

Thiophene Linked Porphyrin Derivatives for Dye Sensitized Solar Cell

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Porphyrins have long been studied as promising components of molecular electronic and photonic devices.¹ Since the earliest reports of the efficient charge injection into nanocrystalline TiO₂ by covalently bound zinc tetrakis(4-carboxyphenyl)porphyrin (ZnTCPP), the photosensitization of TiO₂ electrodes by porphyrins has been extensively studied.²

Inferior performances of porphyrins 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 Sorét band broad and weak Q bands strong by extension of the porphyrin π -system by modifying a β -position.³

It is known that attachment of a thienyl unit induced a bathochromic shift, an intensification of the absorptivity and an increased lifetime of the excited-state.⁴ Siebbeles found 4-ethyl

group of *meso*-phenyl exhibit a maximum charge separation efficiency over other porphyrin derivatives.⁵

At this moment, to explore nature of the linker between porphyrin and anchoring group, β -substituted porphyrins 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**³ and **4**⁶ 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.⁷

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.⁸

DSSC based on synthesized dyes were fabricated according to reference.⁹ Quantity of anchoring dye and cell efficiency depend on dye dipping time (2×10^{-4} M in EtOH) in the absence of co-adsorbate. The longer dipping time increased the cell efficiency of KS-1 (2 h: $\eta = 0.9\%$, 24 h: $\eta = 1.5\%$) but decreased those of KS-2 (2 h: $\eta = 2.2\%$, 24 h: $\eta = 1.4\%$) and KS-3 (2 h: $\eta = 2.5\%$, 24 h: $\eta = 1.8\%$) even though the quantity of anchored dye were increased in all cases. These results show that KS-2

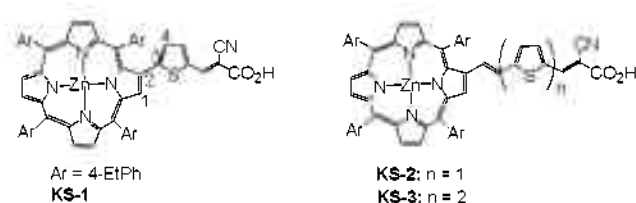
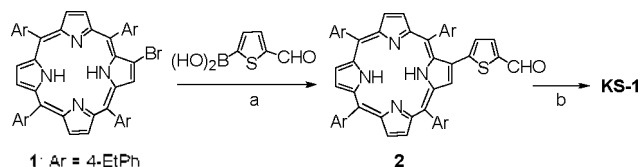
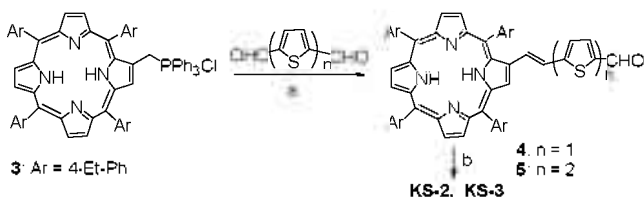


Figure 1. Chemical structure of dyes.



Scheme 1. (a) Pd(PPh₃)₄, K₂CO₃/toluene, reflux, 2 days (25%); (b) (i) Zn(OAc)₂/CH₂Cl₂-MeOH, rt, 5 h; (ii) cyanoacetic acid, piperidine/CH₃CN, reflux, overnight (56%)



Scheme 2. (a) (i) DBU/CH₂Cl₂, rt, 30 min; (ii) I₂, rt, overnight (69% for **4**, 81% for **5**); (b) (i) Zn(OAc)₂/CH₂Cl₂-MeOH, rt, 5 h; (ii) cyanoacetic acid, piperidine/CH₃CN, reflux, overnight (81% for KS-2, 76% for KS-3)

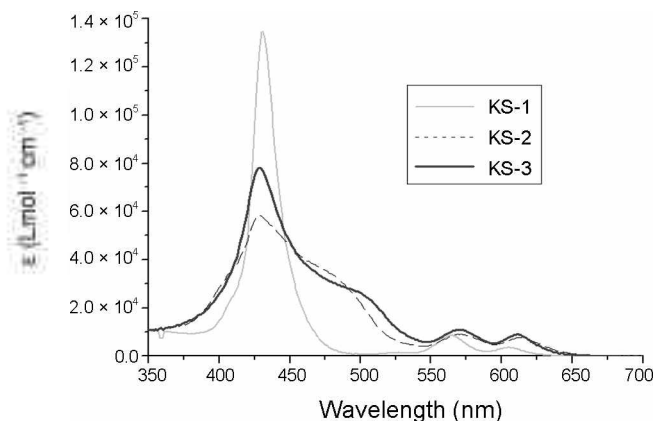


Figure 2. UV-Vis spectra of dyes in THF solution.

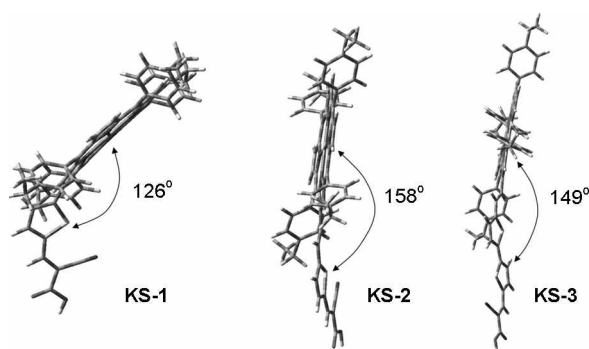


Figure 3. Optimized structures of dyes.

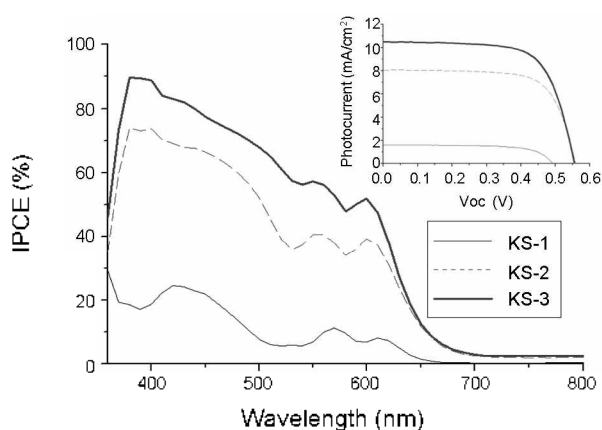


Figure 4. IPCE spectra for DSSC based on dyes under AM 1.5 irradiation.

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). J_{sc} 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 TiO_2 . (quantity of anchored dye on TiO_2 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^{-8} 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).⁸ Porphyrin ring plane of KS-1 is largely bent from the linker group, leading to steric hindrance between porphyrin moiety and surface of TiO_2 .

The elimination of the C=C double bond of KS-2 giving KS-1 was done to prevent the possible photoisomerization which could

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

Dyes	J_{sc} (mA cm^{-2})	V_{oc} (V)	ff	η^a (%)
KS-1	1.6	0.49	67.5	0.5
KS-2	11.8	0.60	63.9	3.2
KS-3	13.0	0.61	65.9	4.0

^aPerformances of DSSCs were measured with 0.16 cm^2 working area. Electrolyte: 0.6 M DMPI in I₂, 0.1 M LiI, 0.5 M TBP in acetonitrile.

decrease efficiency.¹⁰ 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 TiO_2 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 TiO_2 surface into electrolyte.

In conclusion, conformation of dye can affect not only on binding ability to TiO_2 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.

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