Synthesis and properties of novel fluorinated subnaphthalocyanines for organic photovoltaic cells

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ABSTRACT

Novel fluorinated subnaphthalocyanine derivatives were newly designed and synthesized as donor materials for low molecular organic photovoltaic cells using fullerene as an acceptor. They were designed to have the low-lying HOMO energy levels for improvement of open circuit voltage without any expense of short-circuit current density. The HOMO/LUMO energy levels of hexafluoro-, heptafluoro-, dodecafluoro-, tridecafluoro- and the parent subnaphthalocyanine estimated based on the photoelectron spectroscopy were -5.69/-3.93, -5.67/-3.90, -5.96/-4.19, -5.92/-4.11 and -5.30/-3.58 eV, respectively, showing that frontier orbital energy levels can be effectively tuned by fluorination.

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Recently, various efforts have been made to develop organic photovoltaic (OPV) cells, which are attractive in view of their lightness, flexibility, and potential for easy and inexpensive manufacturing processes compared with inorganic ones. However, it is necessary to enhance the photovoltaic conversion efficiency of OPVs. In the field of bilayer pn-junction-based thin film cells, copper phthalocyanine (CuPc) has been commonly used as a small molecular donor material. Mutolo et al. compared boron subphthalocyanine chloride (SubPc in Figure 1) with CuPc as a donor material.¹ They reported that an OPV cell (SubPc/C₆₀) using fullerene (C₆₀) as an acceptor showed increase of the cell power conversion efficiency (η) in comparison with that of CuPc, due to the doubled open circuit voltage (V_{oc}) in the former. η is proportional to the product of the V_{oc} , short-circuit current density (J_{sc}), and the fill factor (FF), in which P_0 is the incident optical power, as shown below in equation (1).

$$\eta = (J_{sc} V_{oc} FF) / P_0 \quad (1)$$

Moreover, it has been demonstrated that V_{oc} is dependent on the energy difference between the highest occupied molecular orbital (HOMO) energy of the donor and the lowest unoccupied molecular orbital (LUMO) energy of the acceptor,² where the energy difference is called the interface energy gap (E_g), as shown in Figure 2. The SubPc/C₆₀ cell showed a higher V_{oc} due to the lower HOMO energy level of SubPc than that of CuPc and the subsequent increase in E_g . The cone-shaped SubPc derivatives are of interest considering steric viewpoints such as

the tendency towards one-dimensional packing and weak intermolecular interaction to create amorphous thin films that lead to a high V_{oc} .^{3,4} There have been several studies about OPVs using SubPcs as donor materials.²⁻¹¹ Nevertheless, it is considered to be disadvantageous from a viewpoint of photochemical properties; that is, SubPc absorbs shorter wavelengths and affects the J_{sc} compared with CuPc. Therefore, there have been also studies on subnaphthalocyanine (SubNc), extended compound of SubPc to have intense bathochromic-shifted absorption band.¹⁰⁻¹² Genoe et al. reported that J_{sc} was improved by using SubNc, while the SubNc/C₆₀ cell afforded a lower V_{oc} depending on the smaller E_g , owing to the higher HOMO energy of SubNc than that of SubPc.¹¹ It is considered that halogenation of heterocycles settles down the HOMO energy levels. In this paper, therefore, we report on the synthesis and properties of partially fluorinated SubNc derivatives focusing on the control of energy levels without alteration of optical properties.

(Figure 1)

(Figure 2)

Elegant molecular design on predicting the energy levels is considered necessary for fabrication of the relevant HOMO and LUMO levels and photochemical properties. Development of the

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new donor derivatives with high photovoltaic performance requires control of the interface energy gap in order to optimize the energy levels, maintaining good absorption properties. Then, the HOMO energy levels of SubPc, SubNc, and fluorinated SubNc derivatives were estimated by DFT calculations along with the excitation energies by TD-DFT method at the B3LYP/6-31G(d,p) level and compared. According to our calculations, F₁₂-SubNc and F₁₃-SubNc were evaluated to have lower HOMO levels than SubPc, and F₆-SubNc and F₇-SubNc to have slightly higher ones than SubPc, while SubNc was evaluated to have much higher HOMO levels compared to others, as shown in Table 1. The lower HOMO energies of fluorinated SubNc derivatives indicate the potential for improvement in photovoltaic performance of the donor/C₆₀ cells.

(Table 1)

Although syntheses and studies of some fluorinated SubPc derivatives have been reported, there has been no report on synthesis of halogenated SubNc derivatives.¹³⁻¹⁶ Scheme 1 shows the synthesis of F₆-SubNc and F₁₂-SubNc. The fluorinated SubNcs were synthesized using a slightly modified cyclotrimerization of the corresponding fluorinated 2,3-naphthalenedicarbonitriles, based on reported methods.¹⁷⁻¹⁹ The precursor, 5,6,7,8-tetrafluoro-2,3-naphthalenedicarbonitrile (**4b**) was synthesized according to a reported method, as shown in Scheme 1,²⁰⁻²² and the preparation of 6,7-difluoro-2,3-naphthalenedicarbonitrile (**4a**) was performed similarly. Diels-Alder reaction of *N*-methylpyrrole with fluorinated benzyne formed by reaction of corresponding benzene derivatives with *n*-butyllithium afforded the fluorinated *N*-methyliminonaphthalenes (**2a,b**) in moderate yields, followed by removal of -CH=CH- with 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine to convert to the fluorinated *N*-methylisindols (**3a,b**) in 57–93 % yields. Then, by addition of dicyanoacetylene to **3**, and successive elimination of the methylamino group by reaction with 3-chloroperoxybenzoic acid (MCPBA), the fluorinated naphthalenedicarbonitrile (**4**) were obtained in 55–91 % yields. The synthesis of 2,3,4,5,11,12,13,14,20,21,22,23-dodecafluorosubnaphthalocyanine boron chloride (F₁₂-SubNc) was accomplished via cyclization of **4b** in the presence of boron chloride in a mixture of *p*-xylene and *o*-dichlorobenzene from 140 °C to 180 °C for 2 h in 44% yield after chromatographic purification. Using a similar method, F₆-SubNc was also synthesized from **4a** in 26% yields. While the synthesis of unsubstituted SubPc generally involves the production of chlorinated byproducts including several chlorides, whose purification is highly difficult, fluorinated SubNc derivatives were relatively purely generated without chlorinated byproducts and were easy to purify. It is considered that fluorides work as protection groups for reaction sites on the aromatic ring and as electron-inductive groups to reduce chlorination of aromatic sites and enable cyclotrimerization at lower temperature.²³⁻²⁵

(Scheme 1)

Furthermore, F₇-SubNc and F₁₃-SubNc were obtained by exchange of the axial chloride of F₆-SubNc and F₁₂-SubNc with fluoride via the modified reaction with AgBF₄ in 70% and 74% yield, respectively, as shown in Scheme 2.²⁶ Fluorinated SubNc derivatives, F₆-, F₇-, F₁₂-, F₁₃-SubNc were newly obtained and characterized by ¹H NMR, ¹⁹F NMR, and MALDI-TOF-MS.

(Scheme 2)

Optical absorption properties of obtained SubNc derivatives (F_n-SubNcs) were verified using UV-Vis spectroscopy in *o*-dichlorobenzene. Figure 3 shows the enhanced Q-band peaks of F_n-SubNcs at around 645 nm keeping large bathochromic-shift (ca. 80 nm) compared with that of SubPc, although they show a little blue-shift from unsubstituted SubNc. This strong absorption at long wavelengths suggests the advantage of light absorption efficiency of F_n-SubNcs/C₆₀ stacked cells over a wide wavelength range.

(Figure 3)

The HOMO energy levels of SubPc, SubNc, F_n-SubNcs, and C₆₀ were verified by experimental measurement of the ionization potential using photo-electron spectroscopy in air (PESA) on the thin film. LUMO levels were rated using optical energy band gaps obtained from the low energy band edges of the UV-vis spectra in the thin films (Figure S15).²⁷ Compared with the spectra in solution, the absorption bands in film state were red-shifted and broadened respectively due to intermolecular interactions. The experimentally obtained HOMO and LUMO energy levels of SubPc, unsubstituted SubNc, F_n-SubNcs, and C₆₀ are illustrated in Figure 4. The HOMO energy levels of F_n-SubNcs were lower than that of unsubstituted SubNc, while the HOMO levels of F₆-SubNc and F₇-SubNc were slightly higher than that of SubPc, and that the downward shift of the HOMO energy level occurred sufficiently by introduction of fluorides in spite of the distorted molecular structure of subnaphthalocyanine. Moreover, it is also shown that the LUMO energy differences between C₆₀ and all F_n-SubNcs ranged from 0.31 to 0.60 eV. Since it was considered that a gap of over 0.4 eV was necessary to generate the driving force for charge separation between donor and acceptor, F₆-SubNc and F₇-SubNc were considered to be more promising.^{29,30} Furthermore, the relative energy levels were in agreement with those evaluated using computational calculations to suggest the simulation effective for band gap control in the group of these compounds.

(Figure 4)

As donor materials for OPV, new fluorinated SubNc derivatives with the low-lying HOMO levels keeping the strong absorption band of long wavelength were designed and synthesized. It was verified using UV-Vis and PESA that the synthesized SubNc derivatives were purposive in the optical and electronic properties of the films. Agreement between the relative energy levels obtained experimentally and those evaluated using computational calculations suggests the potential of elegant band gap control in this group of compounds. Optimization and examination of the performance of bilayer photovoltaic cells using the halogenated SubNc derivatives as donor materials is currently underway and will be reported in the near future.

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Table 1. Calculated orbital energy levels of frontier orbitals of SubPc, SubNc derivatives, and C₆₀

Compounds	HOMO (eV)	LUMO (eV)
SubPc	-5.31	-2.79
SubNc	-4.84	-2.72
F ₆ -SubNc	-5.17	-3.03
F ₇ -SubNc	-5.10	-2.95
F ₁₂ -SubNc	-5.43	-3.32
F ₁₃ -SubNc	-5.37	-3.24
C ₆₀	-5.99	-3.78

Legends

Figure 1. SubPc, SubNc, and new synthesized SubNcs.

Figure 2. Schematic energy level diagrams for CuPc/C₆₀, SubPc/C₆₀, SubNc/C₆₀, and new SubNc/C₆₀.

Figure 3. UV-Vis spectra of SubPc, SubNc, and their fluorinated derivatives.

Figure 4. HOMO and LUMO levels of SubPc, SubNc derivatives, and C₆₀ obtained from the ionization potential and optical band gap. The LUMO energy level of C₆₀ is quoted from literature.²⁸

Scheme 1. Synthesis of fluorinated subnaphthalocyanines.

Scheme 2. Synthesis of axially fluorinated subnaphthalocyanines.

Figures

Figure 1. SubPc, SubNc, and new synthesized SubNcs.

Figure 4. HOMO and LUMO levels of SubPc, SubNc derivatives, and C_{60} obtained from the ionization potential and optical band gap. The LUMO energy level of C_{60} is quoted from literature.²⁸

Figure 2. Schematic energy level diagrams for CuPc/ C_{60} , SubPc/ C_{60} , SubNc/ C_{60} , and new SubNc/ C_{60} .

Figure 3. UV-Vis spectra of SubPc, SubNc, and their fluorinated derivatives.

Schemes

Scheme 1. Synthesis of fluorinated subnaphthalocyanines.

Scheme 2. Synthesis of axially fluorinated subnaphthalocyanines.

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