Electronic Supplementary Information for

Photochemistry of *P,N*-Bidentate Rhenium(I) Tricarbonyl Complexes: Reactive Species Generation and Potential Application for Antibacterial Photodynamic Therapy

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Summary of contents

Figure S1. Spectral changes of **RePNBr** in EtOH (a), DCM (b) and MeCN (c) upon irradiation at 365 nm at 20°C.

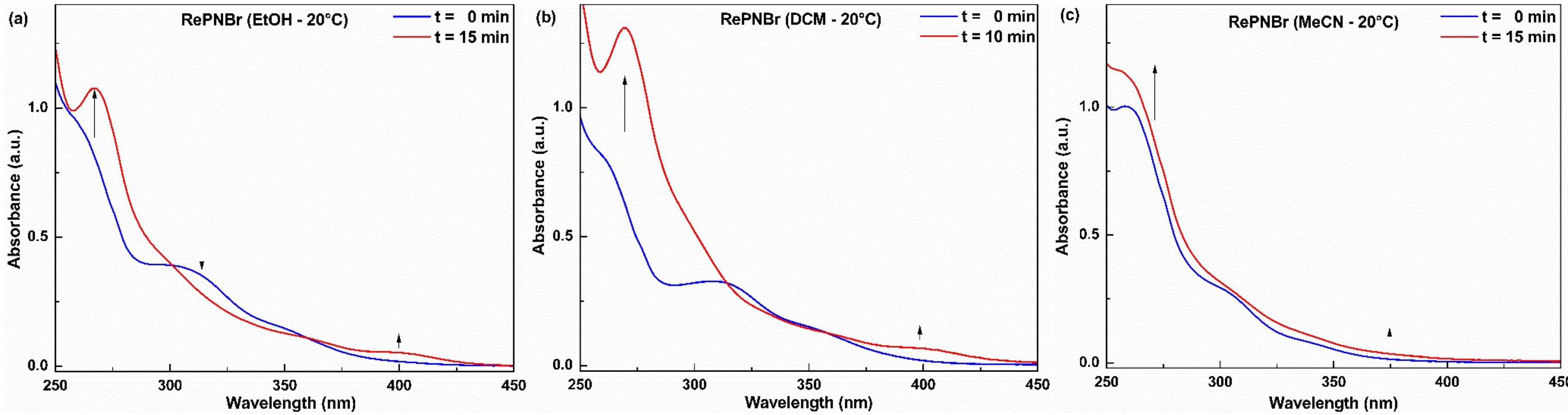


Figure S2. Spectral changes of **RePNNBr** in EtOH (a), DCM (b) and MeCN (c) upon irradiation at 365 nm at 20°C.

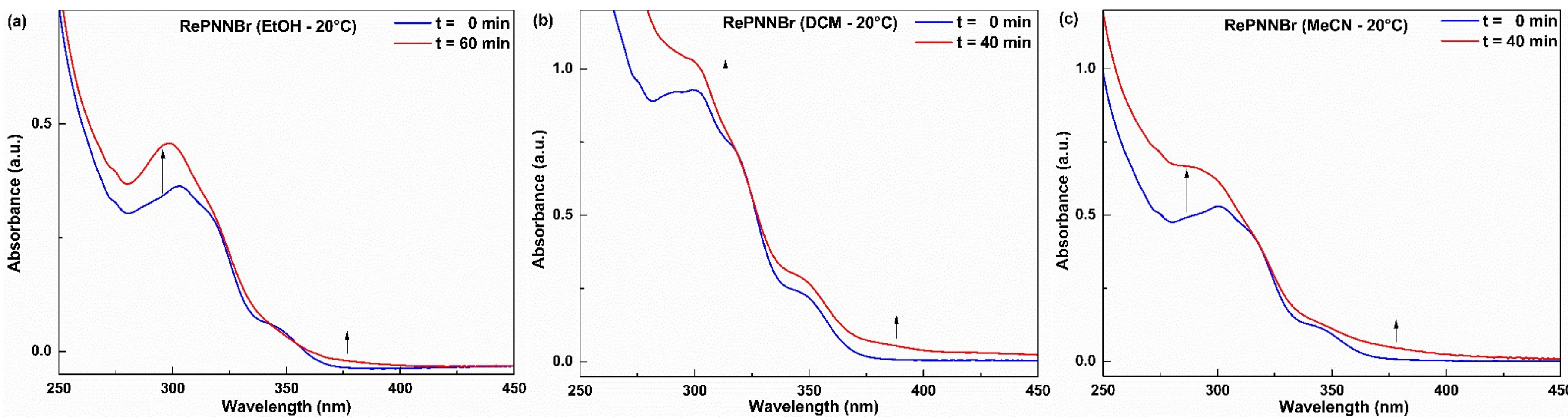


Figure S3. Spectral changes of **RePNTfO** in EtOH (a), DCM (b) and MeCN (c) upon irradiation at 365 nm at 20°C.

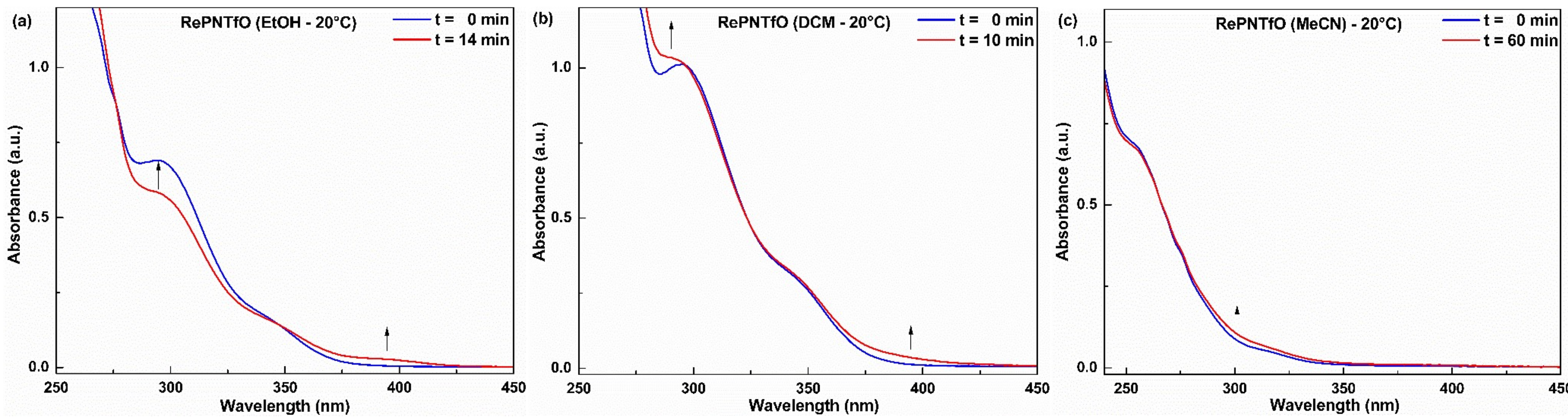


Figure S4. IR (CO-stretching region) spectral change of **RePNBr** (left), **RePNNBr** (center) and **RePNTfO** (right), in DCM with 0 min (blue) and 15 min (red) of irradiation (365 nm) at room temperature.

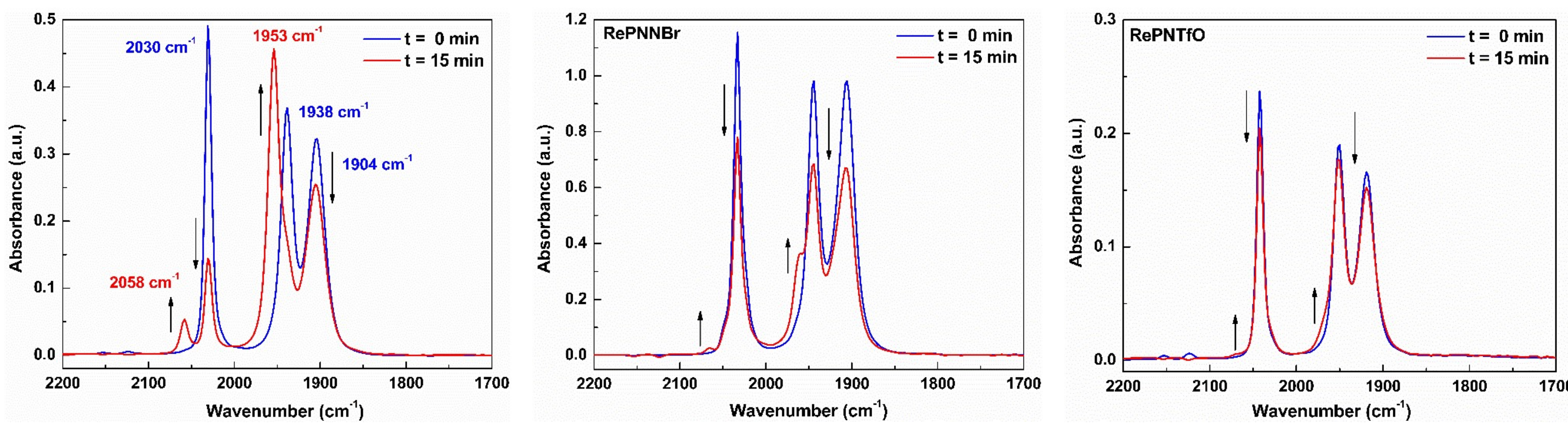


Figure S5. TD-DFT computed spectra for *fac*-**RePNBr** and its *mer*-isomers.

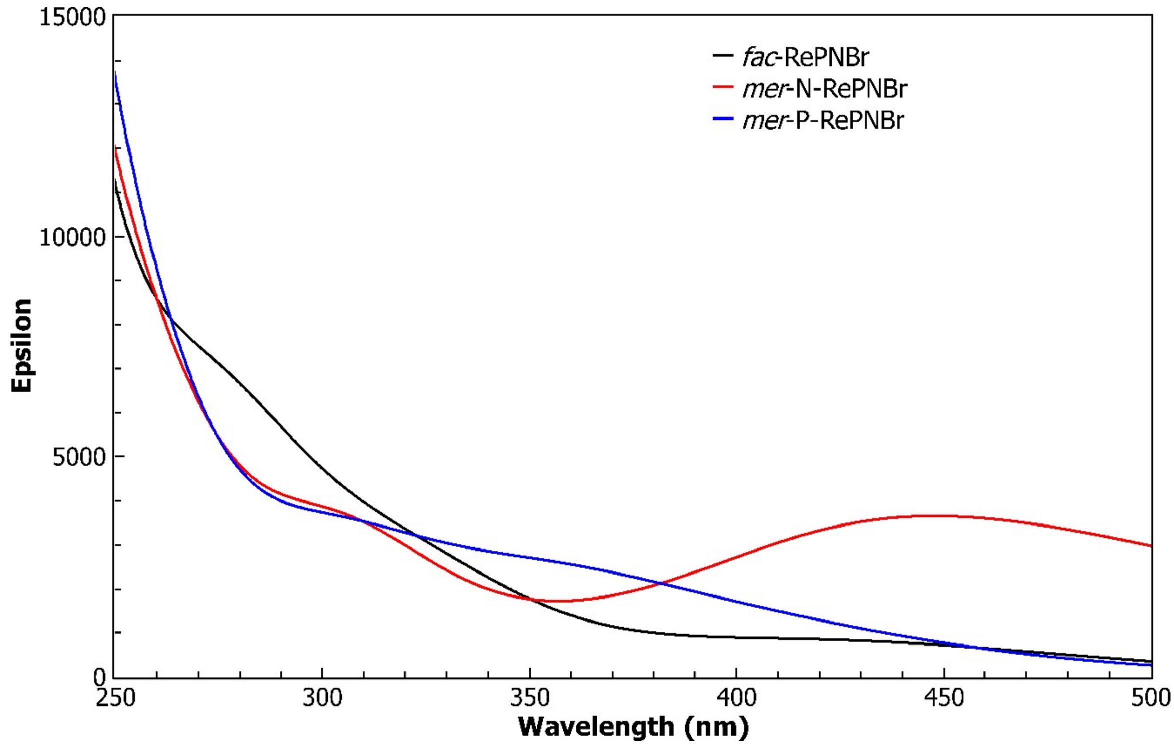
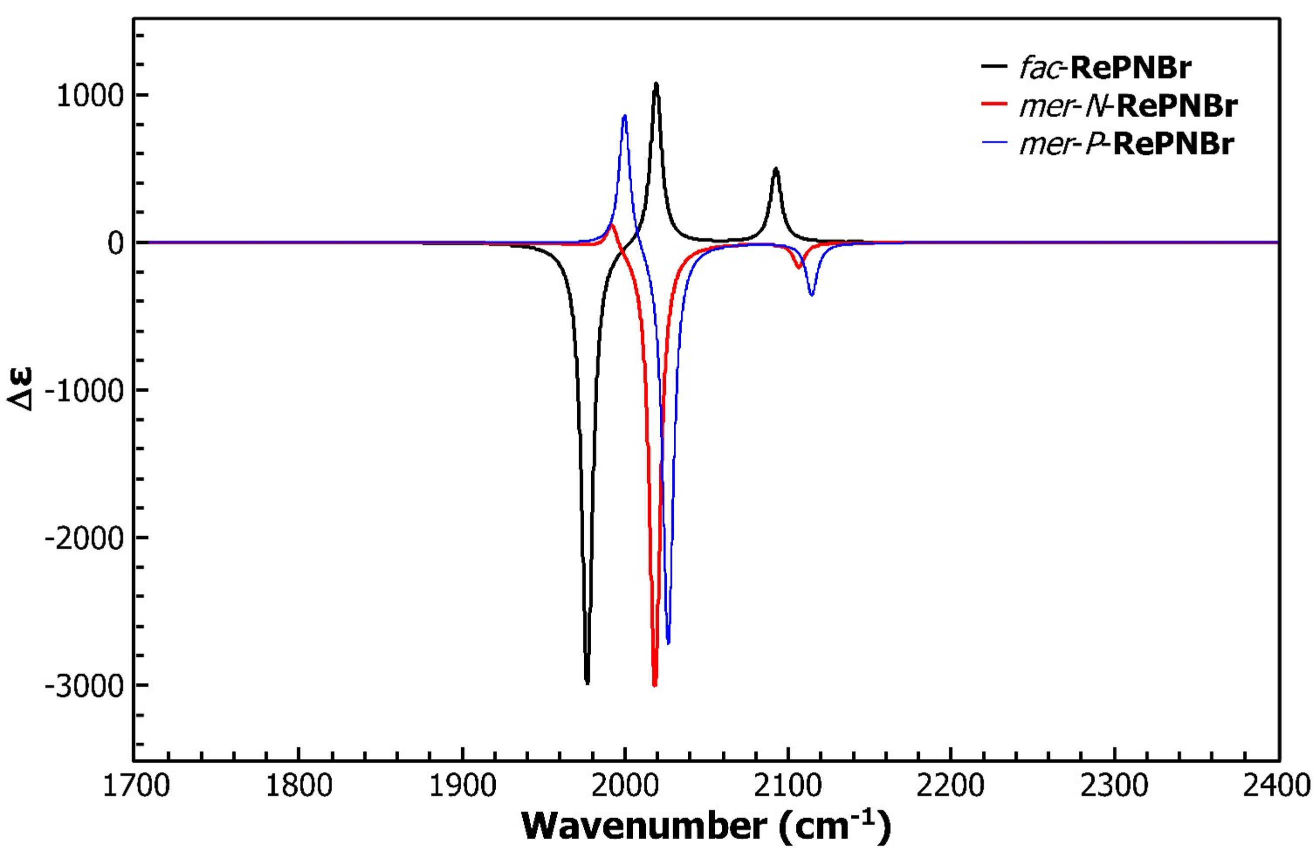


Figure S6. DFT computed Vibrational Circular Dichroism spectra for *fac*-**RePNBr** and its *mer*-isomers.



Derivation of Equation 1.

Our approximation resembles the Hippler's proposal,[1] where the absorbed photons can be considered as a second reactant, being the first elementary process a bimolecular reaction. Consider the following elementary processes in the mechanism:

$$A + I_a \xrightarrow{k_1} A^* \qquad rate = -\frac{d[A]}{dt} = \frac{d[A^*]}{dt} = k_1[A]\, I_a \qquad (1)$$

$$A^* \xrightarrow{k_{prod}} P \qquad rate = -\frac{d[A^*]}{dt} = \frac{d[P]}{dt} = k_{prod}[A^*] \qquad (2)$$

$$A^* \xrightarrow{k_{photoph}} A \qquad rate = -\frac{d[A^*]}{dt} = k_{photoph}[A^*] \qquad (3)$$

and applying SS approximation for excited state concentration, [A*]

$$k_1[A]\, I_a = (k_{prod} + k_{photoph})\, [A^*] \qquad (4)$$

$$[A^*] = \frac{k_1\, I_a}{(k_{prod} + k_{photoph})}[A] \qquad (5)$$

Replacing in eq. 2

$$\frac{d[P]}{dt} = k_{prod}\frac{k_1\, I_a}{(k_{prod} + k_{photoph})}[A] \qquad (6)$$

Under well controlled steady state experimental conditions: irradiation with constant light intensity, geometry unaltered, similar extinction coefficients, the value of I_a is constant, and then, the eq. 6 can be reduced to:

$$\frac{d[P]}{dt} = k_{app}\,[A] \qquad (7)$$

where $k_{app} = k_{prod}\frac{k_1\, I_a}{(k_{prod} + k_{photoph})}$

under above mentioned considerations and conditions, an apparent first order expression can be defined as follows:

$$[P] = [A]_o(1 - e^{-k_{app}\, t}) \qquad (8)$$

where [P] is the photoproduct concentration and [A]o is the initial concentration of the complex. As the [P] can be replaced by $A_p/(\varepsilon_p\, l)$, where A_P and ε_P correspond to the absorbance and molar extinction coefficient of the product, respectively, and l is the optical path, equation 8 can be expressed as:

$$A_P = \varepsilon_P\, l\, [A]_o(1 - e^{-k_{app}\, t}) \qquad (9)$$

1. M. Hippler, *Journal of Chemical Education*, 2003, **80**, 1074.