Appendix A

General Description of Techniques and Measurements
Appendix A

A.1 Physical methods

**UV-vis absorption spectroscopy.** UV-vis absorption spectra were recorded with a Specord600 (AnalytikJena) spectrophotometer in 1 cm (unless stated otherwise) path length quartz cuvettes.

**Mass spectroscopy.** ESI mass spectra of complexes were recorded on a Triple Quadrupole LC/MS/MS mass spectrometer (API 3000, PerkinElmer Sciex Instruments).

**Electron paramagnetic resonance (EPR) spectroscopy.** EPR (X-band, 9.46 GHz) were recorded on a Bruker ECS106 spectrometer in liquid nitrogen (77K). Samples (0.4 mL), monitored by UV-vis absorption spectroscopy, were flash frozen in liquid nitrogen.

**Fourier transform infrared spectroscopy (FTIR) spectroscopy.** FTIR spectra were recorded using a UATR (ZnSe) with a Perkin Elmer Spectrum400, equipped with a liquid nitrogen cooled MCT detector.

**Raman spectroscopy.** Raman spectra at $\lambda_{exc}785$ nm were recorded on a PerkinElmer Raman Station at room temperature. Raman spectra at 532 nm (300 mW at source, Cobolt Lasers) and 473 nm (100 mW at source, Cobolt Lasers) were obtained in an 180° backscattering arrangement, with Raman scattering collected and collimated and subsequently refocused via a pair of 2.5 cm diameter plano-convex lens (f = 7.5 cm and 10 cm, respectively) into a Shamrock300i spectrograph (Andor Technology) with a 1200 L/mm grating blazed at 500 nm and acquired with a Newton DU970N-BV or a iDus-420-BUE2 CCD camera (Andor Technology). The slit width was set at 50 μm and appropriate long pass filter was placed in front of the focusing lens. Raman spectra at 355 nm (10 mW at source, Cobolt Lasers) were acquired in a 180° backscattering arrangement. Raman scattering was collected by a 2.5 cm diameter plano convex lens (f = 7.5 cm). The collimated Raman scattering passed through an appropriate long pass edge filter (Semrock) and was focused by a second 2.5 cm diameter plano convex lens (f = 15 cm) into a Shamrock500i spectrograph (Andor Technology) 2399 L/mm grating blazed at 300 nm, respectively, acquired with an iDus-420-BU2 CCD camera (Andor Technology). The spectral slit width was set to 12 μm. Data were recorded and processed using Solis (Andor Technology) with spectral calibration performed using the Raman spectrum of acetonitrile/toluene, 50:50 (v/v).

**NMR spectroscopy.** $^1$H NMR spectra (400 and 500 MHz) and $^{13}$C NMR spectra were recorded on a Varian Mercury Plus and Varian Inova, respectively. Chemical shifts are denoted relative to the residual solvent peak ($^1$H NMR spectra CD$_3$CN, 1.94 ppm; CD$_3$Cl, 7.26 ppm).

**Electrochemistry.** Electrochemical measurements were carried out on a model CHI760B electrochemical workstation (CH Instruments). Analyte concentrations were typically 0.25–1 mM in acetonitrile containing 0.1 M tetrabutylammonium trifluoromethylsulfonate. A 3 mm diameter Teflon-shrouded glassy carbon working electrode (CH Instruments), a Pt wire auxiliary electrode, and an SCE reference electrode were employed. Unless stated otherwise all potential values are quoted with respect to the SCE. Potentials are reported ±10 mV.

**Spectroelectrochemistry.** Spectroelectrochemical experiments in solution were carried out using an OTTLE cell (a liquid IR cell modified with Infrasil windows and a platinum mesh working and counter electrode and a Ag/AgCl reference electrode) mounted in a Specord600 UV-vis spectrometer with potential controlled by a CHI600C potentiostat. In situ UV-vis absorption spectroelectrochemistry of poly-1 was carried out by initial modification of an ITO electrode by cyclic voltammetry follow by transfer to 2 mm quartz cuvette as an electrochemical cell.
**Irradiation** Typically 2 mL of complex in solvent were purged with Ar in a 1 cm path length cuvette for 5 min before irradiation to remove oxygen. Irradiation was carried out orthogonally to the monitoring beam of the UV-vis absorption spectrometer. LEDs (Thorlabs) were used at 365 nm (M365 F1, 6.10 × 10^−5 einstein s^−1 dm^−3), 490 nm (M490F3, 4.76 × 10^6 einstein s^−1 dm^−3), 565 nm (M565F, 3.19 × 10^6 einstein s^−1 dm^−3), and 300 nm (M300F2, 1.25 × 10^6 einstein s^−1 dm^−3) controlled by T-Cube Light Source & Driver Module (Thorlabs); or a DPSS laser at 355 nm (9.79 × 10^−6 einstein s^−1 dm^−3, Cobolt Lasers). Light intensity at sample was measured with PM10V1 High Power 10 Watt sensor coupled to a FieldMate Power Meter.

**A.2 Colorimetric quantification of formaldehyde**

The formation of formaldehyde was quantified as described in literature. The colorimetric reagent was prepared by dissolving NH₄OAc (15 g, 0.19 mol), acetic acid (0.3 mL, 5.4 mol) and pentane-2,4-dione (0.2 mL, 1.9 mol) in 100 mL water. Take 1 mL reaction solution, diluted 10 times (1 mL solution dissolved in 9 mL water, concentration of formaldehyde should not exceed 8 μg of formaldehyde per mL), then mixed with the other 10 mL of colorimetric reagent. The mixture was put into a 31 °C water bath. Every 2 min, 1 mL mixture was transferred to the cuvette and check the UV-vis absorbance at 420 nm, after around 35 min, the absorbance will reach to its maximum and stable for ca. 10 min. This maximum absorbance was used to calculated the concentration of formaldehyde using equation (1).

\[
C = \frac{A_{420\text{nm}}}{L \times \varepsilon_{420\text{nm}}} \times 20
\]  

Where C is the concentration of formaldehyde in the reaction, A_{420\text{nm}} is the maximum absorbance of the mixture at 420 nm, L is the pathlength of the cuvette, \( \varepsilon_{420\text{nm}} \) is the molar absorptivity of diacetyldihydrolutidine (DDL), which was determined by calibration with solutions containing known amounts of formaldehyde.

**A.3 Estimation of photochemical quantum yield.**

The photo flux of the irradiation for quantum yield measurement is determined by actinometry with potassium ferrioxalate as actinometer, the standard procedure from literature was slightly modified and described in our previous work. The overall photochemical quantum yield was calculated according to literature methods with modification for the photo-reduction process.

The photo reduction of 1 was calculated using equation 1:

\[
-\frac{dC_1}{dt} = \phi_1 \frac{\varepsilon_1 C_1}{A} I (1 - 10^{-A})
\]  

\[
-\frac{dC_1}{dt} \text{ is the rate of change of concentration of } 1 \text{ in M, } I (1 - 10^{-A}) \text{, the light absorbed by the whole sample, } \frac{\varepsilon_1 C_1}{A} \text{ is the fraction of the light absorbed by } 1, \text{ } C_1 \text{ is the concentration of } 1 \text{ in M, } \varepsilon_1 \text{ is molar absorptivity of } 1 \text{ at } \lambda_{\text{irr}}, \text{ } A \text{ is the absorbance when using a 1 cm path length cuvette, } \phi_1 \text{ is quantum yield for the photoreduction, } I \text{ is radiant power (Einstein s}^{-1} \text{L}^{-1}).
\]

\[
-\frac{dC_1}{dt} \cdot \frac{A}{1 - 10^{-A}} = \varepsilon_1 I \phi_1 (C_1)
\]  

With K = \( \varepsilon_1 I \phi_1 \).
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\[- \frac{dC_1}{dt} \cdot \frac{A}{1-10^{-A}} = K(C_1) \quad (E3)\]

With \( f = \int_0^t \frac{1-10^{-D}}{D} dt \), and integration;

\[ \ln \left( \frac{KC_1}{KC_0} \right) = fK \quad (E4) \]

then,

\[ \ln \left( \frac{C_1}{C_0} \right) = fK \quad (E5) \]

linear fitting of \( f \) and \( \ln \left( \frac{C_1}{C_0} \right) \) gives the slope \( K \),

\[ K = \varepsilon_1 I \phi_1, \quad \phi_1 = \frac{K}{\varepsilon_1 \times I} \quad (E6) \]

A.4 References


