Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Effect of Increasing Ligand Conjugation in Cu(I) Photosensitizers on NiO Semiconductor Surfaces

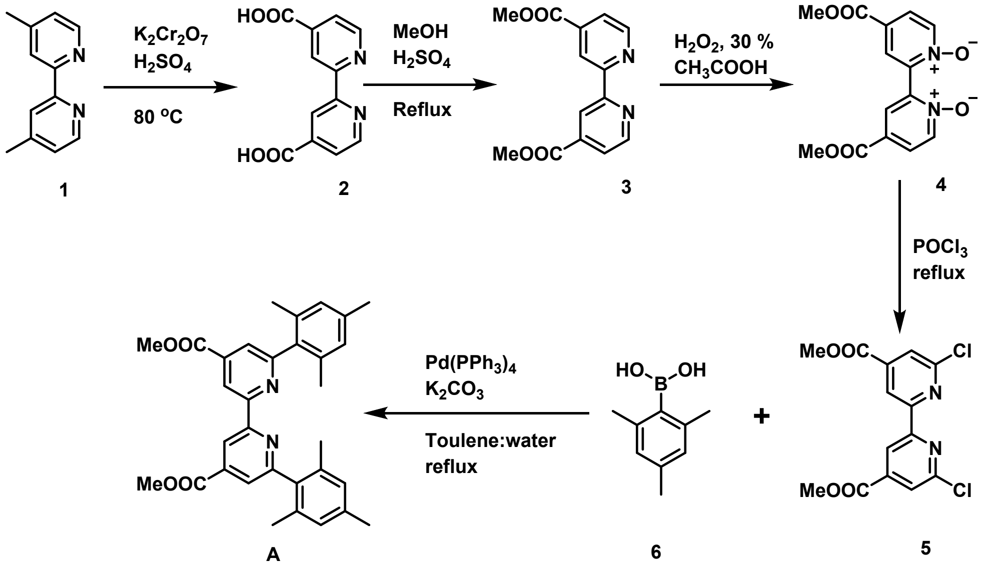
Zujhar Singh[1]*, Joseph D. Chiong*[1]*, Saeid Kamal*[2]*, Marek B. Majewski*[1]***

1. Department of Chemistry and Biochemistry and Centre for NanoScience Research Concordia University, 7141 Sherbrooke Street West, Montreal, Quebec, H4B 1R6, Canada

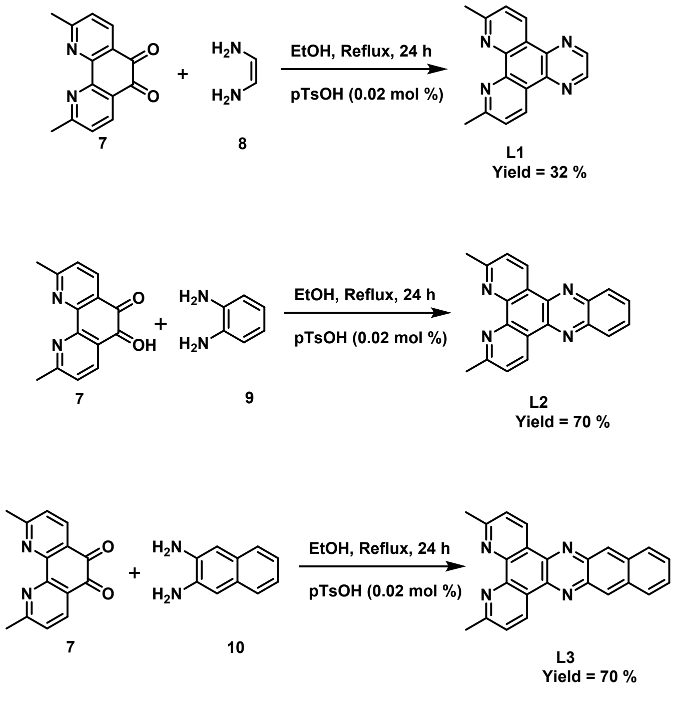
2. Department of Chemistry and Laboratory for Advanced Spectroscopy and Imaging Research (LASIR), The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

E-mail: marek.majewski@concordia.ca

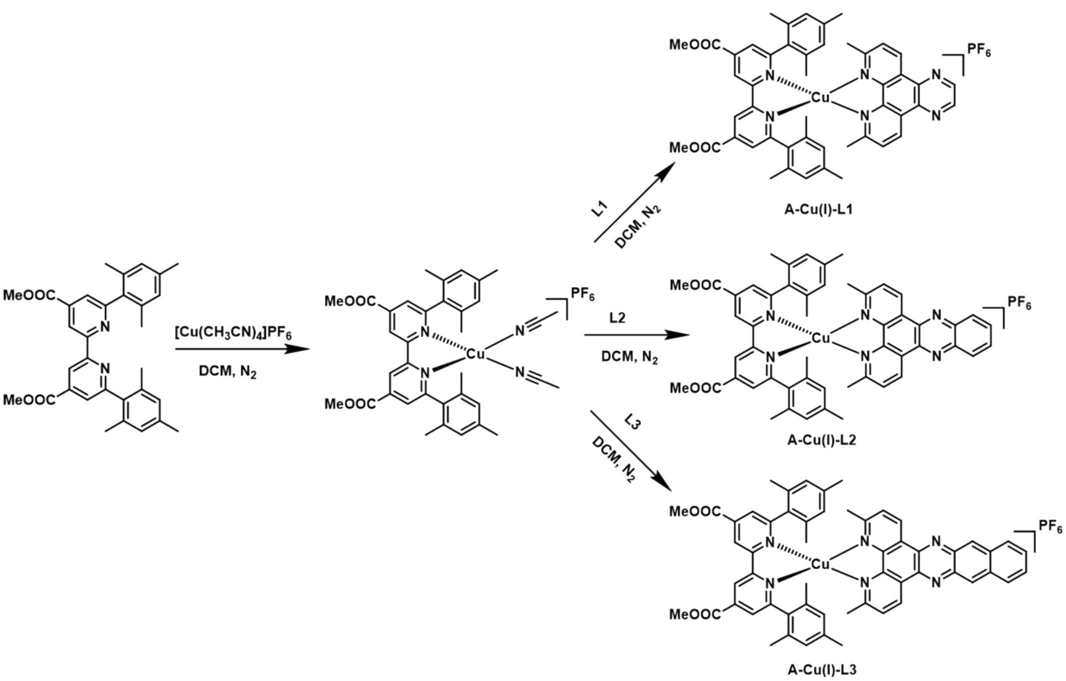
Experimental Procedures



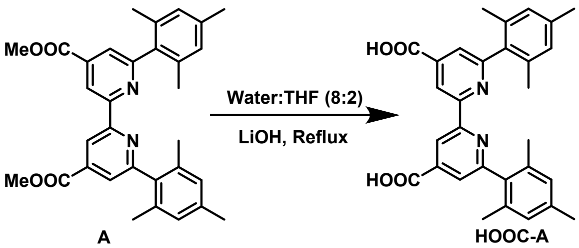
Scheme S1. Synthetic scheme for the synthesis of ligand **A**.



Scheme S2. Synthetic scheme for the synthesis of ligands **L1**, **L2** and **L3**.



Scheme S3. HETPhen synthetic scheme for the synthesis of complexes **A-Cu(I)-L1**, **A-Cu(I)-L2**, and **A-Cu(I)-L3.**



Scheme S4. Synthetic scheme for the preparation of anchoring ligand **HOOC-A**.

Results and Discussions

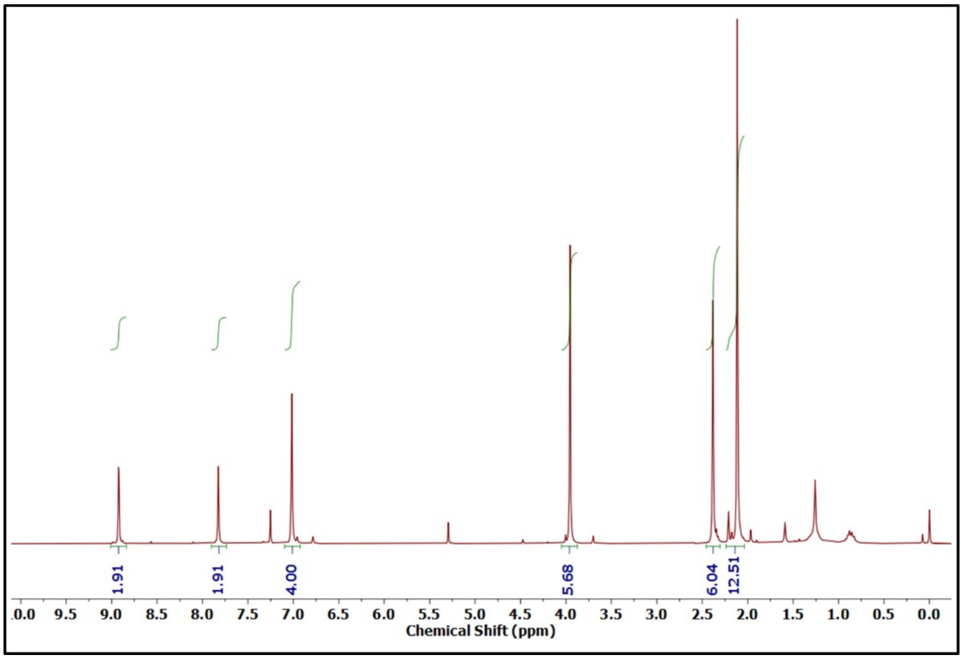


Figure S1. ^{1}H NMR spectra of **A** ($CDCl_3$, 300 MHz).

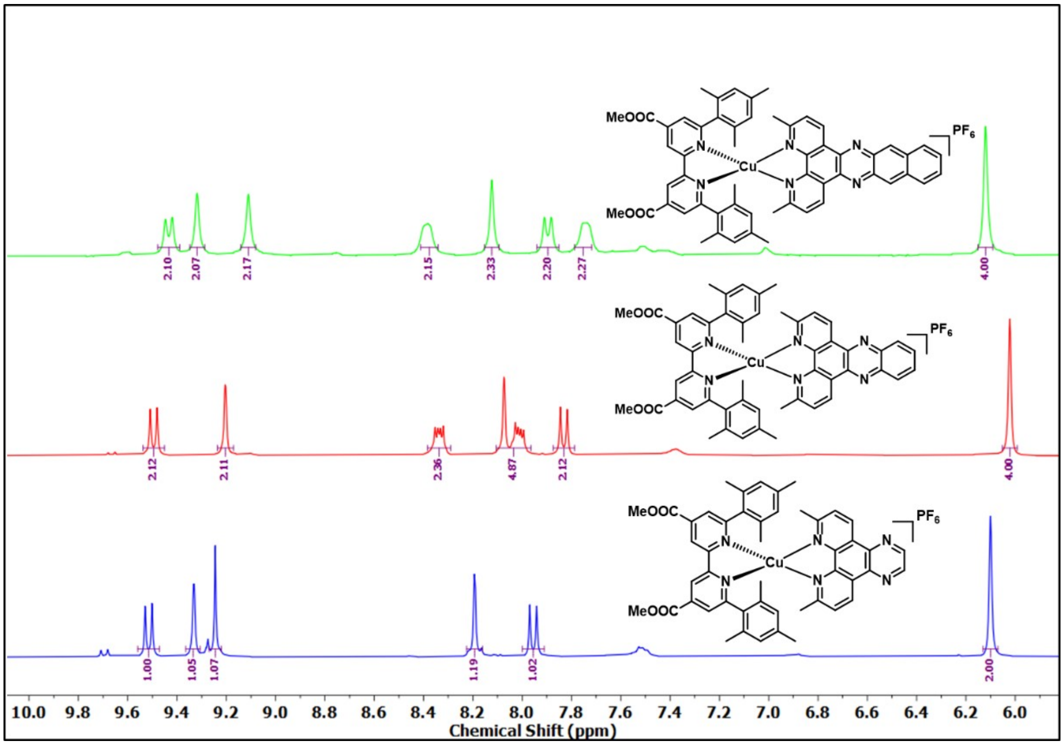


Figure S2. Overlaid ^{1}H NMR spectra of three complexes **A-Cu(I)-L1** (blue), **A-Cu(I)-L2** (red), and A**-Cu(I)-L3** (green) [$(CD_3)_2SO$, 300 MHz].

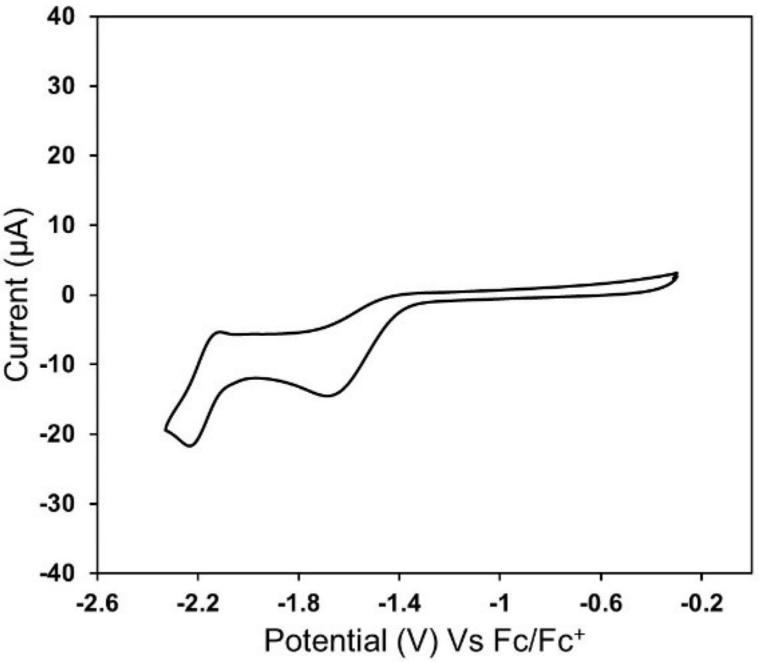


Figure S3. Cyclic voltammograms of reductive side of complex A-Cu(I)-L1. It was recorded in 0.1 M $TBAPF_6$ in DMF at υ = 100 mV/s with a 2 mm Pt button working electrode, Pt mesh as counter electrode, and Ag wire pseudoreference electrode. Potentials are reported vs. the ferrocene/ferrocenium (Fc/Fc^+) redox couple through addition of ferrocene as an internal standard (not shown).

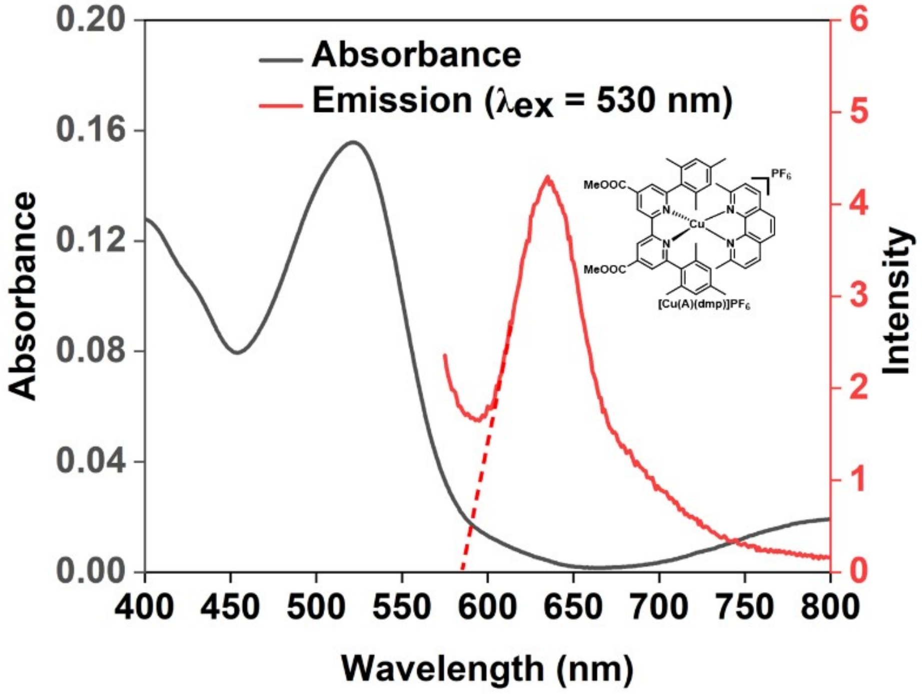


Figure S4. Overlaid photoluminescence (red) and absorbance spectra (black) of [Cu (dmp)(A)]PF_6. Dashed line indicates the intersection of the absorbance and photoluminescence spectra used to calculate E_{00}. Spectra were recorded in deaerated acetonitrile at room temperature (λ_{max} = 530 nm).

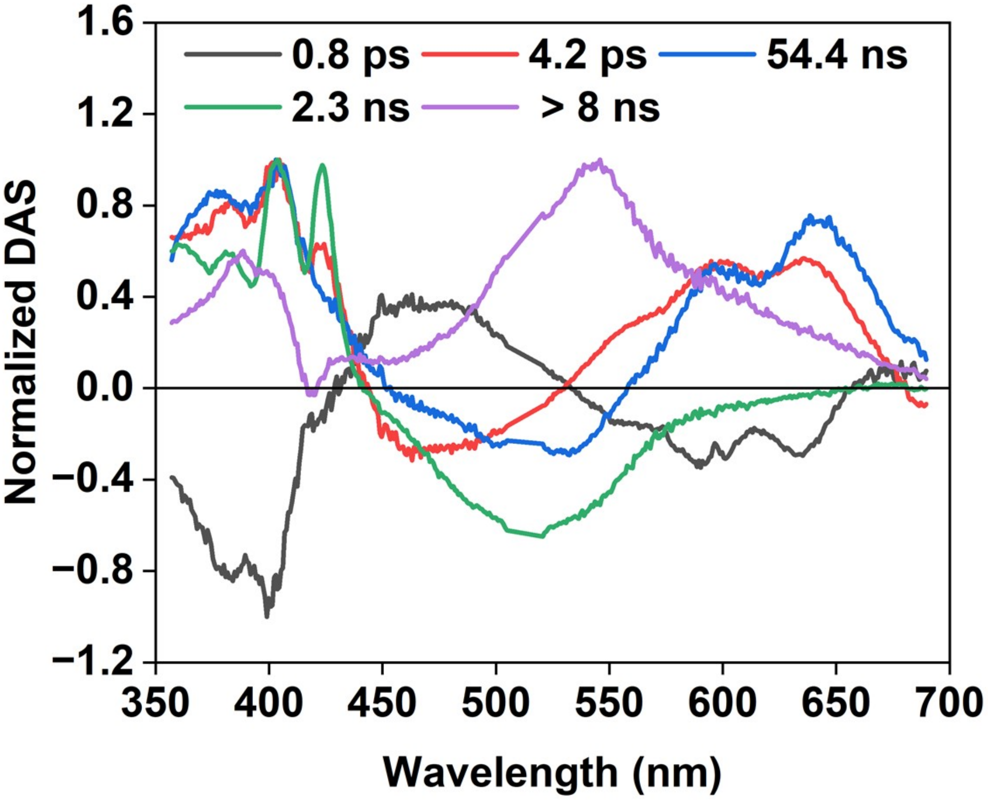


Figure S5. Decay associated spectra of **A-Cu(I)-L3** collected in acetonitrile solution, λ_{ex} = 510 nm, 1 μJ / pulse.

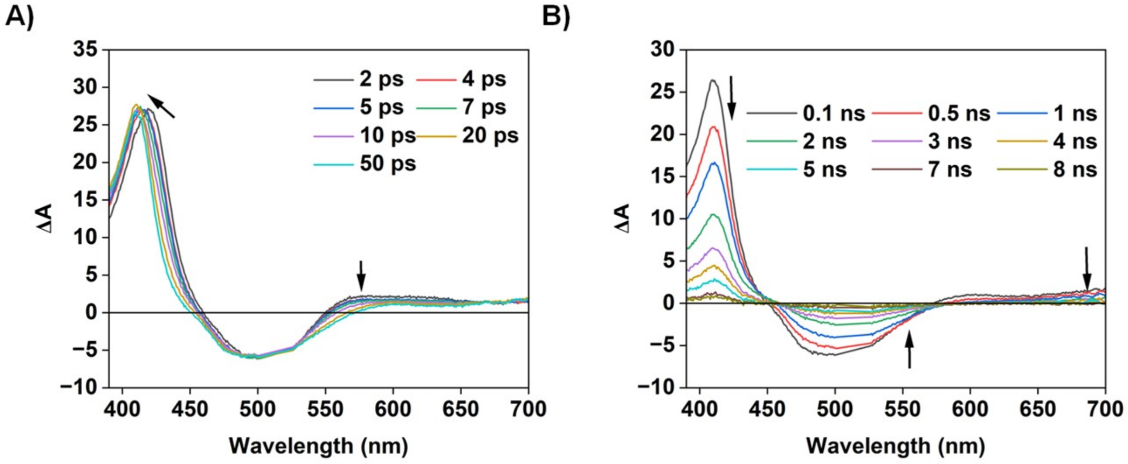


Figure S6. A) Femtosecond transient absorption difference spectra for **A-Cu(I)-L1** at shorter time delays (2-40 ps). B) Femtosecond transient absorption difference spectra for **A-Cu(I)-L1** at longer time delays (50 ps-7 ns) collected in acetonitrile solution, λ_{ex} = 510 nm, 1 μJ / pulse.

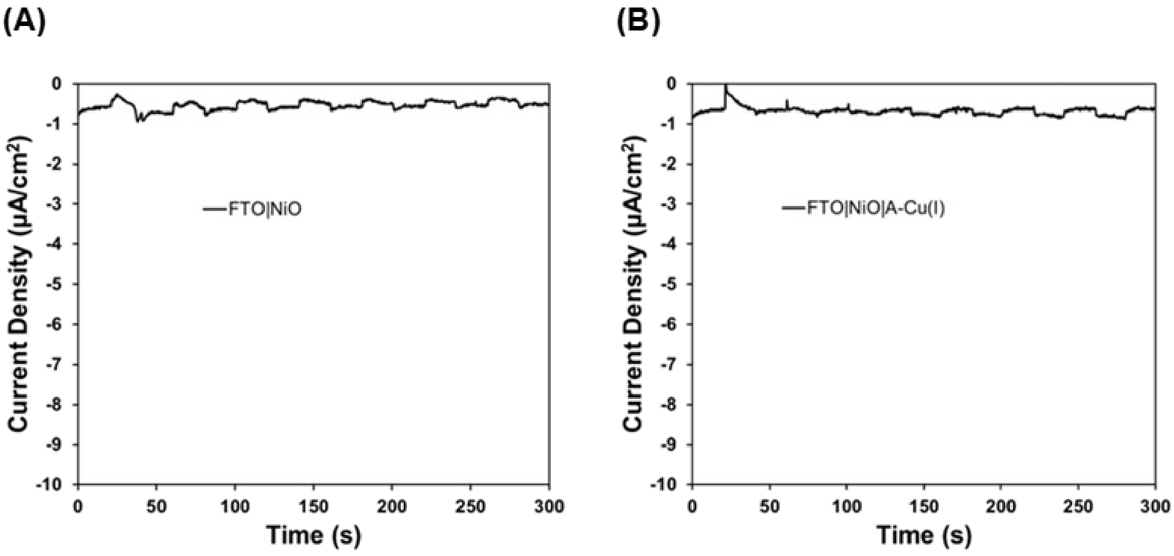


Figure S7. A) Chopped-light chronoamperometry experiment on undecorated semiconductor film FTO|NiO. B) Chopped-light chronoamperometry experiment on partially decorated semiconductor film FTO|NiO|A-Cu(I). Chronoamperograms were recorded in 0.1 M $TBAPF_6$ in acetonitrile at 0V with the film as working electrode, Ag wire as pseudoreference electrode and Pt mesh as the counter electrode.

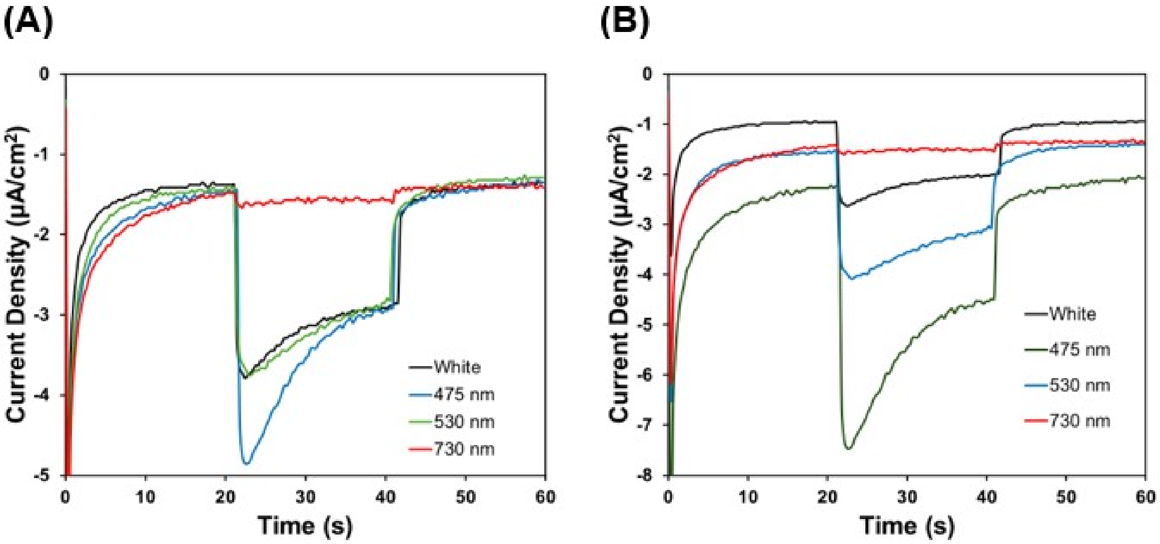


Figure S8. A) Chopped-light chronoamperometry experiment on **NiO|A-Cu(I)-L2** illuminated with a 144 mW/cm^2 single white LED, a 65 mW/cm^2 single blue LED (475 nm), a 92 mW/cm^2 single green LED (530 nm) and a 104 mW/cm^2 single red LED (730 nm). B) Chronoamperogram normalized to 100 mW/cm^2. Chronoamperograms were recorded in 0.1 M TBAPF$_6$ in acetonitrile at −0.4 V with the film as working electrode, Ag wire as pseudoreference electrode and Pt mesh as the counter electrode.