Thiophene Linked Porphyrin Derivatives for Dye Sensitized Solar Cell

Villari A. Nuay, Dong Hee Kim, Sang Hee Lee, and Jaecugn Ko

Department of Chemistry, Kunsan National University, Kunsan 572-701, Korea. E-mail: leeshy@kunsan.ac.kr
1Department of Material Chemistry, Korea University, Jochiwon 339-700, Korea. E-mail: jkjo@korea.ac.kr

Received September 3, 2009, Accepted October 8, 2009

Key Words: Dye sensitized solar cell, Thiophene. Porphyrin. Aggregation

Porphyrians have long been studied as promising components of molecular electronic and photonic devices. Since the earliest reports of the efficient charge injection into nanocrystalline TiO2 by covalently bound zinc tetakis(4-carboxyphenyl)porphyrin (ZnTCPP), the photosensitization of TiO2 electrodes by porphyrians has been extensively studied.

Inferior performances of porphyrians to ruthenium polypyridyl complexes as photosensitizers would be attributed to the limited light absorption. Poor matching to solar light distribution. A strategy to solve this problem is to make a strong and narrow Soret band broad and weak Q bands strong by extension of the porphyrin π-system by modifying a β-position.

It is known that attachment of a thiophene unit induced a bathochromic shift, an intensification of the absorbity and an increased lifetime of the excited-state. Siebbeles found 4-ethyl group of meso-phenyl exhibit a maximum charge separation efficiency over other porphyrin derivatives.

At this moment, to explore nature of the linker between porphyrin and anchoring group, β-substituted porphyrians KS-1, KS-2 and KS-3 containing thiophene linker and ethyl group on meso-phenyl group were synthesized and characterized their photoelectronic properties.

Synthesis of KS-1, KS-2 and KS-3 were readily achieved from key intermediates 1 and 4 using Suzuki coupling reaction and Wittig reaction (Scheme 1 and 2). The UV-Vis spectra of KS-1, KS-2 and KS-3 show a series of bands between 400 and 650 nm due to π-π* transitions on the conjugated macrocycle that are red-shifted with respect to the B- and Q-bands of ZnTCPP.

Absorption intensity of KS-2 and KS-3 at 450 ~ 550 nm were drastically increased compared to ZnTCPP as we expected. However, a narrower absorption spectrum of KS-1 means inefficient conjugation between porphyrin and thiophene ring. In energy minimized structure of KS-1, the thiophene ring plane is largely deviated from porphyrin ring plane (dihedral angle of C1-C2-C3-C4 in Fig. 1: 49 degree) due to the steric hindrance between meso-aryl and thiophene.

DSSC based on synthesized dyes were fabricated according to reference. Quantity of anchoring dye and cell efficiency depend on dye dipping time (2 × 10⁻⁴ M in EtOH) in the absence of co-sorbate. The longer dipping time increased the cell efficiency of KS-1 (2 h: η = 0.9%). 24 h: η = 1.5%), but decreased those of KS-2 (2 h: η = 2.2%, 24 h: η = 1.4%) and KS-3 (2 h: η = 2.5%, 24 h: η = 1.8%) even though the quantity of anchored dye were increased in all cases. These results show that KS-2
and KS-3 have a tendency to undergo aggregation due to its almost planar structure (Fig. 3) which resulted to the reduced cell efficiency. However, the bent structure of KS-1 was able to suppress the aggregation (Fig. 3).

The aggregation problem of KS-2 and KS-3 was resolved by using chenodeoxycholic acid (CDCA) as a co-adsorbate (0.2 mM dye and 10 mM CDCA in THF; dipping time: 24 h) which resulted to more than twice of the analogues without CDCA. (Table 1) Even though KS-2 and KS-3 show similar UV-Vis absorption spectrum and same fashion of IPCE (Fig. 4), Jsc of KS-3 is higher than that of KS-2. Main difference of KS-2 from KS-3 is length of linker and quantity of anchored dye on TiO2 (quantity of anchored dye on TiO2 after 24 h dipping: KS-1: 2.5 × 10^{-8} mol cm^{-2}, KS-2: 4.1 × 10^{-8} mol cm^{-2}, KS-3: 4.6 × 10^{-9} mol cm^{-2}).

The low binding ability of KS-1 can be explained due to the shorter length of linker and bent structure (Fig. 4). Porphyrrin plane of KS-1 is largely bent from the linker group, leading to steric hindrance between porphyrin moiety and surface of TiO2.

The elimination of the C=C double bond of KS-2 giving KS-1 was done to prevent the possible photoisomerization which could decrease efficiency. However, contrary to our expectation, the efficiency of KS-1 is much lower than KS-2. Low efficiency of KS-1 can be explained partly due to very narrow and blue shifted absorption spectrum. Furthermore, it is noteworthy that the quantity of anchored dye KS-1 on TiO2 is lower than those of KS-2 and KS-3. Efficiency of KS-1 was drastically decreased after one week while those of KS-2 and KS-3 were retained. This result shows that low binding ability of KS-1 caused dye desorption from TiO2 surface into electrolyte.

In conclusion, configuration of dye can affect not only its binding ability to TiO2 but also dye aggregation and conjugation. Low efficiency of KS-1 can be explained by narrow absorption spectrum and low binding ability. The low binding ability of KS-1 caused serious dye desorption after cell fabrication. A maximum η value of 4.0% is achieved under AM 1.5 irradiation with a DSSC based on KS-3. To obtain a better η, further optimization of molecular design based on KS-3 and the fabricated fundamental conditions of DSSCs will be studied in detail in our future work.

Acknowledgments. This paper was supported by research funds of Kunsan National University.

References.

8. Optimized structures were obtained at B3LYP/6-31G(d) using QM3.

Table 1. Photovoltaic performances of DSSC using KS-1, KS-2, and KS-3.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Jsc (mA cm^{-2})</th>
<th>Voc (V)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS-1</td>
<td>1.6</td>
<td>0.49</td>
<td>67.5</td>
<td>0.5</td>
</tr>
<tr>
<td>KS-2</td>
<td>11.8</td>
<td>0.60</td>
<td>63.9</td>
<td>3.2</td>
</tr>
<tr>
<td>KS-3</td>
<td>13.0</td>
<td>0.61</td>
<td>65.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Performances of DSSCs were measured with 0.16 cm^{-2} working area. The cell consists of 0.6 M DMF/anisole, 0.05 M LiI, 0.1 M LiCl, 0.5 M TBP in acetonitrile.