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Trifluoroethoxy-Coating Improves the Axial Ligand Substitution of Subphthalocyanine

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Abstract: A novel trifluoroethoxy (TFEO)-coated SubPc (**1**) and various axially functionalised derivatives thereof (**2**) have been efficiently synthesised. The advantage of the TFEO-coating on SubPcs compared to conventional fluorine-coated or uncoated molecules has been clearly demonstrated, as axial derivatisation has been realised in very good yields. Among various SubPcs synthesised, formyl-SubPc **2f** has been further used as a building block for the synthesis of donor–acceptor SubPc–C_{60} hybrid **8**, while iodo-SubPc **2e** has been used for the synthesis of trifluoroethoxy-coated SubPc–Pc dyads **9** and **10**. All of these compounds are highly soluble in all common organic solvents, which greatly facilitates their purification and characterisation. The SubPcs **2a–c** incorporating oligoethylene glycol moieties are attractive from a biological point of view, while SubPcs **8–10** may prove useful for studies of intramolecular electron- and energy-transfer processes.

Keywords: fluorine · phthalocyanines · porphyrinoids · substitution reaction · synthesis

Introduction

Subphthalocyanines (SubPcs), which can be regarded as phthalocyanine (Pc) analogues with lower symmetry, are nonplanar cone-shaped aromatic macrocycles composed of three diimino-isoindoline units *N*-fused around a boron centre.[1] Owing to their curved geometry, as confirmed by X-ray crystallography,[2] these compounds show a reduced tendency for aggregation and have a higher solubility index than phthalocyanines. Their 14 π-electron core also facilitates strong absorption and leads to high emission quantum yields in the visible region. These features make SubPcs promising chromophores with potential applications in optical data storage,[3] nonlinear optics,[4] photosynthetic models for studying energy- and electron-transfer processes,[5] supramolecular chemistry,[6] and photodynamic therapy (PDT).[7] The optoelectronic properties of SubPcs can be fine-tuned by 1) varying their axial ligands and/or 2) peripheral functionalisation.[1,8] However, the peripheral functionalisation approach is not suitable for the synthesis of diverse SubPc derivatives, since the harsh reaction conditions for SubPc formation preclude the incorporation of a number of important functional groups at the peripheral positions. Moreover, this approach is somewhat tedious because an independent phthalonitrile is required for each target SubPc. Therefore, the substitution of axial ligands of SubPcs is the main route for the synthesis of diverse SubPcs, although the chemical yields are not always high. Indeed, Ng et al. have recently reported the synthesis of biologically very effective SubPcs axially substituted with oligoethylene glycol moieties, but the key axial substitution reaction of SubPcs by oligoethylene glycols could only be achieved in low to moderate yields.[7] Recently, we discovered the unique non-aggregation property of trifluoroethoxy (TFEO)-coated phthalocyanines conjugated with deoxyribonucleosides, which are suitable as PDT agents.[9a] We also synthesised TFEO-coated binuclear Pc, in which the two Pcs are covalently linked with a conjugated rigid diyne spacer, and noted its prominent avoidance of intermolecular aggregation.[9b] Fluorophobic

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repulsion is responsible for the observed lack of aggregation, which is seen even in the case of the 18 π-conjugated system. As part of our ongoing research programs directed towards the development of novel functionalised Pcs[9] and the synthesis of fluorine-containing biologically active compounds,[10] we disclose herein the synthesis of novel TFEO-substituted subphthalocyanine (SubPc) **1**, which has proved to be an effective precursor for the synthesis of diverse SubPcs bearing a variety of substituents at their axial position. The electron-withdrawing effect and non-aggregation property of the twelve trifluoroethoxy moieties on **1** have been found to dramatically facilitate nucleophilic axial ligand substitution reactions on the SubPcs. Indeed, the TFEO-coating is revealed to be far more effective than the conventional fluorine-coating or no coating in facilitating this axial ligand substitution reaction.

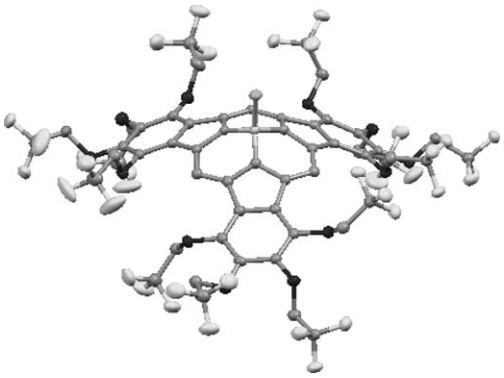
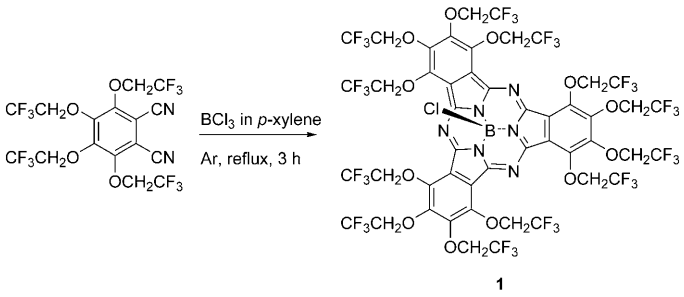


Figure 1. X-ray crystallographic structure of **1** with hydrogen atoms omitted for clarity (CCDC-758071 can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

SubPc **1** was synthesised in 32% yield by cyclotrimerisation of 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile in the presence of boron trichloride in *p*-xylene under reflux conditions (Scheme 1).[11] The SubPc **1** was purified by column



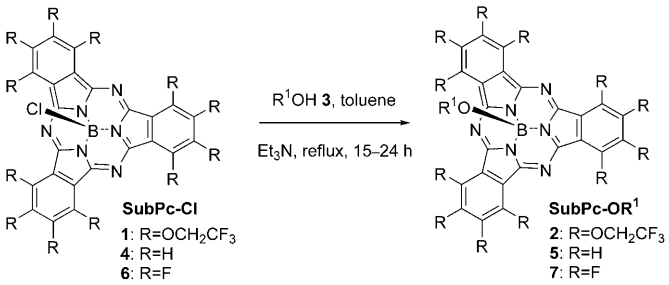
Scheme 1. Synthesis of **1**.

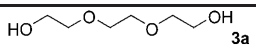
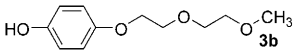
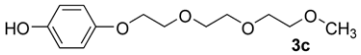
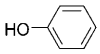
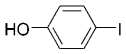
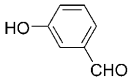
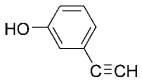
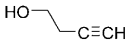
chromatography on silica gel and characterised by ^{1}H and ^{19}F NMR spectroscopies, UV/Vis spectrophotometry, MALDI-TOF mass spectrometry, and FTIR spectroscopy (see the Supporting Information). The molecular structure of **1** was also determined by X-ray diffraction analysis. Single crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from a solution in toluene. As shown in Figure 1, the boron centre is tetracoordinated, thus forming a cone-shaped structure.

Axial substitution reactions of **1** to afford **2** were carried out by classical substitutions of the chlorine atom with various alcohol derivatives **3** in toluene (Table 1). Ethylene glycol **3a** was first selected as a nucleophile due to the difficulty of the axial ligand substitution reaction as well as the biological importance of the corresponding substituted SubPcs.[7] Ng and co-workers reported that the axial ligand substitution of conventional SubPc **4** by **3a** gave the SubPc **5a** bearing an ethylene glycol moiety in just 5% yield[7] (Table 1, entry 1). We attempted a similar substitution reaction using perfluoro-substituted SubPc **6** as the substrate, anticipating that the replacement of all peripheral hydrogen atoms of **4** with fluorine would render the nucleophilic substitution reaction chemically high-yielding. Contrary to our expectations, **6** proved to be unreactive toward **3a** in the presence of triethylamine under reflux conditions (entry 2). We next examined the ligand substitution reaction of our novel SubPc **1** with **3a**. Gratifyingly, the desired compound **2a** was isolated in 68% yield (entry 3), which represents a vast improvement compared with the aforementioned two results (entries 1 and 2). Encouraged by this result, ligand substitution reactions of SubPcs **1**, **4**, and **6** with phenol derivatives **3b** or **3c** bearing a di- or triethylene glycol methyl moiety were evaluated and compared, since SubPcs bearing the units of **3b** or **3c** have been shown to be promising candidates for photodynamic therapy of cancers.[7] While the yields of the ligand substitutions of **4** and **6** to give **5b**,**c** and **7b**,**c** were low (30–41%, entries 4, 5, 7, and 8), TFEO-SubPc **1** gave **2b**,**c** in high yields (83–85%, entries 6 and 9). It should be mentioned that compounds **2a–c** could be easily purified by column chromatography on silica gel using common organic solvents, in marked contrast to the tedious size-exclusion chromatography required for compounds **5a–c**.[7] These results clearly demonstrate that a trifluoroethoxy coating at the periphery of SubPc plays a crucial role in enhancing chemical efficiency and facilitating product isolation.

Motivated by this favourable outcome, we next embarked on the synthesis of a number of TFEO-SubPcs **2d–h** axially substituted with a variety of phenol and alcohol derivatives bearing synthetically useful functional groups such as iodo, formyl, and ethynyl (Table 1, entries 10–14). Substitutions of the chlorine atom by phenol (**3d**) and 4-iodophenol (**3e**) afforded the corresponding products **2d** and **2e** in yields of 81 and 80%, respectively (entries 10 and 11). Formyl and ethynyl substituents as well as aliphatic 3-butyn-1-ol **3h** were also well tolerated under the same conditions, the reactions with **1** affording SubPcs **2f–h** in good yields of 63–73%. All compounds bearing the TFEO groups were purified and

Table 1. Axial ligand substitution reactions of subphthalocyanines.



Entry	SubPc-Cl	R	R^1OH **3**	SubPc-OR^1	Yield [%]
1[a]	**4**	H	 **3a**	**5a**	5
2[b]	**6**	F	**3a**	**7a**	NR
3[c]	**1**	OCH_2CF_3	**3a**	**2a**	68
4[a]	**4**	H	 **3b**	**5b**	30
5[b]	**6**	F	**3b**	**7b**	41
6[c]	**1**	OCH_2CF_3	**3b**	**2b**	83
7[a]	**4**	H	 **3c**	**5c**	37
8[b]	**6**	F	**3c**	**7c**	39
9[c]	**1**	OCH_2CF_3	**3c**	**2c**	85
10[c]	**1**	OCH_2CF_3	 **3d**	**2d**	81
11[c]	**1**	OCH_2CF_3	 **3e**	**2e**	80
12[c]	**1**	OCH_2CF_3	 **3f**	**2f**	73
13[c]	**1**	OCH_2CF_3	 **3g**	**2g**	73
14[c]	**1**	OCH_2CF_3	 **3h**	**2h**	63

[a] Data taken from ref. [7]. [b] Et_3N (1.65 equiv was used). [c] Et_3N (3.5 equiv was used).

then characterised by ^1H and ^{19}F NMR spectroscopies, UV/Vis and fluorescence spectroscopies, MALDI-TOF mass spectrometry, and FTIR spectroscopy (see the Supporting Information). They were found to be appreciably soluble in both polar and less-polar organic solvents, presumably due to the character of the trifluoroethoxy substituents on the SubPc macrocycle. It should be noted that both the ^1H and ^{19}F NMR spectra of the compounds showed extremely resolved, easily assignable signals that were in accordance with the proposed structures and independent of the functional groups present (see the Supporting Information). The high resolution of these spectra is indicative of non-aggregation in the solution state, demonstrating the strong repulsion effect of the trifluoroethoxy groups and SubPc geometry.

The UV/Vis spectra of SubPcs **1** and **2a–c** were recorded in a variety of solvents (chloroform, benzotrifluoride, dioxane, and DMF) at concentrations ranging from 1×10^{-4} M to 1×10^{-6} M. All of these compounds were found to be essentially non-aggregated, irrespective of the solvent and concentration, and were characterised by sharp absorption bands in the B-band region at around 330 nm and in the Q-band region at around 600 nm. Figure 2 shows representative examples of the absorption spectra of SubPc **1** and **2a–c** in chloroform at 1×10^{-5} M. Similar non-aggregation behaviour was also found in a variety of other solvents at different concentrations (Figure 2 and the Supporting Information). It is interesting to note that the shape and size of these spectra did not change even after the addition of pyridine as a metal-coordinating molecule that is known to disrupt aggregation (see also Figure S53 in the Supporting Information for colour graphics). Compared with literature data,[1b,7] the Q-band absorption maxima of **1** and **2a–c** are red-shifted by 30–35 nm due to the strong electron-withdrawing effect of the twelve appended trifluoroethoxy groups. Almost superimposable singlet ground-state transitions of the compounds demonstrate that the macrocyclic π-system is not perturbed by the various axial ligands. As compounds **2a–c** may have potential application as PDT agents,[7] the observed non-aggregation property is extremely important because intermolecular aggregation facilitates an efficient nonradiative energy relaxation pathway, greatly shortening the excited-state lifetimes.[12]

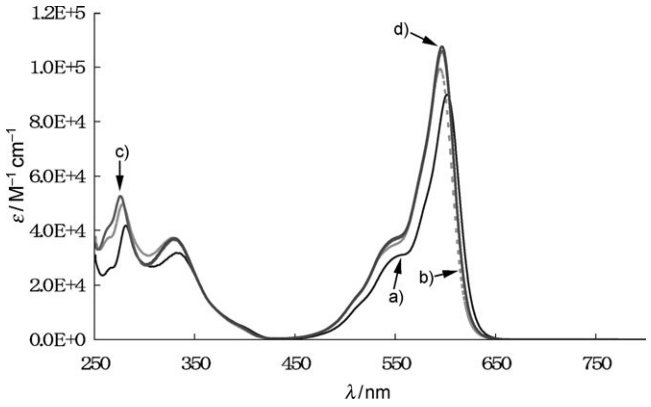


Figure 2. UV/Vis absorption spectra of **1** (a), **2a** (b), **2b** (c), and **2c** (d) in $CHCl_3$ (1×10^{-5} M).

Steady-state fluorescence spectra of the SubPcs **1** and **2a–c** were also measured in different organic solvents. The compounds showed very high fluorescence, a further important consequence of the low aggregation tendency (see Figure 3

and the Supporting Information). As shown in Figure 3, SubPc **1** exhibits a strong emission band at 620 nm with a fluorescence quantum yield (ϕ_F) of 0.83, while SubPc **2a** emits at 613 nm with a ϕ_F value of 0.56 in chloroform upon excitation at 530 nm. SubPcs **2b** and **2c** show fluorescence at 612–614 nm with quantum yields in the range 0.05–0.11 (Table 2; see also Figure S71 in the Supporting Information for colour graphics). The fluorescence quenching of the latter two compounds can be attributed to the presence of the phenyl moiety, which is likely to facilitate an intramolecular photo-induced electron-transfer process.[7]

Table 2. Fluorescence quantum yields[a] (ϕ_F) and emission maxima (λ_{em} [nm]) of TFEO-coated SubPcs.

SubPc	$CHCl_3$	$PhCF_3$	Dioxane	DMF
1	0.83 (620)	0.95 (618)	0.85 (621)	–
2a	0.56 (613)	0.63 (610)	–	0.55 (612)
2b	0.06 (614)	0.05 (612)	–	0.11 (614)
2c	0.07 (614)	0.05 (612)	–	0.11 (614)
2d	0.55 (615)	0.55 (613)	0.51 (616)	–
2f	0.47 (618)	–	0.49 (618)	–
8	0.005 (795, 614)	0.005 (612)	0.007 (796, 616)	–
9	0.07 (767, 616)	0.13 (714, 614)	0.24 (718, 617)	–
10	0.005 (796, 615)	–	0.02 (686, 619)	–

[a] Fluorescence quantum yields were calculated using tetraphenylporphyrin (TPP) in benzene as a reference ($\phi_F = 0.11$).[17]

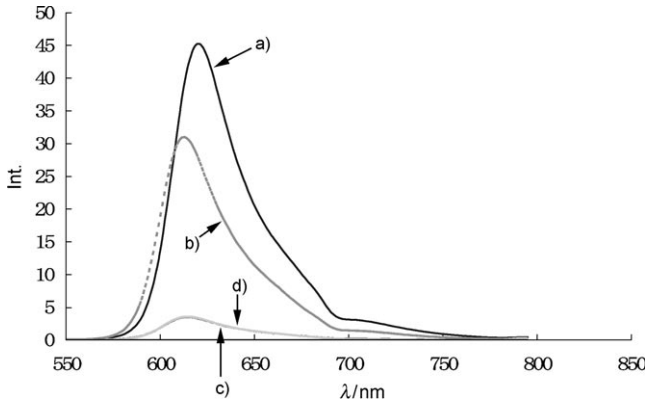
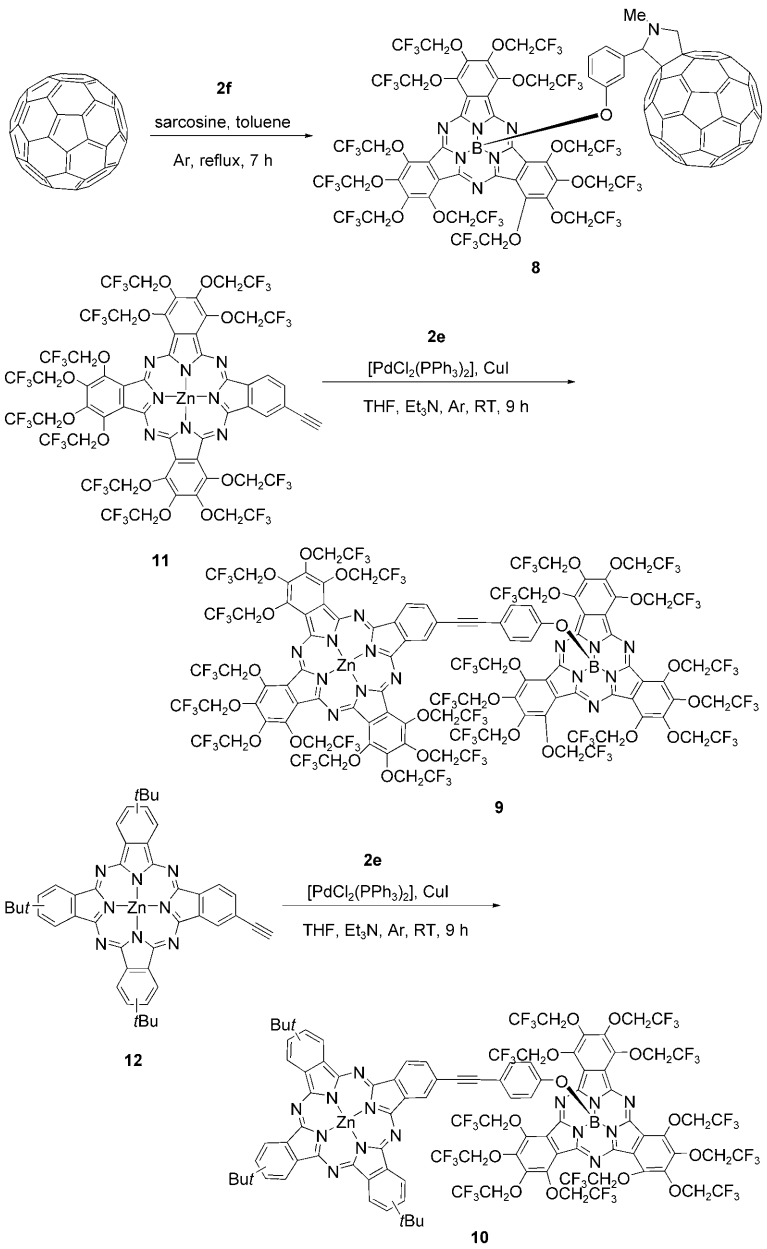


Figure 3. Steady-state emission spectra of **1** (a), **2a** (b), **2b** (c), and **2c** (d) in $CHCl_3$ with excitation at 530 nm.

Photo-induced energy- and electron-transfers are important processes that lead to useful applications in photosynthetic model systems for the conversion of solar energy into profitable chemical energy.[13] In this context, donor–acceptor hybrids with well-defined spacers can mimic the natural photosynthetic process. With this objective, we synthesised trifluoroethoxy-SubPc–C_{60} hybrid **8** along with subphthalocyanine–phthalocyanine dyads **9** and **10** to demonstrate the utility of SubPcs **2** (Scheme 2). SubPc–C_{60} hybrid **8** was prepared by a 1,3-dipolar cycloaddition reaction according to the Prato procedure.[14] Thus, heating a mixture of SubPc **2f** and sarcosine with C_{60} gave compound **8** in 57% yield. On the other hand, SubPc–Pc dyads **9** and **10** were conveniently synthesised by palladium-catalysed Sonogashira cross-couplings of SubPc iodide **2e** and terminal alkynes as the key reaction. For example, homo dyad **9** was synthesised in 70% yield by the cross-coupling of iodo-SubPc **2e** with monoalkynyl TFEO-ZnPc **11** in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ and CuI in anhydrous THF. Similarly, hetero SubPc–Pc hybrid **10** was obtained in a good yield of 56% by the reaction of **2e** with ethynyl-*tert*-butyl zinc Pc **12**. All of these hybrid compounds were purified by column chromatography on silica gel and were characterised by ^1H and ^{19}F NMR spectroscopies, UV/Vis spectrophotometry, MALDI-TOF mass spectrometry, and FTIR spectroscopy (see the Supporting Information).

Absorption spectra were recorded for the hybrid compounds **8**–**10** and their constituent monomers **1**, **11**, and **12** (Figure 4) (see also the Supporting Information). Figure 4 (top) shows the absorption and magnetic circular dichroism (MCD) spectra of a SubPc with twelve CF_3CH_2O- substituents (**1**), and of low-symmetry ZnPc compounds with twelve peripheral CF_3CH_2O- groups and one ethynyl group (**11**) and three peripheral *tert*-butyl groups and one ethynyl group (**12**). These compounds represent the constituent chromophores of the dyads **9** and **10** (middle) and **8** (bottom) giving rise to the spectra in these figures. A comparison of the spectral data reveals many intriguing properties. The major π-π* bands shift to longer wavelength in the order **1**, **12**, and **11**. The absorption coefficients of **1** are smaller than those of **11** or **12**. Of the two Pc compounds, the Q band of **11** is more intense and is red-shifted relative to that of **12**. This red-shift can be ascribed primarily to ligand nonplanarity due to the presence of the bulky CF_3CH_2O- groups at the α-positions.[15,16] The MCD spectra are broadly similar to those of the parent SubPc[17,18] and MPc complexes.[19–21] Derivative-shaped Faraday *A*-terms are observed for each major absorption peak, so three- or fourfold axes of symmetry are clearly retained and the main π-π* excited states remain orbitally degenerate. The MCD intensity of the Q band is enhanced relative to that observed in the B1/B2 (or Soret) band region due to the larger orbital angular momentum change associated with the forbidden Q transition. It should be noted that the MCD intensity of the Q band of SubPc **1** is significantly weaker than those of Pcs **11** and **12** due to the doming of the π-system.

Figure 4 (middle) shows the spectra of dyads comprised of **1** and either **11** (compound **9**) or **12** (compound **10**). Before recording these spectra, we confirmed that the species were well dispersed by carrying out Beer's experiments; that is, it was ensured that the Q band intensified in a linear manner as the concentration was increased. Taking the band shape, position, and intensity of the constituent chromophores into account, Figure 4 (top), the spectra can be approximately expressed as a summation of the spectra of the constituent moieties. The broad B1/B2 band region of **9** can be attributed to an overlap of the n-π* bands of the ether oxygen and π-π* transitions of the ligand π-system.[16] The Q-band intensity of the SubPc moiety (at ca. 600 nm) is much lower than that of the Pc moiety, as would be anticipated based on



Scheme 2. Structures of SubPc–C_{60} dyad **8** and SubPc–Pc dyads **9** and **10**.

Figure 4 (top). The trough and peak observed in the MCD spectrum of **10** at 684 and 669 nm correspond directly to an absorption peak and a shoulder in the intensity. Since these bands are clearly Faraday *B*-terms, there must be a ground-state interaction between the SubPc and Pc moieties.

Figure 4 (bottom) shows the spectra of the SubPc–C_{60} dyad **8**. As is the case with **9** and **10**, the spectra can be viewed as a summation of the spectra of the component SubPc and C_{60} moieties. Most of the absorption band intensity in the 250–300 nm region can be ascribed to the C_{60} moiety.[22] In the MCD spectrum, the intensity associated with the C_{60} moiety is relatively low since **1** has similar intensity in this region; Figure 4 (top).

Steady-state emission spectra of the SubPc dyads were measured in a variety of solvents (see the Supporting Information). Figure 5 shows a representative comparative fluorescence spectrum of SubPc–C_{60} dyad **8** along with that of the precursor formyl-SubPc **2f**, the excited-state interactions between the photo- and redox-active constituents in which are quite revealing (see also Figure S73 in the Supporting Information for colour graphics). A strong quenching of the SubPc fluorescence compared to the reference precursor **2f** is observed, irrespective of the solvent, which can be attributed to a substantial amount of electron-transfer from the SubPc moiety to the fullerene acceptor. It is interesting to note that the TFEO-coated SubPc moiety still acts as a donor in this dyad **8**, since the TFEO-Pc can no longer act as a donor in the TFEO-Pc–C_{60} dyad.[9e] This phenomenon is also supported by fluorescence quantum yield data (Table 2). While SubPc **2f** shows ϕ_F values of 0.47 and 0.49 in $CHCl_3$ and dioxane, respectively, the corresponding values for the SubPc–C_{60} dyad **8** are significantly decreased to 0.005 and 0.007 in the respective solvents.

Conclusion

In conclusion, we have synthesised a novel trifluoroethoxy-coated SubPc (**1**) and various axially functionalised derivatives thereof (**2**). The advantage of the TFEO-coating of the SubPc compared to conventional fluorine-coated or uncoated molecules is clearly apparent as axial derivatisation has been realised in very good yields. Some of the resulting products have been further used as building blocks for synthesising a donor–acceptor SubPc–C_{60} hybrid and trifluoroethoxy-coated SubPc–Pc dyads. All of the prepared compounds are highly soluble in all common organic solvents (see the Supporting Information),[23] which facilitates their easy purification and characterisation and may also prove to be of considerable interest in fields such as catalysts for organic reactions or dyes for solar cells. The

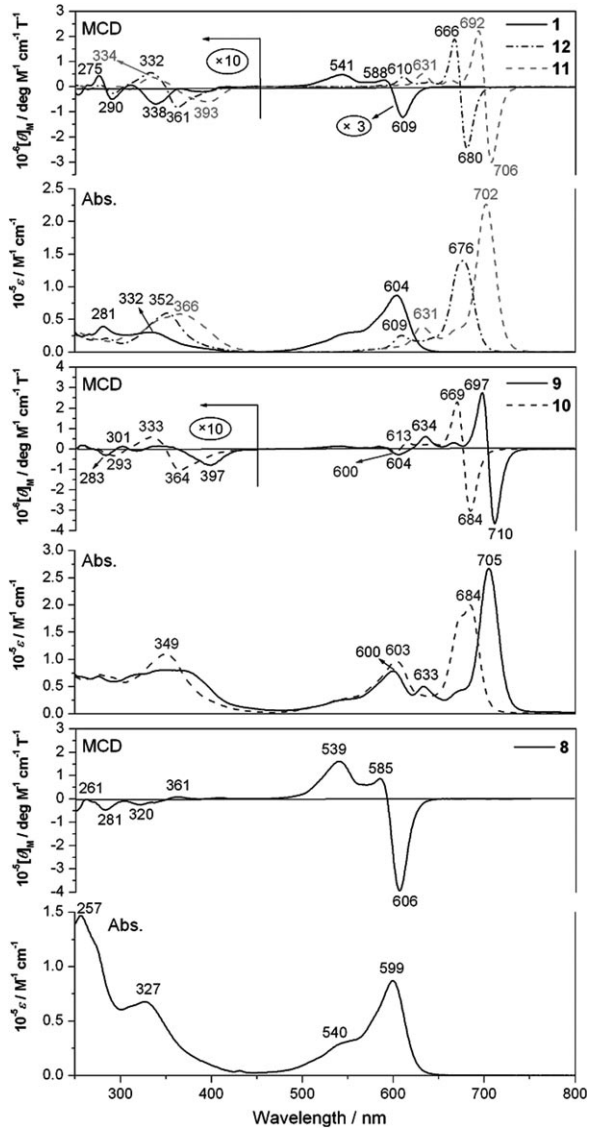


Figure 4. Absorption and MCD spectra of monomeric **1**, **11**, **12** (top), SubPc–Pc dyads **9**, **10** (middle), and SubPc–C_{60} dyad **8** (bottom) in dioxane.

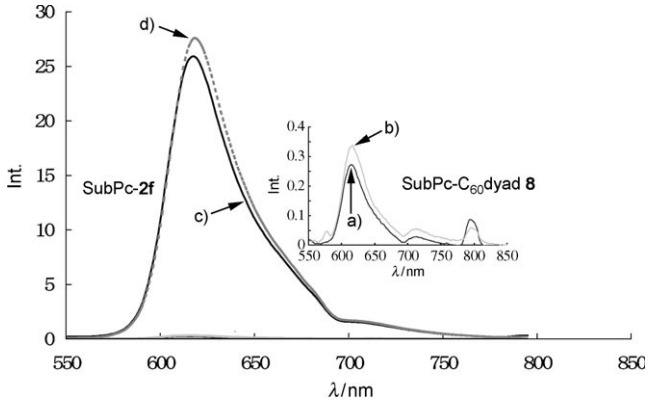


Figure 5. Steady-state emission spectra of SubPc–C_{60} dyad **8** in $CHCl_3$ (a), dioxane (b); SubPc-**2f** in $CHCl_3$ (c) and dioxane (d) with excitation at 530 nm. Inset: Corresponding emission spectra of dyad **8**.

SubPcs **2a–c** are attractive from a biological point of view, while SubPcs **8–10** could be useful for studies of intramolecular electron- and energy-transfer processes, although further investigation is required.

Experimental Section

General methods: All solvents were dried and distilled according to standard procedures. All of the reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm Merck silica gel plates (60F-254). Column chromatography was carried out on a column packed with silica gel 60N (spherical, neutral, size 63–210 μm). ^{1}H and ^{19}F NMR (200 MHz) spectra were recorded on a Varian Gemini-200 spectrometer, while ^{13}C NMR (600 MHz) spectra were recorded on a Bruker-600 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane and internal acetone. Infrared (IR), UV/Vis, and steady-state fluorescence spectra were recorded on a JASCO FTIR-200 spectrometer, V-530 spectrometer, and FP-6200 spectrofluorimeter, respectively. Fluorescence quantum yields were calculated according to a procedure described elsewhere.[17] MALDI-TOF mass spectra were taken on a SHIMADZU Axima CFR Plus and ESI mass spectra were recorded on a SHIMADZU LCMS-2010 EV.

Subphthalocyanine 1: BCl_3 (3.46 mL, 1 M solution in *p*-xylene) was added to dry 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (500 mg, 0.961 mmol) under an argon atmosphere. The reaction mixture was stirred under reflux (≈140 °C) for 3 h. The purple solution was then flushed with argon and the solvent was evaporated. The resulting solid was purified by column chromatography on silica gel, eluting with 10–12% ethyl acetate in hexane, to afford SubPc **1** as a purple solid (163 mg, 32%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.28$ (q, $J = 8.2$ Hz, 12H; $OCH_2 \times 6$), 4.67 ppm (q, $J = 8.2$ Hz, 12H; $OCH_2 \times 6$); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.13$ (t, $J = 7.0$ Hz, 18F; $CF_3 \times 6$), −74.74 ppm (t, $J = 7.0$ Hz, 18F; $CF_3 \times 6$); IR (KBr): $\tilde{\nu} = 3417$, 2973, 1607, 1542, 1492, 1432, 1281, 1238, 1166, 1131, 1092, 1068, 968, 834, 661 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 602 (4.95), 558 (4.49), 331 (4.50), 281 nm (4.62); $PhCF_3$: λ_{max} (log ε) = 599 (4.94), 552 (4.48), 330 nm (4.49); dioxane: λ_{max} (log ε) = 603 (4.94), 558 (4.49), 333 (4.48), 281 nm (4.59); MALDI-TOF MS: *m*/*z*: calcd for $C_{48}H_{24}BClF_{36}N_6O_{12}$: 1606.07; found: 1604.45 (most abundant peak in the isotopic envelope).

Standard procedure (SP) for axial substitution reactions of SubPc 1: A mixture of SubPc **1**, triethylamine, and the requisite alcohol in toluene was heated at reflux (≈120 °C) for 15–24 h under an inert atmosphere. After cooling to room temperature, the solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel using mixtures of ethyl acetate and hexane in different proportions as eluents. In some cases, the product was further purified by recrystallisation.

Subphthalocyanine 2a: According to the SP, SubPc **1** (150 mg, 0.093 mmol) was reacted with triethylene glycol **3a** (0.075 mL, 0.56 mmol) by refluxing in toluene (10 mL) containing triethylamine (0.046 mL, 0.327 mmol) for 20 h. The resulting crude purple product was subjected to column chromatography on silica gel, eluting with 30–40% ethyl acetate in hexane. SubPc **2a** was isolated as a purple solid (109 mg, 68%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.36$–5.22 (m, 12H; $OCH_2 \times 6$), 4.66 (q, $J = 8.2$ Hz, 12H; $OCH_2 \times 6$), 3.48–3.44 (m, 2H; CH_2OH), 3.39–3.31 (m, 4H; CH_2CH_2OH, CH_2), 3.15–3.10 (m, 2H; CH_2), 2.68 (t, $J = 4.6$ Hz, 2H; $BOCH_2CH_2$), 1.68 ppm (t, $J = 4.6$ Hz, 2H; $BOCH_2$); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.13$ (t, $J = 7.0$ Hz, 18F; $CF_3 \times 6$), −74.78 ppm (t, $J = 7.0$ Hz, 18F; $CF_3 \times 6$); IR (KBr): $\tilde{\nu} = 3446$, 2972, 1733, 1670, 1542, 1492, 1458, 1433, 1282, 1238, 1165, 1127, 1067, 1017, 969, 853, 663 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 595 (4.92), 548 (4.46), 330 (4.50), 278 nm (4.62); $PhCF_3$: λ_{max} (log ε) = 592 (4.89), 547 (4.44), 327 nm (4.45); DMF: λ_{max} (log ε) = 594 (4.88), 549 (4.43), 321 nm (4.49); MALDI-TOF MS: *m*/*z*: calcd for $C_{54}H_{37}BF_{36}N_6O_{16}$: 1720.18; found: 1718.59 (most abundant peak in the isotopic envelope).

Subphthalocyanine 2b: According to the SP, SubPc **1** (150 mg, 0.093 mmol) was reacted with 4-(3,6-dioxaheptoxy)phenol **3b**[7] (119 mg, 0.56 mmol) by refluxing in toluene (10 mL) containing triethylamine (0.046 mL, 0.327 mmol) for 15 h. The resulting crude purple product was subjected to column chromatography on silica gel, eluting with 30% ethyl acetate in hexane. The product was further purified by recrystallisation from chloroform/hexane to furnish SubPc **2b** as a purple solid (138 mg, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.36 (d, J=9.0 Hz, 2H; Ar-H), 5.34 (d, J=9.0 Hz, 2H; Ar-H), 5.22 (q, J=8.2 Hz, 12H; $OCH_2\times$ 6), 4.66 (q, J=8.0 Hz, 12H; $OCH_2\times$6), 3.90–3.85 (m, 2H; CH_2), 3.75–3.70 (m, 2H; CH_2), 3.67–3.62 (m, 2H; CH_2), 3.55–3.50 (m, 2H; CH_2), 3.35 ppm (s, 3H; CH_3); ^{19}F NMR (188 MHz, $CDCl_3$): δ=−74.08 (t, J= 7.9 Hz, 18F; $CF_3\times$6), −74.77 ppm (t, J=7.9 Hz, 18F; $CF_3\times$6); IR (KBr): $\tilde{\nu}$=2973, 1541, 1492, 1459, 1432, 1282, 1238, 1216, 1165, 1130, 1068, 1016, 970, 854, 753, 662 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$)=597 (5.00), 553 (4.55), 329 (4.54), 276 nm (4.70); $PhCF_3$: λ_{max} ($\log\varepsilon$)=594 (4.98), 550 (4.52), 328 nm (4.51); DMF: λ_{max} ($\log\varepsilon$)=597 (4.96), 552 (4.52), 326 nm (4.51); MALDI-TOF MS: m/z: calcd for $C_{59}H_{39}BF_{36}N_6O_{16}$: 1782.19; found: 1781.64 (most abundant peak in the isotopic envelope).

Subphthalocyanine 2c: According to the SP, SubPc **1** (150 mg, 0.093 mmol) was reacted with 4-(3,6,9-trioxadecoxy)phenol **3c**[7] (144 mg, 0.56 mmol) by refluxing in toluene (10 mL) containing triethylamine (0.046 mL, 0.327 mmol) for 16 h. The resultant crude product was subjected to column chromatography on silica gel, eluting with 30–35% ethyl acetate in hexane. The product was further purified by recrystallisation from chloroform/hexane to afford SubPc **2c** as a purple solid (144 mg, 85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.36 (d, J=9.0 Hz, 2H; Ar-H), 5.34 (d, J=9.0 Hz, 2H; Ar-H), 5.22 (q, J=8.2 Hz, 12H; $OCH_2\times$ 6), 4.66 (q, J=8.2 Hz, 12H; $OCH_2\times$6), 3.89–3.84 (m, 2H; CH_2), 3.75–3.70 (m, 2H; CH_2), 3.67–3.59 (m, 6H; $CH_2\times$3), 3.53–3.48 (m, 2H; CH_2), 3.35 ppm (s, 3H; CH_3); ^{19}F NMR (188 MHz, $CDCl_3$): δ=−74.08 (t, J= 7.9 Hz, 18F; $CF_3\times$6), −74.77 ppm (t, J=7.9 Hz, 18F; $CF_3\times$6); IR (KBr): $\tilde{\nu}$=2971, 1541, 1492, 1459, 1432, 1283, 1238, 1165, 1129, 1067, 1017, 970, 854, 753, 662 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$)=597 (4.99), 553 (4.53), 330 (4.53), 276 nm (4.68); $PhCF_3$: λ_{max} ($\log\varepsilon$)=594 (4.96), 550 (4.50), 328 nm (4.49); DMF: λ_{max} ($\log\varepsilon$)=597 (4.96), 552 (4.52), 327 nm (4.51); MALDI-TOF MS: m/z: calcd for $C_{61}H_{43}BF_{36}N_6O_{17}$: 1826.22; found: 1824.27 (most abundant peak in the isotopic envelope).

Subphthalocyanine 7b: Dodecafluorosubphthalocyanato boron(III) chloride **6**[11] (50 mg, 0.077 mmol) was reacted with 4-(3,6-dioxaheptoxy)phenol **3b**[7] (98.5 mg, 0.464 mmol) by refluxing in toluene (4.5 mL) containing triethylamine (0.018 mL, 0.128 mmol) for 24 h. The resulting crude purple product was subjected to column chromatography on silica gel eluting with 30% ethyl acetate in hexane to furnish SubPc **7b** as a purple solid (26 mg, 41%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.30 (dd, J=6.8, 2.2 Hz, 2H; Ar-H), 5.24 (dd, J=6.6, 2.2 Hz, 2H; Ar-H), 3.90–3.85 (m, 2H; CH_2), 3.74–3.70 (m, 2H; CH_2), 3.66–3.62 (m, 2H; CH_2), 3.55–3.50 (m, 2H; CH_2), 3.36 ppm (s, 3H; CH_3); ^{19}F NMR (188 MHz, $CDCl_3$): δ= −136.20 (dd, J=18.9, 4.5 Hz, 6F), −146.87 ppm (dd, J=19.6, 4.5 Hz, 6F); IR (KBr): $\tilde{\nu}$=3446, 2882, 1650, 1533, 1485, 1428, 1394, 1264, 1223, 1164, 1113, 991, 966, 835, 773, 742, 715, 640 cm^{-1}; ESI MS: m/z: calcd for $C_{35}H_{15}BF_{12}N_6O_4$: 822.11; found: 845.10 $[M+Na]^+$.

Subphthalocyanine 7c: Dodecafluorosubphthalocyanato boron(III) chloride **6**[11] (50 mg, 0.077 mmol) was reacted with 4-(3,6,9-trioxadecoxy)phenol **3c**[7] (119 mg, 0.464 mmol) by refluxing in toluene (4.5 mL) containing triethylamine (0.018 mL, 0.128 mmol) for 24 h. The resulting crude product was subjected to column chromatography on silica gel eluting with 40% ethyl acetate in hexane to afford SubPc **7c** as a purple solid (26 mg, 39%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.31 (dd, J=6.5, 2.1 Hz, 2H; Ar-H), 5.26 (dd, J=6.8, 2.2 Hz, 2H; Ar-H), 3.89–3.85 (m, 2H; CH_2), 3.74–3.69 (m, 2H; CH_2), 3.68–3.60 (m, 6H; $CH_2\times$3), 3.54–3.50 (m, 2H; CH_2), 3.36 ppm (s, 3H; CH_3); ^{19}F NMR (188 MHz, $CDCl_3$): δ=−136.23 (dd, J=19.5, 5.7 Hz, 6F), −146.87 ppm (dd, J=19.0, 5.6 Hz, 6F); IR (KBr): $\tilde{\nu}$=3481, 2878, 1650, 1533, 1485, 1429, 1395, 1264, 1222, 1162, 1112, 994, 965, 836, 773, 742, 714, 675, 640 cm^{-1}; ESI MS: m/z: calcd for $C_{37}H_{19}BF_{12}N_6O_5$: 866.13; found: 889.10 $[M+Na]^+$.

Subphthalocyanine 2d: SubPc **1** (85 mg, 0.053 mmol) and phenol **3d** (25 mg, 0.265 mmol) were placed in a 20 mL round-bottomed flask and then dry toluene (2 mL) and Et_3N (0.026 mL, 0.185 mmol) were added under N_2 atmosphere. The reaction mixture was stirred under reflux (≈120°C) for 24 h, and then the solvent was evaporated. The residual purple solid was subjected to column chromatography on silica gel eluting with 10–12% ethyl acetate in hexane. SubPc **2d** was isolated as a purple solid (71 mg, 81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.86–6.74 (m, 3H; Ar-H), 5.41 (d, J=7.2 Hz, 2H; Ar-H), 5.22 (q, J=8.0 Hz, 12H; $OCH_2\times$6), 4.66 ppm (q, J=8.0 Hz, 12H; $OCH_2\times$6); ^{19}F NMR (188 MHz, $CDCl_3$): δ=−74.10 (t, J=8.0 Hz, 18F; $CF_3\times$6), −74.77 ppm (t, J= 8.0 Hz, 18F; $CF_3\times$6); IR (KBr): $\tilde{\nu}$=3421, 2979, 1493, 1459, 1431, 1281, 1237, 1166, 1129, 1068, 1018, 970, 854, 755, 662 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$)=597 (4.97), 550 (4.51), 331 (4.51), 276 nm (4.64); $PhCF_3$: λ_{max} ($\log\varepsilon$)=594 (4.98), 547 (4.52), 328 nm (4.52); dioxane: λ_{max} ($\log\varepsilon$)=597 (4.97), 550 (4.52), 330 (4.52), 275 nm (4.64); MALDI-TOF MS: m/z: calcd for $C_{54}H_{29}BF_{36}N_6O_{13}$: 1664.13; found: 1663.38 (most abundant peak in the isotopic envelope).

Subphthalocyanine 2e: SubPc **1** (285 mg, 0.177 mmol) was reacted with 4-iodophenol **3e** (195 mg, 0.887 mmol) by refluxing in toluene (5 mL) containing triethylamine (0.087 mL, 0.621 mmol) for 24 h. The resulting crude purple product was purified by column chromatography on silica gel eluting with toluene/hexane (70:30) to give SubPc **2e** as a purple solid (253 mg, 80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.12–7.08 (m, 2H; Ar-H), 5.29–5.24 (m, 2H; Ar-H), 5.24–5.15 (m, 12H; $OCH_2\times$6), 4.73–4.60 ppm (m, 12H; $OCH_2\times$6); ^{19}F NMR (188 MHz, $CDCl_3$): δ=−74.05 (t, J=8.0 Hz, 18F; $CF_3\times$6), −74.77 ppm (t, J=8.0 Hz, 18F; $CF_3\times$6); IR (KBr): $\tilde{\nu}$=3442, 2971, 1492, 1460, 1431, 1282, 1238, 1215, 1166, 1129, 1068, 1018, 970, 834, 753, 662 cm^{-1}; MALDI-TOF MS: m/z: calcd for $C_{54}H_{28}BF_{36}IN_6O_{13}$: 1790.03; found: 1789.32 (most abundant peak in the isotopic envelope).

Subphthalocyanine 2f: According to the SP, SubPc **1** (80 mg, 0.05 mmol) was reacted with 3-hydroxybenzaldehyde **3f** (30 mg, 0.25 mmol) by refluxing in toluene (2 mL) containing triethylamine (0.024 mL, 0.174 mmol) for 16 h. The resulting crude purple product was purified by column chromatography on silica gel eluting with 20% ethyl acetate in hexane. The product was further purified by recrystallisation from toluene/hexane to afford formyl-SubPc **2f** as a purple solid (61 mg, 73%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=9.68 (s, 1H; CHO), 7.22–7.18 (m, 1H; Ar-H), 7.03–6.96 (m, 1H; Ar-H), 5.82–5.78 (m, 2H; Ar-H), 5.26 (q, J= 8.2 Hz, 12H; $OCH_2\times$6), 4.66 ppm (q, J=8.0 Hz, 12H; $OCH_2\times$6); ^{19}F NMR (188 MHz, $CDCl_3$): δ=−74.08 (t, J=8.1 Hz, 18F; $CF_3\times$6), −74.77 ppm (t, J=8.1 Hz, 18F; $CF_3\times$6); IR (KBr): $\tilde{\nu}$=3442, 2977, 1698, 1492, 1432, 1281, 1239, 1166, 1130, 1104, 1067, 1017, 970, 854, 753, 662 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$)=599 (4.97), 551 (4.52), 331 (4.57), 275 nm (4.69); dioxane: λ_{max} ($\log\varepsilon$)=600 (4.95), 552 (4.51), 332 (4.55), 274 nm (4.68); MALDI-TOF MS: m/z: calcd for $C_{55}H_{29}BF_{36}N_6O_{14}$: 1692.13; found: 1690.70 (most abundant peak in the isotopic envelope).

Subphthalocyanine 2g: According to the SP, SubPc **1** (50 mg, 0.031 mmol) was reacted with 3-hydroxyphenylacetylene **3g** (0.017 mL, 0.156 mmol) by refluxing in toluene (1 mL) containing triethylamine (0.015 mL, 0.109 mmol) for 21 h. The resulting crude purple product was subjected to column chromatography on silica gel eluting with 12% ethyl acetate in hexane. SubPc **2g** was isolated as a purple solid (38.4 mg, 73%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.88–6.72 (m, 2H; Ar-H), 5.49–5.42 (m, 2H; Ar-H), 5.30–5.19 (m, 12H; $OCH_2\times$6), 4.66 (q, J=8.2 Hz, 12H; $OCH_2\times$6), 2.94 ppm (s, 1H; CH); ^{19}F NMR (188 MHz, $CDCl_3$): δ= −74.10 (t, J=7.9 Hz, 18F; $CF_3\times$6), −74.77 ppm (t, J=7.9 Hz, 18F; $CF_3\times$ 6); IR (KBr): $\tilde{\nu}$=3438, 3304, 2974, 1492, 1458, 1431, 1281, 1238, 1166, 1130, 1067, 1016, 970, 853, 662 cm^{-1}; MALDI-TOF MS: m/z: calcd for $C_{56}H_{29}BF_{36}N_6O_{13}$: 1688.13; found: 1686.54 (most abundant peak in the isotopic envelope).

Subphthalocyanine 2h: According to the SP, SubPc **1** (50 mg, 0.031 mmol) was reacted with 3-butyn-1-ol **3h** (0.012 mL, 0.156 mmol) by refluxing in toluene (1 mL) containing triethylamine (0.015 mL, 0.109 mmol) for 17 h. The resulting crude purple product was purified by column chromatography on silica gel eluting with 20% ethyl acetate in hexane. SubPc **2h** was obtained as a purple solid (32 mg, 63%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.35–5.17 (m, 12H; $OCH_2\times$6), 4.72–4.59 (m, 12H; $OCH_2\times$6), 2.35 (s, 1H; CH), 1.69–1.57 (m, 2H; CH_2), 1.49–

1.43 ppm (m, 2H; CH_2); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.11$ (t, $J =$ 8.1 Hz, 18F; $CF_3 \times 6$), −74.77 ppm (t, $J = 8.1$ Hz, 18F; $CF_3 \times 6$); IR (KBr): $\tilde{\nu} = 3421$, 3309, 2973, 1492, 1459, 1433, 1281, 1237, 1215, 1165, 1127, 1068, 1018, 969, 854, 834, 754, 732, 662 cm^{-1}; MALDI-TOF MS: m/z: calcd for $C_{52}H_{29}BF_{36}N_6O_{13}$: 1640.13; found: 1638.57 (most abundant peak in the isotopic envelope).

TFEO-subphthalocyanine–C_{60} dyad 8: A solution of SubPc **2f** (38 mg, 0.022 mmol), C_{60} fullerene (18 mg, 0.025 mmol), and sarcosine (*N*-methylglycine) (6 mg, 0.067 mmol) in dry toluene (15 mL) was heated under reflux conditions for 7 h. The solution was then cooled to room temperature and concentrated under vacuum. The resulting crude mixture was subjected to column chromatography on silica gel eluting with toluene/hexane (4:1) to give SubPc–C_{60} dyad **8** as a blue solid (31 mg, 57%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.1$–6.9 (m, 1H; Ar-H), 6.80 (t, $J =$ 7.7 Hz, 1H; Ar-H), 5.94–5.66 (m, 1H; Ar-H), 5.34–5.08 (m, 13H; Ar-H, $OCH_2 \times 6$), 4.73 (br d, $J = 9.6$ Hz, 1H; CH_2-pyrr), 4.59 (q, $J = 8.0$ Hz, 12H; $OCH_2 \times 6$), 4.42 (br s, 1H; CH-pyrr), 3.99 (br d, $J = 9.4$ Hz, 1H; CH_2-pyrr), 2.54 ppm (s, 3H; CH_3); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.03$ (t, $J = 7.9$ Hz, 18F; $CF_3 \times 6$), −74.68 ppm (t, $J = 8.1$ Hz, 18F; $CF_3 \times 6$); ^{13}C NMR (150.9 MHz, $CDCl_3$): $\delta = 156.2$, 153.9, 153.2, 148.7, 146.5, 146.4, 146.2, 146.15, 146.1, 145.9, 145.7, 145.3, 145.2, 145.1, 145.0, 144.8, 144.6, 144.4, 144.3, 144.2, 144.1, 143.8, 143.7, 143.6, 143.3, 142.2, 142.0, 141.65, 141.6, 141.5, 141.4, 141.3, 141.1, 141.0, 140.9, 140.5, 139.2, 139.0, 138.8, 138.5, 136.2, 136.1, 135.4, 135.3, 126.5, 125.9, 124.7, 124.1, 122.8, 122.2, 121.0, 120.4, 120.2, 71.9, 71.7, 71.6, 71.4, 71.3, 71.2, 71.1, 70.9, 69.6, 68.9, 39.4 ppm; IR (KBr): $\tilde{\nu} = 3435$, 2961, 1604, 1491, 1428, 1281, 1238, 1215, 1166, 1127, 1067, 1020, 970, 855, 662 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 598 (4.95), 549 (4.51), 429 (3.62), 326 (4.87), 257 nm (5.35); $PhCF_3$: λ_{max} ($\log\varepsilon$) = 597 (4.93), 549 (4.50), 429 (3.61), 326 nm (4.86); dioxane: λ_{max} ($\log\varepsilon$) = 599 (4.94), 546 (4.50), 430 (3.61), 327 (4.86), 255 nm (5.28); MALDI-TOF MS: m/z: calcd for $C_{117}H_{34}BF_{36}N_7O_{13}$: 2439.17; found: 2437.20 (most abundant peak in the isotopic envelope).

TFEO-subphthalocyanine–phthalocyanine hybrid 9: A 30 mL round-bottomed flask was charged with SubPc **2e** (35 mg, 0.0195 mmol), 23-ethynyl-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) **11**[9b] (43.5 mg, 0.024 mmol), [$PdCl_2(PPh_3)_2$] (2 mg, 0.0028 mmol), and CuI (0.5 mg, 0.0026 mmol). Dry tetrahydrofuran (2.5 mL) and dry triethylamine (0.5 mL) were then added under an argon atmosphere, and the mixture was stirred for 9 h at room temperature and then concentrated under vacuum. Water was added to the residual crude mixture, and the resulting mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent, the crude solid was purified by column chromatography on silica gel, eluting first with CH_2Cl_2/MeOH (50:1) and then with hexane/dioxane (7:3) to afford SubPc–Pc hybrid **9** as a greenish-blue solid (47 mg, 70%). ^{1}H NMR (200 MHz, [D_6]acetone): $\delta = 9.02$ (br, 2H; Ar-H), 8.12 (br, 1H; Ar-H), 7.30 (d, $J = 8.4$ Hz, 2H; Ar-H), 5.76 (d, $J = 8.4$ Hz, 2H; Ar-H), 5.65 (q, $J = 8.4$ Hz, 16H; $OCH_2 \times 8$), 5.28–5.11 (m, 16H; $OCH_2 \times 8$), 5.03–4.85 ppm (m, 16H; $OCH_2 \times 8$); ^{19}F NMR (188 MHz, [D_6]acetone) $\delta = -72.57$ to −73.20 (m, 36F; $CF_3 \times 12$), −73.65 ppm (m, 36F; $CF_3 \times 12$); IR (KBr): $\tilde{\nu} = 3436$, 2972, 1602, 1488, 1456, 1431, 1278, 1240, 1162, 1068, 1014, 969, 853, 833, 753, 662 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 761 (5.22), 720 (4.96), 598 (4.80), 322 (4.91), 275 nm (4.88); $PhCF_3$: λ_{max} ($\log\varepsilon$) = 702 (5.38), 631 (4.68), 596 (4.78), 351 nm (4.93); dioxane: λ_{max} ($\log\varepsilon$) = 704 (5.40), 633 (4.70), 599 (4.79), 355 (4.95), 275 nm (4.83); MALDI-TOF MS: m/z: calcd for $C_{112}H_{55}BF_{72}N_{14}O_{25}Zn$: 3438.17; found: 3441.01 (most abundant peak in the isotopic envelope).

TFEO-subphthalocyanine–*t*Bu-phthalocyanine hybrid 10: A 30 mL round-bottomed flask was charged with SubPc **2e** (45 mg, 0.025 mmol), 23-ethynyl-2(3),9(10),16(17)-tri-*tert*-butylphthalocyaninate zinc(II) **12**[24] (24 mg, 0.031 mmol), [$PdCl_2(PPh_3)_2$] (2 mg, 0.0028 mmol), and CuI (0.5 mg, 0.0026 mmol). Dry tetrahydrofuran (2.5 mL) and dry triethylamine (0.5 mL) were then added under an argon atmosphere, and the mixture was stirred for 9 h at room temperature and then concentrated under vacuum. Water was added to the residual crude mixture, and the resulting mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent, the blue solid was purified by column chromatography on silica gel, eluting first with CH_2Cl_2/MeOH (98:2) and then with hexane/dioxane (3:1) to give TFEO-SubPc–*t*BuPc hybrid **10** as a blue solid (34 mg, 56%). ^{19}F NMR (188 MHz, [D_6]acetone): $\delta = -72.89$ (br, 18F; $CF_3 \times 6$), −73.61 ppm (t, $J = 8.0$ Hz, 18F; $CF_3 \times 6$); IR (KBr): $\tilde{\nu} = 3437$, 2964, 1612, 1490, 1458, 1429, 1281, 1239, 1167, 1129, 1068, 1017, 969, 923, 833, 749, 661 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$) = 686 (4.91), 598 (4.96), 550 (4.55), 382 (4.80), 334 (4.95), 300 (4.93), 277 nm (4.93); dioxane: λ_{max} ($\log\varepsilon$) = 683 (5.30), 603 (4.99), 546 (4.45), 349 (5.06), 278 nm (4.88); MALDI-TOF MS: m/z: calcd for $C_{100}H_{67}BF_{36}N_{14}O_{13}Zn$: 2430.38; found: 2432.77 (most abundant peak in the isotopic envelope).

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