

# Supporting Information

## New Light-Harvesting Molecular Systems Constructed with a Ru(II) Complex and a Linear-shaped Re(I) Oligomer

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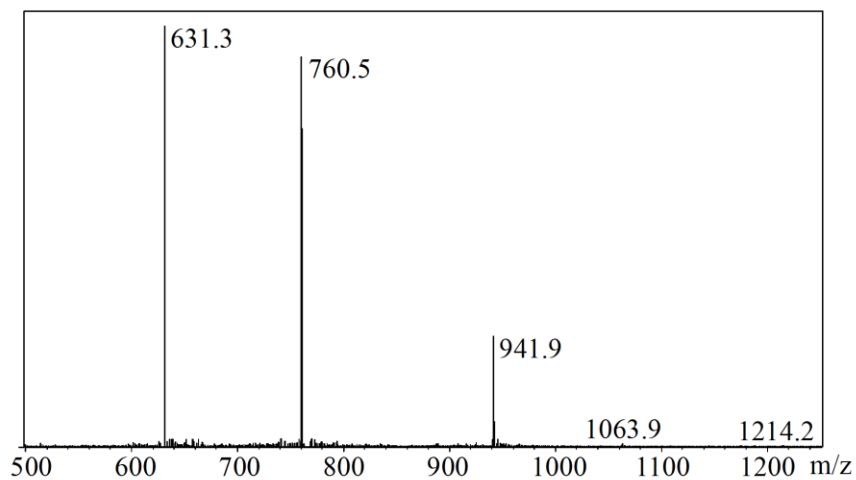


Figure S1. ESI-MS spectrum of **Ru-Re5**<sup>7+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>7</sub> dissolved in MeCN.

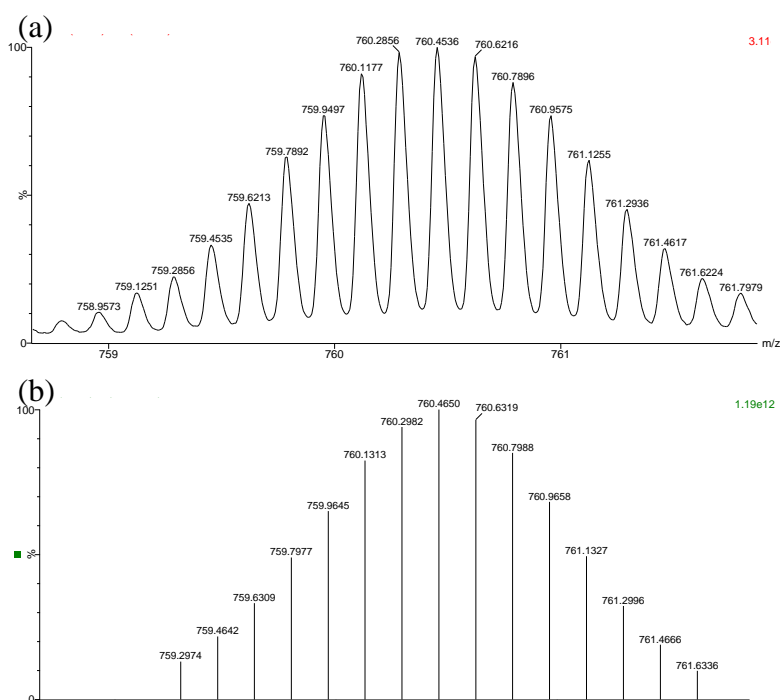


Figure S2. Peaks corresponding to  $[\mathbf{M} + (\text{PF}_6^-)]^{6+}$  in the ESI-TOFMS spectrum of **Ru-Re5**<sup>7+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>7</sub> (a), and the calculated isotope distribution pattern (b).

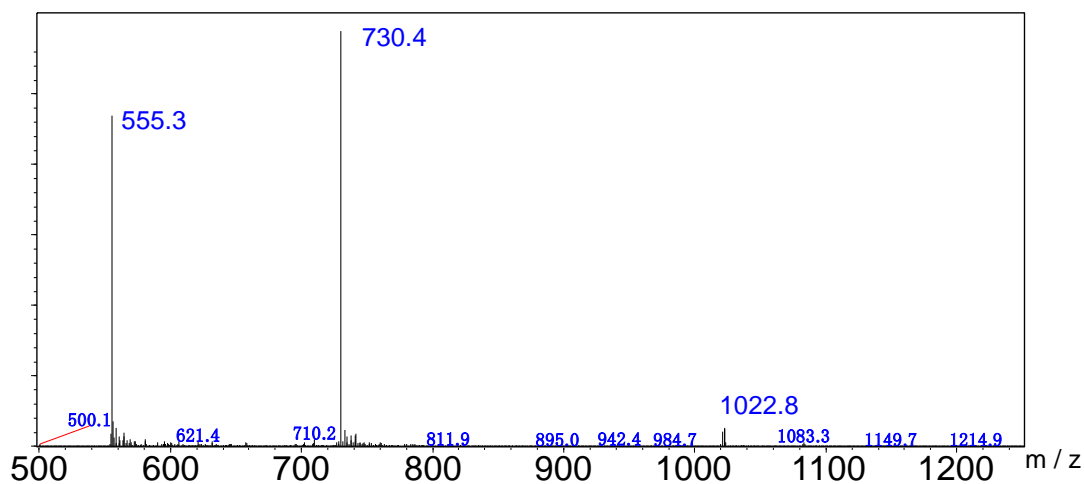


Figure S3. ESI-MS spectrum of **Ru-Re3A**<sup>5+</sup>(PF<sub>6</sub>)<sub>5</sub> dissolved in MeCN.

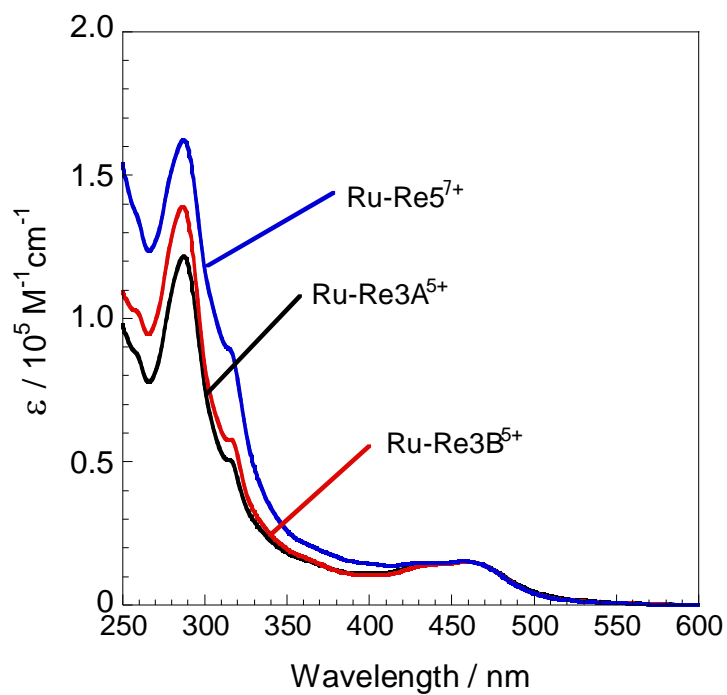


Figure S4. UV/vis absorption spectra of **Ru-Re3A**<sup>5+</sup> (black line), **Ru-Re3B**<sup>5+</sup> (red line) and **Ru-Re5<sup>7+</sup>** (blue line) in MeCN solutions.

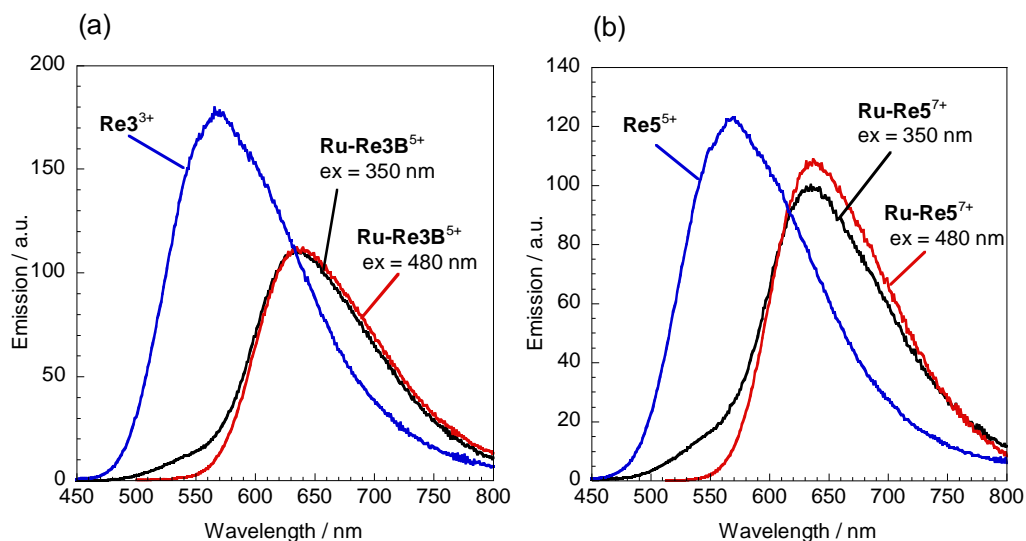


Figure S5. Emission spectra from degassed MeCN solutions containing the Ru(II)-Re(I) multinuclear complexes by excitation using 350- and 480-nm light and the corresponding Re(I) oligomers by excitation using 350-nm light: (a) **Ru-Re3B<sup>5+</sup>** and **Re3<sup>3+</sup>**; (b) **Ru-Re5<sup>7+</sup>** and **Re5<sup>5+</sup>**. They are standardized by the number of absorbed photons at the excitation wavelength.

### Calculations of the energy transfer rate constants from the terminal Re(I) unit to the interior

#### Re(I) unit ( $k_1(\text{Re3}^{3+})$ ) and the radiative and non-radiative rates from each Re(I) units in **Re3<sup>3+</sup>**.

The emission decay of **Re3<sup>3+</sup>** could be fitted with the following double-exponential functions: with  $\tau = 15$  ns and 893 ns which can be attributed to the emission from the terminal and the interior Re(I) units, respectively.

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (\text{S1})$$

Therefore, the energy transfer rate constant from the excited terminal Re(I) unit to the interior Re(I) unit ( $k_1(\text{Re3}^{3+})$  in Scheme 3e) can be calculated using the summed rate constant of the radiative and non-radiative decay from the terminal Re(I) unit ( $k_r(\text{Re3}^{3+}, \text{terminal}) + k_{nr}(\text{Re3}^{3+}, \text{terminal})$ ) and the following equation:

$$k_1(\text{Re3}^{3+}) = \frac{1}{15 \times 10^{-9}} - [k_r(\text{Re3}^{3+}, \text{terminal}) + k_{nr}(\text{Re3}^{3+}, \text{terminal})] \quad (\text{S2})$$

The emission decay of the dimer Re(I) complex,  $[(\text{CO})_3(\text{dmb})\text{Re-PP-Re}(\text{dmb})(\text{CO})_3]^{2+}$  (**Re2<sup>2+</sup>**), has a similar structure as the terminal Re(I) unit in **Re3<sup>3+</sup>** and could be fitted to a single-exponential with 537 ns. If  $[k_r(\text{Re3}^{3+}, \text{terminal}) + k_{nr}(\text{Re3}^{3+}, \text{terminal})]$  is the same to that of **Re2<sup>2+</sup>** ( $1.9 \times 10^6 \text{ s}^{-1}$ ), the  $k_1(\text{Re3}^{3+})$  can be calculated as  $6.5 \times 10^7 \text{ s}^{-1}$ .

### Calculation of the energy transfer efficiency in Ru-Re3A<sup>5+</sup>

The energy transfer efficiencies from the Re(I) units to the Ru(II) unit in **Ru-Re3A<sup>5+</sup>** were calculated using the following two equations, and all of the estimated energy transfer rate constants are given in the Results and Discussion section.

From the excited terminal Re(I) unit:

$$\begin{aligned} \eta_{\text{ET1}} &= \frac{k_1(\text{Ru} - \text{Re3A}^{3+}) + k_3(\text{Ru} - \text{Re3A}^{3+})}{k_r(\text{Ru} - \text{Re3A}^{3+}, \text{terminal}) + k_{nr}(\text{Ru} - \text{Re3A}^{3+}, \text{terminal}) + k_1(\text{Ru} - \text{Re3A}^{3+}) + k_3(\text{Ru} - \text{Re3A}^{3+})} \quad (\text{S3}) \\ &= \frac{6.5 \times 10^7 + 5.8 \times 10^7}{1.1 \times 10^6 + 6.5 \times 10^7 + 5.8 \times 10^7} \\ &= 99 \% \end{aligned}$$

From the interior Re(I) unit:

$$\begin{aligned} \eta_{\text{ET2}} &= \frac{k_2(\text{Ru} - \text{Re3A}^{3+})}{k_r(\text{Ru} - \text{Re3A}^{3+}, \text{interior}) + k_{nr}(\text{Ru} - \text{Re3A}^{3+}, \text{interior}) + k_2(\text{Ru} - \text{Re3A}^{3+})} \quad (\text{S4}) \\ &= \frac{6.4 \times 10^6}{1.1 \times 10^6 + 6.4 \times 10^6} \\ &= 85 \% \end{aligned}$$

### Calculation of the emission decay kinetics in Ru-Re5<sup>7+</sup>

The **Ru-Re5<sup>7+</sup>** is constructed with the following four different types of chromophores: the terminal Re(I) unit (**Re-V**), two interior Re(I) units (**Re-III** and **Re-IV**) and the Ru(II) unit (**Ru**) (Scheme S1).

After UV irradiation, all of the chromophores can absorb photons and become the  $^3\text{MLCT}$  excited state. Each of the excited states is relaxed through the intrinsic decay process (radiative and non-radiative relaxation) and various energy-transfer processes, and these time profiles should follow the set of rate equations (eqs. S5). We define  $k_{\text{Ru}}$ ,  $k_{\text{Re-V}}$ ,  $k_{\text{Re-III}}$ , and  $k_{\text{Re-IV}}$  as the intrinsic decay rates of **Ru**, **Re-V**, **Re-III** and **Re-IV** excited states, respectively. The energy-transfer rate between the **Re-III** and **Re-IV** chromophores is represented by  $k_m$ . The following relationships are true:

$$\begin{aligned}
\frac{d\text{Ru}(t)}{dt} &= -k_{\text{Ru}}\text{Ru}(t) + k_2(\text{Ru} - \text{Re}5^{7+})\text{Re-III}(t) + k_3(\text{Ru} - \text{Re}5^{7+})\text{Re-IV}(t) + k_4(\text{Ru} - \text{Re}5^{7+})\text{Re-V}(t) \\
\frac{d\text{Re-V}(t)}{dt} &= -(k_{\text{Re-V}} + k_1(\text{Ru} - \text{Re}5^{7+}) + k_4(\text{Ru} - \text{Re}5^{7+}))\text{Re-V}(t) \\
\frac{d\text{Re-III}(t)}{dt} &= -(k_{\text{Re-III}} + k_m + k_2(\text{Ru} - \text{Re}5^{7+}))\text{Re-III}(t) + k_m\text{Re-IV}(t) \\
\frac{d\text{Re-IV}(t)}{dt} &= -(k_{\text{Re-IV}} + k_m + k_3(\text{Ru} - \text{Re}5^{7+}))\text{Re-IV}(t) + k_m\text{Re-III}(t) + k_1(\text{Ru} - \text{Re}5^{7+})\text{Re-V}(t)
\end{aligned} \tag{S5}$$

where  $\text{Ru}(t)$ ,  $\text{Re-V}(t)$ ,  $\text{Re-III}(t)$ , and  $\text{Re-IV}$  are the concentration of the  $^3\text{MLCT}$  excited states of the **Ru**, **Re-V**, **Re-III**, and **Re-IV** chromophores at time  $t$ .

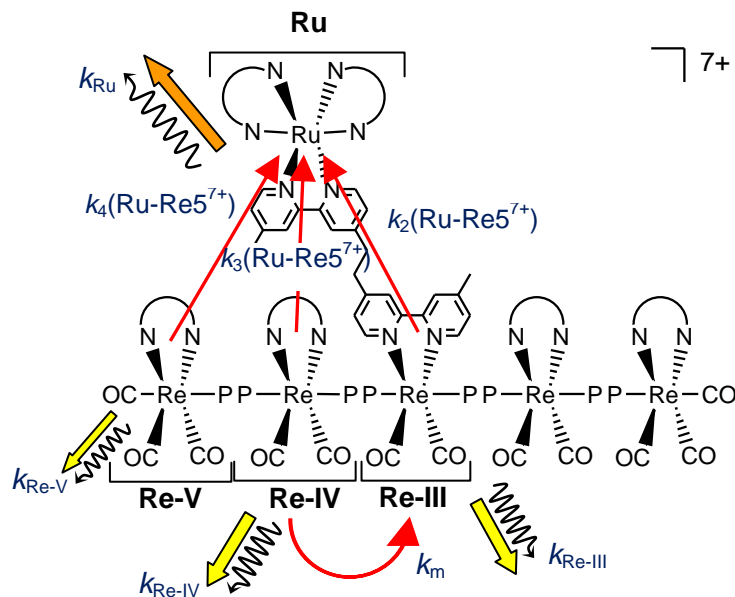
The rate equations (eqs. S5) may be rewritten:

$$\begin{aligned}
\frac{d\text{Ru}(t)}{dt} &= -k_{\text{Ru}}\text{Ru}(t) + k_2(\text{Ru} - \text{Re}5^{7+})\text{Re-III}(t) + k_3(\text{Ru} - \text{Re}5^{7+})\text{Re-IV}(t) + k_4(\text{Ru} - \text{Re}5^{7+})\text{Re-V}(t) \\
\frac{d\text{Re-V}(t)}{dt} &= -\alpha\text{Re-V}(t) \\
\frac{d\text{Re-III}(t)}{dt} &= -(\beta - \delta)\text{Re-III}(t) + k_m\text{Re-IV}(t) \\
\frac{d\text{Re-IV}(t)}{dt} &= -(\beta + \delta)\text{Re-IV}(t) + k_m\text{Re-III}(t) + k_1(\text{Ru} - \text{Re}5^{7+})\text{Re-V}(t)
\end{aligned} \tag{S5'}$$

where the parameters  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\mu$  are defined as follows:

$$\begin{aligned}
\alpha &= k_{\text{Re-V}} + k_1(\text{Ru} - \text{Re}5^{7+}) + k_4(\text{Ru} - \text{Re}5^{7+}) \\
\beta &= \frac{1}{2} \{ (k_{\text{Re-III}} + k_m + k_2(\text{Ru} - \text{Re}5^{7+})) + (k_{\text{Re-IV}} + k_m + k_3(\text{Ru} - \text{Re}5^{7+})) \} \\
\delta &= \frac{k_3(\text{Ru} - \text{Re}5^{7+}) - k_2(\text{Ru} - \text{Re}5^{7+})}{2}
\end{aligned} \tag{S6}$$

$$\mu = \frac{1}{2} \sqrt{4k_m^2 + (k_3(\text{Ru} - \text{Re}5^{7+}) - k_2(\text{Ru} - \text{Re}5^{7+}))^2} \tag{S7}$$



Scheme S1. Relaxation processes in **Ru-Re5<sup>7+</sup>**.

The decay functions of the excited states at time  $t$  are calculated as the solution of eqs. S5 or S5' rate equations.

The initial concentrations of the excited states are assumed to be follows:

$$\begin{aligned}
 \text{Ru}(0) &= \text{Ru}_0 \\
 \text{Re-V}(0) &= 2(\text{Re-V}_0) \\
 \text{Re-III}(0) &= \text{Re-III}_0 \\
 \text{Re-IV}(0) &= 2(\text{Re-IV}_0)
 \end{aligned}
 \tag{S8}$$

The set of rate equations (eqs. S5) can be solved analytically. The solutions are the sums of the one to four exponential functions that have the common decay rate constants ( $\alpha$ ,  $\beta + \mu$ ,  $\beta - \mu$ , and  $k_{\text{Ru}}$ ) for each chromophores. The solutions of eqs. S5 for the **Re-V**, **Re-III**, **Re-IV**, and **Ru**, are calculated as follows:

(1) the decay function of **Re-V** is

$$\text{Re-V}(t) = 2(\text{Re-V}_0)e^{-\alpha t} \tag{S9}$$

(2) the decay function of **Re-III** is

$$\text{Re-III}(t) = A_{1\text{Re-III}}e^{-\alpha t} + A_{2\text{Re-III}}e^{-(\beta+\mu)t} + A_{3\text{Re-III}}e^{-(\beta-\mu)t} \tag{S10}$$

where  $A_{1\text{Re-III}}$ ,  $A_{2\text{Re-III}}$  and  $A_{3\text{Re-III}}$  are the pre-exponential factors that were defined as follows:

$$\begin{aligned}
 A_{1\text{Re-III}} &= \frac{2k_m k_1 (\text{Ru} - \text{Re}5^{7+})}{(\alpha - \beta + \mu)(\alpha - \beta - \mu)} T_0 \\
 A_{2\text{Re-III}} &= -\frac{k_m k_1 (\text{Ru} - \text{Re}5^{7+})}{(\alpha - \beta - \mu)\mu} T_0 - \frac{\delta + 2k_m - \mu}{2\mu} B_0 \\
 A_{3\text{Re-III}} &= \frac{k_m k_1 (\text{Ru} - \text{Re}5^{7+})}{(\alpha - \beta + \mu)\mu} T_0 + \frac{\delta + 2k_m + \mu}{2\mu} B_0
 \end{aligned} \tag{S11}$$

(3) the decay function of **Re-IV** is

$$\text{Re-IV}(t) = A_{1\text{Re-IV}} e^{-\alpha t} + A_{2\text{Re-IV}} e^{-(\beta+\mu)t} + A_{3\text{Re-IV}} e^{-(\beta-\mu)t} \tag{S12}$$

where  $A_{1\text{Re-IV}}$ ,  $A_{2\text{Re-IV}}$  and  $A_{3\text{Re-IV}}$  are the pre-exponential factors that were calculated as follows:

$$\begin{aligned}
 A_{1\text{Re-IV}} &= -\frac{2(\alpha - \beta + \delta)k_1 (\text{Ru} - \text{Re}5^{7+})}{(\alpha - \beta + \mu)(\alpha - \beta - \mu)} T_0 \\
 A_{2\text{Re-IV}} &= -\frac{(\delta + \mu)k_1 (\text{Ru} - \text{Re}5^{7+})}{2(\alpha - \beta - \mu)\mu} T_0 + \frac{2\mu + 2\delta - k_m}{2\mu} B_0 \\
 A_{3\text{Re-IV}} &= \frac{(\delta - \mu)k_1 (\text{Ru} - \text{Re}5^{7+})}{(\alpha - \beta + \mu)\mu} T_0 + \frac{2\mu - 2\delta + k_m}{2\mu} B_0
 \end{aligned} \tag{S13}$$

(4) the decay function of **Ru** is

$$\text{Ru}(t) = f_{\text{Ru1}}(t) e^{-k_{\text{Ru}} t} \tag{S14}$$

where

$$f_{\text{Ru1}}(t) = f_{\text{Ru2}}(t) + \int_0^t f_{\text{Ru3}}(s) ds \tag{S15}$$

The first and the second term in eqs. S15 should be substituted with the following:

$$\begin{aligned}
 f_{\text{Ru2}}(t) &= \text{Ru}_0 \\
 f_{\text{Ru3}}(s) &= \frac{1}{2(\alpha - \beta - \mu)(\alpha + \beta - \mu)\mu^2} f_{\text{Ru4}}(s) \\
 f_{\text{Ru4}}(s) &= A_{1\text{Ru}} e^{-(\alpha - k_r)s} + A_{2\text{Ru}} e^{-(\beta + \mu - k_r)t} + A_{3\text{Ru}} e^{-(\beta - \mu - k_r)t}
 \end{aligned} \tag{S16}$$

where  $A_{1\text{Ru}}$ ,  $A_{2\text{Ru}}$  and  $A_{3\text{Ru}}$  are the pre-exponential factors that were calculated as follows:



$$\begin{aligned}
A_{1\text{Ru}} &= 2[k_4(\text{Ru} - \text{Re}5^{7+}) - \frac{k_1(\text{Ru} - \text{Re}5^{7+})\{k_2(\text{Ru} - \text{Re}5^{7+})k_m - (\alpha - \beta + \delta)k_3(\text{Ru} - \text{Re}5^{7+})\}}{(\alpha - \beta + \mu)(\alpha - \beta - \mu)}]T_0 \\
A_{2\text{Ru}} &= \frac{k_1(\text{Ru} - \text{Re}5^{7+})\{(\delta + \mu)k_3(\text{Ru} - \text{Re}5^{7+}) - k_2(\text{Ru} - \text{Re}5^{7+})k_m\}}{(\alpha - \beta - \mu)\mu}T_0 \\
&\quad - \frac{2k_2(\text{Ru} - \text{Re}5^{7+})(2k_m - \mu + \delta) + k_3(\text{Ru} - \text{Re}5^{7+})(k_m - 2\mu - 2\delta)}{2\mu}B_0 \\
A_{3\text{Ru}} &= \frac{k_1(\text{Ru} - \text{Re}5^{7+})\{(\mu - \delta)k_3(\text{Ru} - \text{Re}5^{7+}) + k_2(\text{Ru} - \text{Re}5^{7+})k_m\}}{(\alpha - \beta + \mu)\mu}T_0 \\
&\quad + \frac{k_2(\text{Ru} - \text{Re}5^{7+})(2k_m + \mu + \delta) + k_3(\text{Ru} - \text{Re}5^{7+})(k_m + 2\mu + 2\delta)}{2\mu}B_0
\end{aligned} \tag{S17}$$

Using the following equation for the exponential functions,

$$e^{-kt} \int_0^t e^{-(m-k)t} dt = \frac{1}{m-k} (e^{-kt} - e^{-mt}) \tag{S18}$$

Ru(t) is represented by the sum of the four exponential functions:

$$\text{Ru}(t) = C_{1\text{Ru}} e^{-k_{\text{Ru}} t} + C_{2\text{Ru}} e^{-\alpha t} + C_{3\text{Ru}} e^{-(\beta + \mu)t} + C_{4\text{Ru}} e^{-(\beta - \mu)t} \tag{S19}$$

where  $C_{1\text{Ru}}$ ,  $C_{2\text{Ru}}$ ,  $C_{3\text{Ru}}$ , and  $C_{4\text{Ru}}$  are the pre-exponential factors that were calculated as follows:

$$\begin{aligned}
C_{1\text{Ru}} &= \text{Ru}_0 + \frac{A_{1\text{Ru}}}{\alpha - k_{\text{Ru}}} + \frac{A_{2\text{Ru}}}{\beta + \mu - k_{\text{Ru}}} + \frac{A_{3\text{Ru}}}{\beta - \mu - k_{\text{Ru}}} \\
C_{2\text{Ru}} &= -\frac{A_{1\text{Ru}}}{\alpha - k_{\text{Ru}}} \\
C_{3\text{Ru}} &= -\frac{A_{2\text{Ru}}}{\beta + \mu - k_{\text{Ru}}} \\
C_{4\text{Ru}} &= -\frac{A_{3\text{Ru}}}{\beta - \mu - k_{\text{Ru}}}
\end{aligned} \tag{S20}$$

The observed emission intensity in the emission decay measurement should be proportional to the linear combination of the concentrations of the excited states Re-V(t), Re-III(t), Re-IV(t) and Ru(t). Therefore the emission decay function should follow the sum of no more than four exponential functions, as follows:

$$I_{em}(t) = A_1 e^{-\alpha t} + A_2 e^{-(\beta+\mu)t} + A_3 e^{-(\beta-\mu)t} + A_4 e^{-k_m t} \quad (S21)$$

where

$$\begin{aligned} k_{obs1} &= \alpha = k_{Re-V} + k_1(\text{Ru} - \text{Re5}^{7+}) + k_4(\text{Ru} - \text{Re5}^{7+}) \\ k_{obs2} &= \beta + \mu = \frac{1}{2}(2k_{Re-III} + 2k_m + k_2(\text{Ru} - \text{Re5}^{7+}) + k_3(\text{Ru} - \text{Re5}^{7+}) + \sqrt{4k_m^2 + (k_2(\text{Ru} - \text{Re5}^{7+}) - k_3(\text{Ru} - \text{Re5}^{7+}))^2}) \\ k_{obs3} &= \beta - \mu = \frac{1}{2}(2k_{Re-IV} + 2k_m + k_2(\text{Ru} - \text{Re5}^{7+}) + k_3(\text{Ru} - \text{Re5}^{7+}) - \sqrt{4k_m^2 + (k_2(\text{Ru} - \text{Re5}^{7+}) - k_3(\text{Ru} - \text{Re5}^{7+}))^2}) \\ k_{obs4} &= k_{Ru} \end{aligned} \quad (S22)$$

and  $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$  are the parameters that represent the contributions of each of the exponential components.

The energy-transfer rate constants are derived as a solution of the set of eqs S22, as follows:

$$\begin{aligned} k_1(\text{Ru} - \text{Re5}^{7+}) &= k_{obs1} - k_{Re-V} - k_{Ru} \\ k_2(\text{Ru} - \text{Re5}^{7+}) &= \frac{1}{2}[(k_{obs2} + k_{obs3}) - 2(k_{Re-III} + k_m) + \sqrt{(k_{obs2} - k_{obs3})^2 - 4k_m^2}] \\ k_3(\text{Ru} - \text{Re5}^{7+}) &= \frac{1}{2}[(k_{obs2} + k_{obs3}) - 2(k_{Re-IV} + k_m) - \sqrt{(k_{obs2} - k_{obs3})^2 - 4k_m^2}] \\ k_4(\text{Ru} - \text{Re5}^{7+}) &= k_{Ru} \end{aligned} \quad (S23)$$

Because all of the observed decay rate constants,  $k_{obs1}$ ,  $k_{obs2}$ ,  $k_{obs3}$  and  $k_{obs4}$  should be positive real numbers, the following limiting condition exists for the rate constants,  $k_2(\text{Ru}-\text{Re5}^{7+})$ ,  $k_3(\text{Ru}-\text{Re5}^{7+})$  and  $k_m$ :

$$(k_{obs2} - k_{obs3})^2 - 4k_m^2 \geq 0 \quad (S24)$$

Therefore, the energy-migration rate between the **Re-III** and **Re-IV** chromophores,  $k_m$ , has the following upper limit:

$$\begin{aligned} k_m &\leq \frac{k_{obs2} - k_{obs3}}{2} \\ &= \frac{1.4 \times 10^7 s^{-1} - 6.7 \times 10^6 s^{-1}}{2} = 3.6 \times 10^6 s^{-1} \end{aligned} \quad (S25)$$