

Chapter8

Concluding remarks

In the dye-sensitized solar cells, sensitizer is a pivotal and unique component with a function of light-harvesting. Its spectral response overlap with the solar emission will affect the device photocurrent to a large extent. Therefore, the simulation of the absorption spectra has a preliminary evaluation on their light-harvesting ability. The calculated wavelength, oscillator strength and transition energies for the most relevant transitions of the electronic absorption bands of these dyes in vacuum phase are obtained through TD-DFT and CIS-DFT calculations.

The aggregation of the dye, electronic structure also affects photovoltaic performance significantly. In DSSCs, one of the most important features for a metal substituted organic dye is intramolecular charge transfer (ICT) from electron donating part to the electron accepting part. The electronic structures of HOMO-1, HOMO, LUMO and LUMO+1 of the six metals substituted Phthalocyanine (SiCl₂Pc, SiO₂Pc, ZnCl₂Pc, NiPc, CuPc, CoPc) dyes are studied, and all these dyes have good electron-separated states. The electron densities of HOMO of metal substituted Phthalocyanine dyes are localized on the donor and the bridge, whereas the electron density of LUMO is mainly localized on the bridge and acceptor units (mostly in the

anchoring group), so the electronic transitions of metal substituted Phthalocyanine dyes from HOMO to LUMO could lead to intramolecular charge transfer from the donor units to the anchoring groups through the conjugated bridge. Therefore, when the dyes are anchored on the surface of TiO₂, the LUMO centered on the anchoring moiety should enhance the orbital overlap with the titanium 3d orbital and subsequently favor the electron injection to the conduction band of TiO₂.

We know that LUMO energy levels of the six dyes are much higher than that of TiO₂ conduction band edge (ca -4.0 eV). Thus, molecules in excited states of all metal substituted Phthalocyanine have a strong ability to inject electrons into TiO₂ electrodes. The HOMO of all dyes are all lower than that of I⁻/I₃⁻ (ca -4.8 eV), therefore, these molecules that lose electrons could be restored by getting electrons from electrolyte. The order of the LUMO energy gaps is NiPc (-3.67 eV) < ZnCl₂Pc (-3.51 eV) < CuPc (-3.49 eV) < SiCl₂Pc (-3.44 eV) < CoPc (-2.99 eV) < SiO₂Pc (-2.98 eV), thus, the order of the driving forces for electron injection from molecular excitation state of the dyes to TiO₂ electrode is SiO₂Pc > CoPc > SiCl₂Pc > CuPc > ZnCl₂Pc > NiPc. The order of the HOMO-LUMO gaps is NiPc (1.47 eV) < ZnCl₂Pc (1.82 eV) < CuPc (1.42 eV) < SiCl₂Pc (1.89 eV) < CoPc (1.87 eV) < SiO₂Pc (2.57 eV). With the HOMO-LUMO gap decrease, more photons at the longer-wavelength side would be absorbed to excite the electrons into the unoccupied molecular orbital, which increases the short circuit current

density and further enhances the conversion efficiency of the corresponding solar cell.

The simulated absorption spectra of these dyes are studied in the help of TD-DFT and CIS-DFT method. Simulated absorption spectra results showing a red-shift of the absorption maximum from $\text{SiO}_2\text{Pc} > \text{CoPc} > \text{SiCl}_2\text{Pc} > \text{CuPc} > \text{ZnCl}_2\text{Pc} > \text{NiPc}$. The absorption spectral features in visible and near-UV region were assigned based on the qualitative agreement to TD-DFT and CIS-DFT calculations. The absorptions are all ascribed to $n \rightarrow \pi^*$ transition. This also indicates that, in order to $\text{NiPc} < \text{ZnCl}_2\text{Pc} < \text{CuPc} < \text{SiCl}_2\text{Pc} < \text{CoPc} < \text{SiO}_2\text{Pc}$ could harvest more light at the longer-wavelength side, which is beneficial to further increase the photo-to-electric conversion efficiency of corresponding solar cell. Based on the analysis of geometries, electronic structures, and electronics absorption spectrum properties of metal substituted phthalocyanine, the role of metals in phthalocyanine is as follows: it enlarged the distance between electron donor group and semiconductor surface, and decreased the timescale of the electron injection rate, resulted in giving lower conversion efficiency. This indicates that the choice of the appropriate conjugate bridge in dye sensitizer is very important to improve the performance of DSSC.