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Design, synthesis and optical properties of unsymmetrical subphthalocyanine trimer connected by phloroglucinol via axial positions

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An unsymmetrical subphthalocyanine trimer consisting of three different subphthalocyanine units was synthesized. Its optical and physical properties were investigated by UV/Vis, fluorescence spectrometry, cyclic voltammetry and computations. Energy transfer from the non-substituted subphthalocyanine unit to the perfluorinated subphthalocyanine unit via a trifluoroethoxy substituted unit is suggested.

Subphthalocyanines (SubPcs) are concave macrocycles with a unique curved 14-π-conjugated system.[1] Similar to their larger homologues of phthalocyanines (Pcs),[2] SubPcs are expected to serve as functional dyes and pigments for application in devices such as organic solar cells, optical storage and others due to their unique structural, electronic, and optical properties. In addition to their utility as functional dyes, they are also attractive as molecular cages and flasks.[3] The convex–concave interaction of SubPcs and fullerenes has been reported.[4] In contrast to the flat-shaped π-conjugated macrocycles of Pcs, SubPcs show a higher tendency of non-aggregation which improves their solubility in organic solvents. These unique properties are likely to be related to their curved π-conjugation system and bowl-like geometry.[5] Recent encouraging progress of SubPcs as an alternative to fullerene[6] and a remarkable power conversion efficiency of 8.4% were achieved as fullerene-free organic solar cells.[7] A fluorinated SubPc fused dimer, when used as an electron acceptor in an organic solar cell, showed 4% efficiency.[8] In this context, we are interested in the design and synthesis of novel SubPc derivatives as novel materials for organic solar cells. In 2010, we reported the synthesis of a trifluoroethoxy (CF$_3$CH$_2$O, TFEO)-coated SubPc and disclosed its considerable efficiency for an axial ligand substitution reaction with a variety of oxygen nucleophiles.[9] This substitution reaction was next applied to
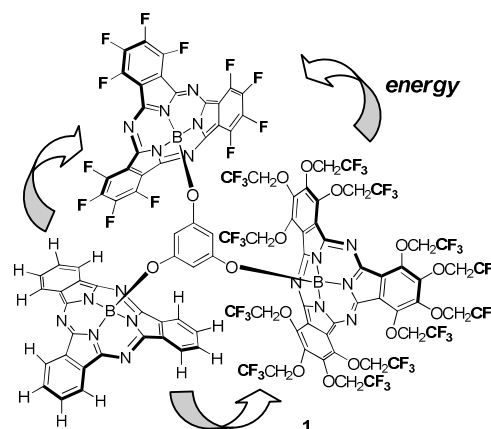

Fig 1. Subphthalocyanine axial trimer **1** and expected energy transfer

the synthesis of a SubPc homodimer and heterodimers having hydroquinine as a linker.[10] It should be noted that a distinct energy/electron transfer process was observed in the heterodimers, and TFEO-SubPc acted as an electron acceptor, while non-substituted SubPc (H-SubPc) acted as a donor in the process. As an extension of this research, we were interested in the unsymmetrical SubPc trimer **1** consisting of three different SubPc moieties, H-SubPc, TFEO-SubPc and perfluorinated SubPc (F-SubPc), which is expected to indicate the step-wise continuous electron transfer process from the H-SubPc moiety to F-subPc and/or F-subPc via TFEO-SubPc units according to their degrees of donor/acceptor properties. These step-wise continuous electron transfer process would attract chemists as tools for development of novel electron/energy transfer system as well as photocatalysis for organic reactions.[7,8,11,14] We report herein the design and synthesis of unsymmetrical, axially linked SubPc trimer **1** connected with phloroglucinol (Fig. 1). The stepwise constriction of **1** from a monomer or dimer to trimer using our TFEO-axial activation method and Torres's silver triflate method[11] is the key for the success of this preparation. A spectrophotometric and electrochemical investigation of trimer **1** and the computations of

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each SubPc unit suggested electron transfer from the H-SubPc units to F-subPc and/or F-subPc via TFEO-SubPc.

Unsymmetrical SubPc trimer **1** having different substituents at each peripheral position of the SubPc unit, such as $-OCH_2CF_3$, -F and -H, was designed based on a previous observation using SubPc hetero dimers. The synthesis of SubPc trimer **1** is shown in Scheme 1. First, the axial substitution of TFEO-SubPc **2a** with 1 equiv. of phloroglucinol was carried out under our previous conditions to provide phloroglucinol-attached TFEO-SubPc **4** in 22% yield. Next, we attempted the connection of F-SubPc **2b** and **4** under reflux conditions providing dimer **5**, but the reaction did not preceded since F-SubPc **2b** showed poor axial reactivity. Thus the axial substitution of F-SubPc **2b** was performed after activating its axial position by silver triflate, i.e., the Torres method, to furnish corresponding unsymmetrical dimer **5** in 24% yield. Finally, the axial substitution reaction of H-SubPc **2c** was performed using the Torres method to afford the desired trimer **1** in 46% yield (Scheme 1). Trimer **1** showed high solubility in common organic solvents and was purified by column chromatography on a silica gel. It was characterized by ^{1}H and ^{19}F-NMR, MALDI-TOF mass spectrometry and FTIR spectroscopy. The ^{1}H NMR spectra of trimer **1** showed unique peaks at 2.6, 2.8 and 2.9 ppm corresponding to three protons of the central benzene ring which are strongly shielded by the diatropic magnetic currents of three different SubPc moieties. Other peaks corresponding to outlying trifluoroethoxy substituents of the TFEO-SubPc unit appeared between 4.5 ppm and 5.2 ppm, and an outlying proton of H-SubPcs appeared around 7.9 ppm and 8.7 ppm. The ^{19}F NMR spectrum of trimer **1** showed two types of fluorine peaks according to the peaks of trifluoroethoxy substituents of the TFEO-SubPc unit around −75 ppm and outlying fluorine substituents of the F-SubPc unit around −137 ppm and −140 ppm. The MALDI-TOF MS spectrum of trimer **1** showed a peak split with a characteristic isotopic pattern corresponding to its molecular ion.
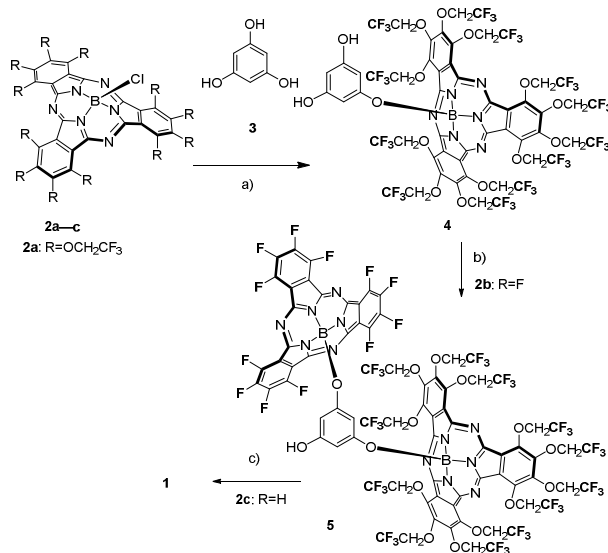
Scheme 1. Synthesis of SubPc trimer **1**: a) phloroglucinol (5.0 equiv.), triethylamine (4.0 equiv.), toluene, reflux, 22%; b) F-SubPc **2b** (1.2 equiv.), silver trifluoromethanesulfonate (1.5 equiv.), *N,N*-diisopropylethylamine (1.5 equiv.), toluene, 24%; c) H-SubPc **2c** (2.0 equiv.), silver trifluoromethanesulfonate (3.0 equiv.), *N,N*-diisopropylethylamine (3.0 equiv.), toluene, 46%.
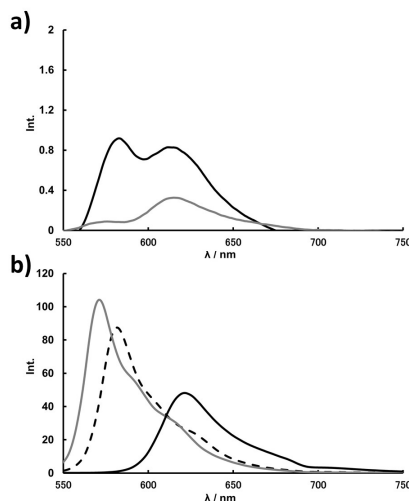
The optical feature of trimer **1** was next investigated. The UV/Vis spectra of trimer **1** were recorded in dioxane and trifluorotoluene, and a concentration range of 1×10^{-6} M to 1×10^{-4} M was examined (Fig. 2). Trimer **1** is present mainly as monomers irrespective of the concentration and is characterized by sharp absorption bands in the B- (335 nm) and Q-band (600 nm) regions. Trimer **1** showed a weak peak at 600 nm (ε_{max} [10^{-5} M] = 4.5×10^4) and a stronger absorption peak at 566 nm (ε_{max} [10^{-5} M] = 1.0×10^5) in the Q-band region in dioxane. The longer wavelength peak originates in absorption of the TFEO-SubPc unit and the shorter wavelength peak consists of two interlaced peaks corresponding to F-SubPc and H-SubPc. The shape of the absorption spectrum is formed by summing up the absorption spectra of TFEO-SubPc (λ_{max} = 603 nm, ε_{max} [10^{-5} M] = 8.7×10^4), F-SubPc (λ_{max} = 572 nm, ε_{max} [10^{-5} M] = 6.3×10^4) and H-SubPc (λ_{max} = 564 nm, ε_{max} [10^{-5} M] = 4.4×10^4). These results also suggest that three subphthalocyanine units absorb light independently and do not disturb each π system. The characteristics of the absorption spectra of trimer **1** in trifluorotoluene were almost the same as those in dioxane.
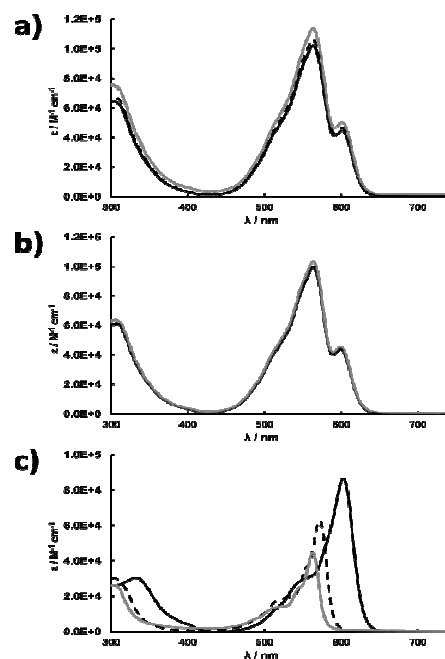
Fig. 2 UV/Vis spectra of trimer **1** in a) dioxane and b) trifluorotoluene at 1×10^{-4} M (black), 1×10^{-5} M (broken line) and 1×10^{-6} M (gray), and c) SubPc monomer (TFEO-SubPc: black, F-SubPc: broken line, and H-SubPc: gray) in dioxane at 1×10^{-5} M.
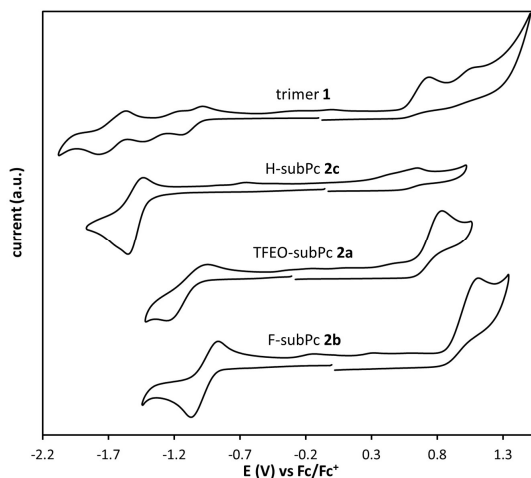
The steady-state fluorescence spectrum of trimer **1** was measured in dioxane and trifluorotoluene (Fig. 3). Trimer **1** showed two weak emission peaks at 582 nm and 614 nm upon excitation at 530 nm in dioxane. The emission peak at the lower energy originates in the emission of TFEO-SubPc and the emission at the higher energy occurs from the F-SubPc unit in dioxane. Moreover,

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the emission peak contributed by the H-SubPc unit was buried in the emission band from the F-SubPc unit. On the other hand, the emission peak of the H-SubPc unit (576 nm) was observed in addition to the peak of the TFEO-SubPc unit (615 nm) in trifluorotoluene by reducing the emission peak of the F-SubPc unit. Trimer **1** showed very small fluorescence quantum yields (Φ_f = 0.02 in dioxane and 0.007 in trifluorotoluene), which were determined by using zinc phthalocyanate in 1-chloronaphthalene as reference (Φ_f = 0.30),[12] by comparison with SubPc monomers. This result suggests electronic communication between each SubPc moiety of trimer **1**. It is inferred that energy transfer occurs from the H-SubPc unit to the F- or TFEO-SubPc unit. Energy transmission was also suggested by the steady-state fluorescence spectra. Although both peaks are quenched, the values of quenching around 570 nm originating from the H-SubPc unit are more significant than the other peak, which implies energy/electron transfer from the H-SubPc unit to the F- or TFEO-SubPc moiety.

Fig. 4 Cyclic voltammograms of subPc trimer **1** and subPc monomer **2a-c** in THF.

Table 1 Half-wave redox potentials of subPc trimer **1** and subPc monomer **2a-c** (V vs Fc/Fc$^+$) in THF.

compound	$E_{1/2red}^{3}$	$E_{1/2red}^{2}$	$E_{1/2red}^{1}$	$E_{1/2ox}^{1}$	$E_{1/2ox}^{2}$
trimer **1**	-1.67	-1.30	-1.06	0.640	0.985
H-subPc **2c**			-1.49	0.590	
TFEO-subPc **2a**			-1.10	0.727	
F-subPc **2b**			-0.962	1.00	

Fig. 3. Steady-state fluorescence spectra of a) trimer **1** in dioxane (black) and trifluorotoluene (gray), and b) SubPc monomer (TFEO-SubPc: black, F-SubPc: broken line, and H-SubPc: gray) in dioxane.

Cyclic voltammograms (CV) of trimer **1** and subPc monomer **2a-c** in THF are summarized in Fig. 4 and Table 1. Trimer **1** exhibited three reduction peaks at -1.06, -1.30 and -1.67 V that are attributed to an independent reduction process of each subPc unit in the cathodic scan. In the anodic scan of trimer **1**, two oxidation processes were observed at 0.640 and 0.985 V. The first reduction process of the subPc monomer was observed at -1.49 V in H-subPc **2c** and easier reduction processes occurred in TFEO-subPc **2a** and F-subPc **2b** at -1.10 and -0.962 V, respectively. On the other hand, fluorine-containing subPc **2a,b** showed a more difficult oxidation process than H-subPc **2c** (**2a**: 0.727, **2b**:1.00, and **2c**: 0.590 V). These results indicate that the molecular orbital energy of subPc was stabilized by introducing a strong electron-withdrawing fluorine atom.

To discuss the electron transfer process between each of the three SubPc units, we carried out DFT calculations using Gaussian09 program[13], which gave the distribution of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of **1** and **2a-c**. The molecular geometries of **1** and **2a-c** were optimized at the B97D/6-31G* level. The partial molecular orbital energy diagrams calculated at the B3LYP/6-31G* level using the optimized geometries are shown in Fig 5. Further details of the calculations are shown in supporting information. The relationship of the HOMO energy levels of SubPc and that of LUMO energy levels are as follows: H-SubPc **2c** > TFEO-SubPc **2a** > F-SubPc **2b**. This result agrees with the trend of the CV measurement and suggests that intramolecular energy transfer in trimer **1** should occur in three patterns: H-SubPc to F-SubPc, H-SubPc to TFEO-SubPc and TFEO-SubPc to F-SubPc (Fig. 1). Even though LUMO is generated by two orbitals in monomer SubPc **2**, degenerated orbitals are configured in trimer **1** due to a reduction of molecular symmetry. The energy level of LUMO+2 and LUMO+3 of **1** is close to the LUMO of **2a**. Furthermore, the distribution of LUMO+2 and LUMO+3 of **1** is localized in the TFEO-SubPc unit (Fig. 6). These results indicate that LUMO+2 and LUMO+3 of **1** originate from the LUMO of **2a**. On the other hand, LUMO to LUMO+1 of **1** are attributed to LUMO of **2b** according to an orbital energy level and distribution map. The HOMO of different SubPc monomers configures three occupied molecular orbitals in **1**. HOMO, and HOMO-**1** and HOMO-**2** of **1** originate from HOMO of **2c**, **2a** and **2b**, respectively. As a result, HOMO of **1** distributes mainly on the H-SubPc unit while LUMO on the TFEO-SubPc unit.
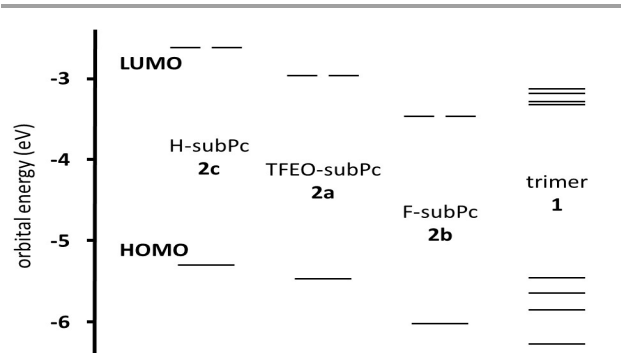
Fig. 5. Partial molecular orbital energy diagram.

LUMO+3 (676) LUMO+2 (675) LUMO+1 (674) LUMO (673)

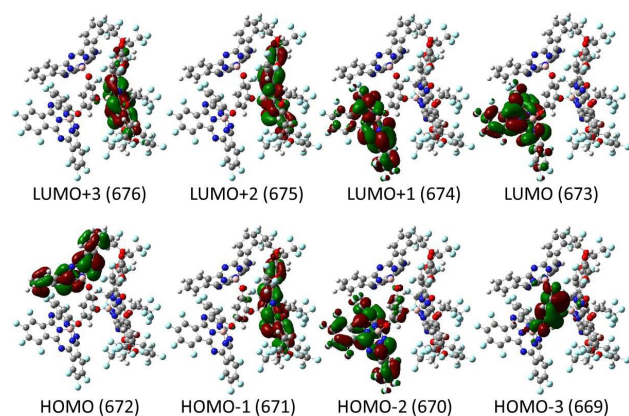HOMO (672) HOMO-1 (671) HOMO-2 (670) HOMO-3 (669)

Fig. 6. Distribution of molecular orbitals of trimer **1**. The numbers in parentheses indicate orbital number.

Conclusions

In conclusion, we have synthesized novel SubPc trimer **1** made up of TFEO-SubPc, F-SubPc and H-SubPc bridged at the axial position via a phloroglucinol linker and investigated its optical properties by UV-Vis and fluorescence spectra. The UV-Vis spectra of **1** show a spectrum shape composed of the absorption of TFEO-SubPc **2a**, F-SubPc **2b** and H-SubPc **2c**. This result indicates that each subphthalocyanine unit of **1** is electronically independent. On the other hand, the steady-state fluorescence spectra of **1** show quenched peaks which suggest energy transfer from H-SubPc to F-SubPc via TFEO-SubPc units, and/or directly H-SubPc to F-SubPc units. DFT calculations strongly support this phenomenon. These results would attract chemists as tools for development of novel electron/energy transfer system[7,8,14] as well as photocatalysis for organic reactions.[15]

Acknowledgements

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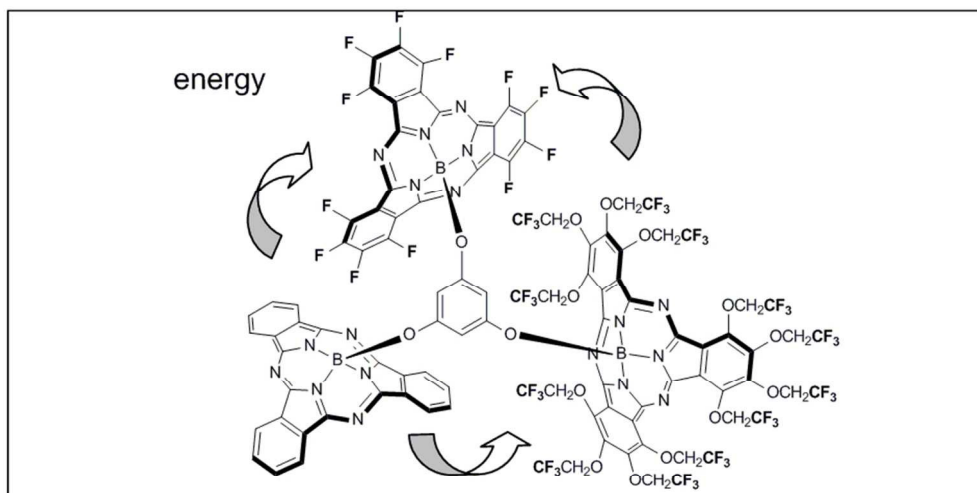
Energy transfer from the non-substituted subphthalocyanine unit to the perfluorinated subphthalocyanine unit via a trifluoroethoxy substituted unit is suggested.

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