

# Supporting Information

## Photo-Injection of High Potential Holes into $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ Nanoparticles by Porphyrin Dyes

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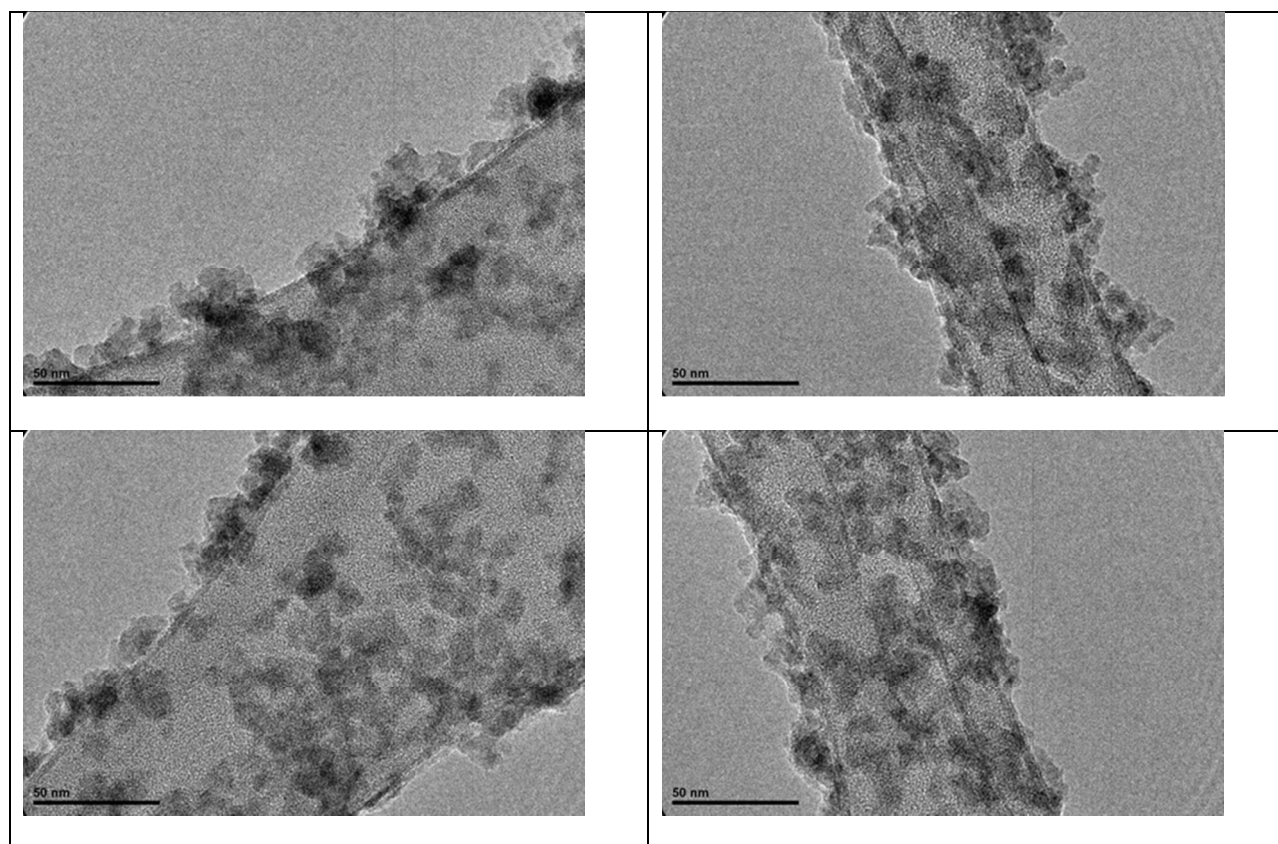
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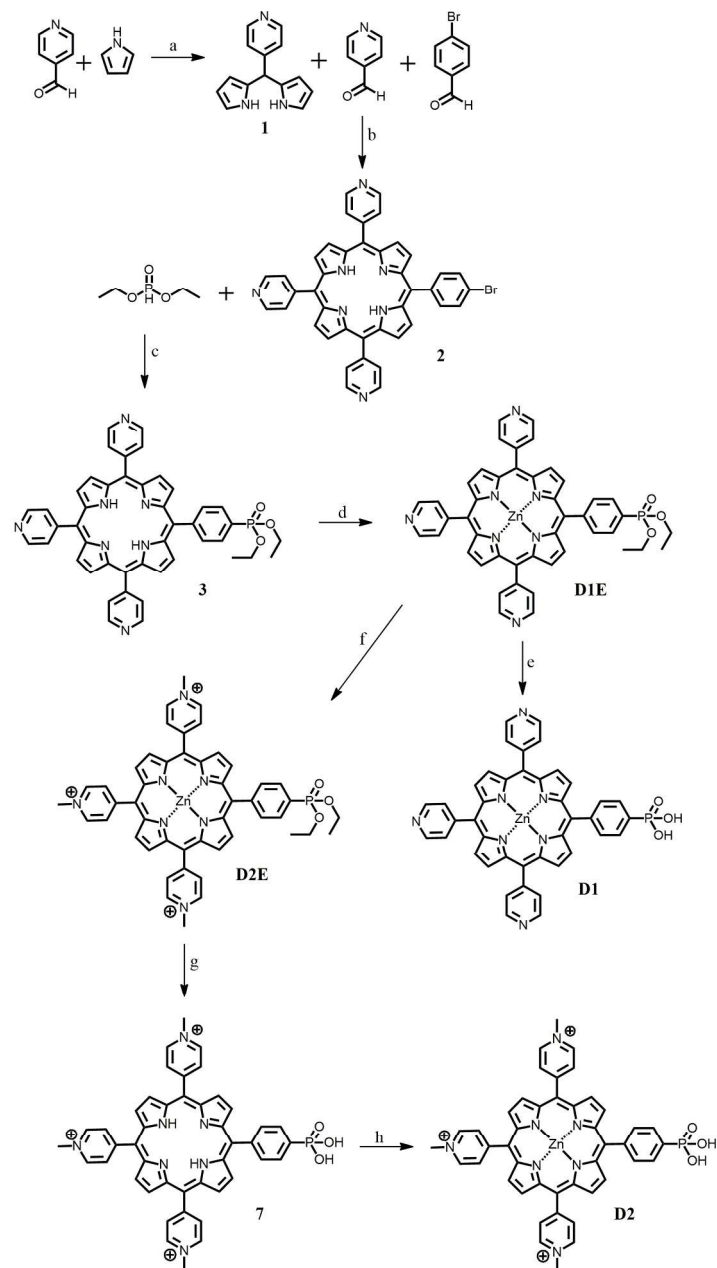
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KEYWORDS:  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  nanoparticles, hole injection, p-type semiconductors, dye-sensitized solar cell, optical properties.

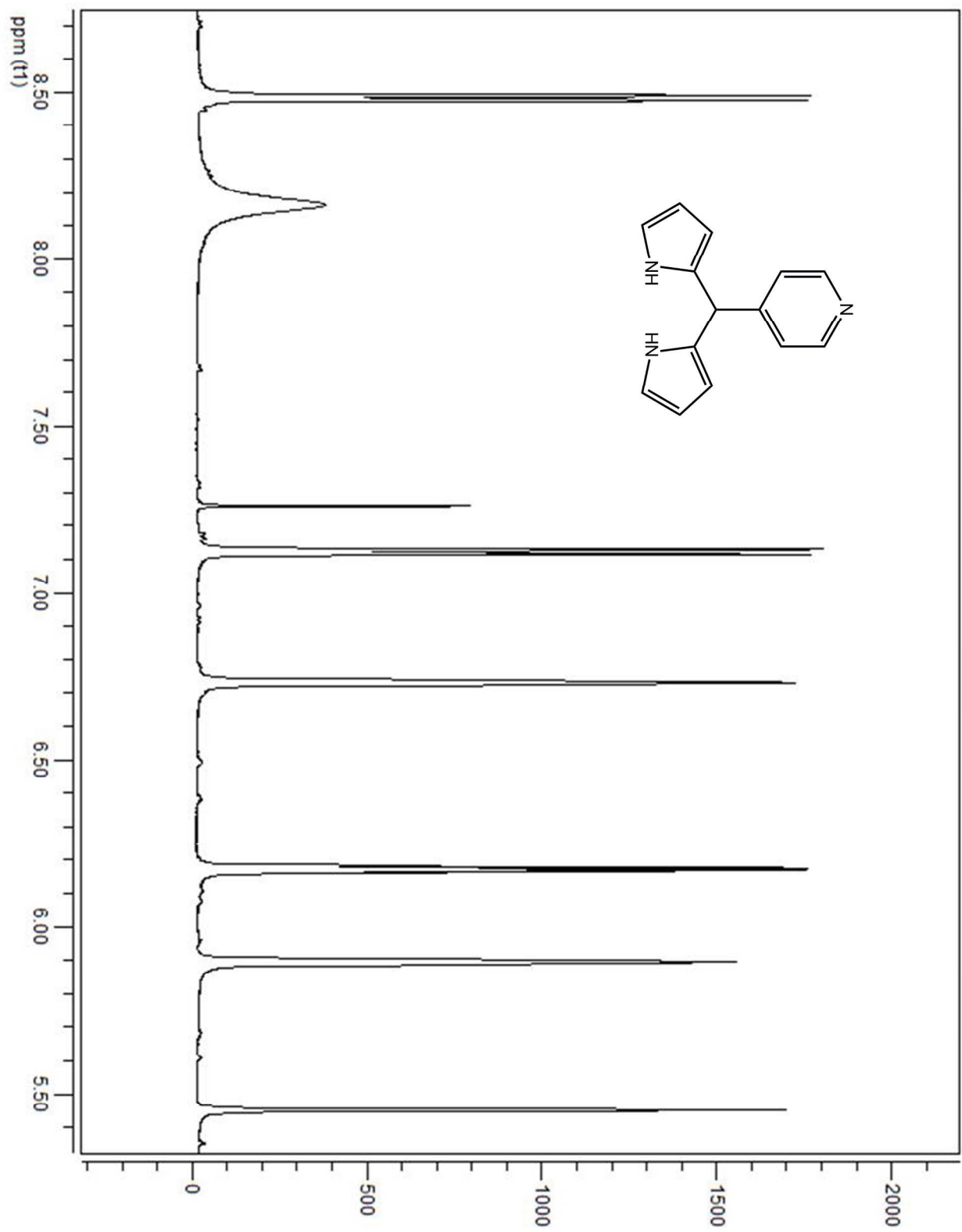
**Figure S1.** Representative HR-TEM images of NP-Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub>.



## Dye synthesis

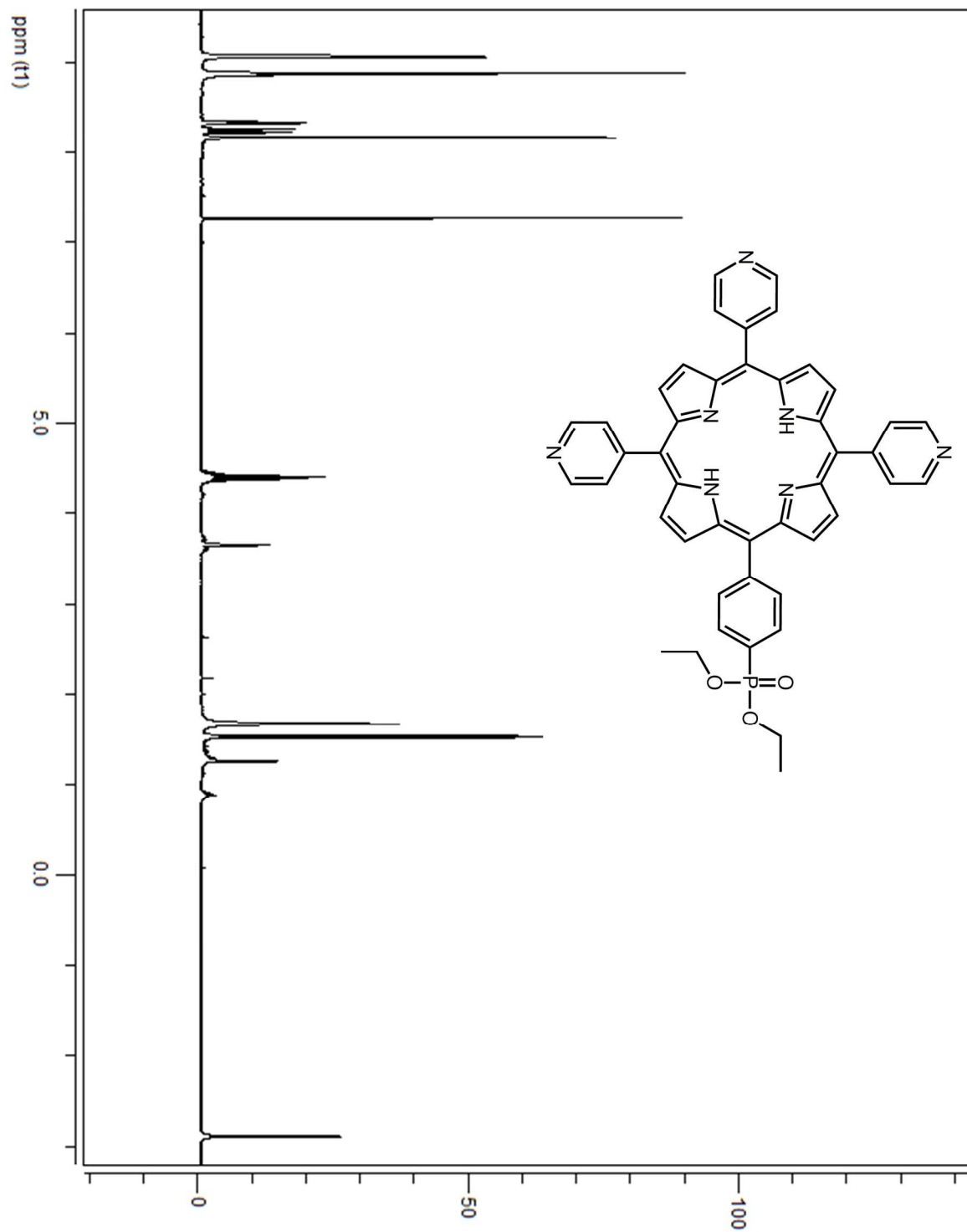


**Scheme S1.** Reagents and conditions: (a) Ar/85 °C/24 h, 53% yield; (b) propionic acid, reflux/45 min, 5.5% yield; (c) diethyl phosphite/ $\text{Pd}(\text{PPh}_3)_4$ /toluene/TEA, Ar/80 °C/18 h, 23% yield; (d)  $\text{ZnOAc} \cdot 2\text{H}_2\text{O}$ /THF/DCM, 60 °C/12 h, 32 % yield; (e) TMS-Br/ $\text{CHCl}_3$ /TEA, 60 °C/18 h, 100% yield; (f) MeI/DMF, Ar/100 °C/1 h then room temperature/12 h, 100% yield; (g) TMS-Br/ACN/TEA, 65 °C/12 h, 100 % yield; (h)  $\text{ZnOAc} \cdot 2\text{H}_2\text{O}$ /THF/ $\text{H}_2\text{O}$ , 60 °C/2 h, 100% yield.

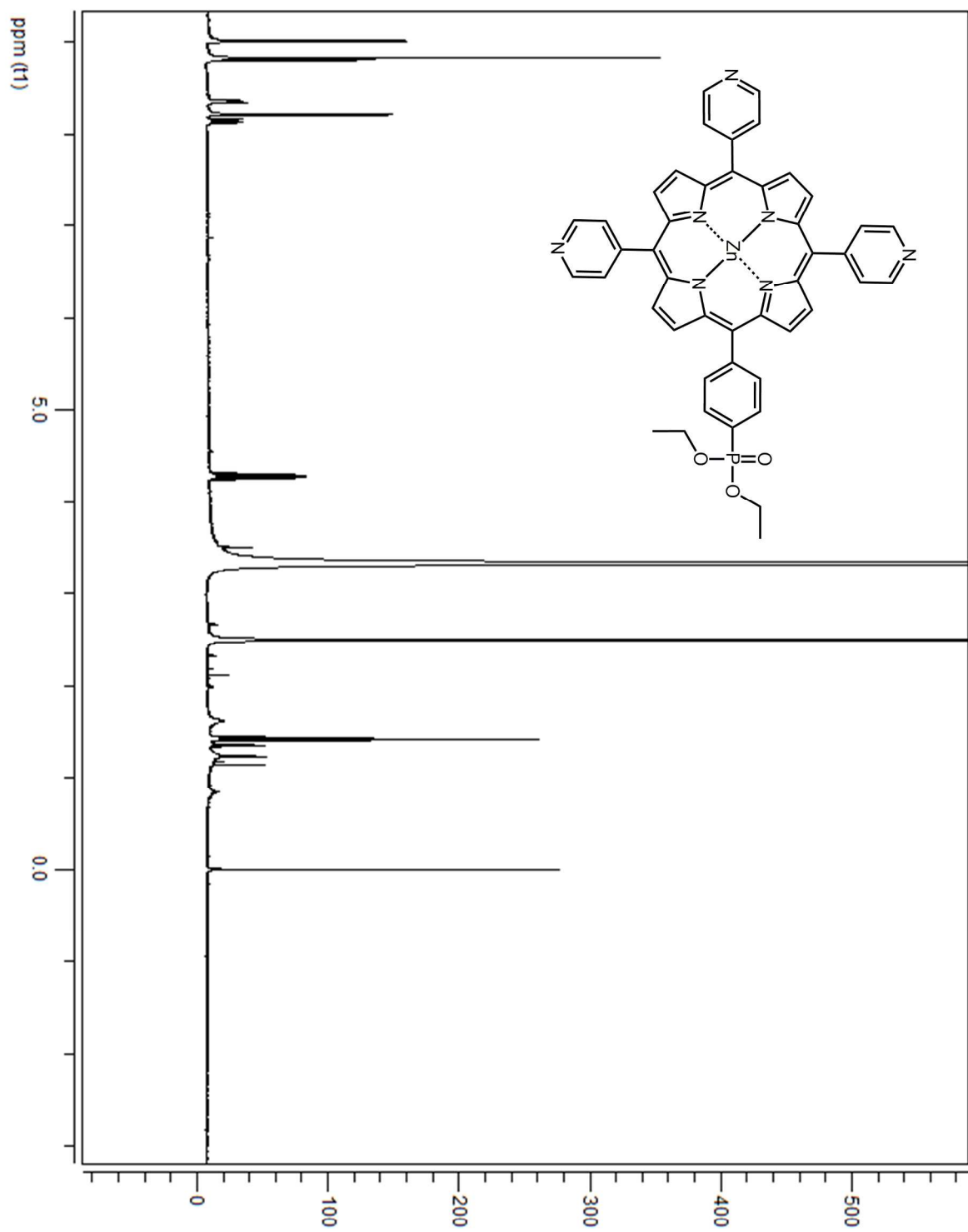


**Figure S2.**  $^1\text{H}$ -NMR of **1** in  $\text{CDCl}_3$ .

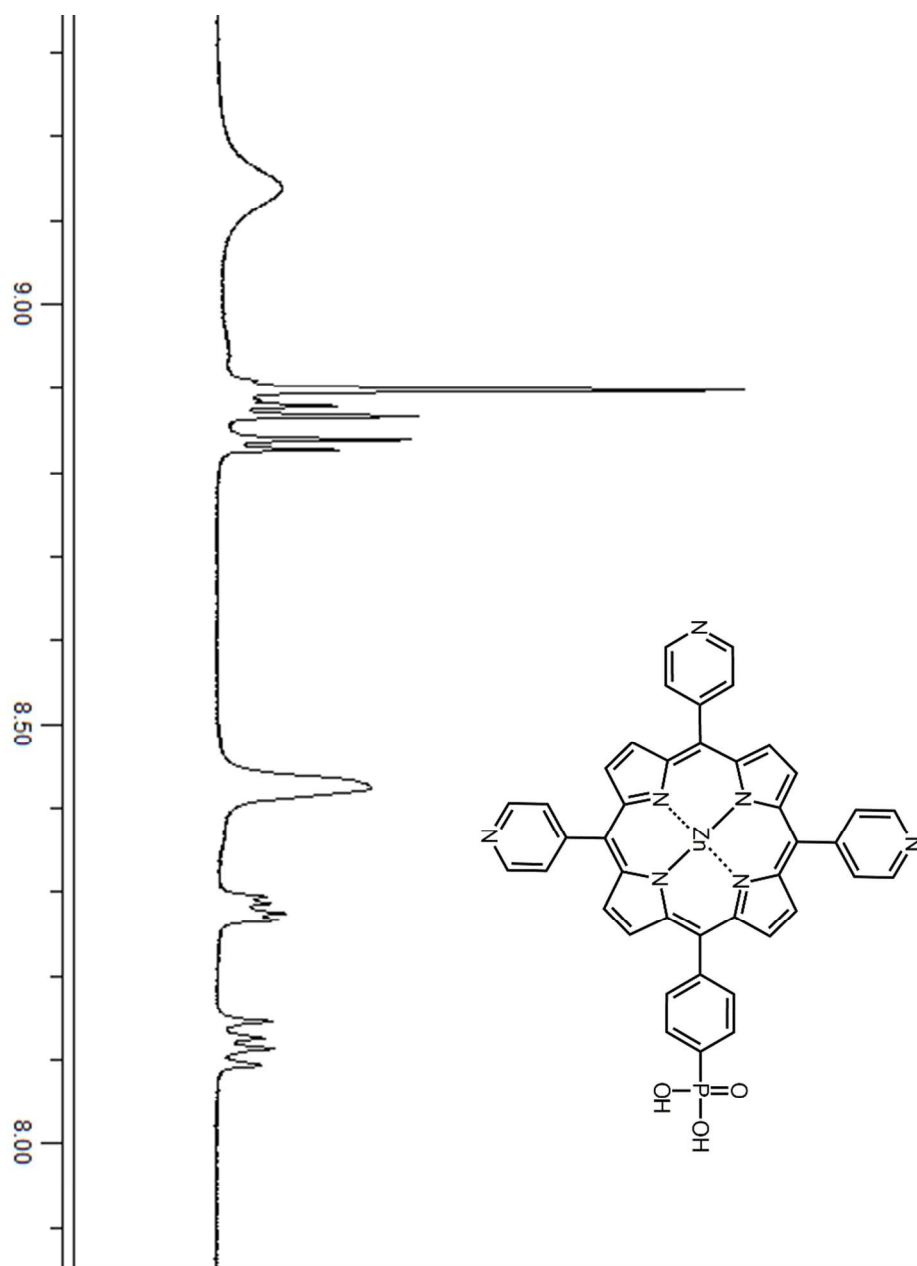




**Figure S4.**  $^1\text{H}$ -NMR of **3** in  $\text{CDCl}_3$ .

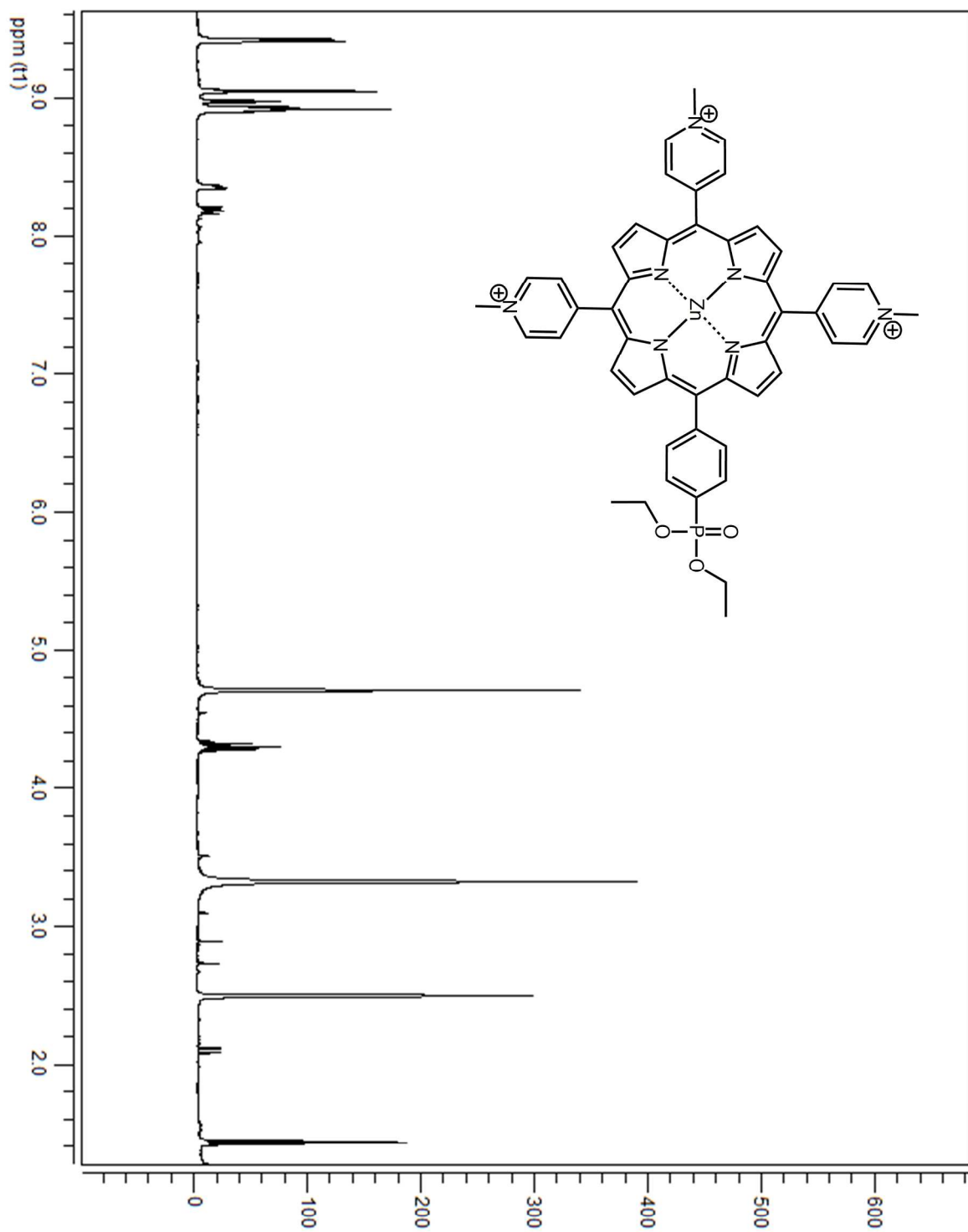


**Figure S5.**  $^1\text{H}$ -NMR of DIE in  $\text{DMSO}-d_6$ .

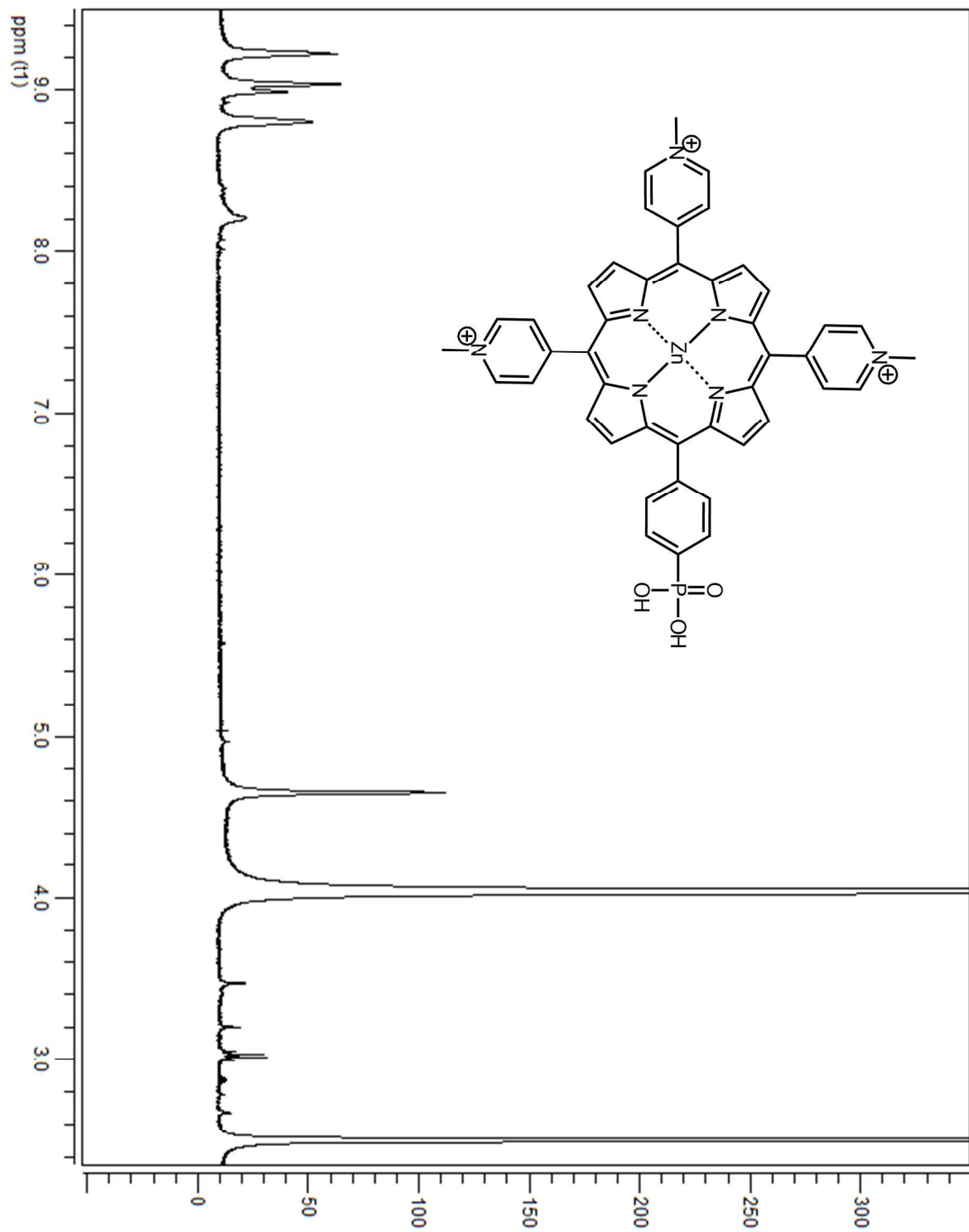


**Figure S6.**  $^1\text{H}$ -NMR of D1 in  $\text{DMSO}-d_6$ .



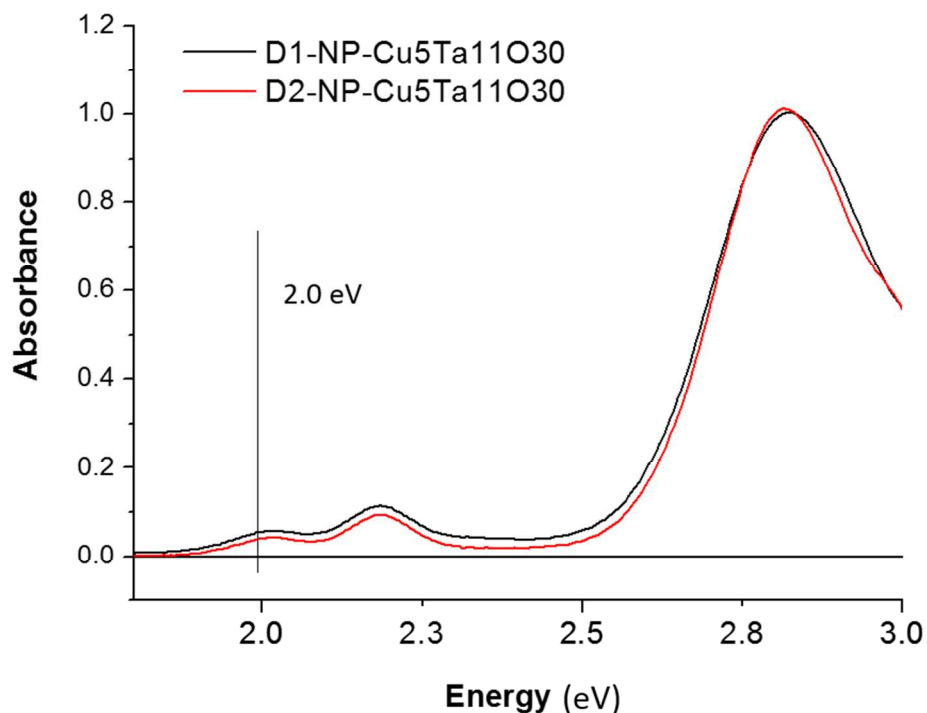


**Figure S7.**  $^1\text{H}$ -NMR of D2E in  $\text{DMSO}-d_6$ .



**Figure S8.**  $^1\text{H}$ -NMR of D2 in DMSO- $d_6$ /D $_2$ O.

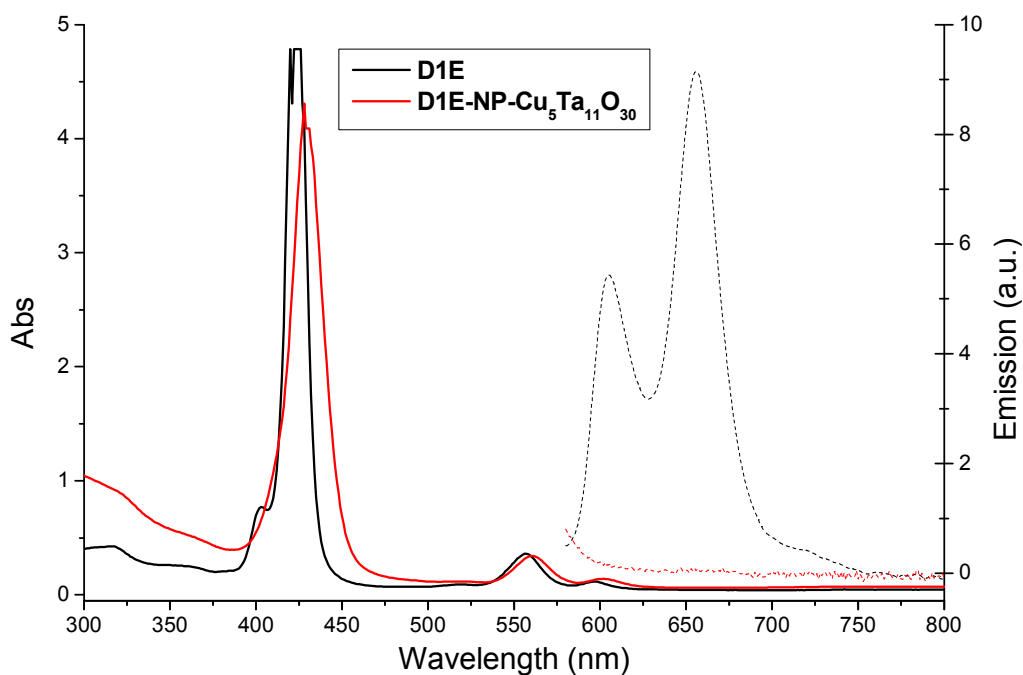
## Determination of $E_{00}$ of D1 and D2



**Figure S9.** Absorption spectra in ethanol for: a) D1-Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub> (black line) and b) D2-NP-Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub> (red line).

## Photophysics of D1 in its ester form attached to NP-Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub>.

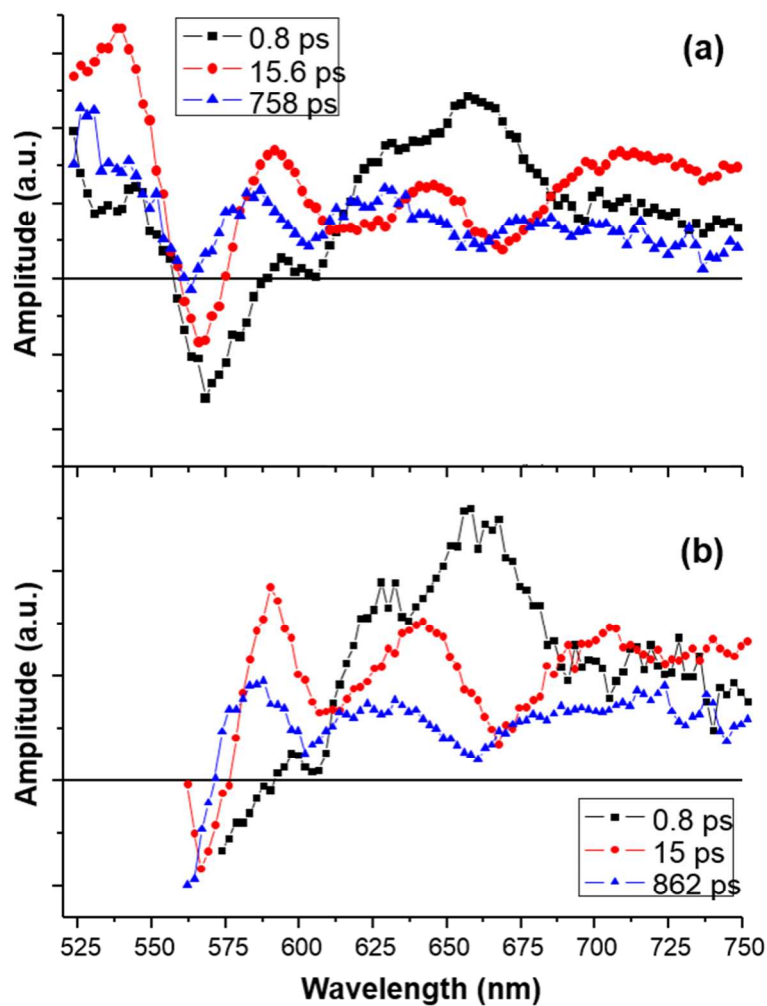
Following the same procedure described on the main manuscript, D1 in ester form (D1E) was attached to NP-Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub>. Figure S3 shows how the Soret Q bands of attached D1E shift toward the red and the emission of the dye is completely quenched presumably because the hole injection into the semiconductor.



**Figure S10.** Absorption spectra (solid lines) and emission spectra upon 560 nm excitation (dash lines) in ethanol for D1E–NP–Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub> (red) and D1E (black).

Femtosecond transient absorption experiments were performed to establish the kinetics of the photoinduced hole transfer reactions in D1E–NP–Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub>, in ethanol solution. Global analysis of the transient absorption data for D1E–NP–Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub> (Fig. S11) reveals three lifetimes of 800 fs, 15.6 ps, 758 ps and a nondecaying component (not shown) upon excitation at 426 nm (Fig. S4a) and 560 nm (Fig S4b). Since some NP–Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub> band gap absorption can be registered at 426 nm, spectra with excitation at 560 nm excitation were recorded finding the same overall features and confirming that the small band gap absorption at 426 nm can be neglected in front of the huge Soret band absorption. The 800 fs DAS can be attributed to the recombination of the charge separated state of the D1E<sup>•+</sup>–NP–Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub>(e<sup>+</sup>) (inverted kinetics),

showing ground state bleaching around 560 and 610 nm and induced absorption associated with  $\text{D1E}^{\bullet-}$  between 620 nm and 700 nm. The 15.6 ps DAS can be attributed to the hole injection from  $\text{D1E}^*$  to the valence band of the  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  showing ground state bleaching around 560 and 610 nm and decay of the stimulated emission around 620 and 670 nm. The 758 ps DAS can be attributed to decay of the singlet excited state of the non-attached(physisorbed)/aggregated dye, which is not involved in the hole injection process, ground state bleaching and stimulated emission bands are slightly blue shifted. Due to the high nonhomogeneity (heterogeneity) of the system, obtained lifetimes do not correspond to single species. These lifetimes represent an average of the decay of several slightly different species. For  $\text{D1E-NP-Cu}_5\text{Ta}_{11}\text{O}_{30}$  there is likely some population with very fast formation of charge separate state ( $<100$  fs), this would explain high amplitude of 0.8 ps DAS in such inverted kinetics case, but overall the rate of decay of the charge-separated species is greater than the average effective rate of formation.



**Figure S11.** Decay-associated-spectra in ethanol measured by fs transient absorption upon excitation at **a)** 426 nm and **b)** 560 nm for D1E-NP-Cu<sub>5</sub>Ta<sub>11</sub>O<sub>30</sub>.

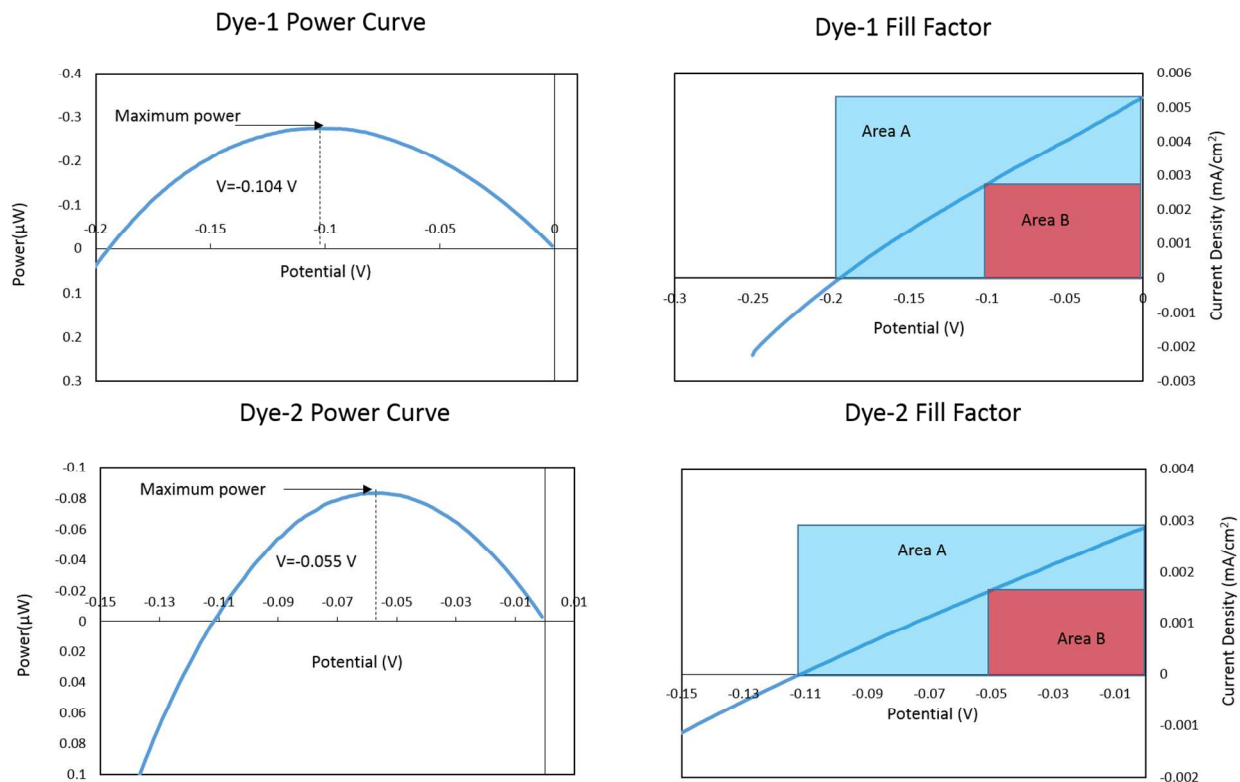
### DSSC Efficiency Calculations

Fill factor and efficiency for the DSSCs were calculated by using Equations S1 and S2:

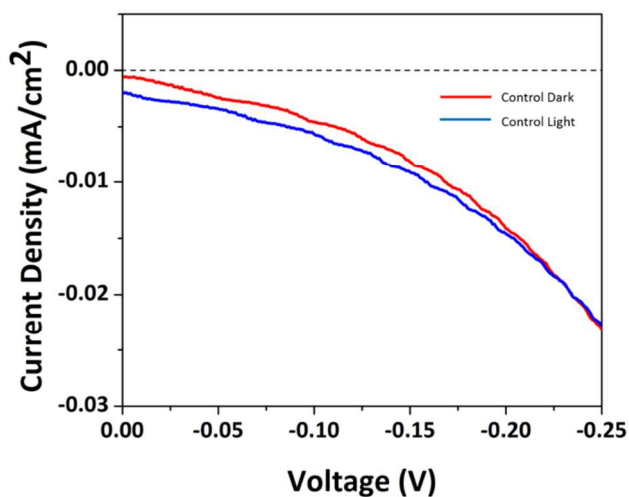
$$ff = \frac{I_{mp}V_{mp}}{I_{sc}V_{oc}} = \frac{Area\ B}{Area\ A} \quad (S1)$$

$$\eta = I_{sc}V_{oc} \left( \frac{ff}{I_c} \right) \quad (S2)$$

Where  $ff$  is the fill factor,  $I_{mp}$  is maximum power current,  $V_{mp}$  is maximum power voltage,  $I_{sc}$  is the short circuit current,  $V_{oc}$  is the open circuit potential,  $I_c$  is incident power from the light source ( $100 \text{ mW/cm}^2$ ) and  $\eta$  is the photo-conversion efficiency (PCE) [1] and is graphically shown in Figure S5. Current-potential scans were performed on a CH-Instruments CH-620a potentiostat under simulated solar irradiance using an AM 1.5 G filter (Oriel). Scans were started near the open circuit voltage and scanned towards the short circuit condition (0.0 V) at a scan rate of  $10 \text{ mV s}^{-1}$ . The semiconducting film served as the working electrode, while the Pt deposited FTO served as the counter and reference electrode. Power curves were made by multiplying the voltage and currents obtained and plotting against the voltage range used, shown in Figure S5. Shown in Figure S6 are the i-v curves for the control experiments in the absence of sensitizing dye. Currents from the control are negligible and do not show any large changes between dark and light conditions, indicating that the dye must be present for any photoinjection to occur.



**Figure S12:** Power-voltage ( $P$ - $V$ ) curves and fill factor ( $ff$ ) plots for Dye-1 (top) and Dye-2 (bottom) on nanoparticle  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  films.

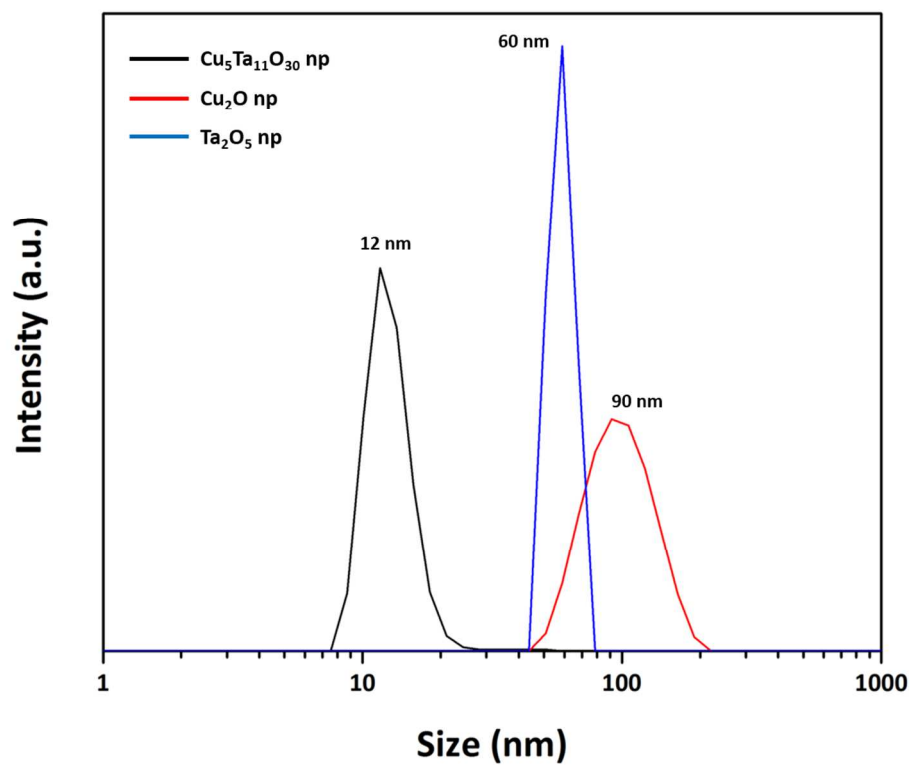


**Figure S13.** Control  $i$ - $v$  curves for  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  nanoparticle films without dye.

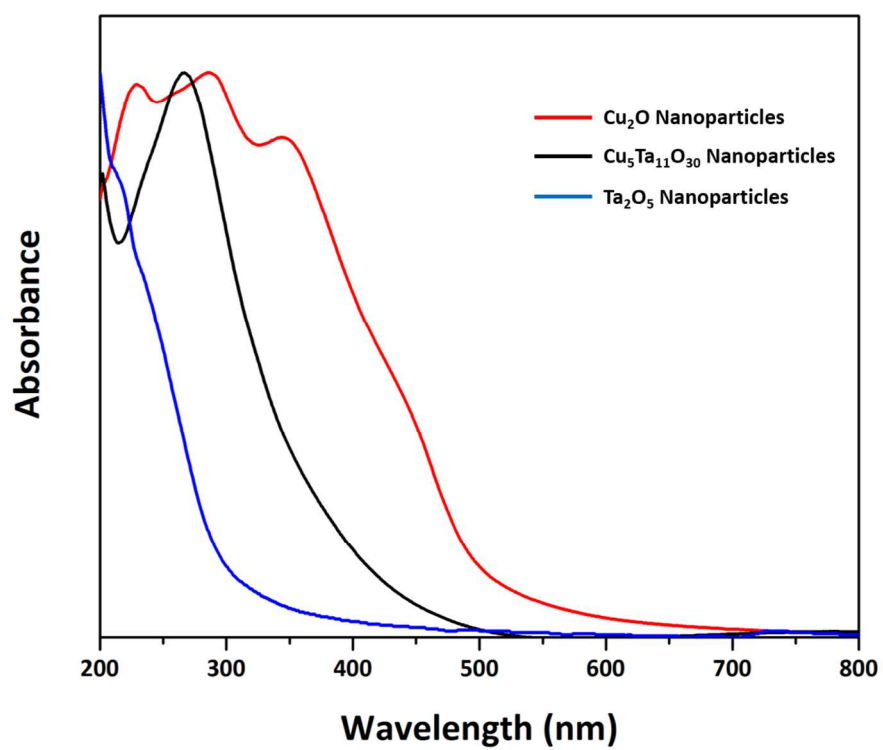


	<u>Dye-1</u>	<u>Dye-2</u>
$V_{oc}$ (V)	0.2	0.11
$I_{sc}$ (A)	5.28E-06	2.85E-06
$I_{mp}$	2.64E-06	1.51E-06
$V_{mp}$	0.104	0.055
FF	2.60E-01	2.65E-01
$\eta$	2.75E-04	8.31E-05

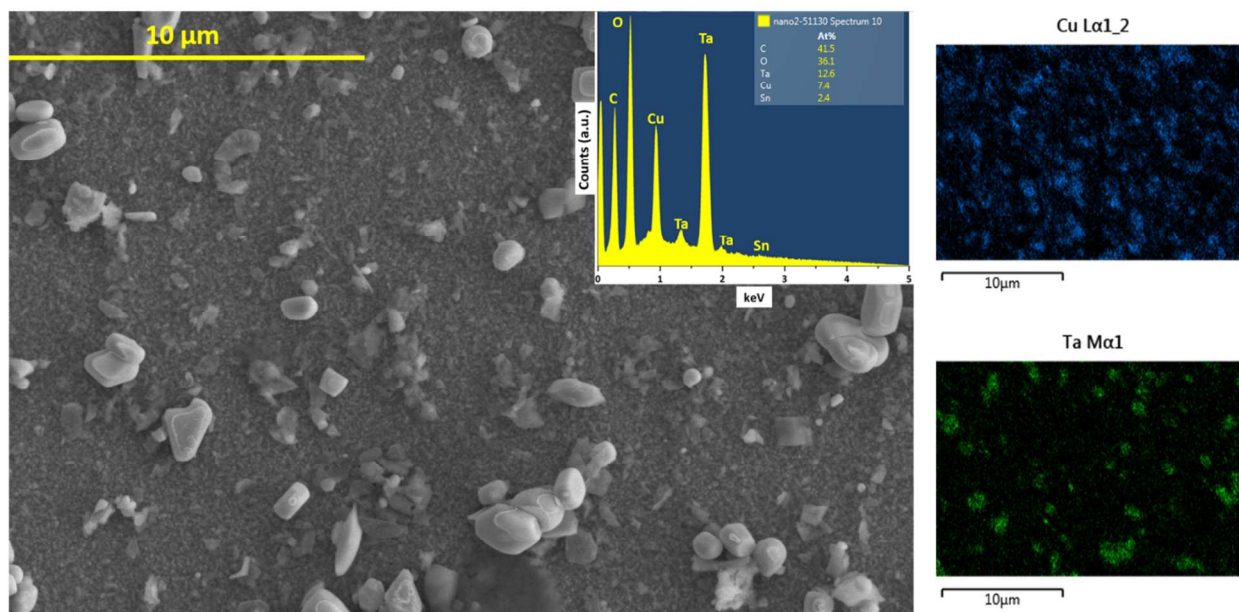
**Table S1.** Table of Parameters Determined in the Efficiency Calculations.



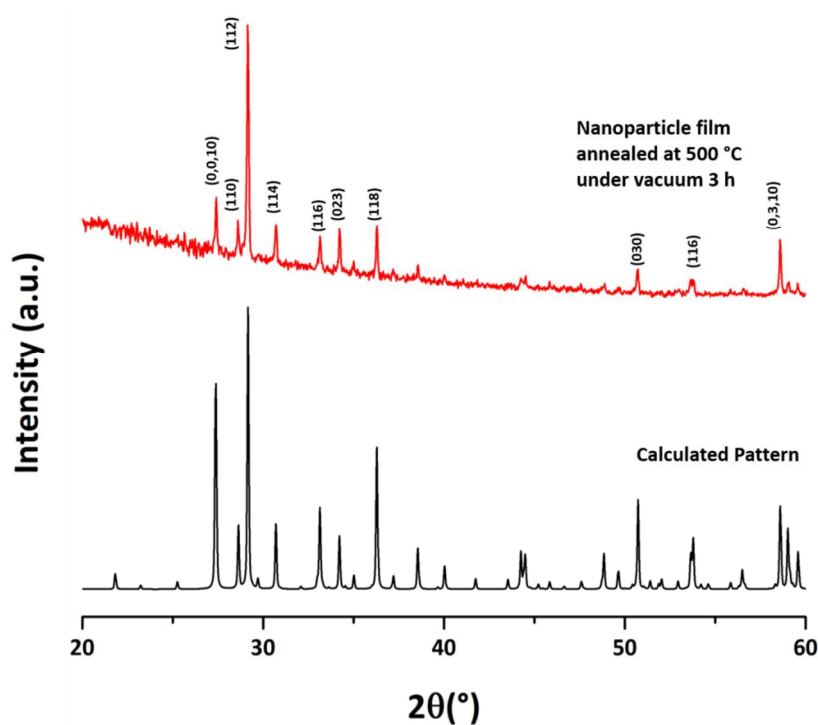
**Figure S14.** Particle size distributions of  $Cu_2O$  (red) and  $Ta_2O_5$  (blue) nanoparticle precursors and  $Cu_5Ta_{11}O_{30}$  nanoparticle product (black).



**Figure S15.** UV-Vis of suspended  $\text{Cu}_2\text{O}$  (red),  $\text{Ta}_2\text{O}_5$  (green) and  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  (black) nanoparticles.



**Figure S16.** FESEM image of an annealed film of  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  nanoparticles in solution with elemental mapping of Cu and Ta (right). Inset: EDS spectrum of the area.



**Figure S17.** Powder X-ray diffraction pattern of the  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  film (upper), and comparison to a calculated pattern based on the known crystalline structure of  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  (lower).

## EXPERIMENTAL SECTION

**Materials.** For the  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  nanoparticles: copper sulfate (anhydrous, 99%), tantalum pentachloride (99.9%), ascorbic acid (anhydrous, 99.9%), sodium hydroxide (99%) and copper(I) chloride (anhydrous, 99.9%) were all purchased from Alfa Aesar. 200 proof anhydrous ethanol was purchased from Koptek.

**High Resolution Transmission Electron Microscopy.** TEM micrographs were collected using a Philips CM200 TEM at 200kV, Cs 1.2 mm, PTP Resolution: 0.25nm Focused Probe: 0.5nm and Imaging Modes: TEM/STEM. TEM micrographs were analyzed using *Digital Micrograph*<sup>TM</sup> software [2].

**Powder X-ray Diffraction.** The  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  products were characterized by powder X-ray diffraction using an Inel X-ray diffractometer and  $\text{Cu K}\alpha_1$  radiation ( $\lambda=1.54056 \text{ \AA}$ ) from a sealed tube X-ray generator (30 mA, 35 kV). A curved position sensitive detector (CPS-120) was used in transmission mode.

**Steady State Absorption and Fluorescence.** Spectra were recorded in 1 cm path length cuvettes with the following spectrophotometers: diode array HP 8452, Shimadzu - UV-IR (2041PC), and Hitachi double beam UV/Vis spectrophotometer (U-2800). Steady-state fluorescence spectra were measured using a Photon Technology International MP-1 spectrometer and corrected for detection system response and excitation source intensity as a function of wavelength. Excitation was provided by a 75 W xenon-arc lamp and single-grating monochromator. Fluorescence was detected at  $90^\circ$  to the excitation beam via a single-grating

monochromator and an R928 photomultiplier tube having S-20 spectral response and operating in the single photon counting mode.

***Time Resolved Absorption.*** Femtosecond to nanosecond transient absorption measurements were acquired with a kilohertz pulsed laser source and a pump-probe optical setup. Laser pulses of 100 fs at 800 nm were generated from an amplified, mode-locked titanium sapphire kilohertz laser system (Millennia/Tsunami/Spitfire, Spectra Physics). Part of the laser pulse energy was sent through an optical delay line and focused onto a 3 mm sapphire plate to generate a white light continuum for the probe beam. The remainder of the pulse energy was used to pump an optical parametric amplifier (Spectra Physics) to generate excitation pulses, which were selected using a mechanical chopper. The white light generated was then compressed by prism pairs (CVI) before passing through the sample. The polarization of the pump beam was set to the magic angle (54.7°) relative to the probe beam and its intensity was adjusted using a continuously variable neutral density filter. The white light probe was dispersed by a spectrograph (300 line grating) onto a charge-coupled device (CCD) camera (DU420, Andor Tech.). The final spectral resolution was about 2.3 nm for over a nearly 300 nm spectral region. The instrument response function was ca. 100 fs. The decay-associated spectra (DAS) were obtained by fitting globally the transient absorption kinetic traces over a selected wavelength region simultaneously as described by equation (1) (parallel kinetic model).[3]

$$\Delta A(\lambda, t) = \sum_{i=1}^n A_i(\lambda) \exp(-t / \tau_i) \quad (1)$$

where  $\Delta A(\lambda, t)$  is the observed absorption change at a given wavelength at time delay  $t$  and  $n$  is the number of kinetic components used in the fitting. A plot of  $A_i(\lambda)$  versus wavelength is called

a DAS and represents the amplitude spectrum of the  $i^{\text{th}}$  kinetic component, which has a lifetime of  $\tau_i$ . Random errors associated with the reported lifetimes obtained from transient absorption measurements were typically  $\leq 5\%$ . Rigorous analysis of time resolved emission and absorption data in a non-homogeneous system requires the use of a model which considers a distribution of multi-exponential decays to describe the kinetics of each transient species and thus accounts for the distribution of available environments in the heterogeneous system. In our analysis we used the minimum number of exponential components that adequately fitted the experimental data within the experimental error. Thus it is likely that the reported decay components correspond to a weighted mean value of the actual distribution of constants associated with each species.

***Dynamic Light Scattering Measurements.*** Dynamic light scattering measurements were performed on a Malvern Zetasizer Nano S with detector  $173^\circ$  from the incident beam and a laser wavelength of 633 nm. Nanoparticles of  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Ta}_2\text{O}_5$  were separately suspended in ethanol and measurements were taken at a temperature of  $25^\circ\text{C}$ , with single size distributions observed for each sample.  $\text{Ta}_2\text{O}_5$  and  $\text{Cu}_2\text{O}$  precursor nanoparticles have size distributions centered around 60 nm and 90 nm, respectively, with  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  nanoparticles having a lower size distribution centered around 12 nm. This is due to the dissolution of the precursors in the  $\text{CuCl}$  flux and then re-crystallization at a smaller size.

***Electronic Absorption Spectroscopy of Nanoparticle Solutions.*** Electronic absorption spectra were taken of suspended particles in ethanol using a Shimadzu UV 3600. The suspensions of  $\text{Cu}_2\text{O}$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  show different absorption profiles shown in Figure S8.  $\text{Cu}_2\text{O}$  absorbs around 2.3 eV,  $\text{Ta}_2\text{O}_5$  absorbs around 4.0 eV and  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$  absorbs around 3.0 eV.

***Field Emission Scanning Electron Microscopy and Energy Dispersive Spectroscopy (FESEM/EDS).*** FESEM/EDS measurements were taken on an FEI Verios 460L field emission scanning electron microscope. Nanoparticle films were deposited from an ethanol solution, then annealed at 200 °C for 2 h under dynamic vacuum. Images show nanoparticle films on fluorine doped tin oxide (FTO) with a Cu-Ta ratio of 2:1, in agreement with the Cu-Ta ratio in  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ . Small amounts of Sn are also detected from the FTO substrate. Elemental mapping shows the coverage of Cu and Ta across the entire area of the film.

***X-ray Diffraction of Annealed Films.*** Suspended nanoparticles in ethanol were deposited on fluorine doped tin oxide (FTO) and allowed to dry in air leaving a film of the nanoparticles. The film was heated to 500 °C for 3 h under dynamic vacuum and allowed to cool to room temperature before removing from the tube furnace. Scotch tape was then used to remove the film from the FTO and taken for X-ray diffraction (XRD). Diffraction patterns of the material match the calculated pattern for  $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ , with peaks indexed in Figure S17. Preferential orientation is observed for the thin films with dominant diffraction on the (112) reflection.

## REFERENCES

1. Odobel, F.; Pellegrin, Y. Recent Advances in the Sensitization of Wide-Band-Gap Nanostructured p-Type Semiconductors. Photovoltaic and Photocatalytic Applications. *J. Phys. Chem. Lett.* **2013**, *4*, 2551-2564.
2. Mitchell, D.R.; Schaffer, B. Scripting-Customized Microscopy Tools for Digital Micrograph. *Ultramicrosc.* **2005**, *103*, 319-332.
3. Van Stokkum, I.H.M.; Larsen, D.S.; Van Grondelle, R. Global and Target Analysis of Time-Resolved Spectra. *Biochim. Biophys. Acta* **2004**, *1657*, 82-104.