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Synthesis of Phthalocyanines with a Pentafluorosulfanyl Substituent at Peripheral Positions

Norihito Iida,[a] Kenta Tanaka,[a] Etsuko Tokunaga,[b] Satoru Mori,[b] Norimichi Saito,[c] and Norio Shibata*[a, b]

The pentafluorosulfanyl (SF_5) group is more electronegative, lipophilic and sterically bulky relative to the well-explored trifluoromethyl (CF_3) group. As such, the SF_5 group could offer access to pharmaceuticals, agrochemicals and optoelectronic materials with novel properties. Here, the first synthesis of phthalocyanines (Pcs), a class of compounds used as dyes and with potential as photodynamic therapeutics, with a SF_5 group directly attached on their peripheral positions is disclosed. The key for this work is the preparation of a series of SF_5-containing phthalonitriles, which was beautifully regio-controlled by a stepwise cyanation via *ortho*-lithiation/iodination from commercially available pentafluorosulfanyl arenes. The macrocyclization of the SF_5-containing phthalonitriles to SF_5-substituted Pcs required harsh conditions with the exception of the synthesis of β-SF_5-substituted Pc. The regiospecificity of the newly developed SF_5-substituted Pcs observed by UV/Vis spectra and fluorescence quantum yields depend on the peripheral positon of the SF_5 group.

The pentafluorosulfanyl (SF_5) group likely has the greatest potential to alter the properties of original compounds when it is introduced into suitable positions on parent molecules, due to its specific physical and chemical properties.[1] Despite the first appearance of this unique motif in the 1950s, the chemistry of the SF_5 group is one of the least explored in fluorine chemistry, causing it to be dubbed as the "forgotten functional group".[2] The SF_5 group has an octahedral geometry, and the sulfur atom is in a hypervalent state with five fluorine atoms surrounding it, imparting SF_5 group with greater electronegativity, lipophilicity and steric size relative to the well-explored trifluoromethyl (CF_3) group. Indeed, the electronegativity of SF_5 is closer to that of a nitro (NO_2) group, and the size of SF_5 is equivalent to a *tert*-butyl group.

The SF_5 group has been nicknamed "super CF_3" for good reason.[3] The field of CF_3 chemistry has blossomed over the past decades to become an extremely rich area of a variety of research fields, including pharmaceuticals, agrochemicals and optoelectronic materials,[4] and SF_5-containing compounds could represent the next epoch in these areas.[5] Examples of SF_5-containing analogues of CF_3-substituted drugs and functional materials have seen success to varying degrees.[6] Although the synthetic methods to access SF_5-containing compounds were previously limited and tedious,[2] the discovery by Umemoto in 2008 of an efficient construction of an SF_5 unit on a benzene ring from a aryl disulfide[2b] allowed simple SF_5-substituted arenes (**1**) to become commercially available with the collaboration of Ube Industries Ltd.[7] Even the synthesis of SF_5-substituted pyridines **2** was recently achieved by Dolbier[8] under modified Umemoto conditions. By virtue of these facts, it is hoped that direct functionalization of readily available simple SF_5-substituted arenes at all positions of the aromatic ring would allow for the synthesis of more complex SF_5-containing molecules,[9] including SF_5-containing macrocycles.

Phthalocyanines (Pcs) are heterocyclic macrocycles and are used as artificial blue or green organic dyes with high robustness.[10] Pcs are very popular pigments (e.g., Pigment Blue 16, Pigment Green 7, etc.) with big sales worldwide, but they have also been extensively researched in industry and academia for the development of organic solar cells, semiconductors, optical recording materials and medicinal agents for photodynamic therapy of cancer due to their strong optical absorption at wavelengths longer than 650 nm. Since these optical properties of Pcs vary significantly with substitutions on peripheral positions, the design and synthesis of Pcs with various substitutions has attracted much attention.[11] In particular, strong electron-withdrawing substituents, such as NO_2 remarkably decrease the basicity of the parent macrocycle, resulting in an increase in the stability of the Pc towards oxidation.[12] However, Pcs suffer from poor solubility in organic solvents. Fluoro-functionalized Pcs have thus emerged as lipophilic and stabilized Pcs to overcome these shortfalls.[13] These fluorinated Pcs are also expected to exhibit novel and unique properties, and trifluoroethoxy-Pcs[13c] and perfluoroisopropyl Pc[13a,b] are two representative examples of this compound class. Many reports have documented the synthesis of Pcs having fluorinated functional groups on peripheral positions[13] but there is no example of the synthesis of Pcs having an SF_5 moiety directly in their peripheral positions.[14] As part of our research program on fluorinated Pcs,[15] we report herein the synthesis of directly functionalized SF_5-substituted Pcs **3a**–**c**, and disclose the regio-

[a] N. Iida, K. Tanaka, Prof. N. Shibata
Department of Frontier Materials, Nagoya Institute of Technology
Gokiso, Showa-ku, Nagoya 466-8555 (Japan)
E-mail: nozshiba@nitech.ac.jp

[b] E. Tokunaga, S. Mori, Prof. N. Shibata
Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555 (Japan)

[c] N. Saito
Pharmaceutical Division, Ube Industries, Ltd.
Seavans North Bldg., 1-2-1 Shibaura, Minato-ku, Tokyo 105-8449 (Japan)

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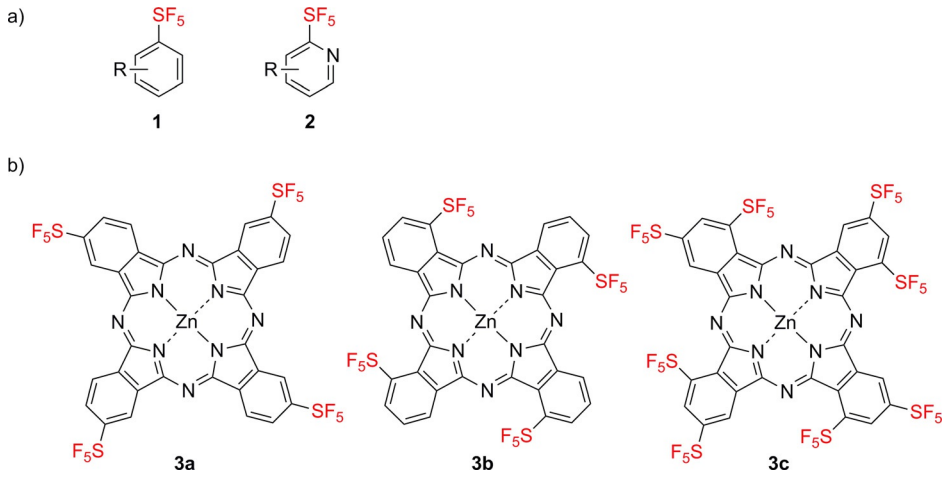
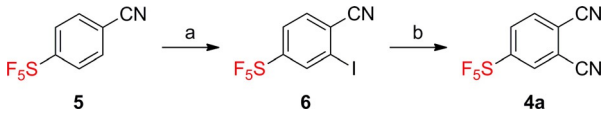


Figure 1. a) Commercially or readily available SF_5-substituted arenes **1** and SF_5-containing heteroarenes (i.e., SF_5-substituted pyridine **2**), reported elsewhere; b) newly developed SF_5-containing macrocyles (i.e., phthalocyannes; SF_5-Pcs **3a–c**), described here.

specific optical properties of these derivatives for the first time (Figure 1).

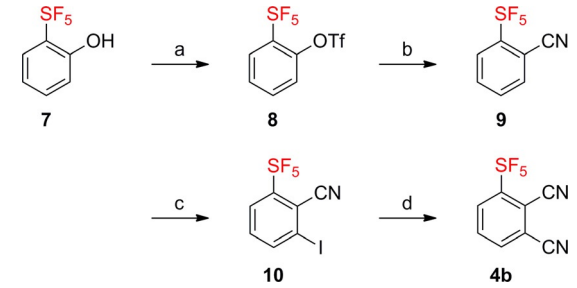
The critical departure point for the synthesis of SF_5-substituted Pcs **3** was how to create a series of SF_5-phthalonitriles **4** from commercially available SF_5-substituted arenes. First, the synthesis of 4-(pentafluorosulfanyl)phthalonitrile **4a** as a precursor for β-SF_5-substituted Pc **3a** was attempted. The regioselective *ortho*-lithiation of 4-(pentafluorosulfanyl)benzonitrile (**5**) using a strong bulky base, lithium tetramethylpiperidide (LiTMP), was followed by iodination with I_2 to furnish **6** in 38% yield. The iodo-function of **6** was next converted into a cyano group using copper(I) cyanide in dimethylformamide (DMF) at 110 °C to give **4a** in 43% yield (Scheme 1).



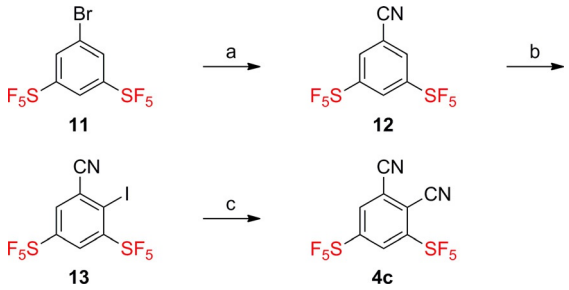
Scheme 1. Synthesis of **4a** via stepwise *ortho*-lithiation/iodination/cyanation process. *Reagents and conditions*: a) LiTMP (2.0 equiv), I_2 (1.1 equiv), THF, −80 °C, 38% yield; b) CuCN (3.0 equiv), DMF, 110 °C, 43% yield.

The synthesis of **4b**, the precursor for α-SF_5-substituted Pc **3b**, was next examined using commercially available 2-hydroxyphenylsulfur pentafluoride (**7**) (Scheme 2). Treatment of **7** with triflic anhydride in the presence of triethylamine in dichloromethane at room temperature provided triflate **8** in 98% yield. The triflate moiety of **8** was converted into a cyano group using a coupling reaction with zinc cyanide under palladium catalysis of tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) to give 2-(pentafluorosulfanyl)benzonitrile (**9**) in 91% yield. The newly functionalized cyano group in **9** was effectively used as a directing group for *ortho*-lithiation under LiTMP conditions followed by treatment with I_2 to provide 2-(pentafluorosulfanyl)-6-iodobenzonitrile (**10**) in 40% yield. Finally, a second cyano group was introduced into **10** via a coupling reaction by copper(I) cyanide in DMF under 140 °C to provide desired α-SF_5-phthalonitrile **4b** in 59% yield.

Finally, the synthesis of 3,5-bis(pentafluorosulfanyl)phthalonitrile (**4c**) from commercially available 3,5-bis(pentafluorosulfanyl)-1-bromobenzene (**11**) was attempted (Scheme 3). Cyanation of bromide **11** proceeded smoothly with potassium ferricyanide and 1-butyl imidazole in the presence of copper(I) iodide to furnish **12** in 74% yield. The *ortho*-lithiation/iodination of **12** required three equivalents of



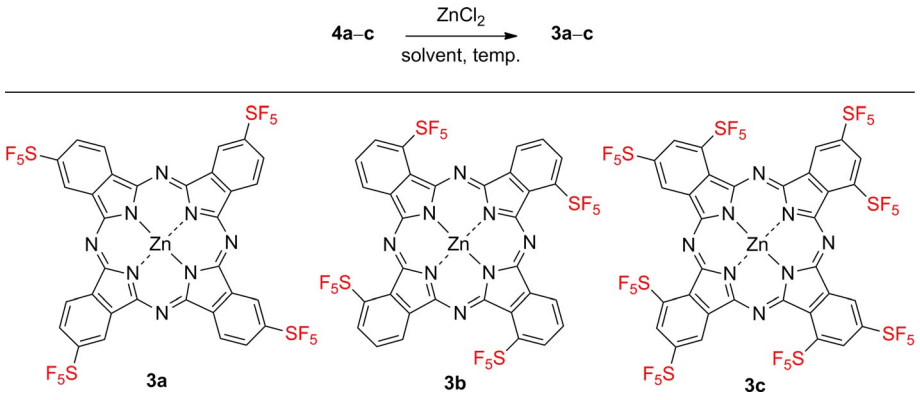
Scheme 2. Synthesis of 3-(pentafluorosulfanyl)phthalonitrile. *Reagents and conditions*: a) Et_3N (1.5 equiv), Tf_2O (1.5 equiv), CH_2Cl_2, r.t., 98% yield; b) $Zn(CN)_2$ (1.2 equiv), $Pd_2(dba)_3$ (1.0 mol%), dppf (2.4 mol%), DMF, 80 °C, 91% yield; c) LiTMP (2.0 equiv), I_2 (2.0 equiv), THF, −80 °C, 40% yield; d) CuCN (1.5 equiv), DMF, 140 °C, 59% yield.



Scheme 3. Synthesis of 3,5-bis(pentafluorosulfanyl)phthalonitrile. *Reagents and conditions*: a) $K_4[Fe(CN)_6]$ (0.8 equiv), CuI (40 mol%), 1-buthyl imidazole (8.0 equiv), toluene, 160 °C, 74% yield; b) LiTMP (3.0 equiv), I_2 (3.0 equiv), THF, −80 °C, 68% yield; c) CuCN (1.0 equiv), DMF, 160 °C, 42% yield.

LiTMP and I_2 in tetrahydrofuran (THF) at −80 °C to give **13** in 68% yield. The desired 3,5-bis(pentafluorosulfanyl)phthalonitrile (**4c**) was obtained in 42% yield by cyanation of **13** under copper(I) cyanide conditions.

With a series of SF_5-phthalonitriles **4** in hand, tetramerization of **4a–c** to SF_5-substituted Pcs **3a–c** was investigated (Scheme 4). Under standard conditions consisting of zinc chlo-



Scheme 4. Synthesis of SF_5-substituted phthalocyanines **3**. *Reagents and conditions*: For **3a**: $ZnCl_2$ (0.33 equiv), *N,N*-dimethylamino ethanol, 140 °C, 10% yield; for **3b**: $ZnCl_2$ (0.31 equiv), 180 °C, solvent-free, 28% yield; for **3c**: $ZnCl_2$ (0.25 equiv), 200 °C, solvent-free, 7.8% yield. All compounds were obtained as a mixture of regioisomers.

ride in *N,N*-dimethyl-2-aminoethanol (DMAE) at 140 °C, 4-(pentafluorosulfanyl)phthalonitrile (**4a**) was converted into β-SF_5-substituted Pc **3a** in 10% yield as a mixture of regioisomers. However, SF_5-phthalonitriles **4b** and **4c** failed to be cyclized under these conditions. This is presumably due to the steric hindrance[14a,15k] and strong electronegativity of the SF_5 group on the neighboring cyano moiety. Finally, desired α-SF_5-substituted Pc **3b** and α,β-SF_5-substituted **3c** were obtained under harsh conditions, that is, without solvent at higher reaction temperatures (180–200 °C), in 28% and 7.8% yield, respectively, as a mixture of regioisomers.

The UV/Vis and fluorescence spectroscopy were used to investigate their optical properties of SF_5-substituted Pcs **3a–c** in dichloromethane, α,α,α-trifluorotoluene (CF_3Ph) and 1,4-dioxane (dioxane) (see Table 1 and Figure 2a; detailed data is provided in the Supporting Information). In dichloromethane, the UV/Vis spectra of α-SF_5-substituted Pc **3b** and α,β-SF_5-substituted **3c** are sharp, while the region of the 630 nm to 640 nm band of β-SF_5-substituted **3a** is broad (Figure 2a). Next, the UV/Vis spectra in CF_3Ph and dioxane were investigated (spectra for **3a** are shown in Figure 2b; spectra for **3b,c**, see Supporting Information). Interestingly, the absorption of β-SF_5 **3a** is remarkably weaker than that of α-SF_5 **3b** and α,β-SF_5 **3c**. The 630 nm region of β-SF_5 **3a** is weak and broad, indicating H-aggregation in CF_3Ph, while both α-SF_5 **3b** and α,β-SF_5 **3c** show sharp spectra of non-aggregation in CF_3Ph. The Q-band of α,β-SF_5 **3c** lies almost in the same blue-shift position as α-SF_5 **3b**, independent of the existence of an additional β-SF_5 group in **3c**, while a red-shift was observed for β-SF_5 **3a**. These results suggest that the effect of an SF_5-substitution at a peripheral α-position is much larger than that at a β-position. The blue-shift caused by α-substitution arises due to the presence of an electron-withdrawing NO_2 group,[16] which is the opposite observation to that seen when an electron-donating *n*-butoxy (*n*BuO) group is present; in that case, α-substitution induces a red-shift of the Q-band.[17]

Table 1. The Q-band values, emission maxima (λ_{em}) and fluorescence quantum yields (Φ_f) of compounds **3** determined from the UV/Vis spectra measured at 1.0×10^{-4} M.

Compd	Solvent	Q-band [nm]	λ_{em} [nm]	Φ_f
3a	CH_2Cl_2	672	676	0.55
3b	CH_2Cl_2	664	672	0.13
3c	CH_2Cl_2	665	685	0.43
3a	CF_3Ph	667	673	0.76
3b	CF_3Ph	662	669	0.25
3c	CF_3Ph	663	684	0.42
3a	dioxane	665	671	0.95
3b	dioxane	660	669	0.31
3c	dioxane	662	685	0.44

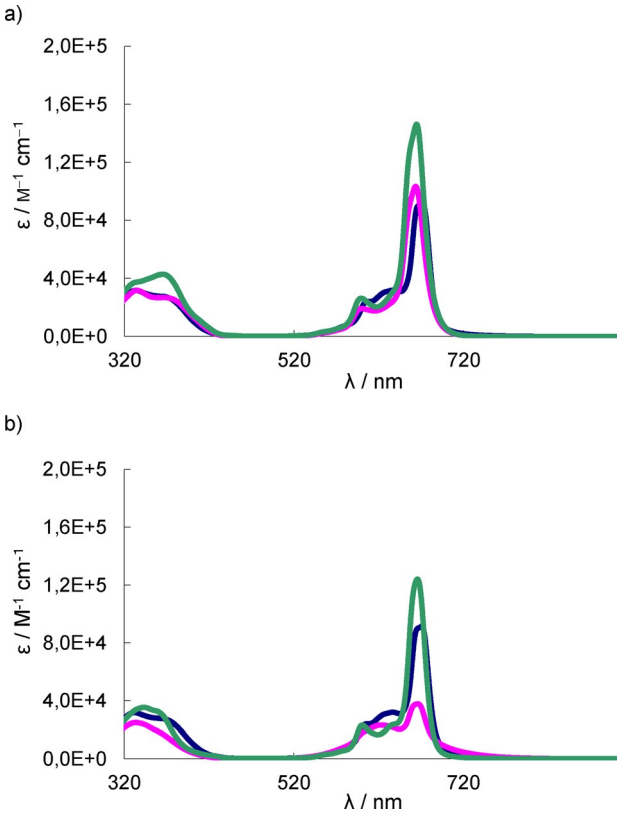


Figure 2. UV/Vis spectra of a) compounds **3** in CH_2Cl_2 at 1.0×10^{-4} M: **3a** (blue), **3b** (pink) and **3c** (green), and b) compound **3a** at 1.0×10^{-4} M in different solvents: CH_2Cl_2 (blue), CF_3Ph (pink), dioxane (green).

To consider the origin of the differences in Q-bands, HOMO–LUMO energy levels of **3a–c** were next calculated by computation, and they were compared with those of conventional zinc phthalocyanine (ZnPc) (DFT/B3LYP/6-31G*) (Figure 3). In all cases, the HOMO levels were stabilized as the number of SF_5

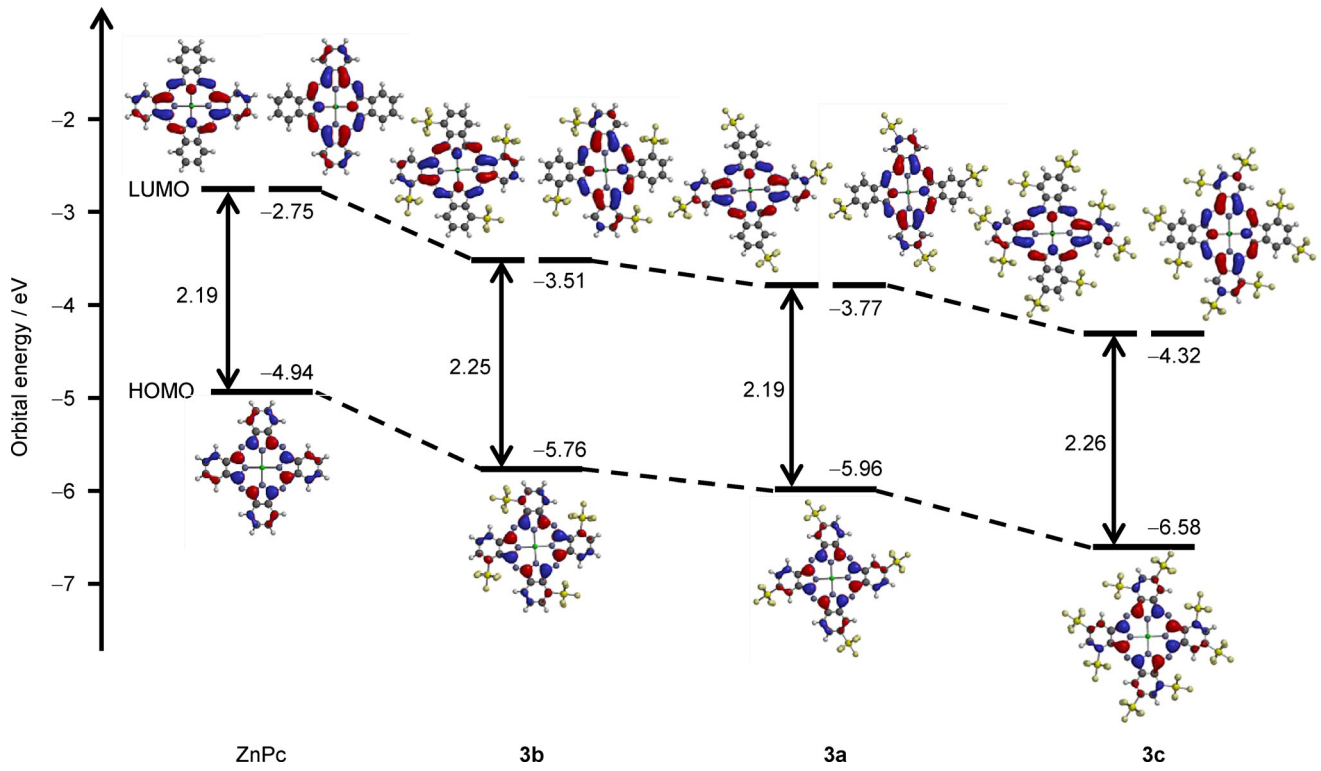


Figure 3. Energy level of frontier molecular orbitals of zinc phthalocyanine (ZnPc) and SF_5-substituted Pcs **3a–c**.

substitutions increased, which is in good agreement with the stabilization of Pcs by electron-withdrawing functional groups. The stabilization effect on the HOMO level by β-SF_5 substitution is slightly stronger than that of α-SF_5 substitution, and approximate additivity was observed for α,β-SF_5 substitution. Energy gaps of HOMO and LUMO correlate well with the Q-band positions of **3a–c** in Table 1. The Q-band of β-SF_5 **3a** is shifted to a long wavelength, which is very consistent with calculations in which the energy gap of HOMO and LUMO of β-SF_5 **3a** is smallest (2.19 eV), while that of α-SF_5 **3b** and α,β-SF_5 **3c** are almost the same (2.25 and 2.26 eV, respectively). These results clearly indicate that a SF_5 group at an α-position increases the energy gap (**3b**: 2.25 eV; **3c**: 2.26 eV), while β-substitution with a SF_5 group does not affect it (energy gap: ZnPc = 2.19 eV; **3a** = 2.19 eV).

Fluorescence of β-SF_5 **3a** is considerably stronger than that of **3b–c**, having a α-SF_5 moiety, especially in dioxane; fluorescence quantum yield of **3a** is very high ($\Phi_f = 0.95$), and fluorescence decreases in the order β-SF_5 **3a** > α,β-SF_5 **3c** > α-SF_5 **3b** (Table 1). It is interesting to note that the electron-donating *n*BuO group on Pcs shows a similar tendency, namely that the Φ_f value becomes smaller with the α-substitution of *n*BuO groups, as reported by Kobayashi and co-workers.[17] They explained this phenomenon as a decrease in the energy gap between HOMO and LUMO, suggesting that the excited states become unstable in systems showing a Q-band at lower energy, due to the ease of electron transfer. However, in our case, electron-withdrawing SF_5 groups were not related to HOMO–LUMO energy gaps. Fundamentally, the effects on optical properties by electron-withdrawing substituents are much smaller than those by an electron-donating group. This indicates that an α-SF_5-substitution induces a non-radiative transition process presumably due to the distortion of the phthalocyanine plane by a bulky SF_5 group on the α-position, while a β-SF_5-substitution inhibits it, although further investigation is required.

In conclusion, a series of directly-substituted SF_5-containing phthalocyanines (Pcs) were regioselectively synthesized from commercial available simple SF_5-substituted arenes by stepwise cyanation via *ortho*-lithiation/iodination. Regiospecific spectroscopic properties were observed. The aggregation of Pcs is controlled regioselectively with the SF_5 substitution at a peripheral α- or a β-position. The effect of SF_5 substitution at a peripheral α-position is much larger than that at a β-position, observed both in the UV/Vis spectra and fluorescence quantum yields, and an approximate but non-linear additivity exists. The electron-withdrawing property of the SF_5 group mainly contributes to the UV/Vis spectra of SF_5-substituted Pcs, while fluorescence quantum yields seem to be affected by the bulkiness of the SF_5 group due to the distortion of the Pc plane. More systematic analysis on the effect of SF_5 substituents is under investigation.

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