

Supporting Information for

Negative Polaron and Triplet Exciton Diffusion in

Organometallic “Molecular Wires”

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Procedure for Fitting Pulse Radiolysis Dynamics to Kinetic Model.

The kinetic data in Figure 3b was fitted using the reactions in Table 1 (table in main text). First we report rate constants for electron attachment, which are needed to evaluate rates of polaron transport, reaction (e) in Table 1. Rate constants for attachment of solvated electrons in THF to oligomers having NDI end caps are listed in Table S-1 below, along with those recently reported for attachment to a series of Pt_n oligomers, n=1-5.¹

Table S-1. Rate Constants for electron attachment to platinum acetylide oligomers (M) in THF at 296 K.

M	k (M ⁻¹ s ⁻¹)	M	k (M ⁻¹ s ⁻¹) ^a
Pt ₂ NDI ₂	1.24 x 10 ¹¹	Pt ₁	9.8 x 10 ¹⁰
Pt ₆ NDI ₂	1.70 x 10 ¹¹	Pt ₂	1.7 x 10 ¹¹
Pt ₁₀ NDI ₂	3.60 x 10 ¹¹	Pt ₃	2.1 x 10 ¹¹
NDIH	4.78 x 10 ¹⁰	Pt ₄	2.5 x 10 ¹¹
		Pt ₅	3.2 x 10 ¹¹

^a Data from ref. ¹

Before fitting the data for Pt₁₀NDI₂, a small contribution to the transient absorption signal arising from the Pt-acetylide chain triplet excited state was subtracted. This correction utilized a measured triplet contribution triplet absorption at 650 nm and the ratio of extinction coefficients for the triplet determined in the photoexcitation experiments. The reaction rate constants were then determined within the set of reactions in Table 1 to account for both geminate and homogeneous recombination with the counter ions by dividing the system into a homogeneous fraction and two geminate fractions. A kinetic model was fit to the data using non-linear least squares fitting in Igor Pro software (Wavemetrics). The kinetic fitting strategy, described in some detail previously,² begins with a description of electron production and decay in neat THF solvent. The solvent parameters are then held fixed during fitting the attachment dynamics to Pt₄, and decay of Pt₄^{•-}, before fitting Pt₁₀NDI₂. In Figure 3, absorbance due to Pt₄^{•-} is seen to grow with a time constant of 0.13 ns. This is faster by a factor of 1.6 than expected from the rate

constant in Table S-1 due to transient terms found for diffusion-controlled reactions of long molecules.^{3,4} A similar increase was found for Pt₁₀NDI₂ measured utilizing decay of absorbance due to solvated electrons at 950 nm. Measurement of fast transport is facilitated by ultrafast production of a fraction of the anions in a “step” process that is complete within the 15 ps instrument time resolution. The step process is due to capture of electrons prior to solvation, which occurs with probability $1 - \exp(-qc)$, where c is the concentration of the Pt₄ or Pt₁₀NDI₂ molecules. As expected, capture of pre-solvation electrons is found to be more effective for Pt₁₀NDI₂, ($q = 72 \text{ M}^{-1}$) than for the shorter Pt₄, ($q = 29.9 \text{ M}^{-1}$), so that 40% of the electrons are captured in the fast “step” process.

Fits to the data find that attachment of solvated electrons, comprising 60% of the total, to Pt₁₀NDI₂ occurs with a pseudo first order rate constant of $(k [\text{Pt}_{10}\text{NDI}_2])^{-1} = 114 \text{ ps}$, which is slower than the 59 ps time of transport for most electrons to the NDI end traps. The step capture is very important, but still this slow attachment reduces accuracy of determination of the transport rate to $\pm 30\%$. Higher accuracy could be obtained if Pt₁₀NDI₂ were soluble to higher concentrations.

A fraction (15%) of the electrons in the chains of Pt₁₀NDI₂ transport much more slowly, $\sim 660 \text{ ps}$. The reason for this slow transport is not known, but we suggest an explanation. Of the electrons that attach to Pt₁₀NDI₂ 60% are geminate: the Pt₁₀NDI₂ anions formed are Coulomb-bound to counter ions, which in THF are solvated protons (RH_2^+ in Table 1) of the manuscript. These geminate Pt₁₀NDI₂^{-•}, RH_2^+ pairs recombine in $\sim 10 \text{ ns}$. The absence of a large, 10 ns decay in the case of Pt₄ tells us that this recombination does not eliminate the anions, but is nonreactive, creating ion-pairs. We speculate that $\sim 15\%$ of the Pt₁₀NDI₂^{-•} anions form (Pt₁₀NDI₂⁻

\cdot, RH_2^+) ion pairs prior to transport of the electronic polarons to the NDI end traps, and that transport of the pairs along the chains is much slower than transport of free polarons.

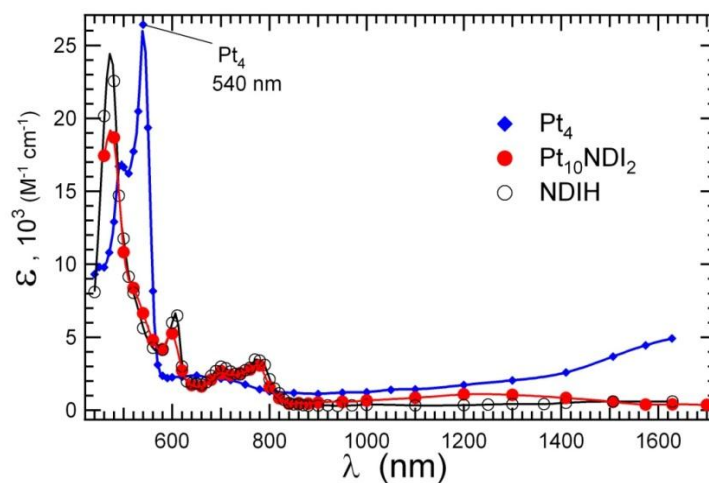


Figure S1. Visible and near infrared spectra of $\text{Pt}_{10}\text{NDI}_2^{\cdot-}$ and $\text{NDIH}^{\cdot-}$ obtained from transient absorptions at ~ 30 ns after pulse radiolysis in THF. The spectra are compared with that for $\text{Pt}_4^{\cdot-}$.

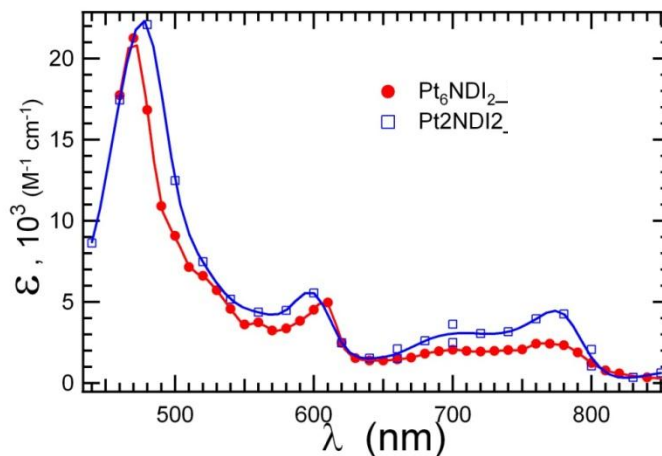


Figure S2. Spectra of $\text{Pt}_2\text{NDI}_2^{\cdot-}$ and $\text{Pt}_6\text{NDI}_2^{\cdot-}$ obtained from transient absorption at ~ 30 ns after pulse radiolysis in THF.

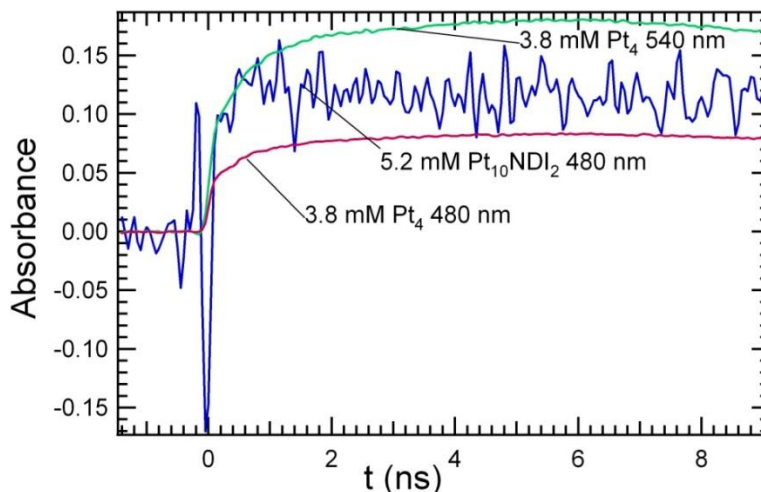


Figure S3. Transient absorption at 480 nm showing the formation of NDI₂^{•-} in a 5.2 mM solution of Pt₁₀NDI₂ in THF. The measurement was taken using a biplanar phototube detector (150 ps nominal time resolution). The data are very noisy due to intense absorption by the Pt₁₀NDI₂ molecules, which reduces the probe light intensity by a factor of ~100 at this high concentration. In addition to noise the data are affected during the first ~300 ps by emission. The noisy measurements on Pt₁₀NDI₂ are compared with observations on Pt₄ at 480 nm, and at the 540 nm spectral maximum of Pt₄^{•-}. The absorption at 480 nm in the Pt₁₀NDI₂ solution, relative to those in the Pt₄ solution, is consistent with nearly complete transfer of electrons to the NDI end groups by ~500 ps.

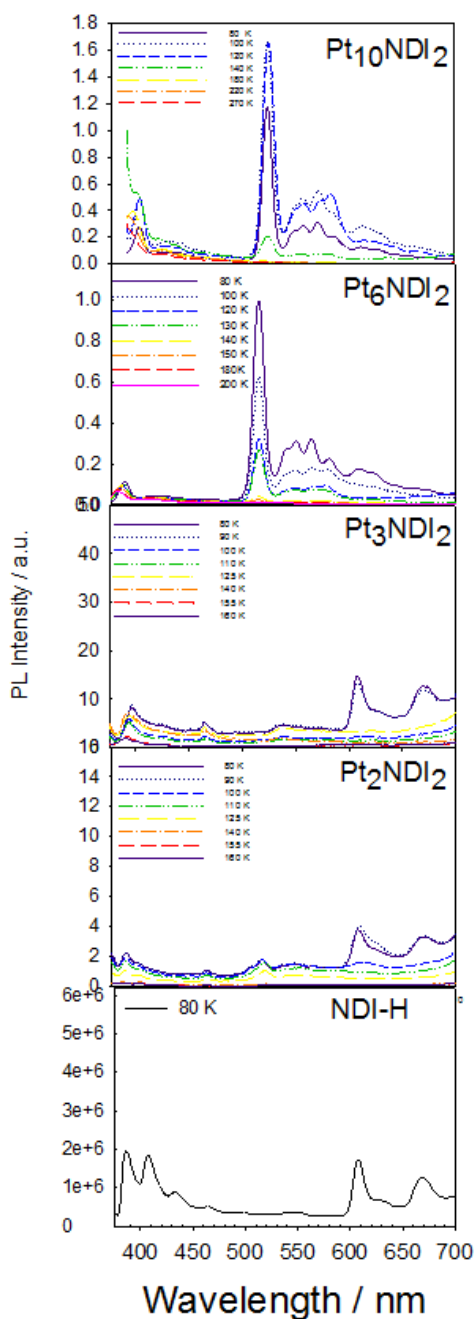


Figure S4. Steady state emission spectra of the Pt_nNDI_2 oligomers and NDI-H in 2-methyltetrahydrofuran solvent at temperatures ranging from 80 – 200 K. Excitation was at 350 nm (absorption of Pt-acetylide chain). The intense phosphorescence band is seen for $\text{Pt}_{10}\text{NDI}_2$ and Pt_6NDI_2 for $T < 130$ K, but it disappears above the solvent glass-to-fluid temperature (~ 140 K). This phosphorescence band is not seen for the shorter oligomers Pt_3NDI_2 and Pt_2NDI_2 , even at very low temperature in the solvent glass.

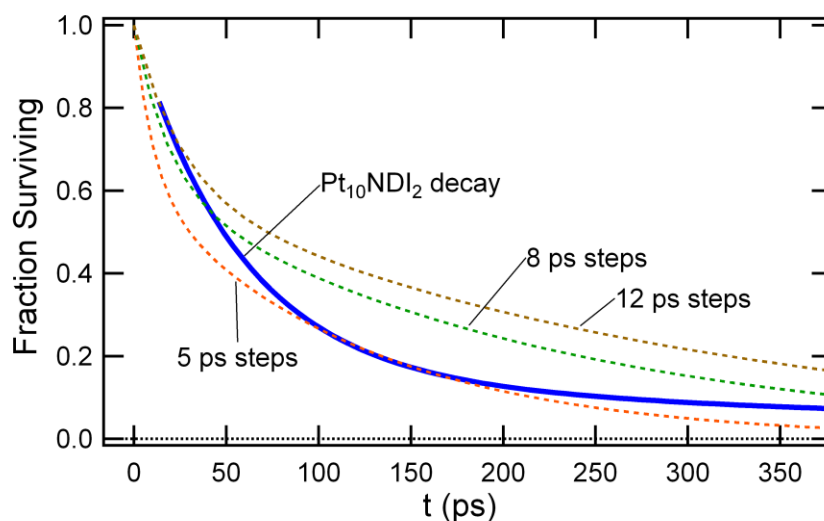


Figure S5. Solid line: Bi-exponential decay function recovered from the fit of the experimental pulse radiolysis data for transport of electrons from the Pt-acetylide chain to the NDI end-group in $\text{Pt}_{10}\text{NDI}_2$ (amplitude = $\alpha_1 \exp\{-k_1 t\} + \alpha_2 \exp\{-k_2 t\}$, with $1/k_1 = 59$ ps, $\alpha_1 = 0.53$ and $1/k_2 = 660$ ps, $\alpha_2 = 0.09$) normalized to 1 at $t = 0$. Broken lines are calculated using the random walk model with the step times indicated in the plot.

References for Supporting Information

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