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Synthesis of an Organic Dye-Sensitizer for Solar Cells Bearing Triphenylamine End-Capped with Pyrene

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Introduction

The huge energy demand as well as the increased concern over the release of greenhouse gases in the atmosphere has sparked a great interest in renewable energy research.¹ Alternative to expensive silicon solar cells are dye-sensitized solar cells (DSSC).² Most dyes follow the donor, π bond linker, and acceptor model, or form complexes with noble metals such as Ru, and could produce energy conversion efficiencies (ECE) in the range of 8-12.3%.³ Recently metal free dyes have been studied more for their low cost synthesis and structural variations which have proven to increase efficiency.⁴ Dyes using triphenylamine (TPA) as a donor were of interest for this research. Recent literature has stated that TPA dyes have ECE from 3.5-5.8%,⁵ and are a focus for further improvement. Therefore, we synthesized an organic dye-sensitizer bearing triphenylamine end-capped with pyrene as a donor moiety (Figure 1). And we investigated its electrochemical and spectroscopic properties. The results show the ability of the dye to absorb light in the visible region. Its redox properties shows that the injection of electron in the conduction band of TiO₂ is viable and that the dye can be regenerated from the redox electrolyte (I^-/I_3^-), (Figure 6).⁶

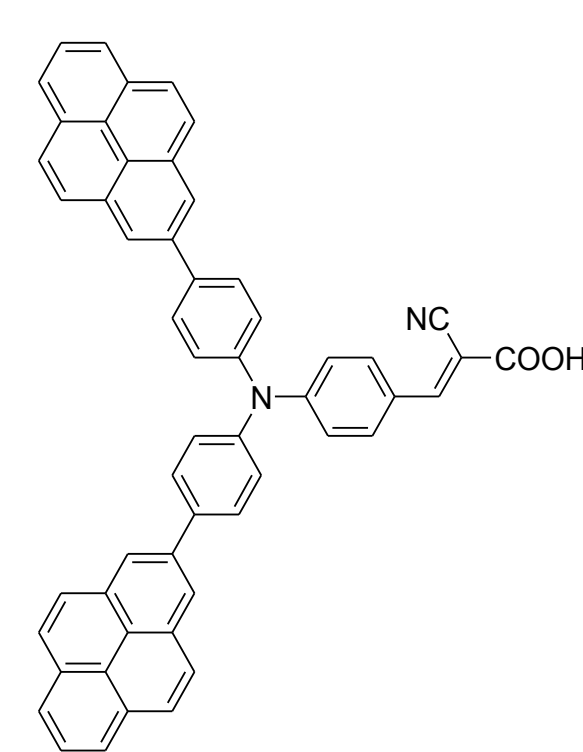


Figure 1. Structure of an organic dye-sensitizer

Materials and Methods

Synthesis of an Organic Dye-Sensitizer

The reagents and solvents for the synthesis of the dye were purchased from VWR and Sigma-Aldrich chemical companies. Solvents were purified and distilled according to standard procedures. The synthesis of an end-capped TPA dye was achieved in three synthetic steps (Scheme 1). The donor moiety, compound **2** was synthesized using Suzuki coupling reaction, by reacting 4,4'-dibromotriphenylamine with pyrene-1-boronic acid in THF with K₂CO₃ and Pd(PPh₃)₄.⁷ The preparation of **3** was accomplished using Vilsmeier-Haak reaction by reacting compound **2** with phosphorous oxychloride in DMF at 0 °C.⁸ And finally the introduction of the acceptor group to produce an organic dye, was achieved using Knoevenagel reaction by reacting **3** with cyanoacetic acid in acetonitrile and piperidine.⁹ The progress of the chemical reactions were monitored by TLC and the purifications of crude intermediates and product were conducted by column chromatography and recrystallization techniques. ¹H NMR spectra were collected in acetone using JEOL 400 MHz instrument.

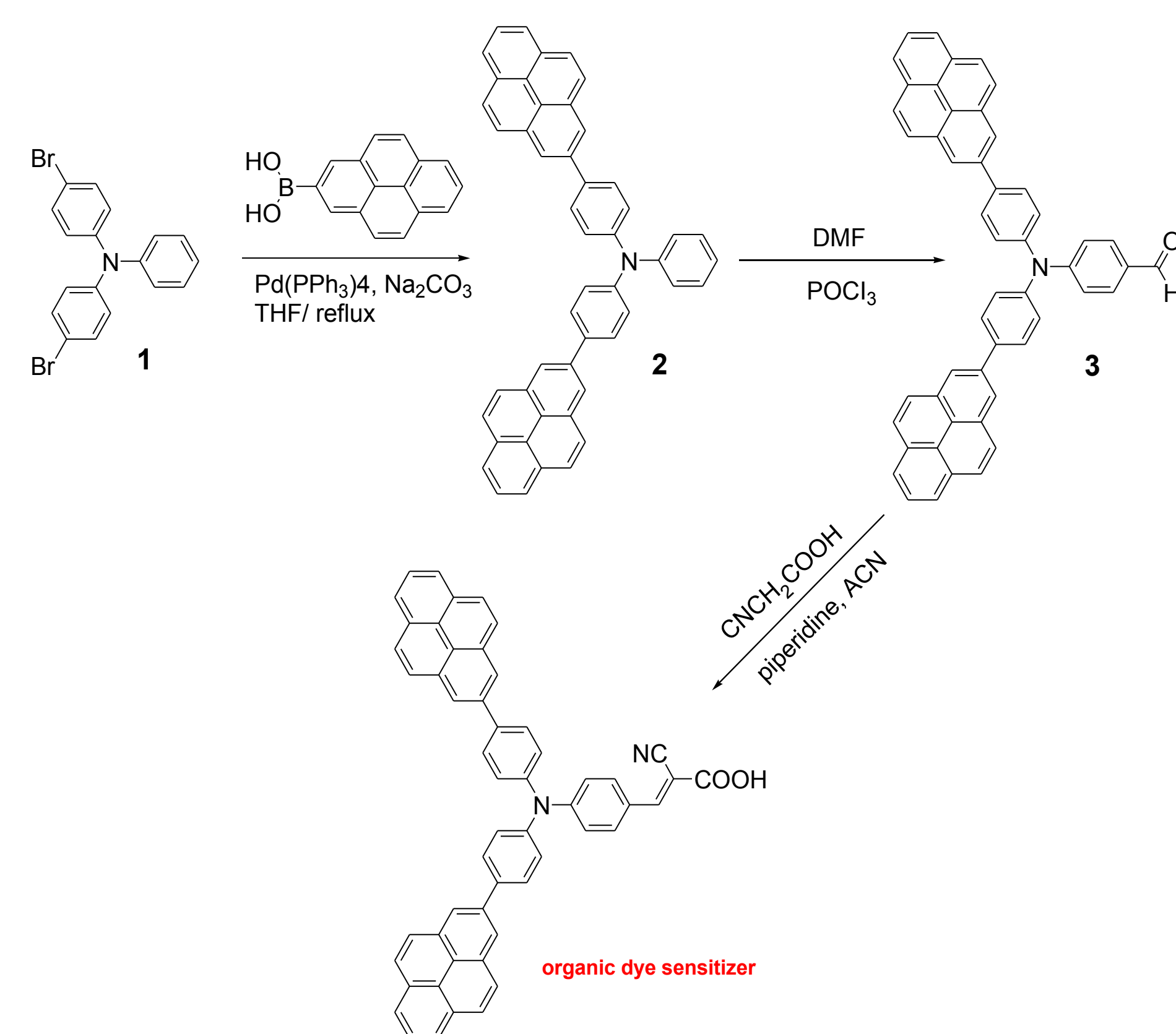
Electrochemical and Spectra Measurements

UV-vis and fluorescence measurements were obtained with Shimadzu spectrometers. The cyclic voltammetric measurements were performed with a three-electrode in a voltammetry cell using CHI Instruments, Electrochemical workstation interfaced with a computer.

Results and Discussions

Characterization of a Dye-Sensitizer

The synthesized dye was characterized by ¹H NMR and IR spectroscopy. The attachment of pyrene to increase the bulkiness of the donor moiety, was confirmed by ¹H NMR (Figure 2). The IR signals at 1700 cm⁻¹ and 2260 cm⁻¹ confirmed the introduction of the functional groups C=O and C≡N respectively in the molecule.



Scheme 1. Synthetic scheme for the preparation of an organic dye-sensitizer

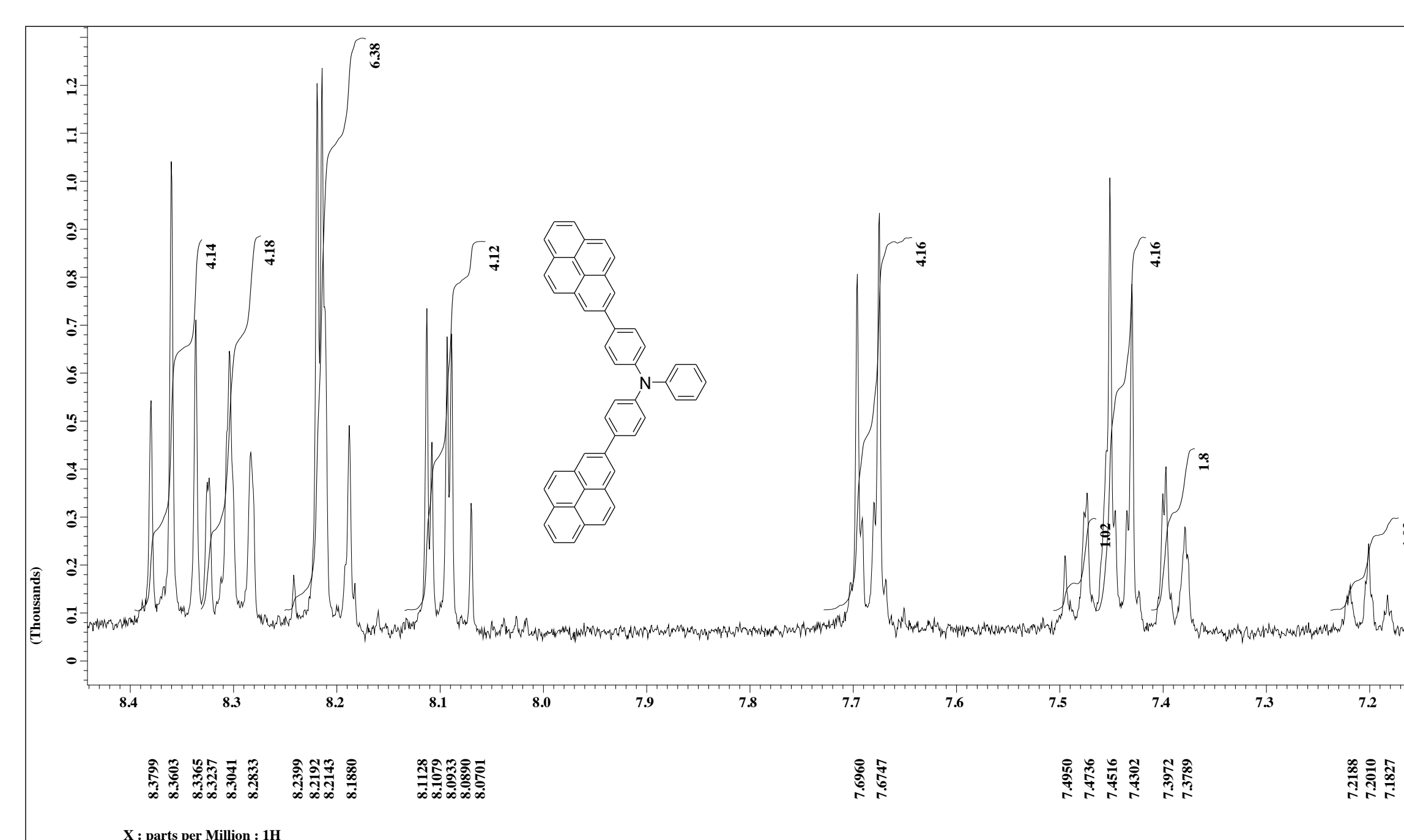


Figure 2. ¹H NMR spectrum of the dye in acetone

Spectroscopic and Redox Properties of the Dye

The UV-vis spectrum of the dye was obtained in CHCl₃ as shown in Figure 3. The absorption spectrum of the dye is red-shifted and extends in the visible region showing that it is able to absorb solar energy. The absorption spectrum shows two major bands at 300-400 nm and 400-550 nm. The UV absorption band at 300-400 nm was attributed to localized aromatic π - π^* transition. And the 400-550 nm visible absorption band was ascribed to intramolecular charge transfer (ICT) transition.¹⁰ In order to measure the oxidation potential corresponding to the HOMO of the synthesized dye, we conducted cyclic voltammetric measurements in CH₂Cl₂. The cyclic voltammogram of a dye in CH₂Cl₂ exhibits two reduction peaks at -1.5 V and -0.6 V vs NHE and an oxidation peak at 1.4 V vs NHE (Fig 4).¹⁰ The HOMO level of the dye is more positive than that of iodine/triiodide (0.4 V vs NHE) and is sufficiently positive to regenerate oxidized dyes from the redox electrolyte (I^-/I_3^-).¹⁰

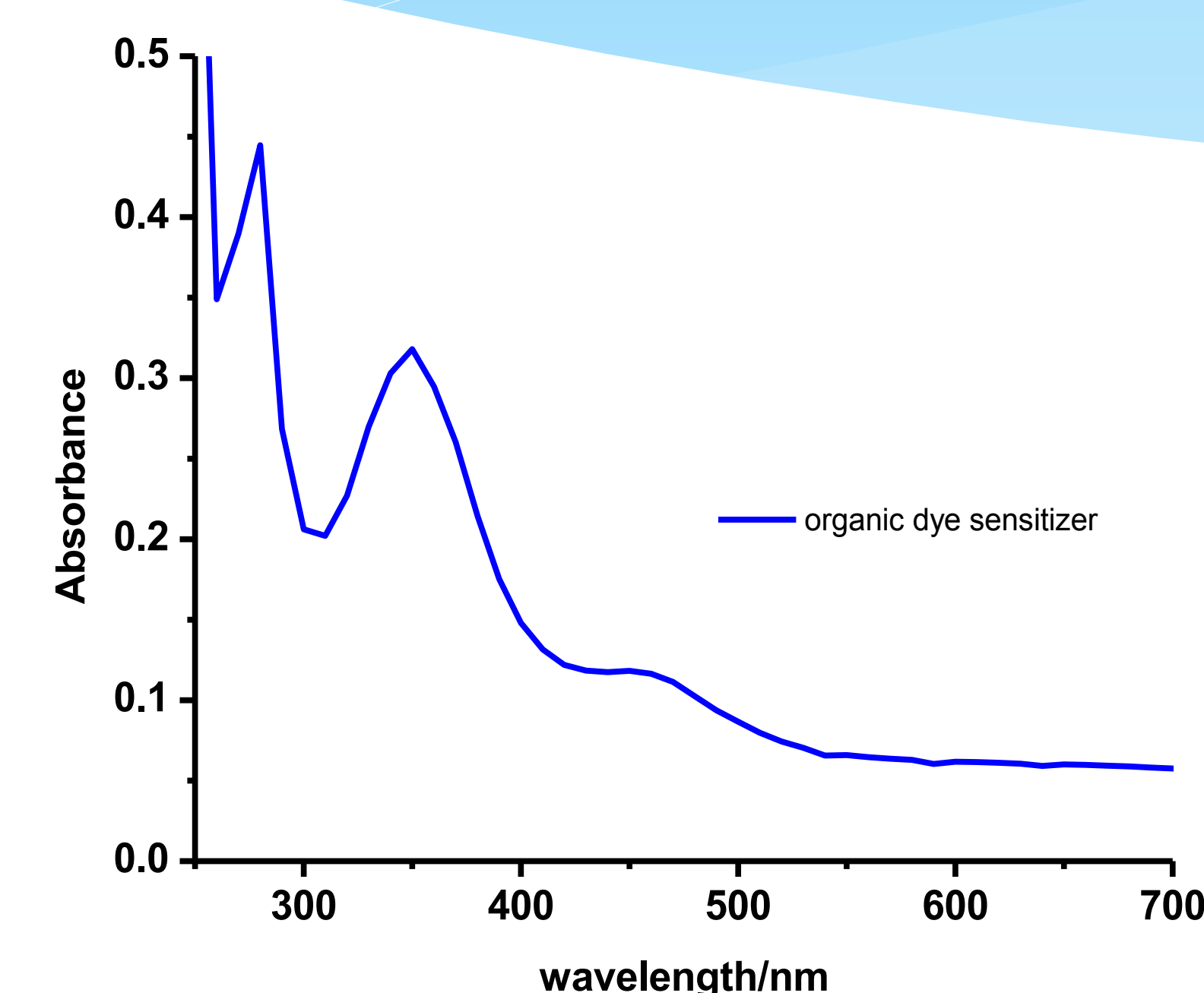


Figure 3. Absorption spectrum of organic dye-sensitizer in CHCl₃

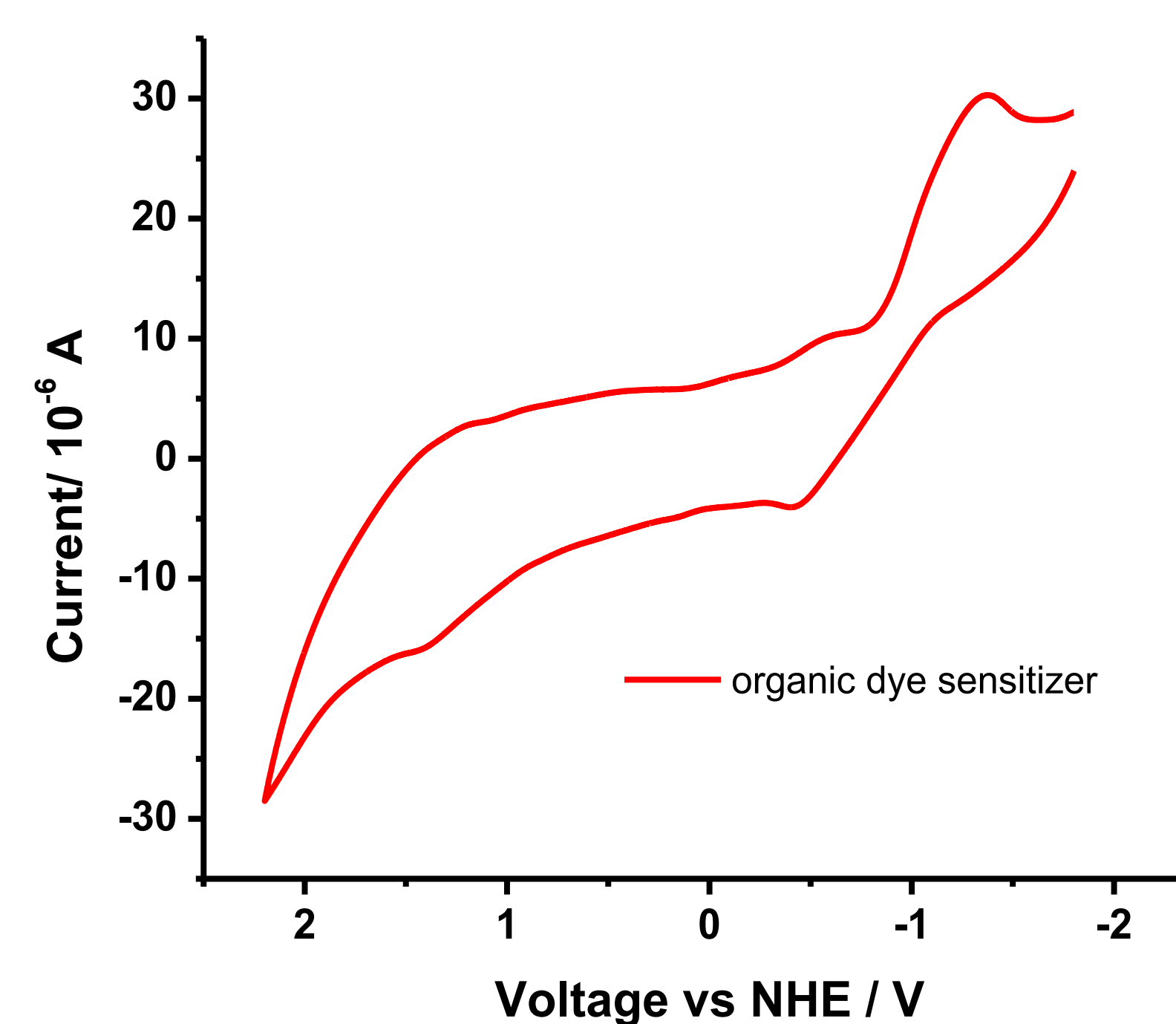


Figure 4. Cyclic voltammograms of dye recorded in dichloromethane (0.1 M TBAP). Sweep rate: 100 mV/s. Working electrode: gold, counter electrode: Pt; reference electrode: Ag/AgCl

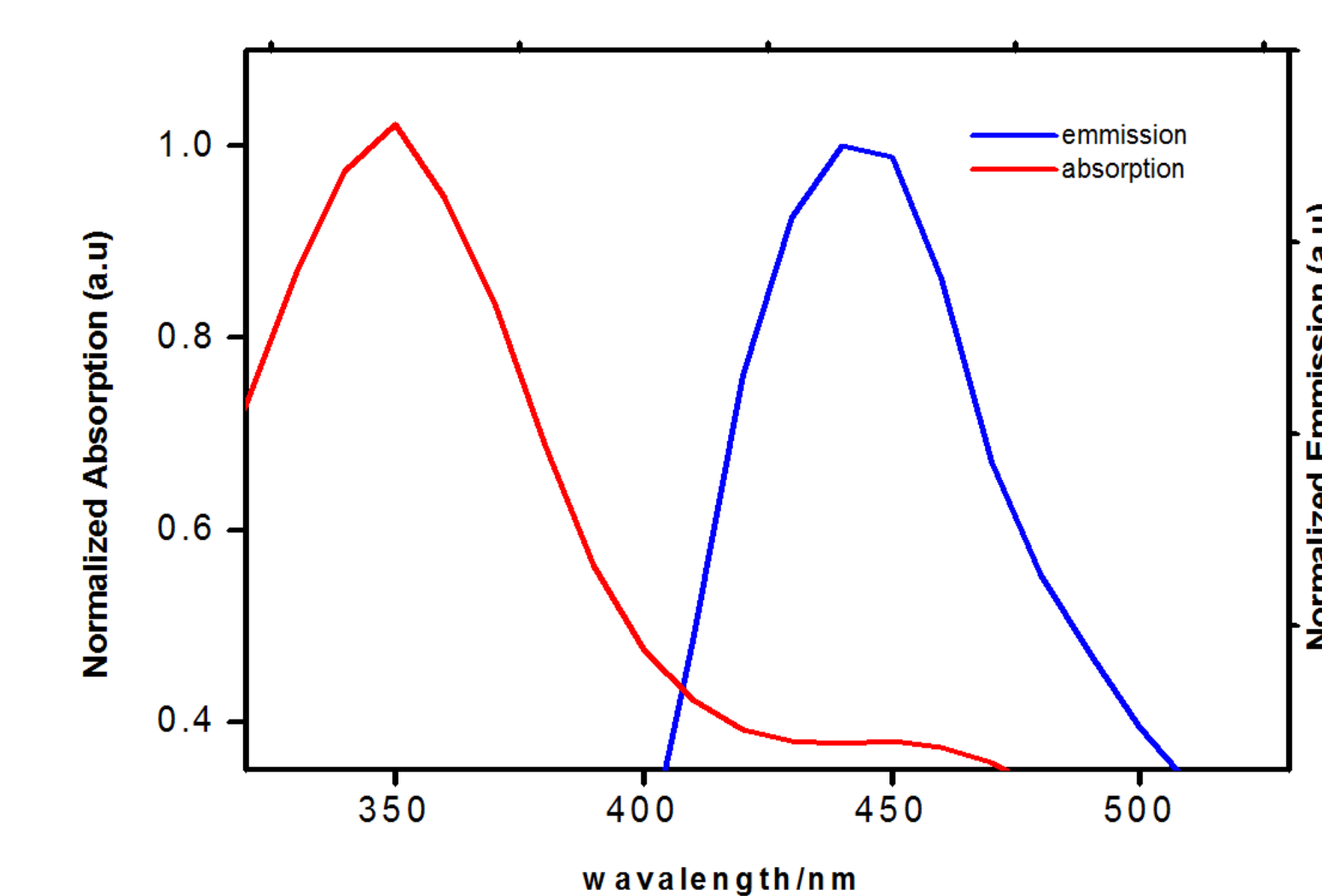


Figure 5. Normalized absorption (red line) and emission (blue line) spectra of an organic dye in chloroform

The LUMO of the dye was obtained by subtracting the zeroth-zeroth (E_{0-0}), estimated from the onset wavelength of the absorption and emission spectrum (Figure 5), from $E-E_{ox}$.¹⁰ The LUMO level of the dye is sufficiently more negative than the conduction band energy level (E_{cb}) of TiO₂ (0.5 V vs NHE) to allow excited electrons to be efficiently injected into the TiO₂ electrode (Figure 6).¹⁰

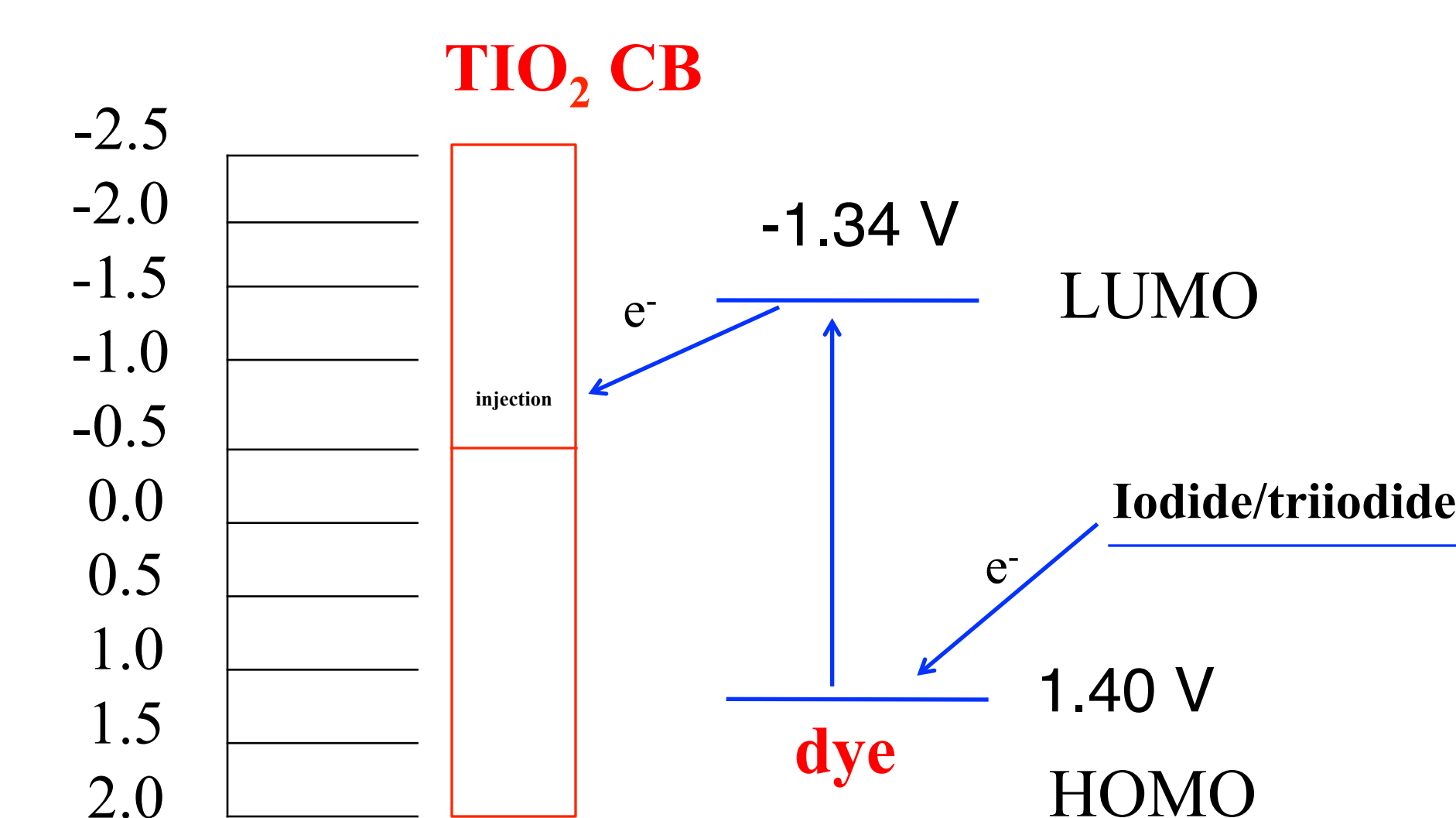


Figure 6. Energy level vs. NHE of the dye

Conclusions

1. We successfully synthesized an organic dye-sensitizer for solar cells
2. The UV/vis spectrum of the dye extends in the visible region where there is maximum solar energy
3. A simple methine unit was chosen as a linker to reduce costs
4. We plan to extend the length of the linker of the dye by incorporating thiophene units in order to broaden the absorption spectrum in the visible region
5. The redox properties of the dye reveal that injection of an electron in the conduction band is viable and that the regeneration of dye is possible from (I^-/I_3^-)
6. Future work will include staining the dye to a ITO-TiO₂ plate and measuring ECE as well as the lifespan of the cell

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