Supporting Information

Watching Intermolecular Light-induced Charge Accumulation on Naphthalene Diimide by Tris(bipyridyl)ruthenium(II) Photosensitizer

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**Figure S1.** Absorption spectra of $[\text{Ru(bpy)}_3]^2+$ (13 $\times$ 10$^{-6}$ M) $[\text{Ru(bpy)}_3]^2+$ + ascorbate (100 mM); and $[\text{Ru(bpy)}_3]^2+$ + ascorbate + NDI (31 $\mu$M).

**Figure S2.** (a) TA spectra at indicated delay times and (b) kinetic trace at 450 nm of $[\text{Ru(bpy)}_3]^2+$ 13 $\times$ 10$^{-6}$ M in deaerated CH$_3$CN/H$_2$O (60:40), $\lambda_{\text{exc}}$ = 460 nm.
Figure S3. (a) TA spectra at indicated delay times and (b) second-order rate plotted for $1/[\text{Ru}^+]$ vs. time at 510 nm of a solution involving $[\text{Ru(bpy)}_3]^{2+}$ 13x10$^{-6}$ M, ascorbate 100 mM in deaerated CH$_3$CN/H$_2$O (60:40), $\lambda_{\text{exc}} = 460$ nm.

Figure S4. TA spectra (a), and temporal evolution (b) of Ru$^+$, NDI$^-$, and NDI$^{2-}$ states at the indicated delay times of the solution $[\text{Ru(bpy)}_3]^{2+}$ (13 $\mu$M), ascorbate (100 mM), and NDI (31 $\mu$M) in deaerated CH$_3$CN/H$_2$O (60:40); Single pump excitation at 460 nm.

Dependence of double charge transfer on the concentration of $[\text{Ru(bpy)}_3]^{2+}$ under single laser excitation

The series TA experiments were performed for different concentrations of $[\text{Ru(bpy)}_3]^{2+}$ in the same conditions of NDI and ascorbate to clarify the dependence of the formation NDI$^{2-}$ on $[\text{Ru(bpy)}_3]^+$. Figure S5 shows the absorption spectra of different concentration of $[\text{Ru(bpy)}_3]^{2+}$ in the same concentrations of NDI and ascorbate.
**Figure S5.** Absorption spectra of different multicomponent systems including the same concentration of NDI and ascorbate, changing concentration of [Ru(bpy)$_3^{2+}$]

Table S1 presents the characteristic times and concentrations of the component species, which were obtained by decomposition analyzing treatment.

<table>
<thead>
<tr>
<th>Time (µs)</th>
<th>$t_{\text{decay}}$ Ru$^+$ [Ru]$^+$ (µM)</th>
<th>$1^{\text{st}}$ $t_{\text{rise}}$ NDI$^{-}$ [NDI$^{-}$] (µM)</th>
<th>$2^{\text{nd}}$ $t_{\text{rise}}$ NDI$^{-}$</th>
<th>$t_{\text{decay}}$ NDI$^-$ [NDI$^-$] (µM)</th>
<th>$t_{\text{rise}}$ NDI$^{2-}$ [NDI$^{2-}$] (µM)</th>
<th>$t_{\text{decay}}$ NDI$^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru 13 µM NDI - asc</td>
<td>5.7(±0.05) 5.5(±0.2)</td>
<td>4.6(± 0.07) 4.3(±0.2)</td>
<td>76(±4)</td>
<td>3266(±158)</td>
<td>9.01(±0.2) 0.67(±0.06)</td>
<td>71.5(±2)</td>
</tr>
<tr>
<td>Ru 28 µM NDI-asc</td>
<td>5.1±0.09 11.7 (±0.3)</td>
<td>3.2±0.05 7.5(±0.3)</td>
<td>89±2</td>
<td>2218±31</td>
<td>9.1±0.3 2(±0.2)</td>
<td>92.8±3.5</td>
</tr>
<tr>
<td>Ru 42 µM NDI-asc</td>
<td>5.2 ±0.1 16±(1)</td>
<td>2.4±0.03 7.8(±0.2)</td>
<td>121±2</td>
<td>2118±24</td>
<td>9.1±0.2 4(±0.2)</td>
<td>127±5</td>
</tr>
</tbody>
</table>

Table S1. The characteristic times and concentrations of the component species involving [Ru(bpy)$_3^{2+}$] (denoted as Ru$^+$), NDI$^{-}$, and NDI$^{2-}$, in which the concentration of NDI$^{-}$ refers to the initial single electron transfer. The solution [Ru(bpy)$_3^{2+}$], ascorbate (100 mM), and NDI (31 µM) in deaerated CH$_3$CN/H$_2$O (60:40); Single pump excitation at 460 nm.
Figure S6. Plot of ΔA of NDI$^{\cdot -}$ at 480 nm (black curve) and NDI$^{2 -}$ corrected in subtracting the contribution of NDI$^{\cdot -}$ at 400 nm (blue curve) versus laser pulse energy of single-pulse excitation after 15 µs. The blue curve is the normalized curve of NDI$^{2 -}$ to be clearer in comparison with NDI$^{\cdot -}$.

Figure S7. TA kinetic traces at 400 nm (corresponding to the absorption of NDI$^{2 -}$), were corrected by removing the contribution of the NDI$^{\cdot -}$ of the solution [Ru(bpy)$_3$]$^{2+}$ (13µM), ascorbate (100 mM), and NDI (31 µM) in deaerated CH$_3$CN/H$_2$O (60:40), upon double-pulse excitation (460 nm, separated by 300 µs, first pump at 10 Hz, second pump at 10 Hz). The corrected kinetic traces were calculated using the method indicated in Figure 3. The red and the green curves show the time traces of the two single pulse excitations with each laser and the black curve presents the kinetic of double pulse excitation.
Figure S8. TA kinetic traces at 480 nm of the NDI$^••$ of the solution [Ru(bpy)$_3$]$^{2+}$ (13 µM), ascorbate (100 mM), and NDI (31 µM) in deaerated CH$_3$CN/H$_2$O (60:40), upon double-pulse excitation (460 nm, separated by 300 µs, first pump at 10 Hz, second pump at 10 Hz). The different intensity between the black curve (kinetic of double-pulse excitation) and the blue curve (kinetic of the total two single pulse together). The final $\Delta A = 0.22 \pm 0.02$ of the NDI$^••$ in double-pulse laser excitation indicates the concentration of 9.5 (±0.5) µM (using a $\Delta \varepsilon_{480} = 23000$ M$^{-1}$.cm$^{-1}$).

Procedure for spectral decomposition

In this paragraph, we describe the process to decompose the measured spectra as a combination of the reference spectra characterizing the four intermediate species Ru$^*$, Ru$^I$, NDI$^•$, NDI$^{2−}$. For each delayed time t, we expressed the transient spectrum as a linear combination of the above basis:

$$\Delta A(t, \lambda) = [Ru^*]_t \times \varepsilon_{Ru^*}(\lambda) + [Ru^I]_t \times \varepsilon_{Ru^I}(\lambda) + [NDI^•]_t \times \varepsilon_{NDI^•}(\lambda) + [NDI^{2−}]_t \times \varepsilon_{NDI^{2−}}(\lambda),$$

where $[Ru^*]_t$, $[Ru^I]_t$, $[NDI^•]_t$, $[NDI^{2−}]_t$ are the set of concentration at time t and $\varepsilon_{Ru^*}(\lambda)$, $\varepsilon_{Ru^I}(\lambda)$, $\varepsilon_{NDI^•}(\lambda)$, $\varepsilon_{NDI^{2−}}(\lambda)$ are the reference absorption spectra of the intermediate species.

In order to determine the set of concentrations, we performed a least square optimization to fit this linear combination with the experimental data.

$$\min_{[Ru^*]_t,[Ru^I]_t,[NDI^•]_t,[NDI^{2−}]_t} [\Delta A^{exp}(t, \lambda) - \Delta A(t, \lambda)]^2$$

Here, $\Delta A^{exp}(t, \lambda)$ is the experimental spectrum and $\Delta A(t, \lambda)$ is the linear model of the transient spectrum at time t.

In Figure S7, we show how a single spectrum is decomposed on a given basis ($\varepsilon_{Ru^*}(\lambda)$, $\varepsilon_{Ru^I}(\lambda)$, $\varepsilon_{NDI^•}(\lambda)$, $\varepsilon_{NDI^{2−}}(\lambda)$).
Figure S9. Decomposition of a single transient spectrum at 7 µs delay time.

Repeating this process for all delayed times, we were able to characterize the dynamics of the different processes occurring in the multi-component photosystem. In the below figure, we present the temporal evolution of the concentrations \([Ru^+], [Ru^2+], [NDI^-], [NDI^{2-}]\) fitted over all our experimental data.

Figure S10. Temporal evolution of the concentration of different intermediate species obtained from spectral decomposition at all delay times.
Numerical solution and data fitting of the Ru-NDI experiment

In this session, we present the details of our numerical simulation of the kinetic equations and the fitting procedure of the concentrations in order to obtain the rate constants characterizing the different reactions. Let us first write down the different light-driven reactions:

1. Ru\(^*\) \rightarrow Ru\(^{II}\) + hv \quad \text{(with rate constant } k_0) \\
2. Ru\(^*\) + asc \rightarrow Ru\(^I\) + asc\(^+\) \quad \text{(with rate constant } k_q) \\
3. Ru\(^I\) + asc\(^+\) \rightarrow Ru\(^{II}\) + asc \quad \text{(with rate constant } k_{rec}) \\
4. Ru\(^I\) + NDI\(^-\) \rightarrow Ru\(^{II}\) + NDI\(^{--}\) \quad \text{(with rate constant } k_{et1}) \\
5. Ru\(^I\) + NDI\(^{--}\) \rightarrow 2NDI\(^{-}\) \quad \text{(with rate constant } k_{et2}) \\
6. NDI\(^{-}\) + NDI \rightarrow 2NDI\(^{-}\) \quad \text{(with rate constant } k_{rec1}) \\
7. NDI\(^2\) + asc\(^+\) \rightarrow NDI\(^-\) + asc \quad \text{(with rate constant } k_{rec1b}) \\
8. NDI\(^{--}\) + asc\(^+\) \rightarrow NDI + asc \quad \text{(with rate constant } k_{rec2})

The system of dynamic equations characterizing the time evolution of the concentrations for different species is given as following:

\[
\begin{align*}
\frac{d[Ru^*]}{dt} &= -k_0[Ru^*] - k_q[asc][Ru^*] \\
\frac{d[Ru^I]}{dt} &= k_q[asc][Ru^*] - k_{et1}[NDI][Ru^I] - k_{et2}[NDI^{--}][Ru^I] - k_{rec}[asc^+][Ru^I] \\
\frac{d[NDI]}{dt} &= -k_{et1}[NDI][Ru^I] + k_{rec2}[asc^+][NDI^{--}] - k_{rec1}[NDI][NDI^{--}] \\
\frac{d[NDI^{--}]}{dt} &= k_{et1}[NDI][Ru^I] - k_{et2}[NDI^{--}][Ru^I] + k_{rec1b}[asc^+][NDI^{--}] \\
&\quad - k_{rec2}[asc^+][NDI^{--}] + 2k_{rec1}[NDI][NDI^{--}] \\
\frac{d[NDI^{2--}]}{dt} &= k_{et2}[NDI^{--}][Ru^I] - k_{rec1b}[asc^+][NDI^{2--}] - k_{corr}[NDI][NDI^{2--}] \\
\frac{d[asc]}{dt} &= -k_q[asc][Ru^*] + k_{rec1b}[asc^+][NDI^{2--}] + k_{rec2}[asc^+][NDI^{--}] \\
\frac{d[asc^+]}{dt} &= k_q[asc][Ru^*] - k_{rec1b}[asc^+][NDI^{2--}] - k_{rec2}[asc^+][NDI^{--}] \\
&\quad - k_{rec}[asc^+][Ru^I]
\end{align*}
\]

with the initial condition at the beginning of these reactions (t=0):

\[ [Ru^*]_0, [NDI]_0, [asc]_0, [Ru^I]_0 = 0, [NDI^{--}]_0 = 0, [NDI^{2--}]_0 = 0, [asc^+]_0 = 0 \]

The above system of ordinary differential equations (ODE) can be solved numerically for a given set of rate constants and a given set of initial values of the concentration. In this paper, we employed the standard ODE method implemented within the Scipy library. This method consists of estimating the vector of derivative of the concentrations as well as the Jacobian of the right-hand side of the equations. Using the analytical formula of these quantities, we can propagate the numerical solution of the concentrations on a given grid of time. In order to better fit the data, we define a time grid with the equivalent timestep to experimental data.
Once the numerical solution can be obtained with the above implementation, we fitted the numerical solution to the data using the least square optimization in order to obtain the best rate constants. Let us denote \( y_t = (y_t^i) \) with \( i = 1 \ldots n \), the numerical solution of the vector of concentrations for a given set of rate constants \( (k_1, k_2, \ldots, k_n) \) and \( c_t = (c_t^i) \) with \( i = 1 \ldots n \), the \( n \) measured concentrations from the pump-pump-probe experiment. Hence the set of concentration is obtained by the following optimization program:

\[
\min \sum_{i=1}^{n} [y_t^i(k_1, k_2, \ldots, k_n) - c_t^i]^2
\]

In the figures below, we present the result of our fitting process with the experimental data described in the paper. With different samples, we obtain a very similar set of the rate constants allowing to fit the experimental data from a very small time scale (sub \( \mu \)s) to very large time scale (5000 \( \mu \)s).

**Figure S11.** Numerical fit to obtain the rate constants of different reactions from (1) to (8).

The set of rate constants obtained from the fit is the following:

- \( k_0 = (1.3 \pm 0.1) \times 10^6 \text{ s}^{-1} \),
- \( k_q = (2.7 \pm 0.3) \times 10^8 \text{ M}^{-1}\text{s}^{-1} \),
- \( k_{rec} = (2.8 \pm 0.3) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \),
- \( k_{ett1} = (5.8 \pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \),
- \( k_{ett2} = (8 \pm 2) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \),
- \( k_{rectb} = (0 \pm 0.2) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \),
- \( k_{rec1} = (5 \pm 1) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \),
- \( k_{rec2} = (4.5 \pm 0.3) \times 10^7 \text{ M}^{-1}\text{s}^{-1} \).