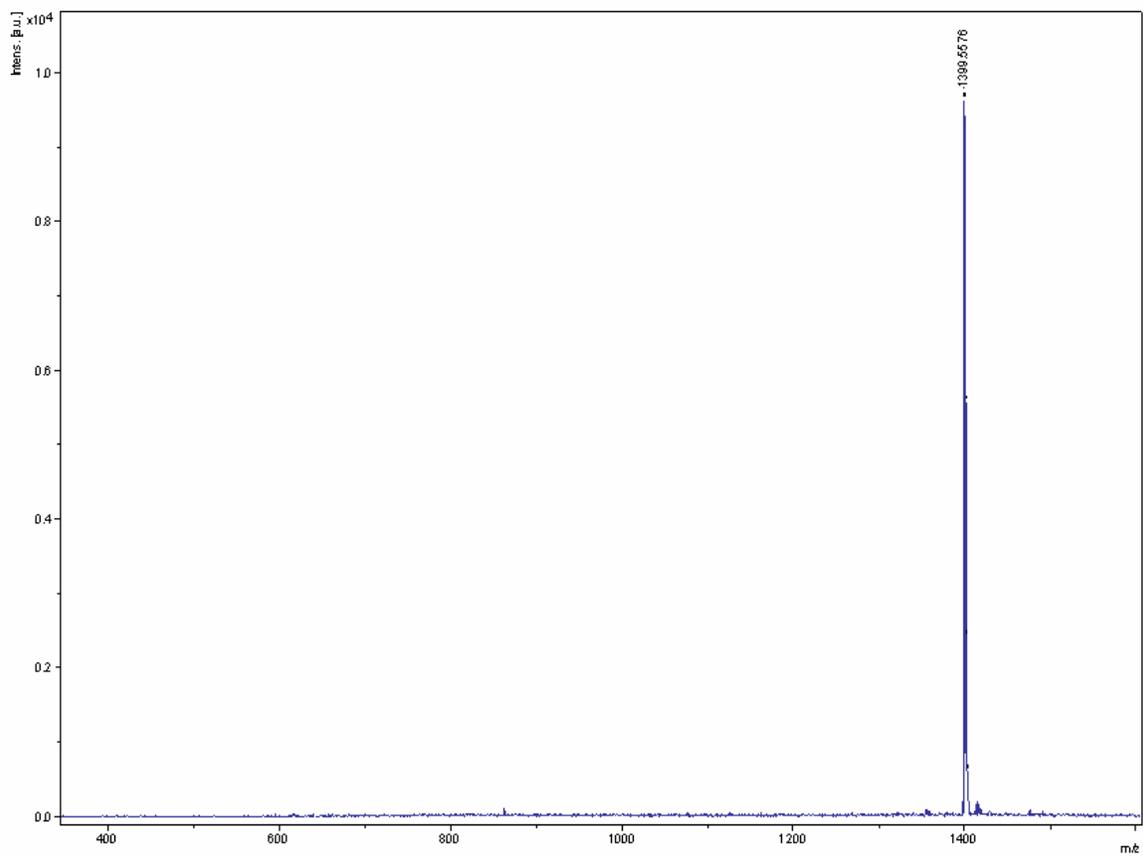


Figure S3. MALDI TOF mass spectrum of $(\text{H}_2\text{P})_2 \mathbf{3}$.

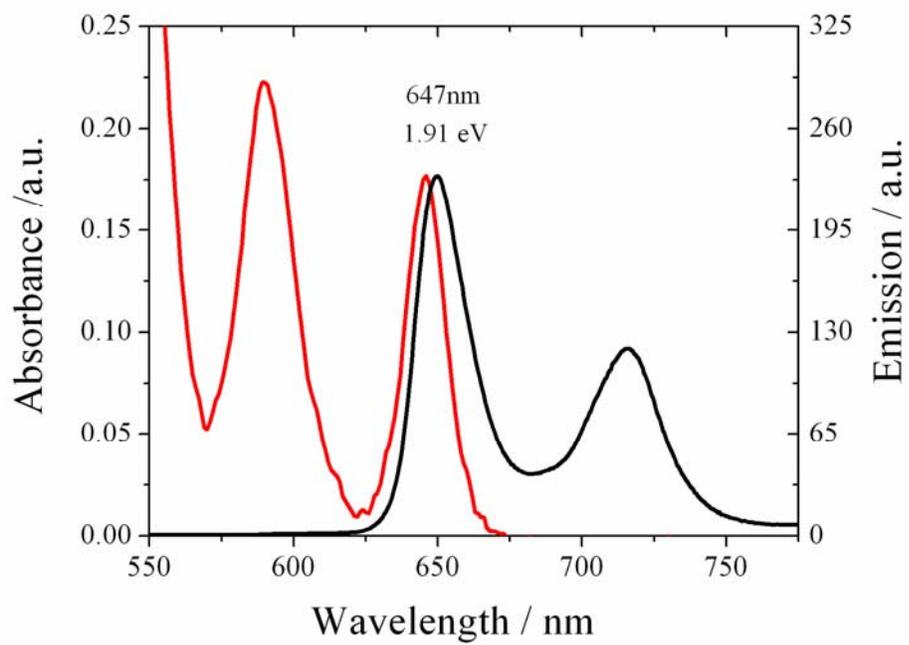


Figure S4. Absorption-emission spectra of CNH-(H₂P)₂ hybrid **6**, obtained in dichloromethane ($\lambda_{\text{exc}} = 420$ nm).

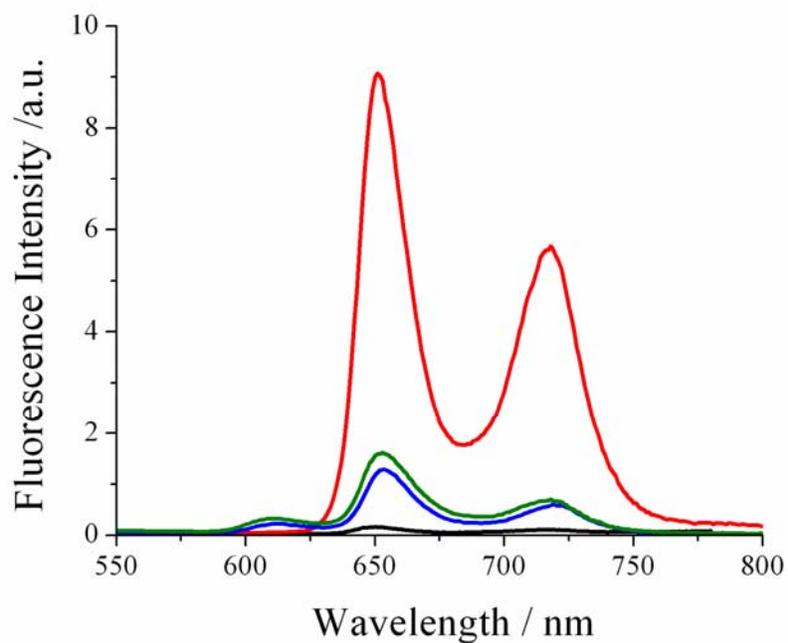


Figure S5. Fluorescence spectra of CNH- $(H_2P)_2$ hybrid **6** in DMF (black), dichloromethane (blue) and toluene (green) as compared with free $(H_2P)_2$ **3** (red) obtained in DMF. The excitation wavelength was 420 nm and the concentrations were adjusted so that the samples exhibited equal absorbance at the excitation wavelength.

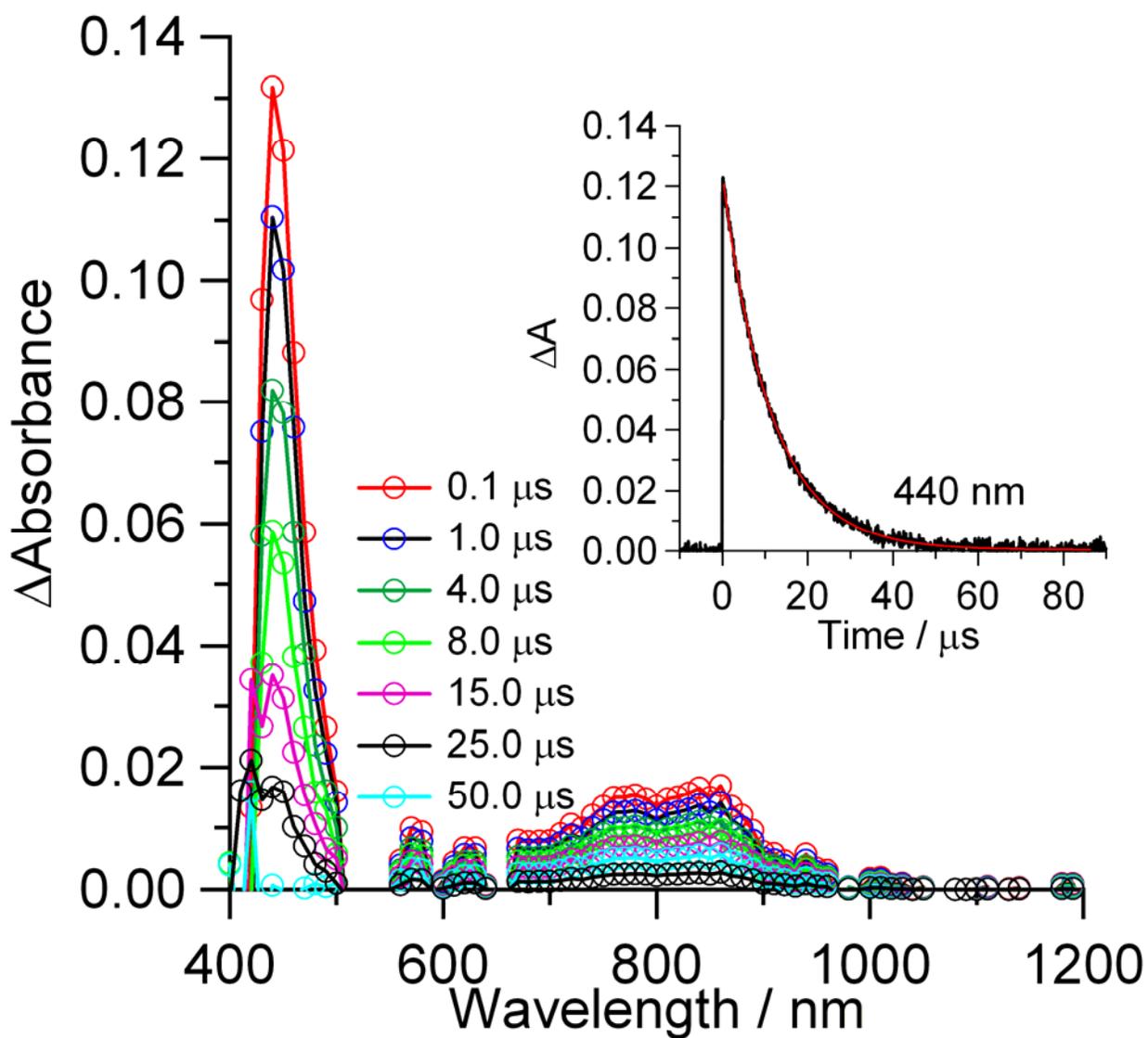


Figure S6. Nanosecond transient absorption spectra of $(\text{H}_2\text{P})_2 \mathbf{3}$ in Ar-saturated CH_2Cl_2 observed by 532 nm (ca. 1 mJ/pulse) laser irradiation. Inset: Absorption-time profiles.

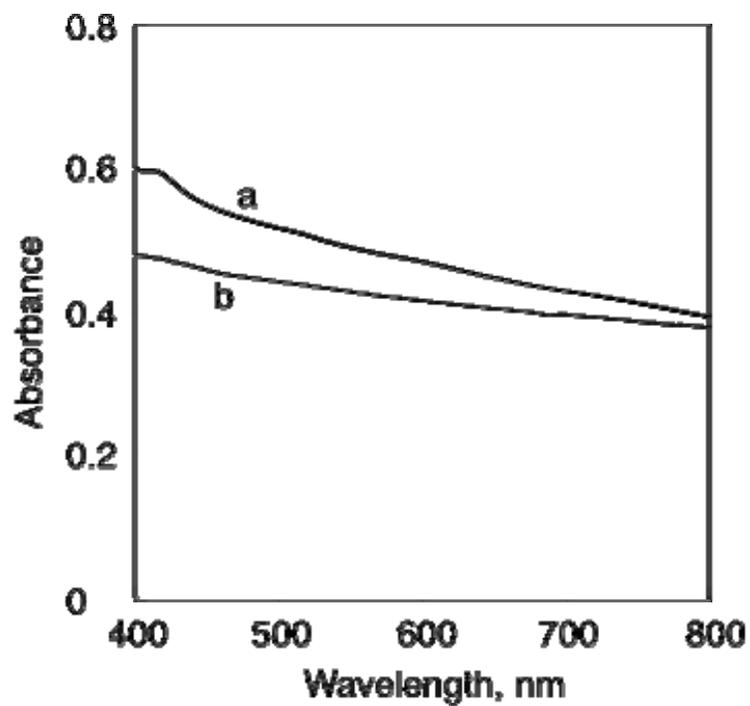


Figure S7. Absorption spectra of (a) OTE/SnO₂/CNH-(H₂P)₂ and (b) OTE/SnO₂/CNH films.