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Axial Ligand Exchange Reactions of *meso*-Aryl Subporphyrins—Axially Fluoro-Substituted Subporphyrin and a μ-Oxo Dimer and Trimer of Subporphyrins

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High reactivity of the boron atom of *meso*-aryl subporphyrins enables the introduction of a broad range of functional groups to its axial position. Axially fluoro-substituted subporphyrins were easily synthesized upon treatment of axially hydroxyl-substituted subporphyrins with $BF_3 \cdot OEt_2$. Homogeneous μ-oxo dimers of subporphyrins were formed by heating monomers in the presence of triethylamine under a high vacuum. A heterogeneous subporphyrin−phthalocyanine−subporphyrin trimer was selectively formed from the respective monomers under similar reaction conditions. Structures of these molecules were elucidated by ^{1}H NMR spectra and a single-crystal X-ray diffraction analysis, and the interactions between neighboring chromophores in the dimeric systems were estimated from absorption and magnetic circular dichroism spectra.

Introduction

Recent growth of interest in expanded and contracted porphyrin analogues stems largely from their unique properties, which originate from their novel larger and smaller macrocyclic π-conjugation systems compared to the well-known 18π-electron conjugation system of porphyrins.[1] Among these, subporphyrin is a comparatively new entry in this class of molecules,[2−4] and it had been anticipated for many years as a real contracted congener of porphyrins. In contrast, its phthalocyanine counterpart, subphthalocyanine, has been known for more than 30 years[5] and has been investigated in a variety of fields as a functional molecule, due to its intense fluorescence and unusual nonlinear optical properties.[6] Subporphyrins known to date exhibit an intense Soret band and rather weak, broad Q bands, both in the shorter wavelength region compared to porphyrins due to their contracted 14π-electron conjugation systems. Most of these subporphyrins comprise a bowl-shaped structure in which a boron atom is coordinated at the center of the molecule in tetrahedral fashion by three nitrogen atoms of pyrrole rings and one axial ligand such as a halogen atom, hydroxy group, or carboxy group.[2,3] Due to this domelike structure, free rotation of the aryl groups at meso positions is allowed in most *meso*-aryl subporphyrins, leading to a much-enhanced coplanarity of the *meso*-aryl substituents and subporphyrin core compared to the case of *meso*-aryl porphyrins. These structural features result in a large perturbation effect of the aryl groups on the optical properties and electronic structures of the subporphyrins.[2] Recently, Osuka et al. utilized this characteristic well to modify two-photon absorption properties and emission behavior by introducing various functional groups to the para positions of *meso*-phenyl substituents via transition-metal-catalyzed substitution reactions of *meso*-*p*-bromophenyl subporphyrins.[7] The coplanarity is also known to facilitate efficient energy transfer from dendritic carbazole moieties at meso positions to subporphyrin cores.[8]

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Another feature of the subporphyrin is the high reactivity of the central boron atom, in which axial ligand exchange reactions take place easily. This reactivity should be useful both for fine-tuning of the properties of subporphyrins and construction of molecular assemblies by using a μ-oxo dimerization reaction. Similar approaches have been undertaken in subphthalocyanine chemistry.[9,10] Torres and coworkers recently reported the substitution reaction of an axial hydroxy group with fluoride and an intriguing columnar packing diagram in the crystal structures of axially fluoro-substituted subazaporphyrin due to a reduction in steric hindrance and a favorable interaction between subazaporphyrin units.[11] Ng and Xu tested heterodimer formation of subphthalocyanine and either porphyrin or phthalocyanine and revealed complexation processes in detail.[12] Inspired by these pioneering studies from the chemistry of phthalocyanine, our recent research along this direction revealed easy replacement of an axial hydroxy substituent with fluoride and the rather less polar nature of axially fluoro-substituted subporphyrin in silica gel columns with only slight changes in other properties such as aromaticity and absorption and fluorescence spectra. This lower polar nature made isolation of the subporphyrins by silica gel much more facile, since axially hydroxy species tend to be adsorbed on silica gel. The axially fluorinated subporphyrin can be converted to the original hydroxy species upon treatment with trifluoroacetic acid followed by water. A μ-oxo dimerization reaction of axially hydroxyl-substituted subporphyrins was first reported by us in 2007,[2b] and recently we found that the conversion yields are totally dependent on the electron-donating properties of *meso*-aryl substituents. This reaction was further utilized to construct a subporphyrin−phthalocyanine−subporphyrin heterotrimer system.

Experimental Section

Instrumentation. Electronic absorption spectra were recorded with a Hitachi U-3410 and a JASCO V-570 spectrophotometers. Magnetic circular dichroism (MCD) spectra were recorded with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet, which produces magnetic fields of up to 1.09 T (1T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla ($[\theta]_M$/deg dm^3 mol^{-1} cm^{-1} T^{-1}). The fluorescence spectrum was measured with a Hitachi F-4500 spectrofluorimeter. ^{1}H NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 594.17 MHz) and a Bruker AVANCE 400 spectrometer (operating as 400.33 MHz) using the residual solvent as the internal reference (δ = 7.260 ppm for $CDCl_3$). High-resolution mass spectra were recorded on a Bruker Daltonics Apex-III spectrometer. X-ray crystallographic studies were carried out on a Rigaku Saturn CCD spectrometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures were derived using the SHELXS-97 program and refined on F^2 using the SHELXL-97 program.

Syntheses. General Procedure for the Syntheses of Axially Fluoro-Substituted Subporphyrins (2a−2c). Axially hydroxyl-substituted subporphyrin (6.2 μmol) was dissolved in CH_2Cl_2 (3 mL), and an excess amount of $BF_3\cdot OEt_2$ (50 μL, 0.40 mmol) was added. The solution was stirred for 30 min at room temperature, and then the solvent was removed. Axially fluoro-substituted subporphyrin was purified using silica gel chromatography ($CHCl_3$) in yields of 95% for **2a**, 92% for **2b**, and 97% for **2c**. Further purification was performed by recrystallization from CH_2Cl_2/MeOH.

Axially Fluoro-Substituted *meso*-Phenylsubporphyrin (2a). ^{1}H NMR ($CDCl_3$): δ 7.63 (t, J = 7.2 Hz, 3H, phenyl-*p*), 7.72 (m, 6H, phenyl-*m*), 8.07 (d, J = 7.2 Hz, 6H, phenyl-*o*), 8.18 (s, 6H, pyrrole-β) ppm. HRMS (ESI-FT-ICR) calcd for $C_{33}H_{21}BN_3FNa$ ([M + Na]$^+$): 512.1705. Found: 512.1701. UV/vis ($CHCl_3$): λ_{max} (ε) 456 (12 000), 369 (157 000) nm.

Axially Fluoro-Substituted *meso*-Anisylsubporphyrin (2b). ^{1}H NMR ($CDCl_3$): δ 4.00 (s, 9H, OCH_3), 7.26 (d, J = 8.6 Hz, 6H, anisyl-*m*), 8.00 (d, J = 8.6 Hz, 6H, anisyl-*o*), 8.15 (s, 6H, pyrrole-β) ppm. HRMS (ESI-FT-ICR) calcd for $C_{36}H_{27}BN_3O_3FNa$ ([M + Na]$^+$): 602.2022. Found: 602.2019. UV/vis ($CHCl_3$): λ_{max} (ε) 494 (13 000), 462 (11 000), 377 (160 000) nm.

Axially Fluoro-Substituted *meso*-(4-Trifluoromethylphenyl)-subporphyrin (2c). ^{1}H NMR ($CDCl_3$): δ 8.00 (d, J = 4.3 Hz, 6H, aryl-*m*), 8.18 (d, J = 4.3 Hz, 6H, aryl-*o*), 8.19 (s, 6H, pyrrole-β) ppm. HRMS (ESI-FT-ICR) calcd for $C_{36}H_{18}BN_3F_{10}Na$ ([M + Na]$^+$): 716.1326. Found: 716.1323. UV/vis ($CHCl_3$): λ_{max} (ε) 456 (13 000), 369 (155 000) nm.

General Procedure for Syntheses of μ-Oxo Dimers of Subporphyrins (3a−3d). Axially hydroxyl-substituted subporphyrin (10 μmol) was dissolved in 3 mL of 100:1 $CHCl_3$/triethylamine, and the solvent was removed. The residue was heated at 85 °C in vacuo for 12 h and subjected to gel permeation chromatography−high-performance liquid chromatography (GPC-HPLC) using 1000:1 $CHCl_3$/triethylamine as an eluent to give **3a−3d** as the first fractions (55% for **3a**, 6% for **3b**, 90% for **3c**, and 84% for **3d**).

μ-Oxo Dimer of *meso*-Phenylsubporphyrin (3a). ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 6H, phenyl-*p*), 7.56 (m, 12H, phenyl-*m*), 7.64 (s, 12H, pyrrole-β), 7.78 (d, J = 7.2 Hz, 12H, phenyl-*o*) ppm. HRMS (ESI-FT-ICR) calcd for $C_{66}H_{42}B_2N_6ONa$ ([M + Na]$^+$): 979.3498. Found: 979.3501. UV/vis ($CHCl_3$): λ_{max} (ε) 469 (9900), 364 (140 000) nm.

μ-Oxo Dimer of *meso*-Anisylsubporphyrin (3b). ^{1}H NMR ($CDCl_3$): δ 7.12 (d, J = 8.8 Hz, 12H, anisyl-*m*), 7.62 (s, 12H, pyrrole-β), 7.75 (d, J = 8.8 Hz, 12H, anisyl-*o*) ppm. UV/vis ($CHCl_3$): λ_{max} (ε) 503 (12 000), 473sh (10 000) and 370 (135 000) nm.

μ-Oxo Dimer of *meso*-(4-Trifluoromethylphenyl)subporphyrin (3c). ^{1}H NMR ($CDCl_3$): δ 7.62 (s, 12H, pyrrole-β), 7.80 (m, 24H, aryl-*o*, *m*) ppm. HRMS (ESI-FT-ICR) calcd for $C_{72}H_{36}B_2F_{18}N_6ONa$ ([M + Na]$^+$): 1387.2741. Found: 1387.2854. UV/vis ($CHCl_3$): λ_{max} (ε) 467 (14 000), 364 (199 000) nm.

μ-Oxo Dimer of *meso*-(3-Pyridyl)subporphyrin (3d). ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 6H, aryl-*m*), 7.73 (s, 12H, pyrrole-β), 8.10 (d, J = 8.0 Hz, 6H, aryl-*o*), 8.83 (d, J = 4.9 Hz, 6H, aryl-*p*), 9.03 (s, 6H, aryl-*o*′) ppm. HRMS (ESI-FT-ICR) calcd for $C_{60}H_{36}B_2N_{12}ONa$ ([M + Na]$^+$): 985.3213. Found: 985.3209. UV/vis ($CHCl_3$): λ_{max} (ε) 465 (7700), 363 (109 000) nm.

Results and Discussion

The axial fluoro-substitution reaction of *meso*-phenyl subporphyrin **1a**,[2a] which we were motivated to investigate by the recent report on subazaporphyrin and subphthalocyanine by Torres et al.,[11] was carried out using $BF_3\cdot OEt_2$ in

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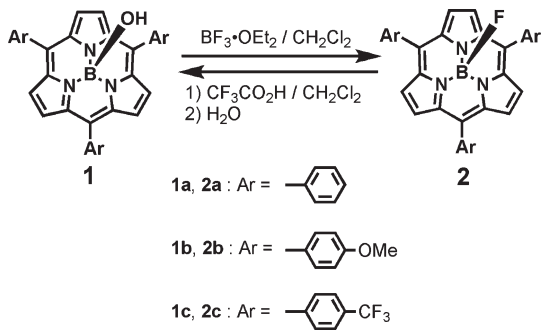
Scheme 1. Synthesis of Axially Fluoro-Substituted Subporphyrins **2a**−**2c**



CH_2Cl_2 at room temperature (Scheme 1). This reaction proceeded almost quantitatively, to give axially fluoro-substituted *meso*-phenyl subporphyrin **2a** in 95% yield. Considering the higher temperature (110 °C) needed for the reaction of subphthalocyanine and the lower yields of both subazaporphyrin and subphthalocyanine, the reactivity of a boron atom in subporphyrin is higher than that of subazaporphyrin and subphthalocyanine. Since quantitative conversion was achieved in the case of subporphyrins having either electron-donating anisyl substituents (**1b**)[2b] or electron-withdrawing trifluoromethyl substituents (**1c**),[2b] aryl groups at meso positions do not appear to have any effect on the yields. Axially fluoro-substituted species can be easily hydrolyzed, to give the original axially hydroxyl-substituted species upon treatment with trifluoroacetic acid in CH_2Cl_2 followed by water. During this investigation, we observed a less polar nature of the fluoro species **2a**−**2c** in silica gel compared to the hydroxyl-substituted species (see the Supporting Information). As was reported elsewhere,[2] axially hydroxyl-substituted subporphyrins tend to be adsorbed on silica gel, and the isolated yields were apparently lower than synthetic yields. The less polar nature of the axially fluoro-substituted species prompted us to test the axial ligand exchange procedure prior to separation of the reaction mixture by silica gel column. Tripyrrolyl borane was reacted with arylaldehyde in refluxing propionic acid for 3−4 h. After removing the solvent, the resultant tar was dissolved in CH_2Cl_2, and $BF_3 \cdot OEt_2$ was added. The mixture was stirred at room temperature for 30 min, and complete conversion of axially hydroxyl-substituted subporphyrins to fluorinated species was monitored by thin-layer chromatography (TLC) analysis. Separation by silica gel column provided axially fluoro-substituted subporphyrins as the first fraction with some tailing due to partial decomposition into hydroxyl-substituted species in the silica gel. Apart from the different behaviors in silica gel, changes in other properties are fairly modest. In the ^{1}H NMR spectra of **2a**, **2b**, and **2c**, a signal due to the protons at β positions is shifted to a lower magnetic field of 8.18, 8.15, and 8.19 ppm, respectively (see the Supporting Information). This slight downfield shift of β protons implies an enhancement of the aromaticity of the subporphyrin core, probably due to an increase in planarity, which was predicted for optimized structures calculated by DFT methods using the B3LYP hybrid functional with 6-31G(d) basis sets (see the Supporting Information). In the UV/vis absorption spectra, slight blue shifts of both the Soret band and Q bands by 3−4 nm were observed, but the absorption and MCD spectra were essentially identical in shape (Figure 1). Furthermore, a blue shift of the fluorescence was observed, and the fluorescence quantum yields were increased (Table 1 and see the Supporting Information).

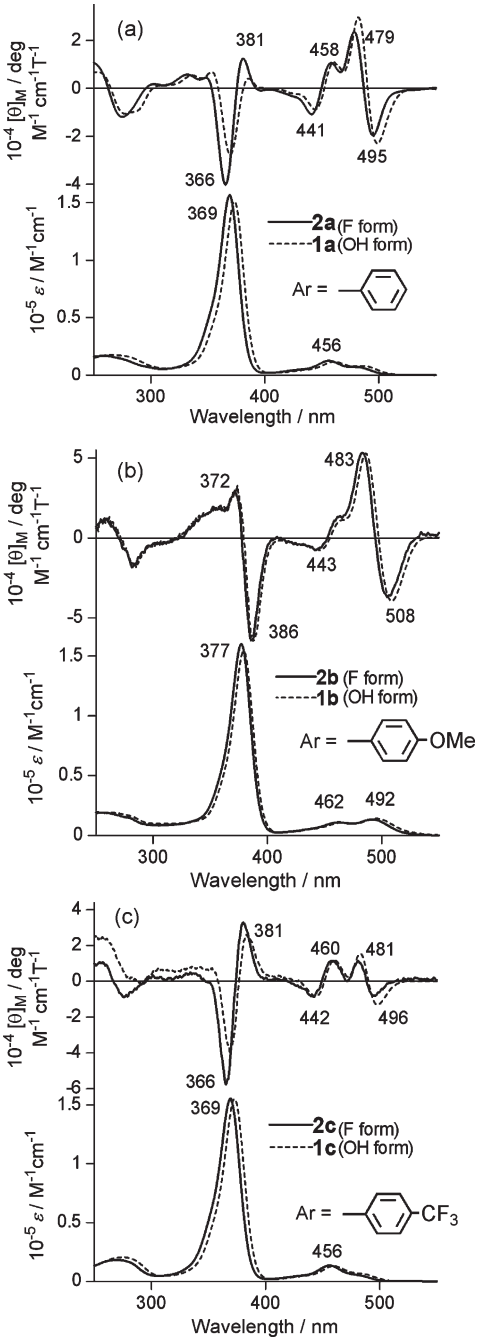


Figure 1. UV/vis (bottom) and MCD (top) spectra of (a) **2a**, (b) **2b**, and (c) **2c** (solid lines) and the corresponding axially hydroxyl-substituted species (**1a**−**1c**; broken lines) in $CHCl_3$.

μ-Oxo bond formation is a useful reaction for building molecular assemblies of subporphyrins. This possibility was first suggested by us with a face-to-face μ-oxo dimer of *meso*-3-pyridyl subporphyrin,[2b] and recently Osuka and Inokuma reported an axially linked slipped-stack subporphyrin dimer by using coordination of carboxy groups of *meso*-phenyl substituents and control of the conformation of the biphenylene-bridged subporphyrin dimer upon μ-oxo bond formation.[13]

(13) (a) Inokuma, Y.; Osuka, A. *Chem. Commun.* **2007**, 2938–2940. (b) Inokuma, Y.; Osuka, A. *Org. Lett.* **2008**, *10*, 5561–5564.

Table 1. Absorption and Fluorescence Properties

compound	absorption[a]	λ_{em} (nm)[b]	Φ_F[c]
1a[d]	486 (8000), 461 (12000), 373 (151000)	516	0.12
1b[d]	496 (14000), 466 (11000), 379 (154000)	536	0.11
1c[d]	480 (7000), 460 (13000), 373 (155000)	510	0.10
2a	456 (12000), 369 (157000)	507	0.15
2b	492 (13000), 462 (11000), 377 (160000)	530	0.19
2c	456 (13000), 369 (155000)	505	0.16
3a	469 (9900), 364 (140000)	533	0.08
3b	503 (12000), 370 (135000)	546	0.10
3c	467 (14000), 364 (199000)	539	0.07

[a] λ/nm (ε/M^{-1} cm^{-1}) data recorded in $CHCl_3$. [b] Data recorded in benzene. [c] Relative to 9,10-diphenylanthracene in benzene (Φ_F = 0.84 excited at 366 nm).[16] [d] See ref 2b.

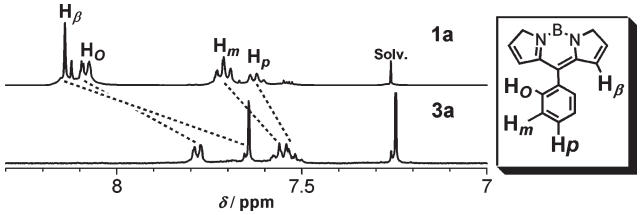
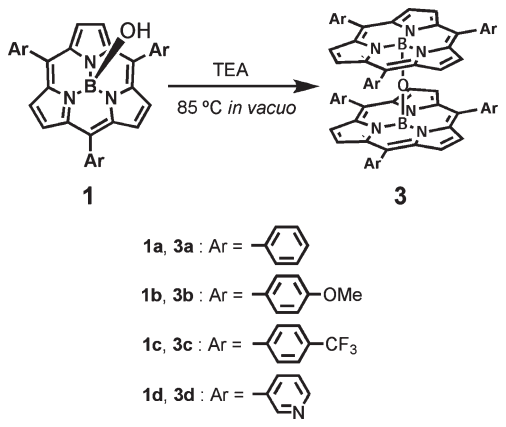


Figure 2. ^{1}H NMR spectra of μ-oxo dimer (**3a**) (bottom) and the corresponding monomer (**1a**) (top) in $CDCl_3$.

Scheme 2. Synthesis of μ-Oxo Dimers **3a**−**3d**



Several reaction conditions under which μ-oxo dimers of subphthalocyanines, porphyrins, and phthalocyanines were formed were tested to synthesize subporphyrin dimers,[9] but no reaction was found suitable for *meso*-aryl subporphyrins. μ-Oxo dimers of subporphyrins were formed under certain reaction conditions such that, after the addition of a small amount of triethylamine, the starting monomers were heated at 85 °C under a high vacuum for 12 h (Scheme 2). This reaction produced μ-oxo dimers in 6−90% yield along with recovery of the starting subporphyrin monomers. The starting monomers (**1a**−**1d**)[2a,2b] and μ-oxo dimers (**3a**−**3d**) were easily separated by recycling GPC-HPLC. The yields were apparently dependent on the *meso*-aryl substituents. In the case of electron-donating phenyl and anisyl substituents, the yields were apparently low, 55% (**3a**) and 6% (**3b**), while subporphyrins having electron-withdrawing substituents such as *p*-trifluoromethylphenyl and 3-pyridyl groups tended to form dimers in high yields of 90% (**3c**) and 84% (**3d**), respectively. The higher yields in the case of subporphyrins having electron-withdrawing substituents can be explained by an increased Lewis acidity of the boron atom as a result of

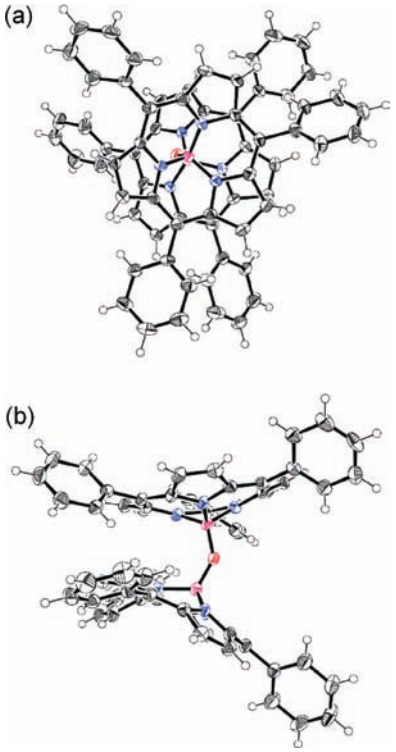


Figure 3. X-ray crystal structure of **3a**, top view (a) and side view (b). The thermal ellipsoids are scaled to the 50% probability level.

the *meso*-aryl substituents. In the ^{1}H NMR spectrum of **3a**, all of the peaks shifted to higher magnetic field due to the aromatic ring current effect of the neighboring subporphyrins (Figure 2). $\Delta\delta$ values of the β and ortho protons are large (0.48 ppm for β protons and 0.29 ppm for ortho protons) compared to those of meta and para protons. Similar changes in the spectra were also observed for other dimers, **3b**−**3d** (see the Supporting Information). The structure of **3a** was finally revealed by single-crystal X-ray diffraction analysis (Figure 3).[14] Two subporphyrin units are linked through a bent B−O−B bond with an angle of 139.6(3)°. The subporphyrin units are twisted by ca. 33° to each other to avoid steric congestion between the *meso*-phenyl substituents. The bowl depth, defined by the height of the boron atom from the mean plane defined by six β-pyrrolic carbon atoms, became deeper than that of the corresponding subporphyrin monomer (1.40 and 1.46 Å for **3a** and 1.29 Å for **1a**[3b]). The UV/vis absorption spectra of **3a**−**3d** all exhibited slight blue shifts of the Soret bands by ca. 10 nm, while the tail of the Soret bands extended to 430 nm, which cannot be observed for the respective monomers (Figure 4). In contrast, the tail of Q bands and emission maximum shifted slightly to the red. The fluorescence quantum yields were slightly decreased, 0.12 for **1a** and 0.08 for **3a** (Table 1). These results can be basically accounted for in terms of exciton coupling theory, which was first applied to porphyrin compounds in the case of a μ-oxo dimer of scandium porphyrins by Gouterman et al. in 1977.[15]

(14) Crystallographic data for **3a**: $C_{68}H_{44}B_2N_6OCl_6$, M_W = 1195.41, monoclinic, space group $P2_1/n$ (no. 14), a = 18.966(5), b = 12.408(3), c = 26.138(6) Å, β = 110.0886(10)°, V = 5777(2) Å^3, Z = 4, ρ_{calcd} = 1.374 g/cm^3, T = −100 °C, 12 893 measured reflections, 5272 unique reflections, R = 0.0755, R_w = 0.2319 (all data), GOF = 0.959.

(15) Gouterman, M.; Holten, D.; Lieberman, E. *Chem. Phys.* **1977**, *25*, 139–153.

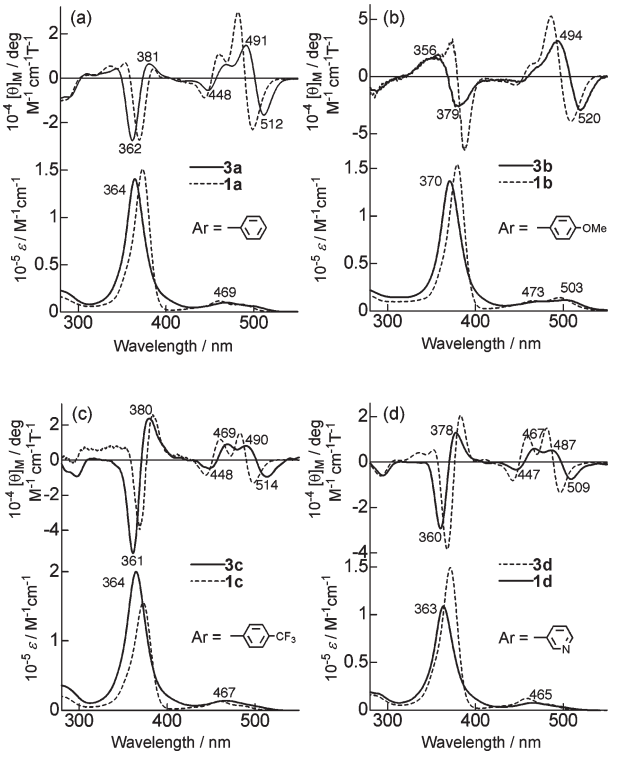


Figure 4. UV/vis (bottom) and MCD (top) spectra of μ-oxo dimers (**3a**−**3d**; solid lines) and the corresponding monomers (**1a**−**1d**; broken lines) in $CHCl_3$.

The μ-oxo dimer of scandium porphyrins showed a similar blue shift and red tail of the Soret band and a red shift of the Q bands. The former was explained by exciton coupling interactions, while the latter was attributed to broadening of the band by solvent effects. The red tail of the Soret band is attributable to a forbidden lower-energy band created by exciton coupling, which becomes partially allowed by symmetry lowering caused by molecular vibration. Since the strength of the dipole moment of the Q band is smaller than that of the Soret band, exciton coupling interactions should be less significant for the Q band, so that inhomogenous solvent broadening due to dimerization is the main factor for the red shift of the Q band. This illustration can also be applied to the μ-oxo dimers of subporphyrins. Since the blue shifts of the Soret band (ca. 10 nm for **3a**) and the decrease of fluorescence quantum yields were small, the extent of exciton coupling interaction can be assumed to be less significant in the μ-oxo dimers of subporphyrins. This would be reasonable considering their nonplanar structures and bent B−O−B bonds.

We further extended this reactivity of the boron atom to construct a heterotrimer system. Phthalocyanines are well-known UV/vis absorbing dyes, exhibiting intense Q bands at around 700 nm. Moreover, similar μ-oxo oligomerization reactivity was seen for silicon phthalocyanines. A heterotrimer system of *meso*-aryl subporphyrins and silicon phthalocyanine is of interest because the resultant trimer system can absorb a wide range of light. Under similar reaction conditions to those of the μ-oxo dimerization reaction, **1a** and octabutoxy silicon phthalocyanine **4** were reacted at 120 °C in a 2:1 molar ratio in the presence of triethylamine under a high

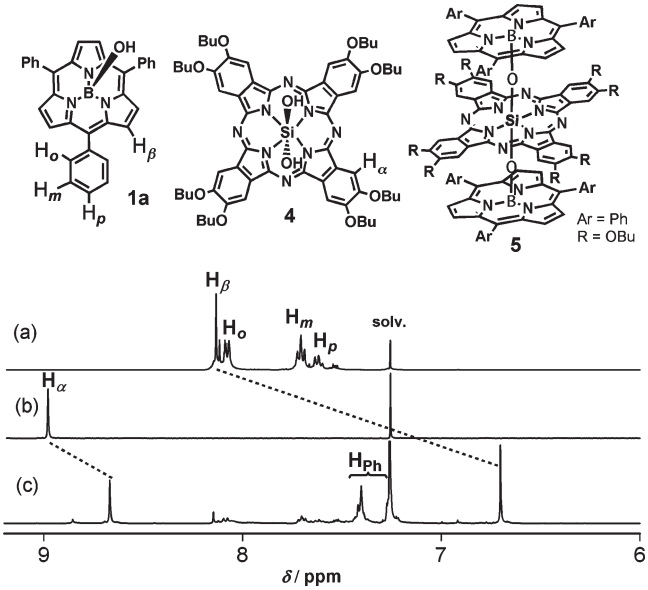


Figure 5. ^{1}H NMR spectra of **1a** (a), **4** (b), and **5** as synthesized (c) in $CDCl_3$.

vacuum, and formation of the subporphyrin−phthalocyanine−subporphyrin heterotrimer **5** was confirmed by MALDI-TOF mass (see Supporting Information) and ^{1}H NMR spectra (Figure 5). In the ^{1}H NMR spectrum, upfield shifts of the signals due to protons at the β positions of **1a** and α-benzo positions of **4** were observed. The 2:3 integration ratio of signals due to the α-benzo and β-pyrrolic protons surely characterized this compound as the target heterotrimer. Unfortunately, however, isolation attempts, either by silica gel or GPC column, led to decomposition of the trimer into the original monomers and subporphyrin−phthalocyanine dimer. Despite the instability of the B−O−Si bond, it is worth noting that the heterotrimer species was selectively formed instead of the formation of subporphyrin−subporphyrin and phthalocyanine−phthalocyanine homodimers. This can be ascribed to the difference in reactivity of silicon and boron in μ-oxo bond formation.

Conclusions

Axial ligand exchange reactions were utilized in order to synthesize novel axially fluoro-substituted subporphyrins (**2a**−**2c**), μ-oxo dimers (**3a**−**3d**), and the μ-oxo subporphyrin−phthalocyanine−subporphyrin hetero timer (**5**). Axially fluoro-substituted subporphyrins exhibited slightly enhanced aromatic character, probably due to rigid structures of the fluorinated species. A drastic change of behavior in silica gel made the column separation of subporphyrin species easier by substituting the axial ligands with fluorine atoms prior to column separation. In our previous work, isolation of subporphyrins from the reaction mixture should be improved as a result of its severe adsorption on silica gel. By using this fluorination reaction, the subporphyrin species was easily isolated. μ-Oxo dimers of subporphyrins were easily synthesized from the respective monomers by heating at 85 °C under a vacuum. Exciton coupling interactions between the subporphyrins were revealed by UV/vis absorption spectra, but the extent was fairly modest, reflecting the nonplanar structure and bent B−O−B bond. A heterogeneous μ-oxo trimer of subporphyrin and silicon phthalocyanine was selectively

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formed from the respective monomers, which was confirmed by the MALDI-TOF mass and ^{1}H NMR spectra. Unfortunately, however, successful isolation of this trimer has not yet been achieved due to facile decomposition into the subporphyrin monomer and μ-oxo dimer of subporphyrin and silicon phthalocyanine. Molecular assembly by using the μ-oxo oligomerization reaction is one of the most promising ways to develop new properties from these simple components, but the stability of the μ-oxo bonding must be controlled. Investigations in this direction are currently being undertaken in our laboratory.

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Supporting Information Available: A picture of TLC development, ^{1}H NMR and fluorescence spectra, optimized structures of **1a** and **2a**, MALDI TOF mass spectrum of **5**, and a CIF file of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.