**Communication**

# Synthesis and Spectroscopic Analysis of *Trans*-A$_2$B$_2$ Metallo-Porphyrin Derivatives as Heterojunction Modulator for Organic Solar Cell

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**ABSTRACT**: The *trans*-A$_2$B$_2$ porphyrin and Ni-porphyrin derivatives were synthesized by Suzuki coupling of bromoporphyrin with arylborate as a key step. The band gaps of those complexes were measured from their absorption, emission and cyclic voltammetric data. All the LUMO energy level of porphyrin derivatives is lower than that of P3HT, and the HOMO energy level is evaluated higher than the HOMO of PCBM.

The organic photovoltaic(OPV) is of great attractive advantages over inorganic based solar cell due to low cost and relatively simple fabrication process in solar energy industry. The low power conversion efficiency (PCE), however, below 10% is remained to be improved for commercial production.[1] The PCE of OPV system is dependent on various components of device: donor-acceptor, size or morphology of the fabricants, and the hole-electron carrier. In the P3HT-PCBM organic photovoltaic, state of the art donor-acceptor matching, the modulator such as porphyrin (PP) has been known to crucial for PCE improve.[2,3] The combination of modulators with donor-acceptor in organic solar cell altered the morphology of P3HT as well as the light harvesting efficiency at the wavelength avoiding overlap with the absorption of donor.

In an effort to develop an efficient modulator for PCE improvement of P3HT-PCBM based organic solar cell, we designed PP derivatives as in Figure 1. Bulky *tert*-butyl group was attached to resist self-interaction of PPs and the Ar group was introduced to modulate the HOMO-LUMO energy level. Here, we report the synthesis of Ni-coordinated PP derivatives and the analysis of HOMO-LUMO energies from their absorption, emission and cyclic voltammetric data
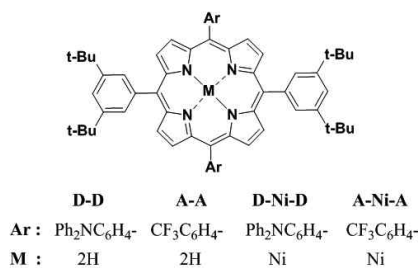


|       | D-D | A-A | D-Ni-D | A-Ni-A |
|-------|-----|-----|--------|--------|
| Ar :  | Ph$_2$NC$_6$H$_4$- | CF$_3$C$_6$H$_4$- | Ph$_2$NC$_6$H$_4$- | CF$_3$C$_6$H$_4$- |
| M :   | 2H  | 2H  | Ni     | Ni     |

**Figure 1**. Chemical structure of PP derivatives.

The synthesis of PPs was processed using Suzuki coupling[4] of PP-bromide **4** with the corresponding arylpinacolborate as in scheme 1. Initially, dipyrromethane **1** (a condensate of pyrrol and formaldehyde)[5] was converted to

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tetrapyrrole (porphyrin ring) **2** by reacting with 3,5-di-*t*-butylbenzaldehyde followed by 2,3,5,6-tetrachloro-1,4-benzoquinone (TCQ)-mediated oxidation in 42% yield. For Ni incorporation, PP **2** was treated Ni(OAc)$_2$ in chloroform-DMF to give metalloporphyrin **3** in quantitative yield. Treatment of PP **3** with *N*-bromosuccinimde NBS and the subsequent Suzuki coupling with the corresponding arylborate generated target complexes, **D-Ni-D** and **A-Ni-A**. For examples of synthetic procedures are as follows:

**5,15-*Bis*(3,5-di-*tert*-butylphenyl)porphyrin (2):** Dipyrro-methane **1** (989 mg, 6.71 mmol) and 3,5-di-*tert*-butylbenzaldehyde (1.47 g, 6.71 mmol) was reacted for 13 h in 0.2 eq of trifluoroacetic acid (100 μl, 1.34 mmol) and then TCQ (3.30 g, 13.4 mmol) was added with reflux for 1.5 h at 70°C. Work-up and column chromatography (5-15% EtOAc in hexane with 1% Et$_3$N) gave PP **2** (42%).[6]

**[5,15-*Bis*(3,5-di-*tert*-butylphenyl)porphyrin] nickel(II) complex (3):** The mixture of PP **2** (115 mg, 0.17 mmol) and Ni(OAc)$_2$·4H$_2$O (0.41 g, 1.63 mmol) in CHCl$_3$/DMF (5:1) was refluxed for 1 d at 120 °C. Work-up and column chromatography (10% EtOAc in hexane with 1% Et$_3$N) gave PP **3** (95%).[7]

**[5,15-Dibromo-10,20-*bis*(3,5-di-*tert*-butylphenyl)porphy-rin] nickel(II) complex (4):** To the solution of PP **3** (100 mg, 0.146 mmol) in pyridine (0.5 ml, 6.2 mmol) was added NBS (39 mg, 0.219 mmol) in CHCl$_3$ (0.5 ml) at 0 °C. After 10 min, at color changing from bright red to deep brown, acetone was added to quench the reaction. Work-up and column chromatography (10-30% EtOAc in hexane with 1% Et$_3$N) gave PP **4** (86%).[8]

**[5,15-*Bis*(4-(trifluoromethyl)phenyl)-10,20-*bis*(3,5-di-*tert*-butylphenyl)porphyrin] nickel(II) complex (5):** The mixture of PP **4** (100 mg, 0.04 mmol), 4,4,5,5-tetramethyl-2-[4-(trifluoromethyl) phenyl]-1,3,2-dioxaborolane (72 mg, 0.27 mmol), Cs$_2$CO$_3$ (86 mg, 0.27 mmol) and Pd(PPh$_3$)$_4$ (5 mg, 0.004 mmol) in toluene/DMF was refluxed for 18h at 120 °C. Work-up and column chromatography (2.5% EtOAc in hexane with 1% Et$_3$N) generated PP **5** (83%).[9]

**Table 1. Absorption and emission properties of PP-derivatives.**

|       | Absorption, λmax (nm) | | Emission (nm) | Eg(eV)* |
|-------|-------|-------|---------|---------|
|       | S-band | Q-band | | |
| **D-D** | 426 | 521, 532 595, 654 | 668, 725 | 1.57 |
| **A-Ni-A** | 418 | 529 | 656, 716 | 1.66 |
| **D-Ni-D** | 428 | 534 | 509, 609 860 | 1.66 |

* Band gap, E$_g$ is calculated by E$_g$ =1240/$\lambda_{onset}$
Measured at 5x10$^{-5}$ wt % concentration in chloroform
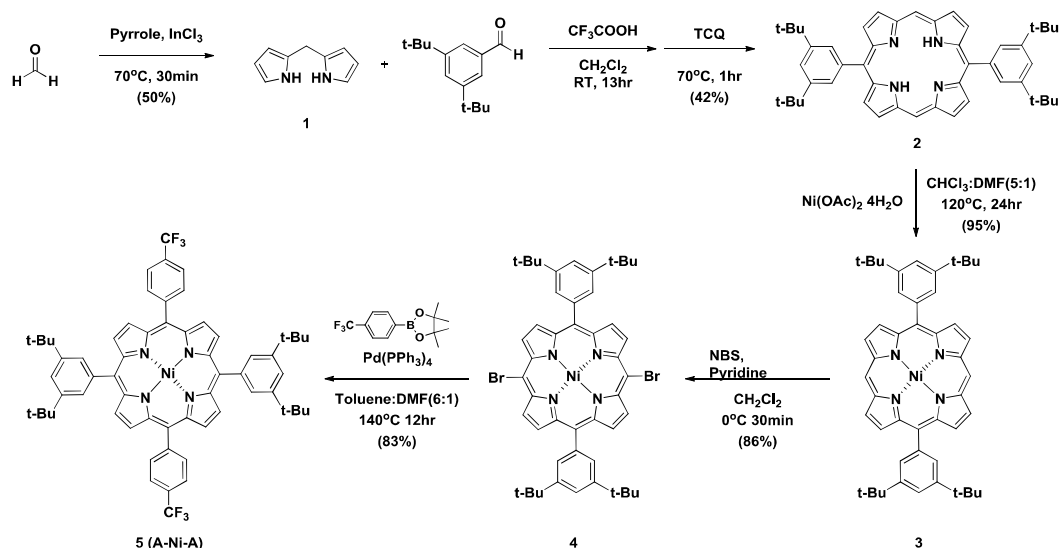
**Scheme 1**. Synthetic route for metalloporphyrin derivatives.

For the spectroscopic analysis of PP derivatives in hand, UV-Vis, PL and CL spectroscopy was observed in $CHCl_3$ and the band gap of PP derivatives was calculated as summarized in Table 1. In addition, CV of PPs was measured (Konkuk University MAT-Fraunhofer ISE Next Generation Solar Cell Research Center) and their HOMO-LUMO energy levels were calculated as shown in Figure 2.

The absorption of PP showed S and Q band as characteristic peaks for porphyrin ring. Metallation of PP did almost not alter the absorption wavelength but had a great influence on the emissions as in cases of **D-D** and **D-Ni-D**.

The HOMO-LUMO band gap was affected by Ni-incorporation resulting 0.09 eV increase. It is noticeable that all the band gap of Ni-PP is equal to 1.66 eV. The LUMO energy of PP is lower than that of P3HT (-2.80eV) and the HOMO energy of PPs higher than the PCBM's HOMO. These results suggested that the designed PPs could play a role of modulation as a hole-carrier between donor P3HT and acceptor PCBM.
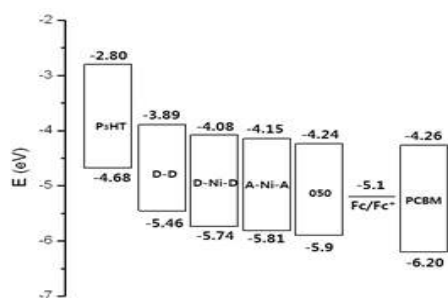


**Figure 2**. HOMO-LUMO energy level of PP derivatives.

In summary, metalloporphyrin derivatives **D-Ni-D** and **A-Ni-A** are designed and synthesized as heterojunction modulators for organic photovoltaics. The HOMO-LUMO energy levels of these porphyrin derivatives located between the HOMO of P3HT(donor) and the LUMO of PCBM(acceptor) suggesting these porphyrin derivatives could be used to increase PCE of OPV.

**KEYWORDS**: Porphyrin, metalloporphyrin, solar cell, band gap, P3HT, PCBM.

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6. ^{1}H NMR (400 MHz, $CDCl_3$) data for PP (**2**): δ(ppm) 10.33 (s, 2H, CH), 9.42 (d, 4H, CH), 9.17 (d, 4H, CH), 8.18 (d, 4H, CH), 7.87 (t, 2H, CH), 1.56 (s, 36H, $CH_3$), -2.98 (s, 2H, NH).
7. ^{1}H NMR (400 MHz, $CDCl_3$) data of PP (**3**): δ(ppm) 9.86 (d, 2H, CH), 9.20 (d, 4H, CH), 8.97 (d, 4H, CH), 7.90 (d, 4H, CH), 7.77 (t, 2H, CH), 1.46 (s, 36H, $CH_3$).
8. ^{1}H NMR (400 MHz, $CDCl_3$) data of PP (**4**): δ(ppm) 10.02 (d, 2H, CH), 9.45 (d, 2H, CH), 8.77 (d, 2H, CH), 7.90 (d, 2H, CH), 7.80 (d, 4H, CH), 7.74 (t, 2H, CH), 1.56 (m, 36H, $CH_3$).
9. ^{1}H NMR (400 MHz, $CDCl_3$) data of PP (**5**): δ(ppm) 8.80 (d, 4H, CH), 8.66 (d, 4H, CH), 8.20 – 7.65 (m, 14H, CH), 1.56 (m, 36H, $CH_3$).