CHEMISTRY
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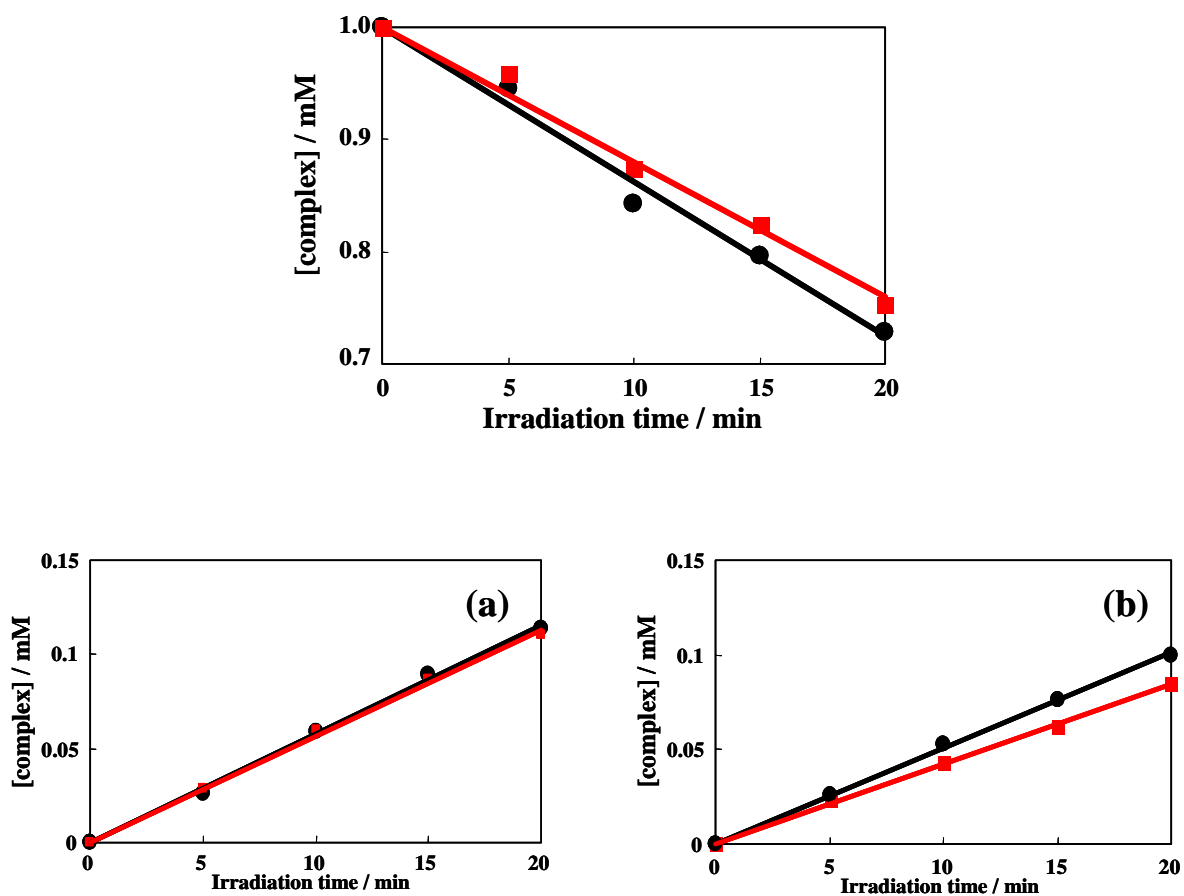## Supporting Information

**Photochemistry of *fac*-[Re(bpy)(CO)₃Cl]****

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Figure S1. Decrease of **1a** (a) and formation of **2a** (b) and **2b** (c) by irradiation to an MeCN solution containing **1a** (1 mM) using 313-nm light under Ar (black) or CO (red) atmosphere.
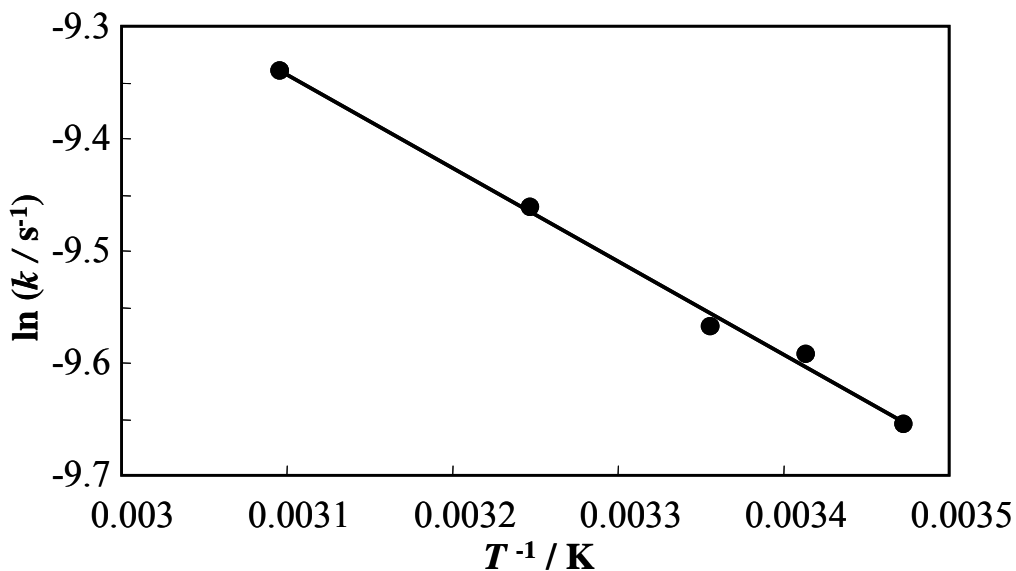
Figure S2 Arrhenius plots for decrease of **1a** by irradiation using 313-nm light in an MeCN solution containing 1.0 mM of **1a** under an Ar atmosphere.
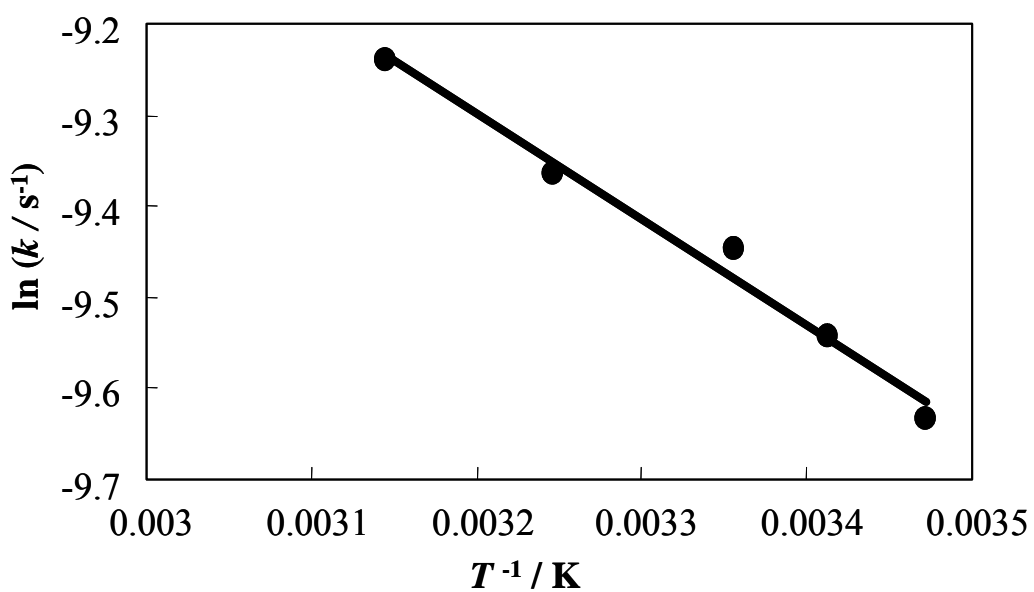

Figure S3 Arrhenius plots for decrease of **1a** by irradiation using 313-nm light in a THF solution containing 1.0 mM of **1a** under an Ar atmosphere.
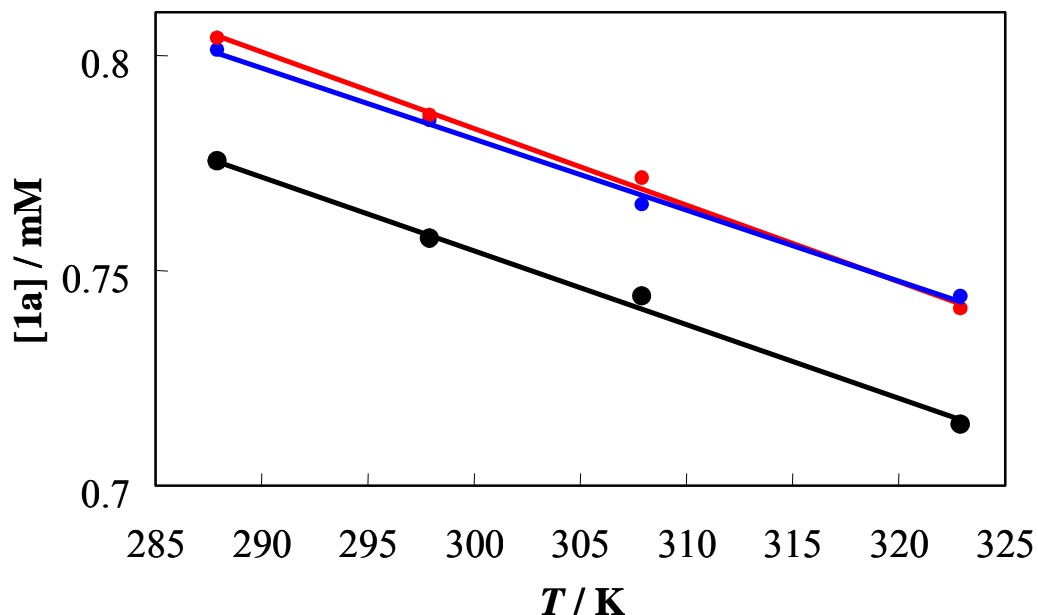
Figure S4. Effects of viscosity of solvent on decrease of **1a** by irradiation: solutions containing 1.0 mM of **1a** were irradiated using 313-nm light for 30 min, 1:1 mixtures of dimethylformamide (the viscosity coefficient is 0.34 mPa•s) – MeCN (0.92 mPa•s) [blue], N,N-dimetylacetoamide (2.14 mPa•s) – MeCN [red].   The result using a neat MeCN solution is also shown [black].
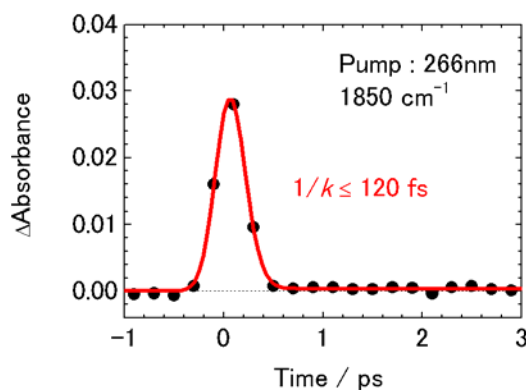
Figure S5. Time profile of the absorbance changes for **1a** in a THF solution following excitation

with a 266-nm laser pulse. The monitoring wavenumber is 1850 cm^{-1}. The solid line is a curve

calculated from a single exponential function convoluted with a laser function.
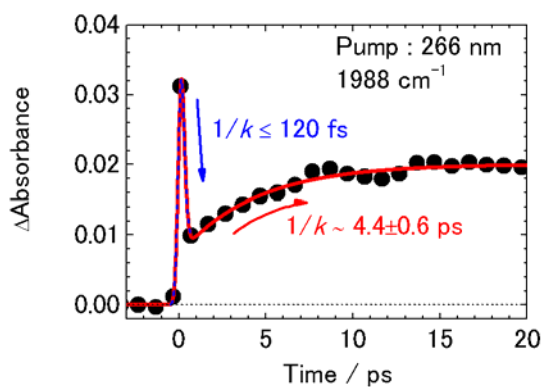
Figure S6. Time profile of the absorbance changes for **1a** in a THF solution following excitation with a 266-nm laser pulse. The monitoring wavenumber is 1988 cm^{-1}. The solid line is a curve calculated from a double exponential function convoluted with a laser function.
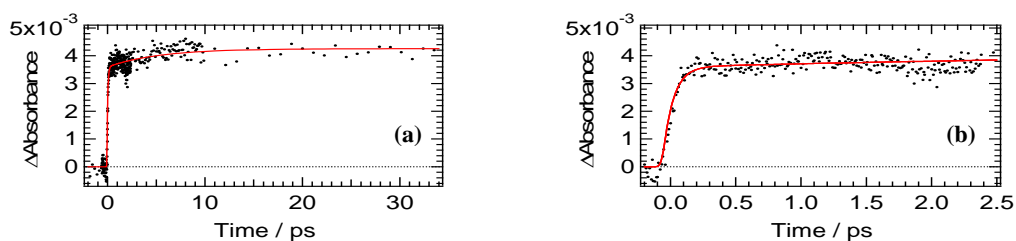
Figure S7. Time profiles of the transient absorbance of **1a** in an MeCN solution following excitation with a femtosecond 370-nm laser pulse. The monitoring wavelength was 475 nm. Solid lines are curves calculated from a triple exponential function with lifetimes of 72 ± 2 fs and 500 ± 10 fs and a 9.7 ± 0.3 ps rise.
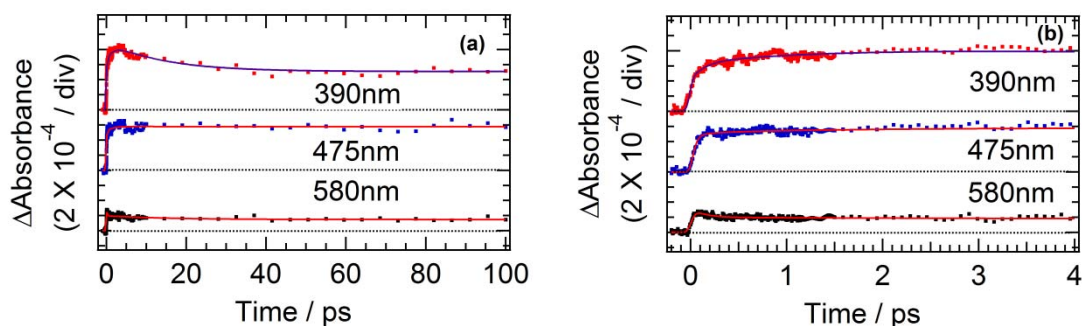
Figure S8. Time profiles of the transient absorbance of **1a** in an MeCN solution following excitation with a femtosecond 270-nm laser pulse. Monitored wavelengths were at 390, 475, and 580 nm. Solid lines are the quadruple exponential function curves with lifetimes of 30 fs, 130 fs, and 14 ps.

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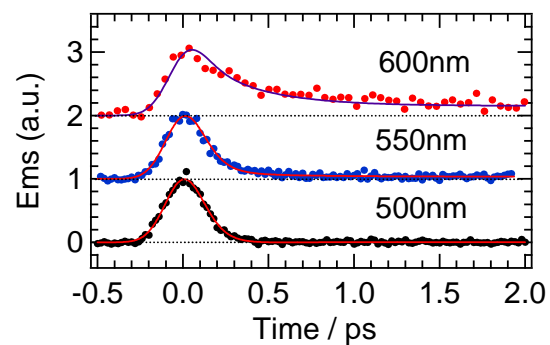
Figure S9. Time profiles of the emission up-conversion signals of **1a** in an MeCN solution following excitation with a femtosecond 400-nm laser pulse. The monitoring wavelengths are 600, 550, and 500 nm. Solid lines are results calculated from a double exponential function and residual signal with lifetimes of 71±2 fs and 360±110 fs.