Electronic Properties of a New Photosensitizer-Dye Derived from a Cadmium Selenide Mediated Retinoid/Carotenoid-Based Complexes of Rhenium (I)

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Abstract:

Two new inorganic-based photosensitizer dyes of rhenium(I) attached to retinoid/carotenoid ligands have been synthesized. All ligands were prepared *via* Knoevenagel condensation reactions of all-trans-retinal (1) and β-apo-8'-carotenal with cyanopyridyl. Electronic UV/Visible absorption spectroscopy shows that these complexes absorb visible light efficiently. Absorption wavelengths are in the 450 nm to 600 nm range. Density Functional Theory (DFT) calculations reveal that the frontier molecular orbitals involved during absorption process occur from the HOMO (highest occupied molecular orbital) to low-energy LUMOs (lowest unoccupied molecular orbital) of the Re metal center. Theoretical treatments also show that these orbitals are located primarily on the polyene chain and the energy gap between them is consistent with the observed optical spectrum. The photosensitizer complexes will be attached to cadmium selenide (CdSe) nanoparticles for enhanced photosensitization.

Introduction:

No one to our knowledge has fabricated a photovoltaic (PVC) device driven by light-harvesting antennae derived from plants and bacteria. In this study, two artificial light-harvesting Re(I)-complexes were synthesized in our lab which mimic the major function of β-carotene and all-*trans*-retinal to harness visible light energy during photosynthesis and vision process, respectively. Figure 1 shows our proposed photocathode and how these light-harvesting dyes can be attached to CdSe nanoparticles for enhanced photosensitization. Here, the Re(I)-complex-CdSe dye are attached *via* chemisorption to a diode containing titanium oxide, TiO_2.

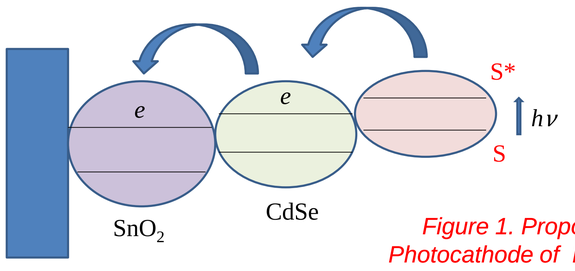
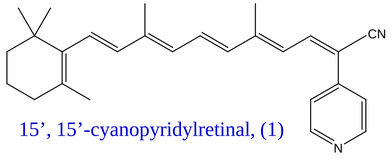
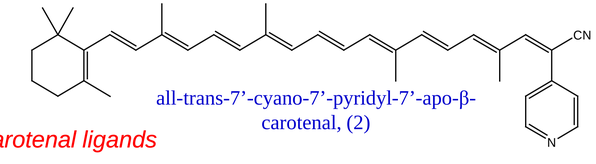


Figure 1. Proposed Photocathode of Dye-Sensitized Solar Cell (DSSC)

Methodology:

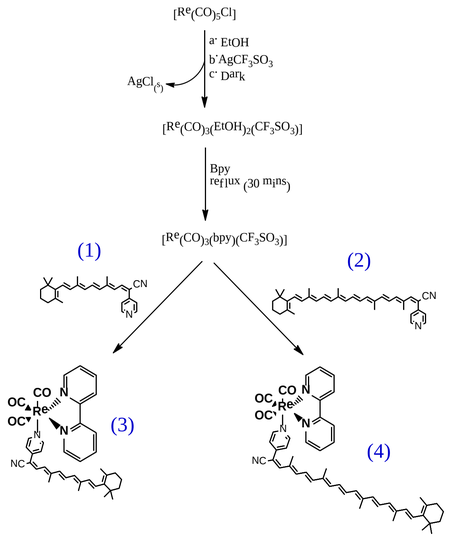


15', 15'-cyanopyridylretinal, (1)



all-trans-7'-cyano-7'-pyridyl-7'-apo-β-carotenal, (2)

Scheme 1. Structures of retinal/carotenal ligands



Scheme 2. Synthesis of Re(I)-complexes

Results and Discussion:

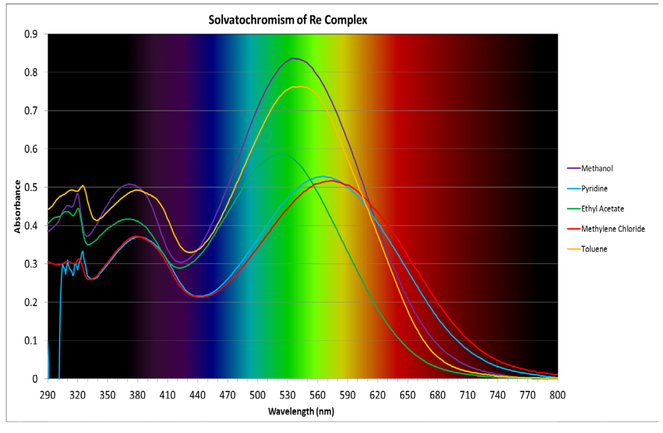


Figure 2. Absorption Spectra of (4) In Various Solvents

Figure 2 shows the absorption spectra of the rhenium (I) – carotenal derivative in various solvents. It is apparent that the absorptivity depends on the polarity of the solvent (solvatochromic behavior). Figures 3 shows the CdSe nanoparticles suspended in 1-octadecene that were synthesized in the lab.

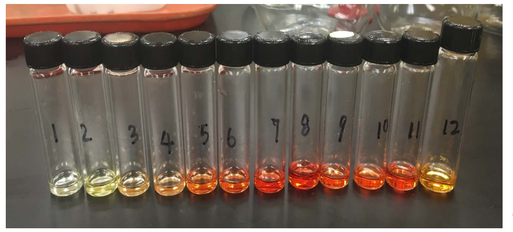


Figure 3. CdSe nanoparticles

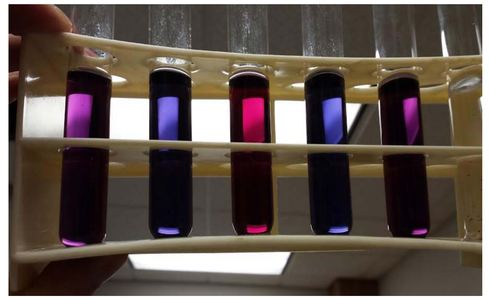
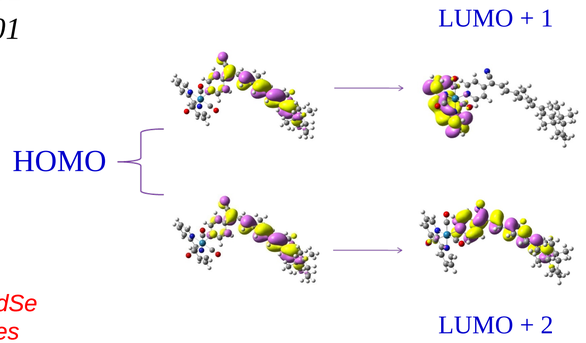


Figure 4. Solvatochromism of (4) In Various Solvents

Figure 3 is a picture of CdSe nanocrystals having varying sizes. The solvents used (left to right in Figure 4) are: methanol, pyridine, ethyl acetate, methylene chloride and toluene. Figure 5 shows the overlay of experimental with theoretical absorption spectra. Results show that theoretical treatments can be used to assign absorption bands and supports the claim that electron density shifts from the polyene HOMO orbitals to the LUMO frontier orbitals of the metal center. The type of PVC device that is proposed in this study is dye-sensitized solar cell (DSSC). Figure 6 shows the mechanism of photosensitization and electron transfer reaction steps that are vital during the solar to electrical energy conversion.



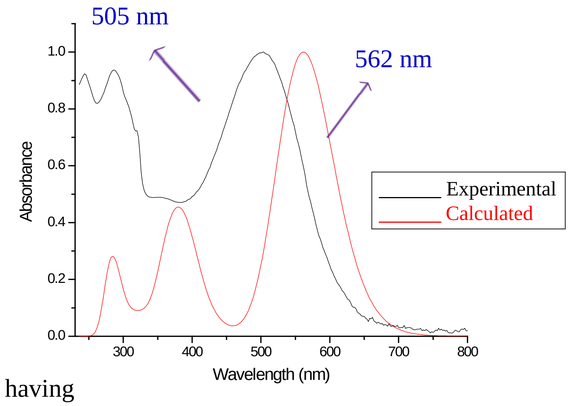


Figure 5. Visible Light Absorption of (6)

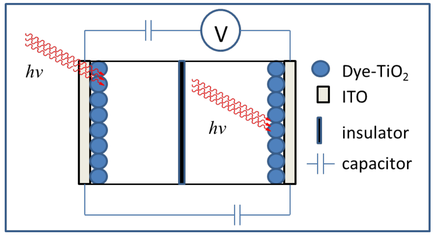


Figure 6. Light-harvesting Mechanism of Proposed PVC

Conclusions:

Inorganic photosensitizer dyes based on a natural product (β-carotene) derivative and rhenium metal were synthesized. Electronic absorption spectroscopy shows that these dyes have strong absorption in the visible spectrum; therefore, they can be used as light-harvesting antenna in dye-sensitized solar cells (DSSCs).

References:

(1) Cruz, A.J.; Siam, K.; Rillema, D.P. *J. Phys. Chem. A* 2011, 115, pp. 1108-1116.

(2) Knoevenagel, E. *Chem. Ber.* **1894**, 27, 2345