

Electronic Supplementary Information

Photochemical Transformation of Lipoic acid-based Ligands: Probing the Effects of Solvent, Ligand Structure, Oxygen and pH

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Table S1. Relative concentration of thiols in the solution of UV-irradiated LA-PEG₇₅₀-OCH₃ in methanol measured in the presence of acid and base, extracted from the Ellman assay. Note that the thiol yield did not significantly change when the acid-to-ligand molar ratio was varied between 1 and 6.

Acid/Base	Acid/base-to-ligand molar ratio	SH (%)
HCl	4	73
H ₂ SO ₄	4	72
HNO ₃	4	75
H ₃ PO ₄	4	65
Ascorbic acid	6	69
Hexanoic acid	6	70
NaOH	4	27

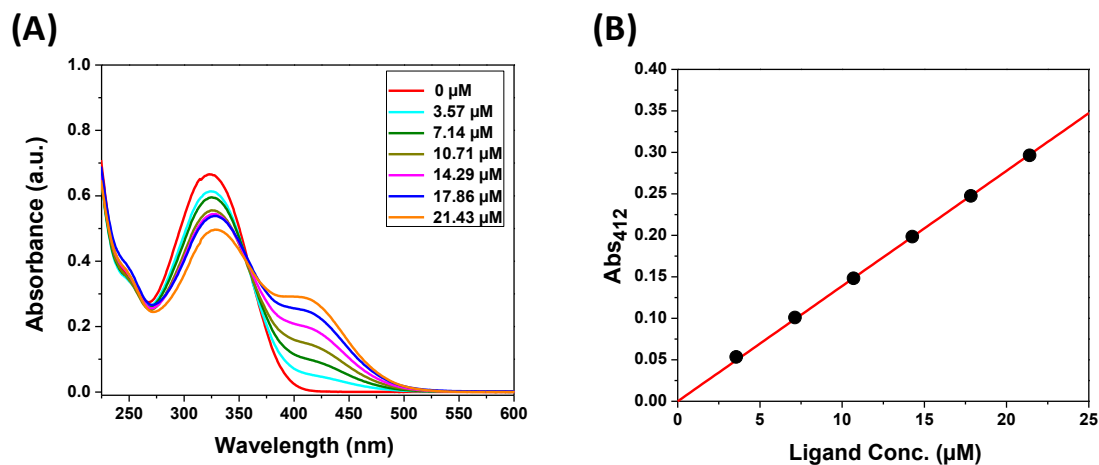


Figure S1. UV spectroscopy data collected from the Ellman assay of cysteine (standard): (A) Absorption profiles, (B) Beer-lambert plot of Abs₄₁₂ vs cysteine concentration. The slope extracted from the linear fit is = 13,890.

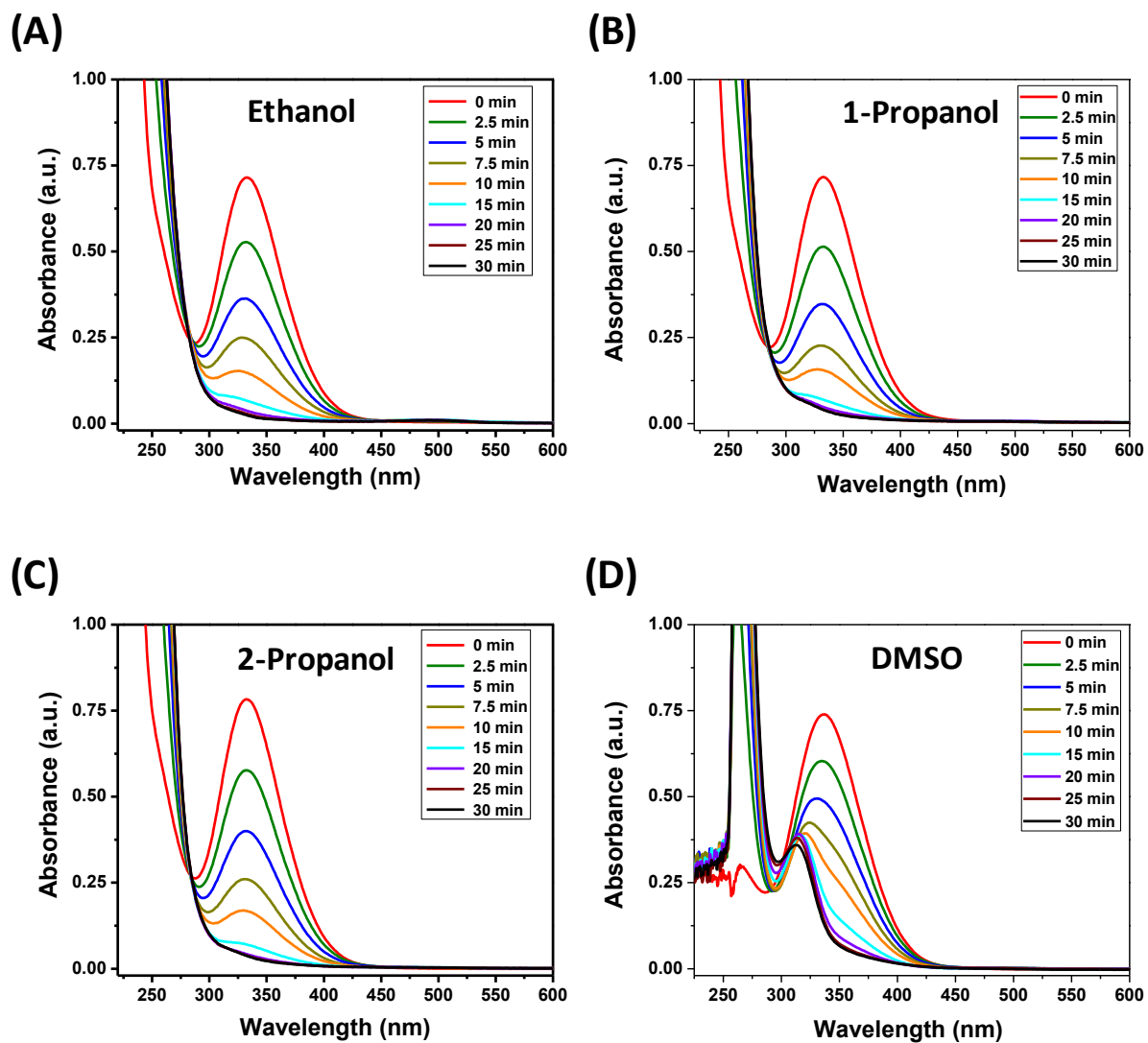


Figure S2. UV-Vis absorbance spectra collected from solutions of LA-PEG₇₅₀-OCH₃* at different times during UV-irradiation in: (A) ethanol, (B) 1-propanol, (C) 2-propanol and (D) DMSO.

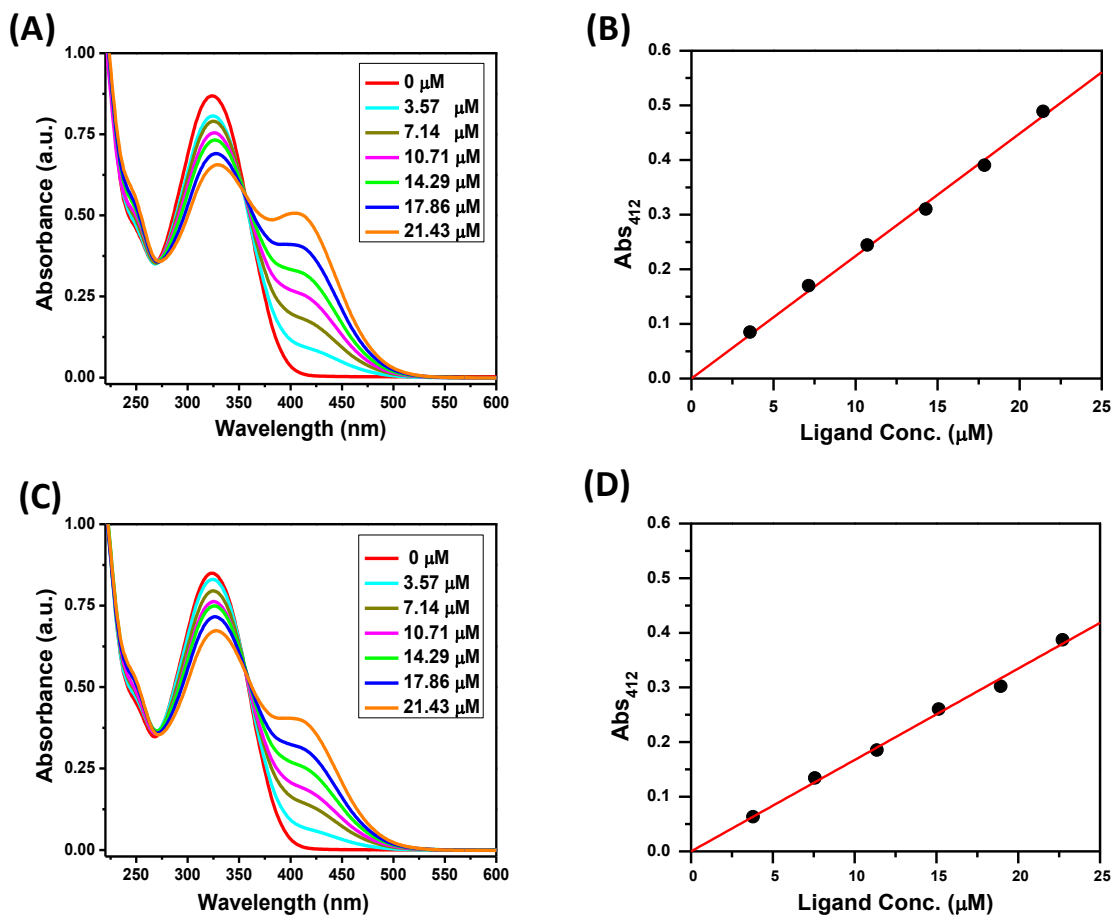


Figure S3. UV-Vis spectroscopy data collected from the Ellman assay of: (A) photo-irradiated LA (LA*), (B) photo-irradiated LA-PEG₇₅₀-OCH₃ (LA-PEG₇₅₀-OCH₃*), both dissolved in methanol. Spectra for six concentrations varying from 0 to ~22 μM are shown. (C) and (D) represent the Beer-Lambert plots of the absorbance at 412 nm versus concentration of LA* and LA-PEG₇₅₀-OCH₃*, respectively; the slope is equal to 23,425 M⁻¹cm⁻¹ for LA* and 17,538 M⁻¹cm⁻¹ for LA-PEG₇₅₀-OCH₃*.

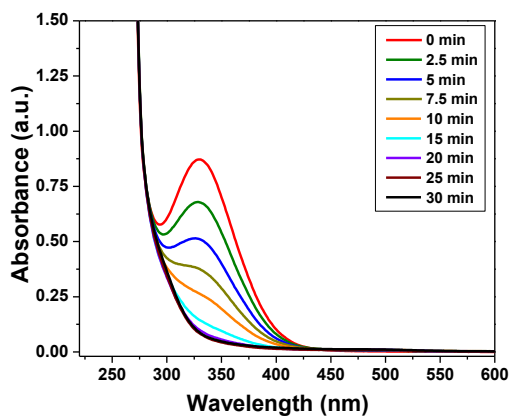


Figure S4. Progression of the UV-Vis absorbance spectra with the UV-irradiation time, collected from methanol solutions of LA-PEG₆₀₀-NH₂* in the presence of added HCl (6 Molar equivalent with respect to ligand).

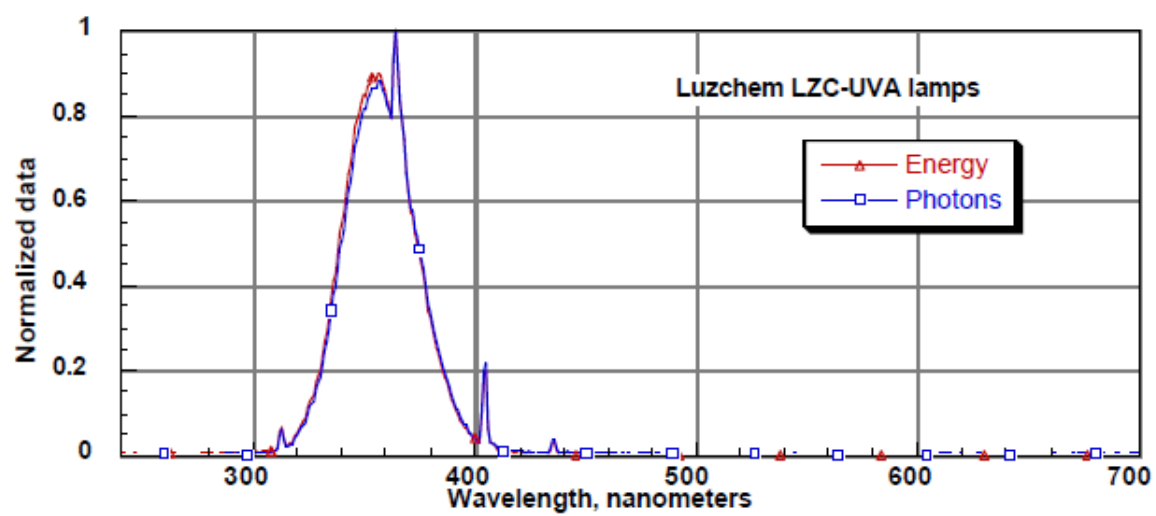


Figure S5. Normalized irradiation spectrum of the Luzchem LZC-UVA lamps used for sample irradiation.



Figure S6. Picture of the UV photoreactor irradiation chamber (Luzchem UV lamp, model LZC 4V). It contains 14 lamps total, 6 installed on top and 8 installed on the sides (4 lamps on each side).