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Synthesis and optical properties of subphthalocyanines axially connected homo- and heterodimers via a hydroquinone linker

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Axially linked trifluoroethoxy (TFEO)-coated subphthalocyanine (SubPc) homo- and heterodimers were synthesized by two different axial ligand substitution methods. TFEO-SubPc homodimers were obtained directly from TFEO-SubPc boron chloride with *o*-, *m*-, and *p*-hydroquinones, while TFEO-SubPc heterodimers were synthesized via stepwise construction using a combination of the TFEO method and Torres's triflate method. The optical properties of dimers obtained were investigated using UV-Vis and fluorescence spectrometry. Electron transfer was observed in the heterodimers, and TFEO-SubPc acted as an electron acceptor in the process. The electron transfer process differs depending on the *o*-, *m*-, and *p*-geometry of the hydroquinone linker, and is supported by computational calculations.

Subphthalocyanines (SubPcs), which are regarded as the lowest homologue of phthalocyanines (Pcs), consist of three diiminoisoindoline fragments attached around a boron center.¹ While the Pcs are principally flat/plane 18- π -conjugated macrocycles,² SubPcs have a unique cone-shaped geometry with a 14- π -conjugation. The curved π -conjugated system is often advantageous in the synthesis of functional materials than a flat π -conjugation due to its reduced tendency for molecular aggregation resulting in a better solubility profile. Moreover, the curved/concave geometry of SubPcs should be useful for molecular recognition of complementary convex π -conjugated molecules such as fullerenes.³ Their strong absorption and high emission quantum yields in the visible region make SubPcs promising chromophores with potential applications in optical data storage,⁴ nonlinear optics,⁵ and photosynthetic models for studying energy- and electron-transfer.⁶ Therefore, the modification and derivatization of SubPcs are of great importance to develop novel functional materials.

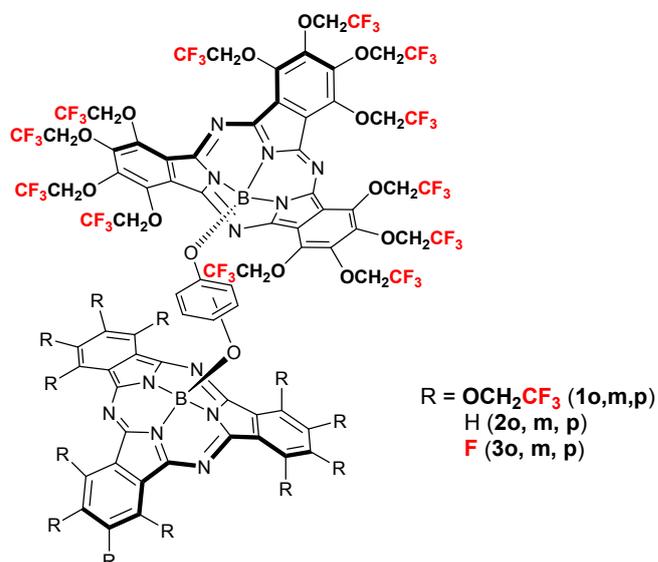


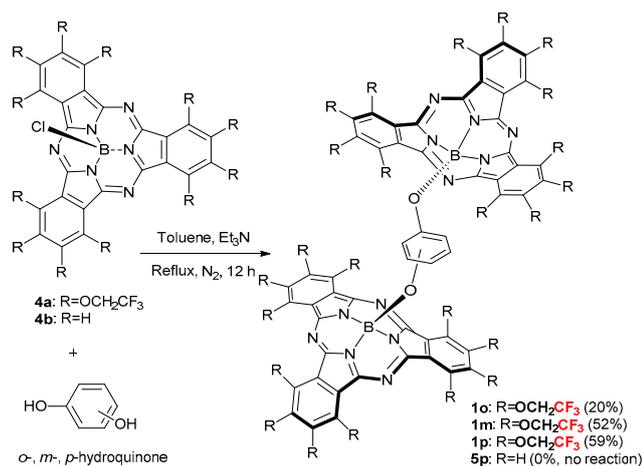
Fig 1. Subphthalocyanine axial substituted dimers

The substitution reaction of the axial ligands on the boron atom in SubPcs is one of the straightforward strategies for the derivatization of SubPcs to construct novel electron transfer systems.⁶ However, the axial substitution of SubPcs generally unreactive and yields are not that high. In this context, our research group reported in 2010 the considerable improvement of the axial ligand substitution of SubPcs by trifluoroethoxy (TFEO)-coating at the periphery of the SubPc macrocycle.⁷ In 2011, Torres et al. further improved the axial substitution of SubPcs by replacing the axial position of SubPcs once in triflate to activate the boron center.⁸ Subsequently, Bender et al. reported that aluminum chloride activates chlorine on the boron of SubPcs to induce the axial substitution reaction.⁹ As an extension of our high-yielding axial substitution methodology using peripheral TFEO-coating of SubPc with Torres's triflate method, we herein disclose the synthesis of novel SubPc homodimers **1** and heterodimers **2** and **3** having hydroquinone as a linker and their spectral investigation. Frontier orbitals of the heterodimer calculated at the B3LYP/6-31G(d) computational level support their optical properties which confirm the donor-acceptor character between TFEO-SubPc and non-substituted SubPc (Fig. 1).

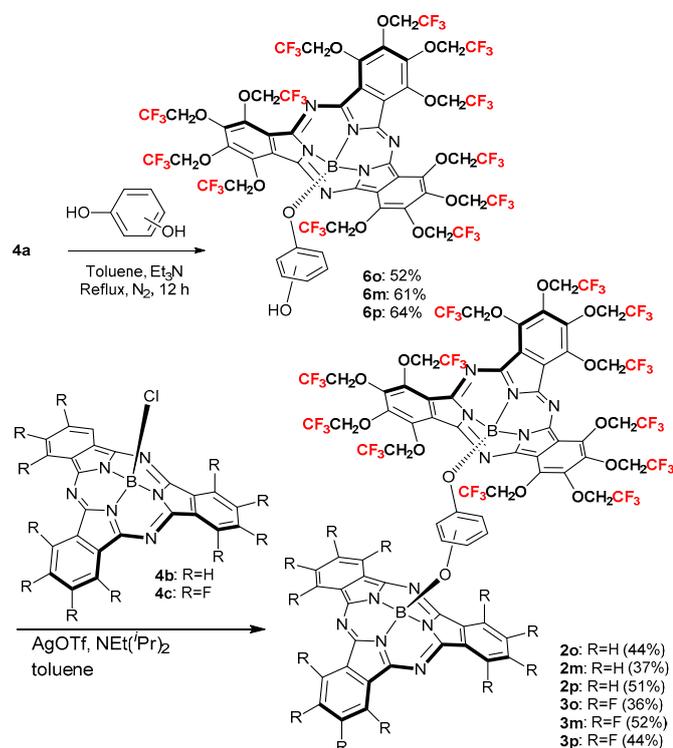
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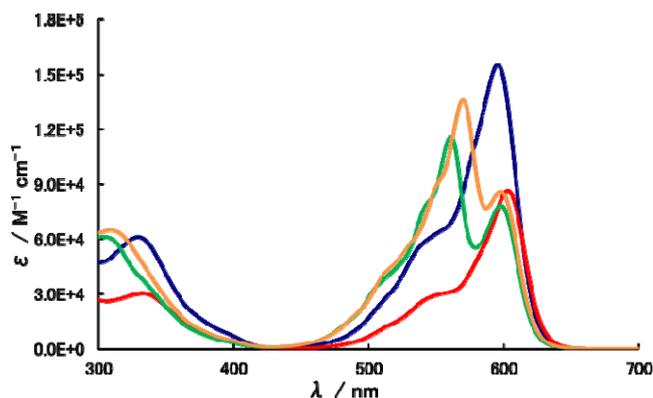


Scheme 1. Synthesis of SubPcs homodimers 1.



Scheme 2. Synthesis of SubPcs heterodimers 2 and 3.

The synthesis of SubPc dimers is shown in Scheme 1. TFEO-SubPc homo-dimers **1o**, **m**, **p** were nicely synthesized by our direct chloro-substitution reaction of TFEO-SubPc **4a** and *o*-, *m*- and *p*-hydroquinones (0.4 equiv) in the presence of triethylamine in toluene under reflux conditions for 12 h. TFEO-SubPc dimers linked with *m*- and *p*-hydroquinones **1m**, **p** were obtained in 52 and 59% yield, respectively, and even sterically hindered *ortho*-substituted dimer **1o** was isolated in 20% yield. It should be mentioned that the effect of the peripheral TFEO-substituent is significant for this substitution reaction, since non-substituted SubPc **4b** did not react with *p*-hydroquinone under the same conditions resulting in no corresponding dimeric product **5p** (Scheme 1).

Fig. 2. UV-vis spectra of homodimer **1p** (blue), heterodimers **2p** (orange) and **3p** (green), and monomer **4a** (red) at 1×10^{-5} M in dioxane.

Syntheses of SubPc hetero-dimers **2o,m,p** and **3o,m,p** were next investigated (Scheme 2). First, the substitution of TFEO-SubPc **4a** with 1 equiv of *o*-, *m*-, and *p*-hydroquinones was carried out under reflux to provide hydroquinone-attached TFEO-SubPcs **6o,m,p**. Then, the substitution of non-substituted SubPc **4b** or perfluorinated SubPc **4c** with **6** was achieved by the Torres's stepwise-activation method with triflate⁸ to furnish hetero SubPc dimers **2o,m,p** and **3o,m,p** linked at the *ortho*-, *meta*-, or *para*-position on the central benzene unit in good yields. All SubPc dimers **1-3** showed good solubility in common organic solvents and were purified by column chromatography on silica gel. They were characterized by ¹H and ¹⁹F NMR, MALDI-TOF mass and FTIR spectroscopy (see ESI). The ¹H NMR spectra of dimers, which exhibit characteristic peaks of central benzene linkers around at 5 ppm, are highly shielded by the diatropic magnetic currents of two SubPc rings. Other peaks corresponding to outlying trifluoroethoxy substituents of TFEO-SubPc appeared between 4.5 ppm and 5.3 ppm, and an outlying proton of H-SubPcs appeared around 7.8 ppm and 8.7 ppm. The ¹⁹F NMR spectrum of dimers showed peaks around -75 ppm for trifluoroethoxy substituents of TFEO-SubPc and -140 ppm for outlying fluorine substituents of F-SubPc. All MALDI-TOF MS spectra of dimers showed a peak split with a characteristic isotopic pattern corresponding to their molecular ion.

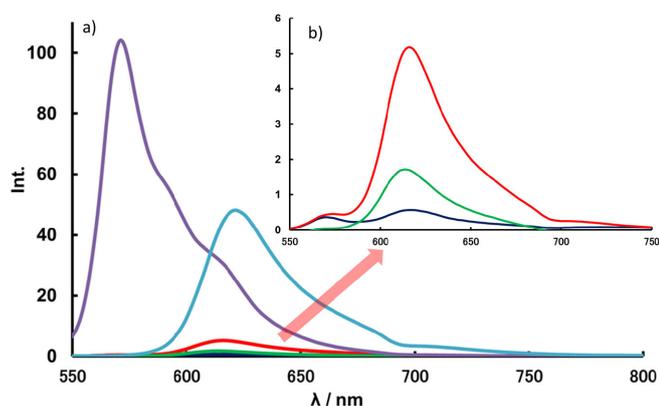
The optical features of dimers **1-3** were next investigated. The UV/Vis spectra of dimers recorded in a variety of solvents (dioxane, trifluorotoluene and dichloromethane) with a concentration range of 1×10^{-6} M to 1×10^{-4} M were examined (see Fig. 2 and Figs. S1-27 in ESI). TFEO-SubPc homo-dimers **1o,m,p** are present mainly as monomers, irrespective of the solvent and concentration, and are characterized by sharp absorption bands in the B- (335 nm) and Q-band (600 nm) regions.¹⁰ The molar extinction coefficient of dimer **1p** ($\epsilon_{\max} [10^{-5} \text{ M}] = 1.55 \times 10^5$) was double that of the TFEO-SubPc monomer **4a** ($\epsilon_{\max} [10^{-5} \text{ M}] = 8.66 \times 10^4$), and most differences in a spectrum caused by the *ortho*-, *meta*- and *para*-positions were not observed. As hetero-dimers, two kinds of peaks, irrespective of the solvent and its concentration, were observed in Q bands corresponding to each SubPc unit. These results suggest that two SubPc units absorb light independently and do not disturb each π system.

Table 1. Fluorescence quantum yields^[a] (Φ_f), emission maxima (λ_{em} [nm]) of dimers upon excitation at 530 nm.

| 1-3 | Φ_f (λ_{em} [nm]) | | |
|-----------------|---------------------------------|------------------|------------------|
| | Dioxane | Trifluorotoluene | Dichloromethane |
| 1o | 0.32 (619) | 0.12 (625) | 0.22 (624) |
| 1m | 0.52 (617) | 0.51 (615) | 0.49 (616) |
| 1p | 0.33 (616) | 0.21 (613) | 0.17 (614) |
| 2o (R-H) | 0.017 (570, 617) | 0.006 (569, 613) | 0.007 (572, 613) |
| 2m (R-H) | 0.11 (574, 616) | 0.031 (570, 614) | 0.041 (575, 613) |
| 2p (R-H) | 0.026 (614) | 0.022 (611) | 0.018 (614) |
| 3o (R-F) | 0.098 (615) | 0.069 (585, 612) | 0.061 (587, 613) |
| 3m (R-F) | 0.52 (616) | 0.15 (614) | 0.17 (614) |
| 3p (R-F) | 0.23 (616) | 0.15 (614) | 0.16 (615) |

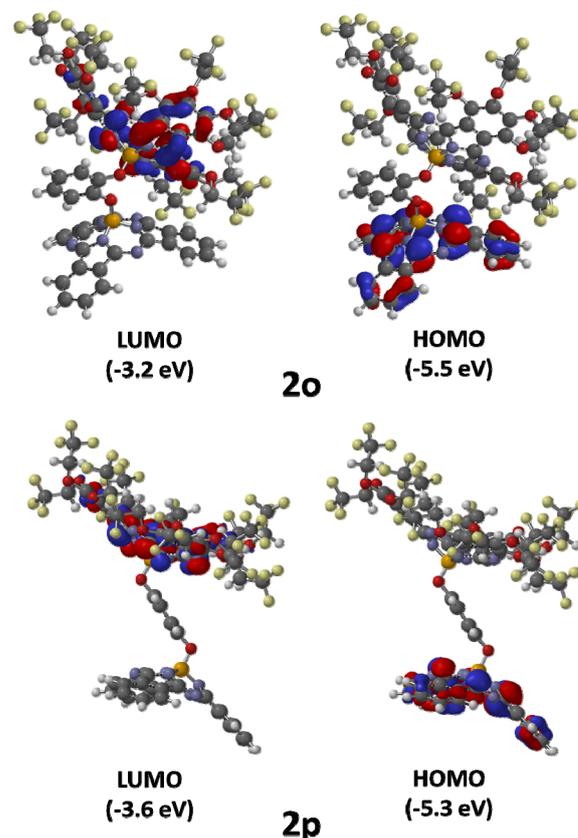
^[a]Determined by using zinc phthalocyanate in 1-chloronaphthalene as reference ($\Phi_f = 0.30$).

The steady-state fluorescence spectra of dimers **1-3** were measured in different organic solvents (see Table 1 and Figs. S28-36 in ESI). The TFE0-SubPc homodimers **1o** and **1p** showed a middle emission band around 617 nm with fluorescence quantum yields (Φ_f) of 0.32 and 0.33, respectively in dioxane upon excitation at 530 nm (Table 1). On the other hand, **1m** showed a higher fluorescence quantum yield ($\Phi_f = 0.52$) in dioxane. These results suggest that electronic communication between the SubPc moieties of dimers linked at *ortho*- and *para*- positions are stronger than the dimers linked at *meta* positions. In the case of heterodimers, the fluorescence of **2o,m,p** decreased significantly in dioxane ($\Phi_f = 0.017$, 0.11 and 0.026), which can be attributed to electron-transfer from the H-SubPc moiety to the TFE0-SubPc moiety.⁶ Especially, Φ_f values of *ortho*-linked SubPc dimer **2o** displayed a striking decrease. On the other hand, the Φ_f values of **3m,p** were not so quenched ($\Phi_f = 0.52$ and 0.23) with the exception of **3o** ($\Phi_f = 0.098$).

**Fig. 3.** Fluorescence spectra of heterodimer **2o** (blue), **2m** (red), **2p** (green), H-SubPc (purple) and TFE0-SubPc (light blue) in dioxane.

Energy transmission was next examined based on both the quantum yield and the steady-state fluorescence. Fig. 3 indicates the fluorescence spectra of heterodimers **2o**, **2m**, **2p**, and monomers H-SubPc, TFE0-SubPc in dioxane. With the comparisons to the fluorescence spectra of the monomers H-SubPc and TFE0-SubPc, the fluorescence spectra of heterodimers **2o**, **2m**, and **2p** are

obviously quenched (Fig. 3a). It should be noted that very small peaks around 570 nm originated to the one half of H-SubPc unit, while the peaks around 616 nm are those of another half of dimers, TFE0-SubPc moiety (Fig. 3b). Although both the peaks are quenched, the values of quenching around 570 nm are more significant than those of around 616 nm, which imply the energy/electron transfer from the H-SubPc unit to the TFE0-SubPc moiety.

**Fig. 4.** Optimized geometry and distribution of molecular orbitals of **2o** and **2p** calculated at the B3LYP/6-31G(d) computational level by Spartan '14.¹²

The optimized geometry and distribution of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of heterodimers **2o** and **2p** were calculated by computational chemistry using Spartan '14 (Fig. 4). These results confirm the donor acceptor character between H-SubPc and TFE0-SubPc moieties. HOMO is localized on the H-SubPc moiety as a donor unit and LUMO is localized on the TFE0-SubPc moiety as an acceptor unit. This result indicates that the electron density of the SubPc macrocycle decreases in response to the electron affinity of 12 TFE0-substituents. These results indicate that fluorescence quenching in heterodimers **2** should be explained by an electron transfer process. More interestingly, the H-SubPc moiety is much closer to the TFE0-SubPc moiety of **2o** than that of **2p**. This result is found to give good agreement with the chemical shift shielding of the hydroquinone ring protons in the ¹H NMR spectra. While **2p** shows 4 protons at same 4.80 ppm (4H, more shielding),

2o has two peaks at 4.97 ppm (2H, more shielding) and 6.14 ppm (2H, less shielding), respectively (see ESI). These differences suggest that the hydroquinone ring of **2p** lies parallel between the two SubPc moieties. On the other hand, the two SubPc units of **2o** are somewhat twisted towards central hydroquinone moiety resulting two SubPc moieties closer. These facts may explain the difference in fluorescence quenching that depends on the *o* and *p* geometries. It has been reported that through-space electron transfer occurs efficiently when the distance between electron donors and acceptors is below 10 Å.¹¹ Therefore, through-space electron transfer probably occurs in addition to through-bond electron transfer in **3o**. A smaller distance between donor (H-SubPc) and acceptor (TFEO-SubPc) moieties allows for an easier direct overlap of frontier orbitals between the donor and acceptor. On the other hand, the H-SubPc and the TFEO-SubPc moieties in **3p** are too distant to allow for through-space electron transfer. Hence, through-bond electron transfer is highly likely to be dominant in **3p**. The observed reduced fluorescence quenching in meta-substituted heterodimer **2m** is understandable since electron transfer through bonding is often not effective in the meta-position of aromatics. The observations of fluorescence quenching in heterodimers **3o,m,p** can be similarly explained, although the significant donor-acceptor characters in **3o,m,p** do not exist between TFEO-SubPc and F-SubPc moieties.

Conclusions

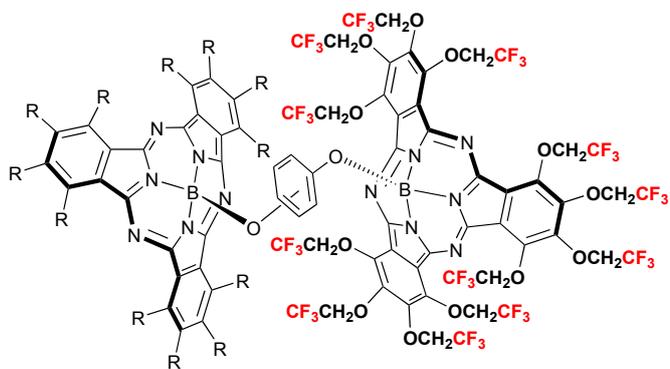
In conclusion, we have synthesized novel SubPc homo- and heterodimers bridged on the axial position via a hydroquinone linker by two types of axial ligand substitution reactions. The optical properties of those compounds were investigated by UV-Vis and fluorescence spectra and calculations. The observed fluorescence quantum yields of dimers suggest that significant energy transmission occurs in heterodimers **2o,m,p**. For *ortho*-substituted heterodimer **2o**, through-space electron transfer probably occurs by the propinquity of TFEO-SubPc and H-SubPc moieties, in addition to regular electron transfer through bonding.

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The electron transfer process between subphthalocyanines differs depending on the *o*-, *m*-, and *p*-geometry of the hydroquinone linker.