

Supporting Information for

Effect of a Phosphonate Anchoring Group on the Excited State Electron

Transfer Rates from a Terthiophene Chromophore to a ZnO Nanocrystal

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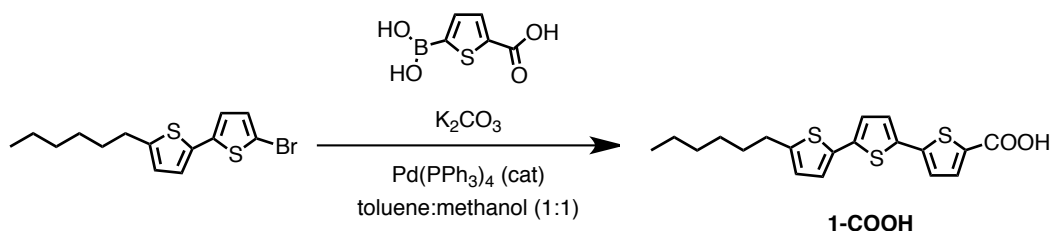
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Synthesis and Characterization of 1-COOH. ¹H NMR spectra were recorded on a JEOL Eclipse 300 MHz spectrometer. The chemical shifts are reported in ppm and referenced to the residual DMSO peak (2.50 ppm). Synthetic procedures were carried out under an inert atmosphere of nitrogen. Pd(PPh₃)₄ (Strem Chemicals Inc.) and 5-borono-2-thiophenecarboxylic acid (Frontier Scientific) were purchased and used as received. 5'-Bromo-5-hexyl-2,2'-bithiophene¹ was prepared as previously reported. **1-COOH** was prepared via Suzuki coupling² as follows:



To a 50 mL two-necked round bottom flask was added K_2CO_3 (0.630 g, 4.56 mmol), 5'-bromo-5-hexyl-2,2'-bithiophene (0.500 g, 1.52 mmol), toluene (5 mL), and methanol (5 mL). The mixture was purged with N_2 for 10 min followed by the addition of 5-borono-2-thiophenecarboxylic acid (0.392 g, 2.28 mmol) and $Pd(PPh_3)_4$ (0.053 g, 0.046 mmol). The mixture was purged with N_2 for an additional 5 min and was then heated to 75 °C for 3 h. After cooling, 20 mL of 0.5 M aqueous HCl was added to the mixture with stirring. The crude material was filtered and washed with hexanes (3 x 5 mL), methanol (3 x 3 mL) and hexanes (2 x 3 mL) to afford 0.422 g (74%) of **1-COOH** as a yellow solid. 1H NMR (DMSO- d_6): δ 7.66 (d, $J = 3.9$ Hz, 1H), 7.43 (d, $J = 3.9$ Hz, 1H), 7.36 (d, $J = 3.9$ Hz, 1H), 7.23 (d, $J = 3.9$ Hz, 1H), 7.19 (d, $J = 3.6$ Hz, 1H), 6.83 (d, $J = 3.6$ Hz, 1H), 2.79 (t, 2H), 1.62 (m, 2H), 1.29 (m, 6H), 0.86 (t, 3H). Note: no carboxylic acid proton was observed. Elem. Anal. Obs. C, 59.53; H, 5.17; Calcd C 60.60; H, 5.35

Electrochemistry. The cyclic voltammetry of **2- PO_3^{2-}** is shown in Figure S1. The first oxidation wave appears at +1.10 V vs Ag/AgCl. In order to approximate the standard reduction potential E^0 for Dye^-/Dye^{2-} , 50 mV ($1/2$ of the commonly observed peak-to-peak separation for a quasi-reversible process) was subtracted from the +1.10 V peak, yielding a value of +1.05 V vs Ag/AgCl. This yields a standard reduction potential of +1.25 V vs NHE, which was used to calculate E^* . The cyclic voltammetry **2- PO_3H_2** exhibits one irreversible oxidation at a standard reduction potential E^0 for Dye^+/Dye of +1.51 V vs NHE.

In the cyclic voltammetry of **1-COO $^-$** the first oxidation wave appears at +0.91 V vs Ag/AgCl. In order to approximate the standard reduction potential E^0 for Dye/Dye^- , 50 mV was subtracted from the +0.91 V peak, yielding a value of +0.86 V vs Ag/AgCl. This yields a potential of +1.05 V vs NHE for the E^0 of Dye/Dye^- , which was used to calculate E^* . The cyclic

voltammetry **1-COOH** yields one quasi-reversible oxidation and a standard reduction potential E^0 for Dye^+/Dye of +1.34 V vs NHE.

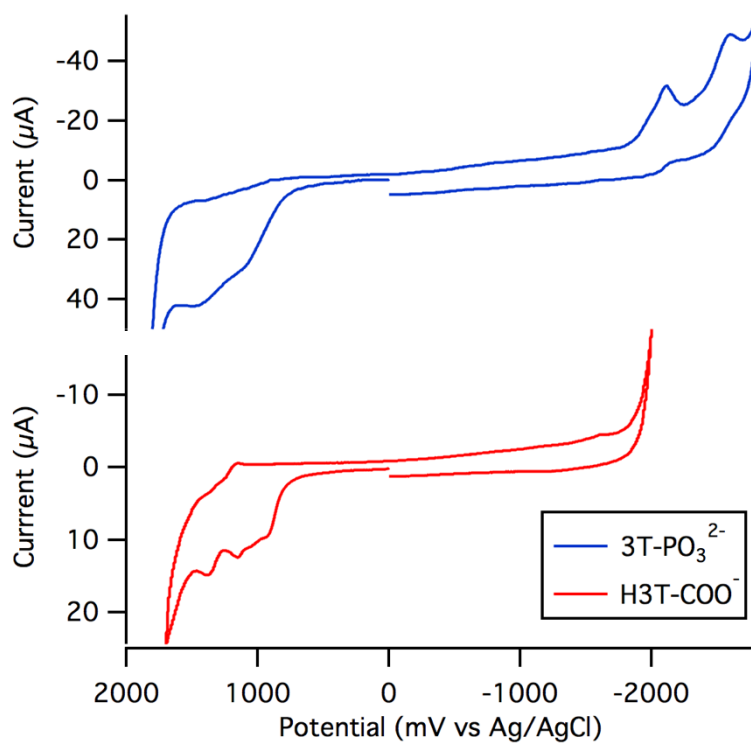


Figure S1: Cyclic voltammetry of **1-COO⁻** and **2-PO₃²⁻** in CH₂Cl₂ or DMF, respectively, using a Ag/AgCl reference electrode, carbon counter electrode, and platinum working electrode. The scan rate 100 millivolts per second.

Electronic Absorption Spectra of the Reaction of $[\text{NO}]^+$ with Dyes. As can be seen in Figure S2, seconds after the addition of $[\text{NO}][\text{PF}_6]$ to a CH_2Cl_2 solution of **1-COOH** there is a decrease in the absorption at 3.2 eV due to **1-COOH** and the appearance of a new peak at 2.19 eV. After 4 minutes, both peaks due to **1-COOH** and the 2.19 eV peak (attributed to the oxidized dye) are replaced with a peak at 2.88 eV attributed to a product or mixture of products that were not further characterized. Due to the low solubility of $[\text{NO}][\text{PF}_6]$ in CH_2Cl_2 , the oxidation of the starting dye is not instantaneous.

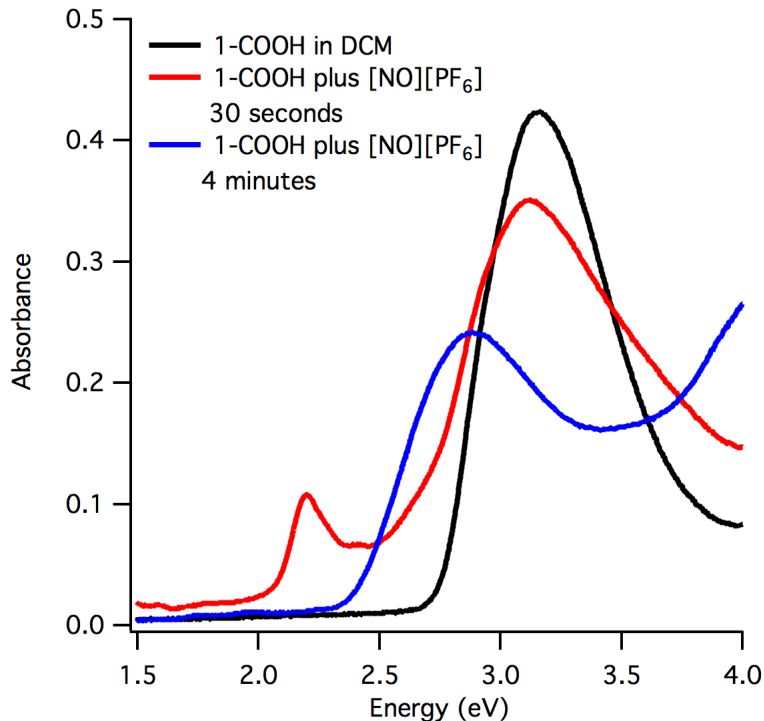


Figure S2: UV-Vis spectra of **1-COOH** in CH_2Cl_2 by $[\text{NO}][\text{PF}_6]$. The black line represents the initial **1-COOH** absorbance. The red line was taken within 30 seconds of the $[\text{NO}][\text{PF}_6]$ addition. The blue line was taken 4 minutes after $[\text{NO}][\text{PF}_6]$ addition.

Figure S3 displays the spectral changes resulting from addition of [NO][PF₆] to an acetonitrile solution of **2-PO₃H₂**. After the initial addition of [NO][PF₆], the **2-PO₃H₂** peak disappears, and the peaks attributed to oxidized dye (2.08 eV) and an unidentified product (2.92 eV) appear, along with peaks at 3.18, 3.32, 3.45, 3.57, and 3.68 eV due to NO.³ The feature at 2.92 eV may be due to the formation of the diphosphonate of sexithiophene based its similar absorbance to the 2.88 eV absorbance observed in the monophosphonic acid of sexithiophene.⁴ This product was not further characterized.

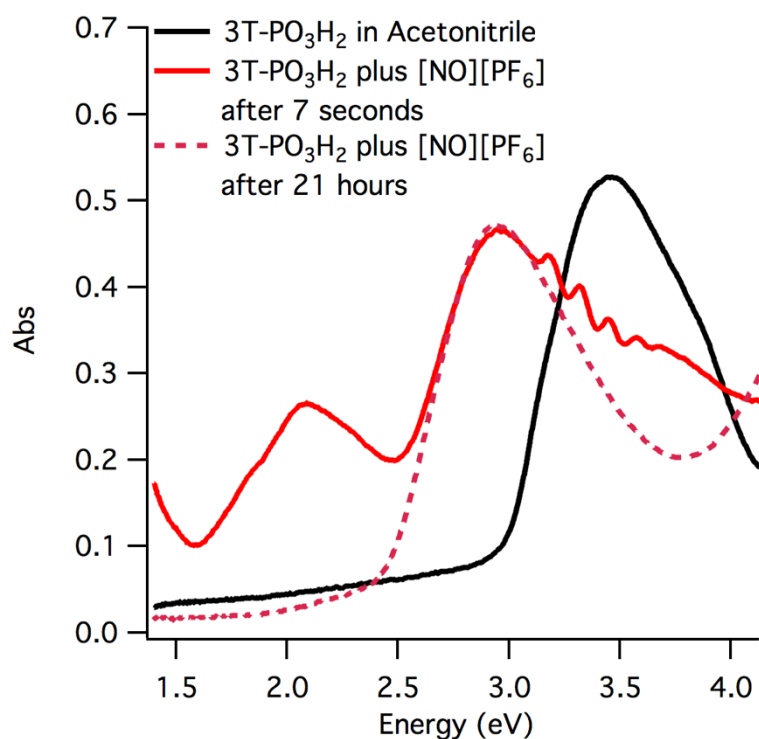


Figure S3: UV-Vis spectra of **2-PO₃H₂** (2.07×10^{-4} M) in CH₃CN (black line), 7 seconds (solid red line) and 21 hours (dashed red line) after addition of 5 mg of [NO][PF₆]. The reaction was conducted under N₂.

Deconvolution of the Ultrafast Spectra of the 2:1 Dye:ZnO NC Solutions. The figures shown below depict the results of the spectral analysis routine. Each figure shows the resulting optimization at the indicated probe delay time. In black, solid line, the raw full frequency data is plotted. The red dashed line depicts the weighted component of the dye transient absorption. The blue dashed line depicts the weighted component of the oxidized dye attached to the reduced nanoparticle transient. The green dashed line depicts the sum of the dye and nanoparticle components and represents the optimized fit to the raw data.

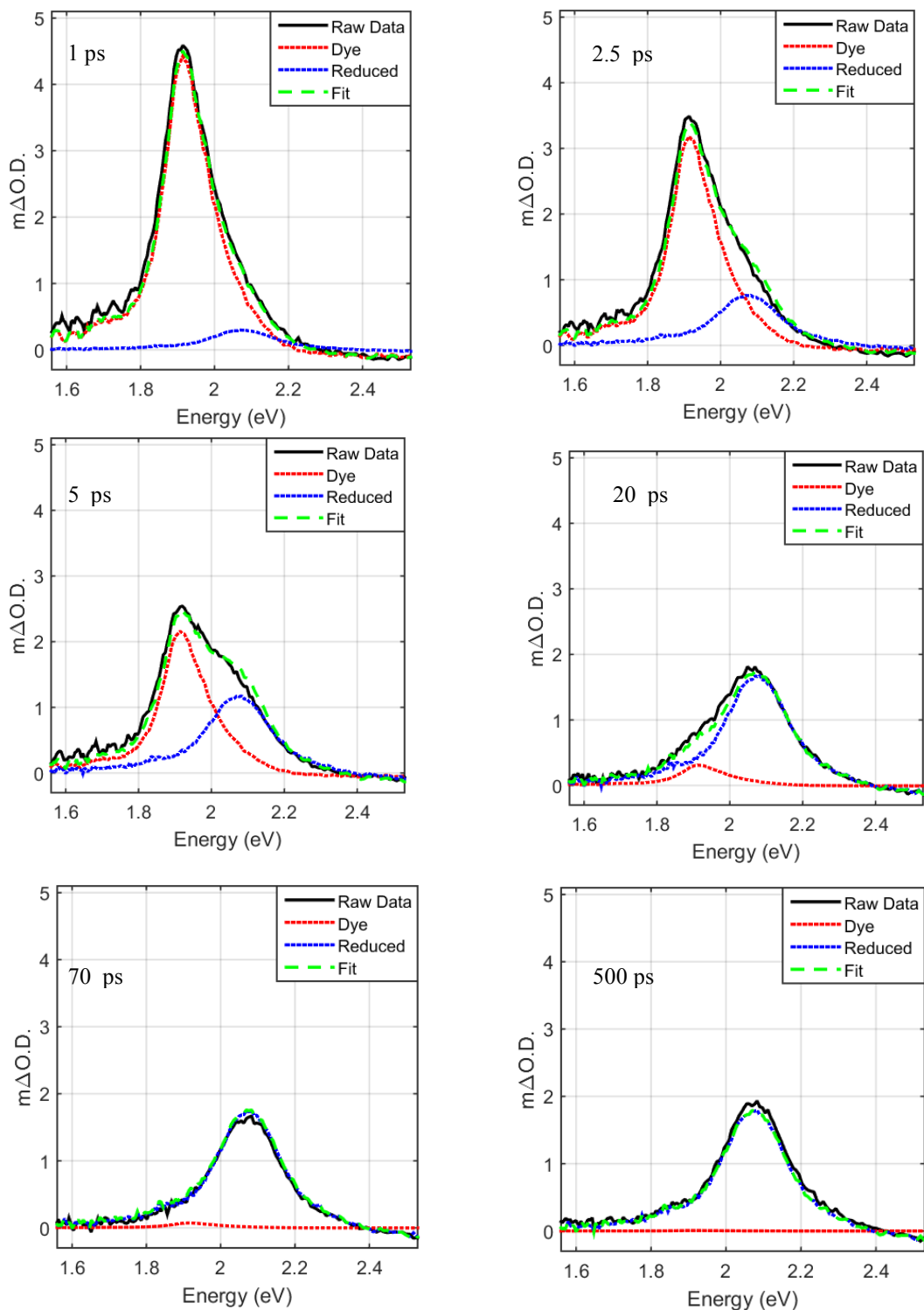


Figure S4. Pump probe spectra of 2:1 phosphonate dye to NC solutions. The dashed red lines labelled “Dye” refer to the transient absorption s of the adsorbed dye excited state. The dashed blue lines labelled “Reduced” refer to the fits to the transient absorption after electron transfer has reduced the NC and oxidized the dye. The dashed green lines are the sum of the two independent contributors to the raw data (solid black lines)

Ultrafast Signal Decay of 20:1 2-PO₃²⁻:ZnO NC Solutions. Figure S5 displays the changes in the TA of the 20:1 2-PO₃²⁻:ZnO NC sample and is modeled with eq. 7. Two exponential functions with lifetimes $\tau_1 = 0.9 \pm 0.1$ ps ($A = 0.52 \pm 0.04$) and $\tau_2 = 7 \pm 1$ ps ($B = 0.41 \pm 0.05$) along with a Heaviside function ($C = 0.07 \pm 0.01$) were required to fit the disappearance of the TA of the singlet excited state.

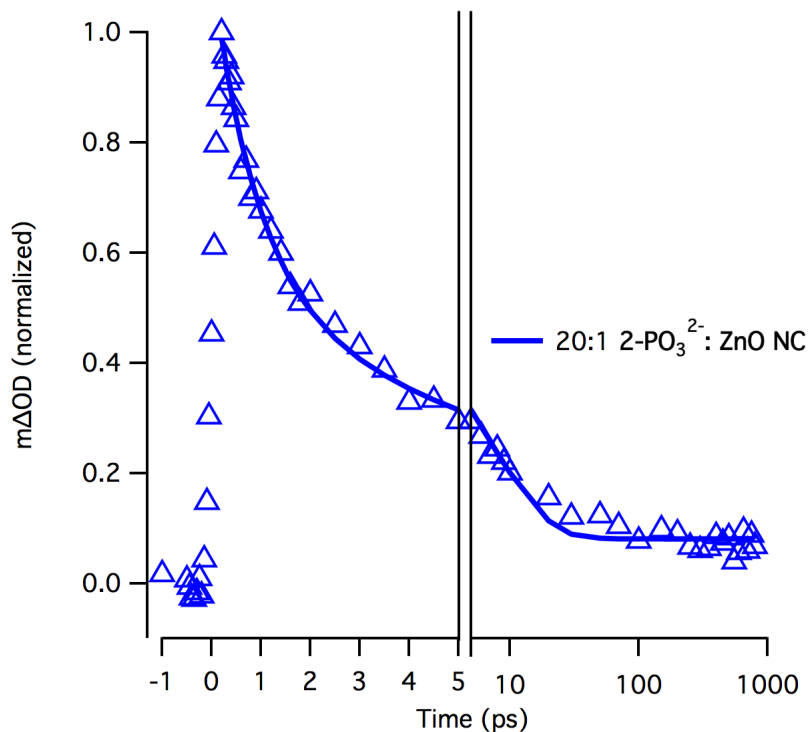


Figure S5: Graph of time dependent changes in the TA at 2.10 eV for 20:1 2-PO₃²⁻: ZnO NC solutions showing the decay (triangles) and fit (blue line) of the transient absorption.

Excitation at 400 nm Does Not Lead to ZnO Emission. In Figure S6 the purple line shows the steady state absorbance of ZnO NCs in methanol and the red lines show the fluorescence of this solution using 360 and 400 nm excitation wavelengths. The black lines show the fluorescence from a methanol solution of 2-PO₃²⁻ (no ZnO NCs) at the same excitation wavelengths. The blue lines show the fluorescence from a 2:1 2-PO₃²⁻:ZnO NC solution using

360 and 400 nm excitation wavelengths. These results demonstrate that irradiation at 400 nm does not excite the ZnO NCs of the diameters used in this study.

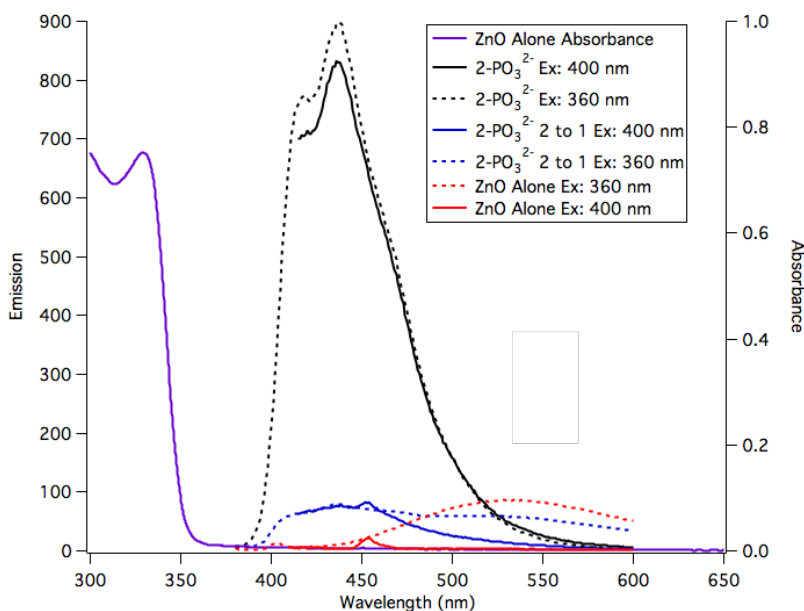


Figure S6: UV-Vis absorption of ZnO, Fluorescence of 2-PO_3^{2-} and 2:1 2-PO_3^{2-} to ZnO NCs excited at 400 nm (solid) and 360 nm (dashed). 2-PO_3^{2-} concentration is 2.26×10^{-6} M and ZnO NC concentration is 1.13×10^{-6} M.

References

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