

*Supporting Information*

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## **Photoinduced Electron Transfer of Nano-Hybrids of Carbon Nanohorns with Amino Group and Tetrabenzoic Acid Porphyrin in Aqueous Media**

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Preparation procedure of  $(\text{CNH-NH-C(=O)-H}_2\text{P(COOH)}_n)$

0.1 mM  $\text{H}_2\text{P(CO}_2\text{H)}_4$  + 1 ml  $\text{CNH-NH}_2$  aqueous solution in 4 ml  $\text{H}_2\text{O}$  (black color)

Heat  $70^\circ\text{C}$  / stirring 2 hr ↓

(Dark brown color solution)

Centrifuge 5 hr

↓  
Mother liquor was removed (pale brown solution) and used for spectroscopic measurements  $(\text{CNH-NH-C(=O)-H}_2\text{P(COOH)}_n)$

↓  
Water was removed under reduced pressure and the solid residue used for TGA and IR measurement.

Scheme S1. Procedures to prepare  $\text{CNH-NH-C(=O)-H}_2\text{P(COOH)}_n$  ( $n \leq 3$ ).

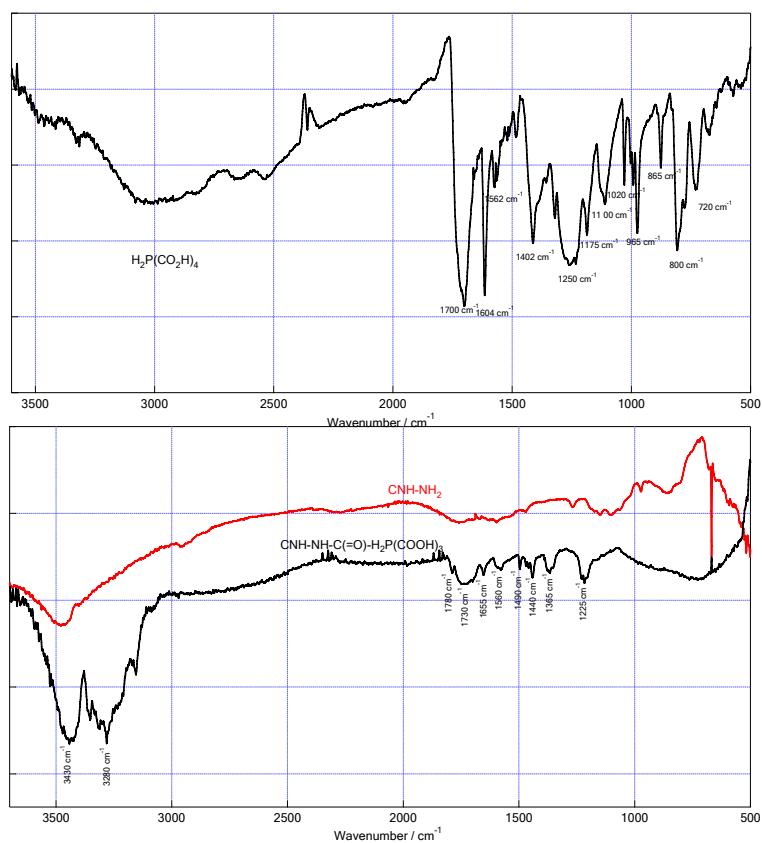


Fig. S1. IR spectra of **CNH-NH<sub>2</sub>** and nanohybrid mixture (**CNH-NH-C(=O)-H<sub>2</sub>P(CO<sub>2</sub>H)<sub>n</sub>**).

Amide, 1650, 3250  $\text{cm}^{-1}$

NH---COOH, 3430  $\text{cm}^{-1}$  (broad); hydrogen bonding

NH---COOH, 3250  $\text{cm}^{-1}$  (sharp); hydrogen bonding

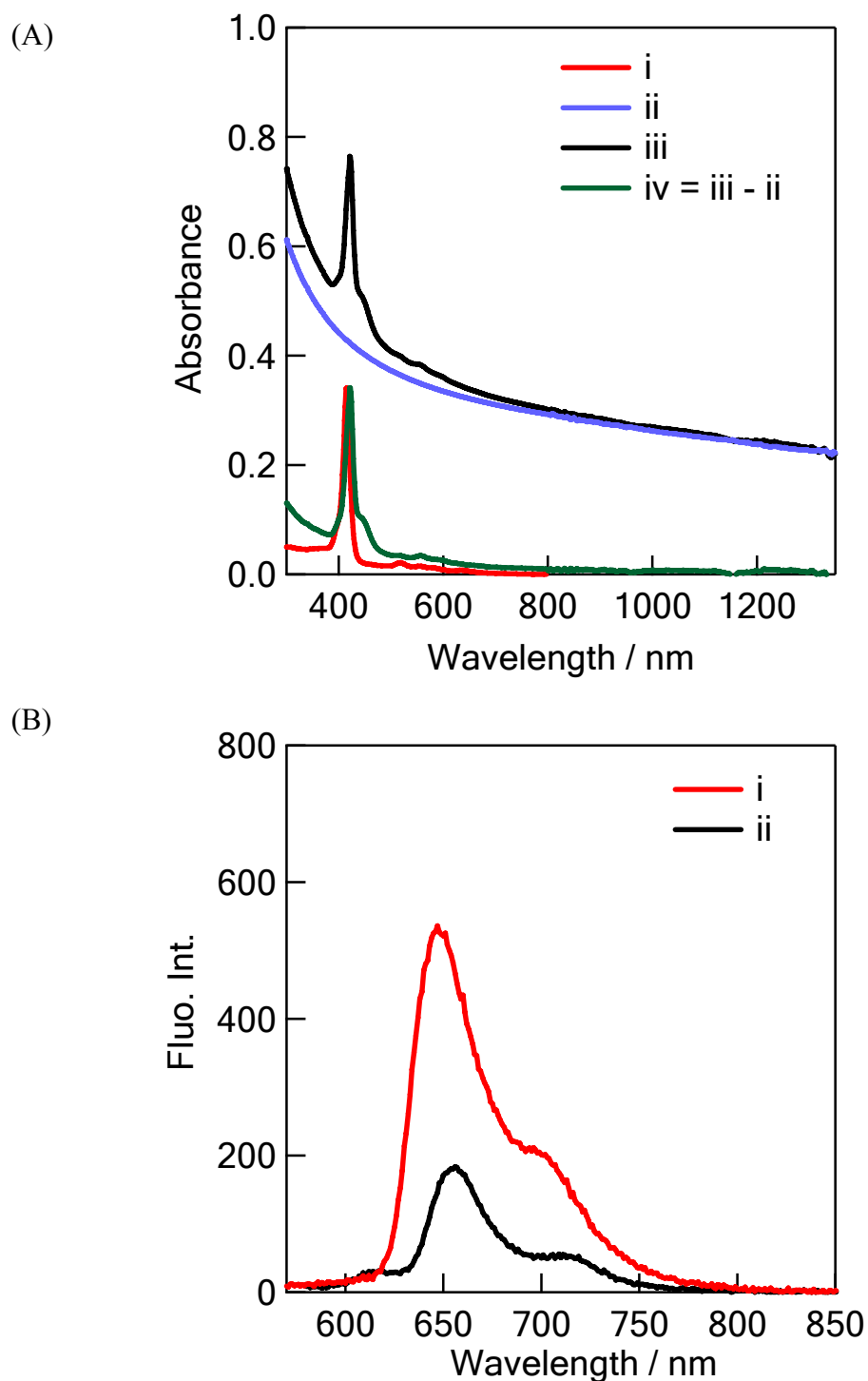


Fig. S2. (A) Steady-state absorption spectra of (i)  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  (0.004 mM) and (ii) **CNH-NH<sub>2</sub>** (iii)  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  nanohybrids with **CNH-NH<sub>2</sub>** (iv) subtracted spectra from spectra (iii) and (ii) in aqueous solution and (B) fluorescence spectra of (i)  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  (0.004 mM) (ii) nanohybrids;  $\lambda_{\text{ex}} = 420$  nm. Fluorescence spectra are measure matching same absorbance at 420 nm.

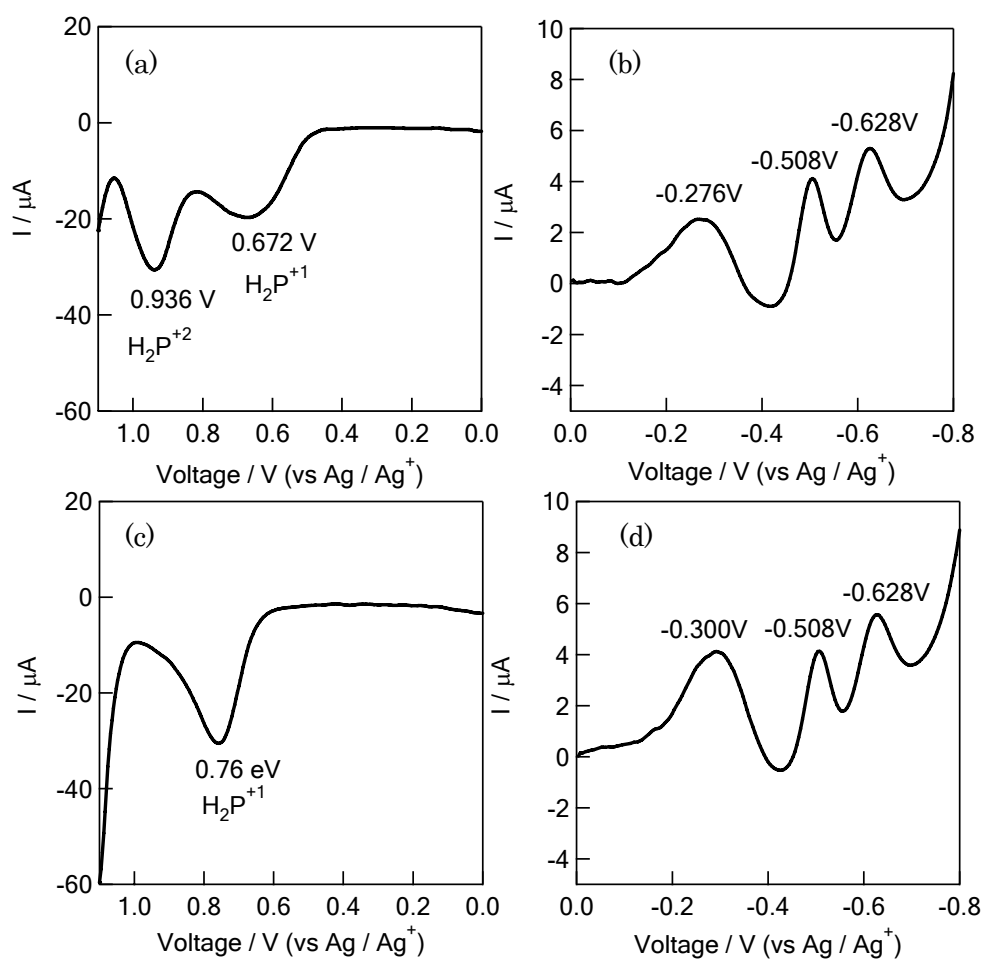


Fig. S3. Differential pulse voltammograms of the (a) and (b)  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  nanohybrids with **CNH-NH<sub>2</sub>**, (c) 0.1 mM  $\text{H}_2\text{P}(\text{COO}^-)_4$  and (d) **CNH-NH<sub>2</sub>** at a scan rate of  $100 \text{ mV s}^{-1}$  in aqueous solution containing KCl (0.1 M) as a supporting electrolyte.

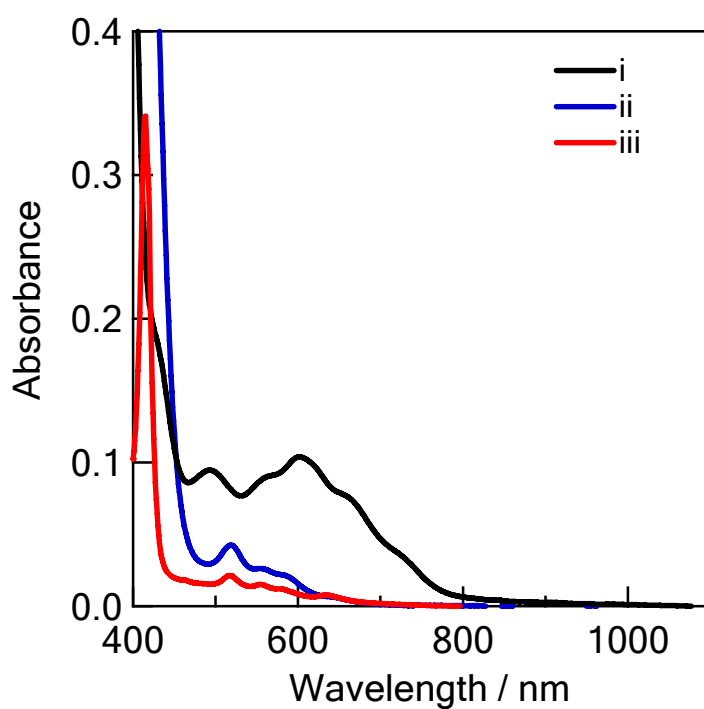


Fig. S4. Steady-state absorption spectral changes observed after repeated 532-nm laser light irradiation of (i)  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  (0.004 mM) in the presence of  $\text{MV}^{2+}$  (0.5 mM) with BNAH (2.0 mM) without  $\text{CNH-NH}_2$  in deaerated  $\text{H}_2\text{O}$  (0.5 cm cell length), (ii) solution-i before laser irradiation, and (iii)  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  (0.004 mM).

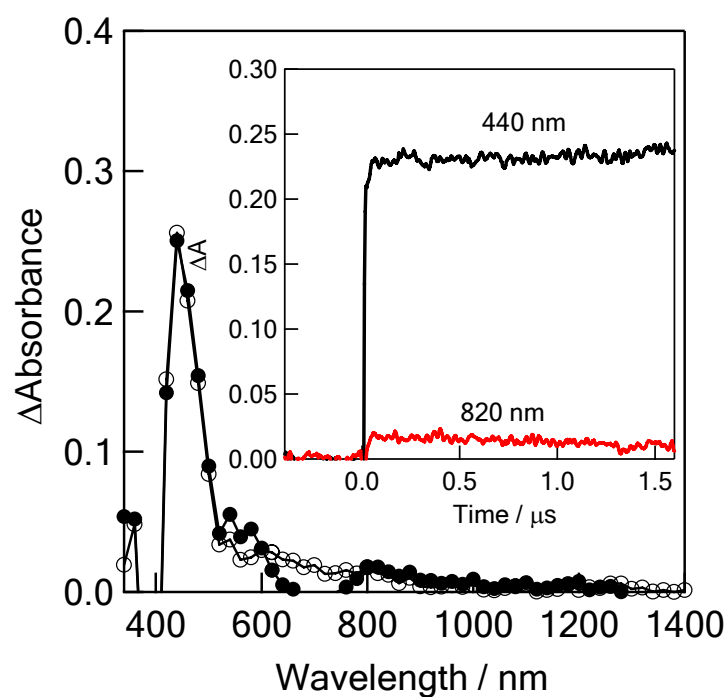


Fig. S5. Nanosecond transient absorption spectra of  $\text{H}_2\text{P}(\text{COOH})_4$  (0.05 mM) observed by 532 nm (ca. 3 mJ/ pulse) laser irradiation in deaerated  $\text{H}_2\text{O}$ ; spectra at 0.1  $\mu$ s ( $\bullet$ ) and 1.0  $\mu$ s ( $\circ$ ). Inset: Absorption-time profiles.

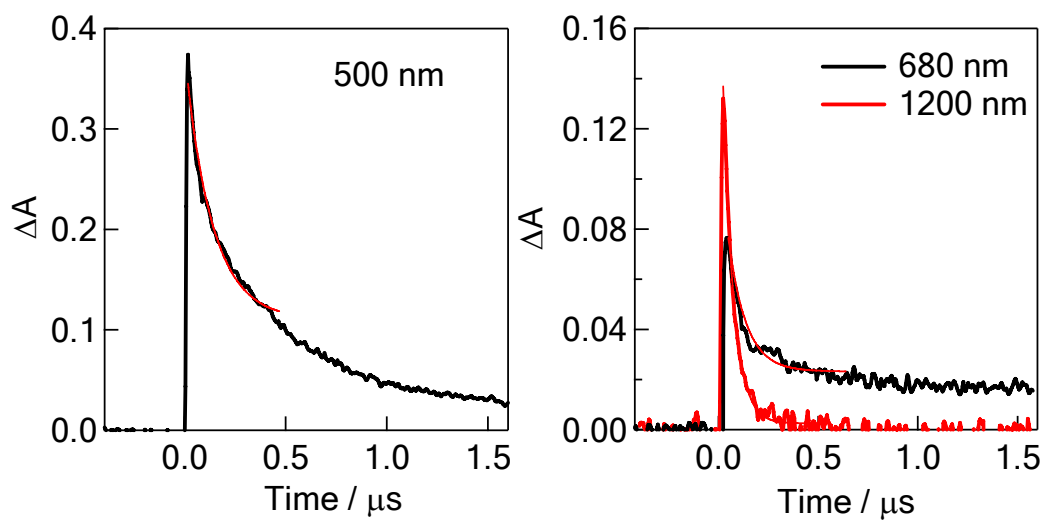


Fig. S6. Absorption-time profiles at 500, 680 and 1200 nm of  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  nanohybrids with **CNH-NH<sub>2</sub>**.



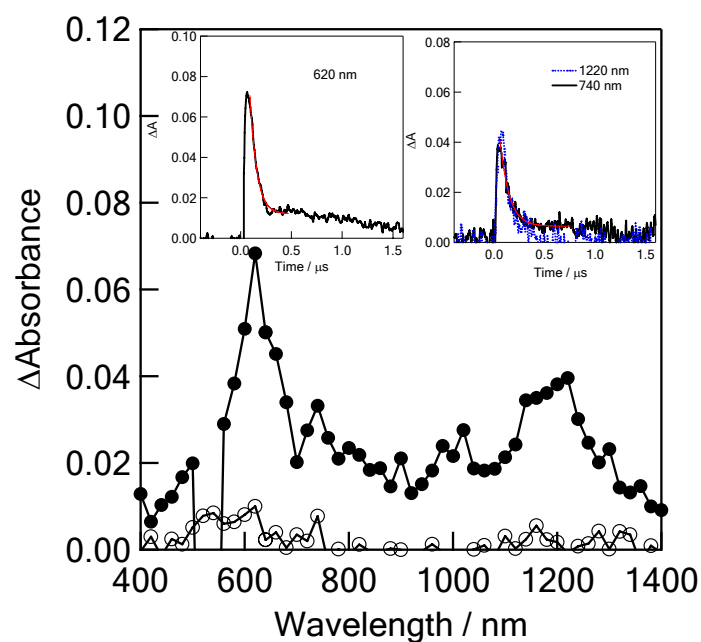


Fig. S7. Nanosecond transient absorption spectra observed by 532 nm (ca. 3 mJ/pulse) laser irradiation of  $\text{H}_2\text{P}(\text{CO}_2\text{H})_4$  nanohybrids with **CNH-NH<sub>2</sub>** in the presence of 0.5 mM  $\text{MV}^{2+}$  and BNAH in deaerated  $\text{H}_2\text{O}$  (at 0.1  $\mu\text{s}$  (●) and 1.0  $\mu\text{s}$  (○)). Inset: Absorption-time profile. The 1200-nm intensity decreased from 0.120 (Figure S4) to 0.04 at immediately after laser light pulse.