


Article

Trifluoroethoxy-Coated Phthalocyanine Catalyzes Perfluoroalkylation of Alkenes under Visible-Light Irradiation [†]

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[†] This manuscript is dedicated to the memory of Professor Kenji Uneyama (1941–2017).

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Abstract: We disclose herein the perfluoroalkylation of alkenes catalyzed by trifluoroethoxy-coated zinc phthalocyanine under irradiation of visible light. Perfluoroalkyl iodides were nicely incorporated into unsaturated substrates, including alkyne, to provide perfluoroalkyl and iodide adducts in moderate to good yields. Trifluoromethylation is also possible by trifluoromethyl iodide under the same reaction conditions. The mechanistic study is discussed.

Keywords: phthalocyanine; photocatalysts; trifluoromethylation; perfluoroalkylation; visible light

1. Introduction

Perfluoroalkyl groups frequently appeared in the libraries of pharmaceuticals, agrochemicals, and functional materials and in the methods for the introduction of perfluoroalkyl groups to organic molecules, causing a massive accumulation of literature over the past few decades [1–5]. Radical perfluoroalkylation of alkenes using perfluoroalkyl halides (Rf-X) under shortwave UV irradiation is one of the classical and well-explored methods for this purpose [6–8]. However, the classical UV irradiation method [9–12] has often suffered from a lack of selectivity, low yields, and complicated reaction devices such as the quartz vessel or the merry-go-round reactor. In recent years, radical perfluoroalkylation has dramatically changed for the sake of discovery of photoredox catalyst systems under visible light irradiation [13–31]. The methods do not require complex reaction devices or harmful UV irradiation because environmentally benign visible lights and photocatalysts are used instead. Besides, high yields and high chemoselectivities are often observed under photo-catalysis without any harsh reaction conditions. Photoredox catalysts containing ruthenium or iridium complexed with polybipyridyl ligands absorbing blue light ($\lambda = 375\text{--}450\text{ nm}$) are mainly explored in this system [13–27]. In recent years, organic dyes such as eosinY or methylene blue have also started to be investigated as organic photoredox catalysts under blue to green light irradiation ($\lambda = \text{ca. } 450\text{--}550\text{ nm}$) [29–31]. Although several metal and non-metal photoredox catalysts have been developed, ruthenium or iridium complexes coordinated by polybipyridyl ligands are surely the most effective catalysts in these transformations, despite the major disadvantage of their high cost.

Phthalocyanines, which are man-made blue color dyes with nearly a century of history [32,33], are 18 π -electron macro-heterocycles consisting of four isoindoline units with a planar structure. Their large conjugated system induces good absorption bands of spectra at 620–700 nm, and their chemical,

thermal, and photo stabilities, low-cost and non-toxicity makes them promising photosensitizers for dye-sensitized solar cell (DSSC) applications [34–36]. From the viewpoint of the successful application of phthalocyanines for DSSC, they should also be very attractive alternative catalysts to Ru(II) polypyridyl complexes for photoredox perfluoroalkylation reactions. In spite of their potential performance as photoredox materials, as mentioned above, research on phthalocyanines for photoredox radical perfluoroalkylation is rarely reported [37,38]. This is presumably due to the notorious low solubility of phthalocyanines in organic solvents [32,33]. In the last several years, we have reported the design and synthesis of a series of trifluoroethoxy-coated phthalocyanines, and revealed their extraordinary non-aggregation property allowing them to become highly soluble in a wide variety of organic solvents [39–45]. We recently reported that trifluoroethoxy-coated boron subphthalocyanine is a very effective catalyst for the radical fluoroalkylation of alkenes and alkynes under energetically lower red light irradiation [46]. However, apart from the advantages of its reactivity following red-light activation ($\lambda = 600\text{--}700\text{ nm}$), boron subphthalocyanine might have a problem, its long-term photo-stability [47–49]. That is, if the reaction requires very long time, catalytic activity would disappear. We disclose herein the radical perfluoroalkylation of alkenes, including alkyne, catalyzed by trifluoroethoxy-coated zinc phthalocyanine under visible light irradiation.

2. Results and Discussion

Initially, perfluoroalkylation of 1-hexenol (**1a**) with perfluorooctyl iodide ($n\text{C}_8\text{F}_{17}\text{I}$) in the presence of a catalytic amount of trifluoroethoxy-coated zinc phthalocyanine (TFEO-ZnPc, 1 mol %) under LED light (white LED, 10 W) irradiation was attempted. The solvent system and additive were selected according to our previous report [46]. The desired perfluoroalkylated product **2aa** was obtained after 1 h in 88% yield (Table 1, Entry 1). Control experiments showed the reaction no longer proceeded without light irradiation, catalyst, or additive (Entries 2–4). The uses of *t*Bu-functionalized zinc phthalocyanine (*t*BuZnPc) or trifluoroethoxy-coated subphthalocyanine (TFEO-SubPc) instead of TFEO-ZnPc decreased product yields (Entries 5, 6). Next, additives were screened and the use of ascorbic acid or Hantzsch ester resulted in a decrease in yields (Entries 7, 8). Finally, study of solvent effect revealed that single solvents such as MeOH, MeCN, or DMSO showed no improvement in yields (Entries 9–11), but an increase in concentration gave higher product yield (Entry 12).

Table 1. Perfluoroalkylation reaction of 1-hexenol with TFEO-ZnPc under visible light irradiation. ^a

Entry	Catalyst (1 mol %)	Additive (0.35 equiv)	Solvent	Yield (%) ^b
1	TFEO-ZnPc	Na ascorbate	MeCN/MeOH	88
2 ^c	TFEO-ZnPc	Na ascorbate	MeCN/MeOH	<5
3	-	Na ascorbate	MeCN/MeOH	<5
4	TFEO-ZnPc	-	MeCN/MeOH	<5
5	<i>t</i> Bu-ZnPc	Na ascorbate	MeCN/MeOH	45
6	TFEO-SubPc	Na ascorbate	MeCN/MeOH	77
7	TFEO-ZnPc	Ascorbic acid	MeCN/MeOH	33

To confirm the reaction mechanism, the time profile of the reaction was investigated. The trifluoromethylation was selected for this purpose due to its longer reaction time (Figure 2). First, trifluoromethylation of **1a** was carried out with optimized conditions for only 1 h and 65% isolated yield of product **1ad** was obtained, even though an excess amount of CF_3I was used (Figure 2a). This result indicates the difficulty of trifluoromethylation compared with other perfluoroalkylations. Next, the time profile was further studied by checking the yields of each reaction time with PhCF_3 as an internal standard with a pause in light irradiation (Figure 2b). The reaction gradually proceeded and gave comparable yields after a 5 h reaction time, while the reaction did not proceed in the dark. These results show good agreement with our previous results [46] and with other reports [19] on the photo-induced radical trifluoromethylation of alkenes with photoredox catalysts.

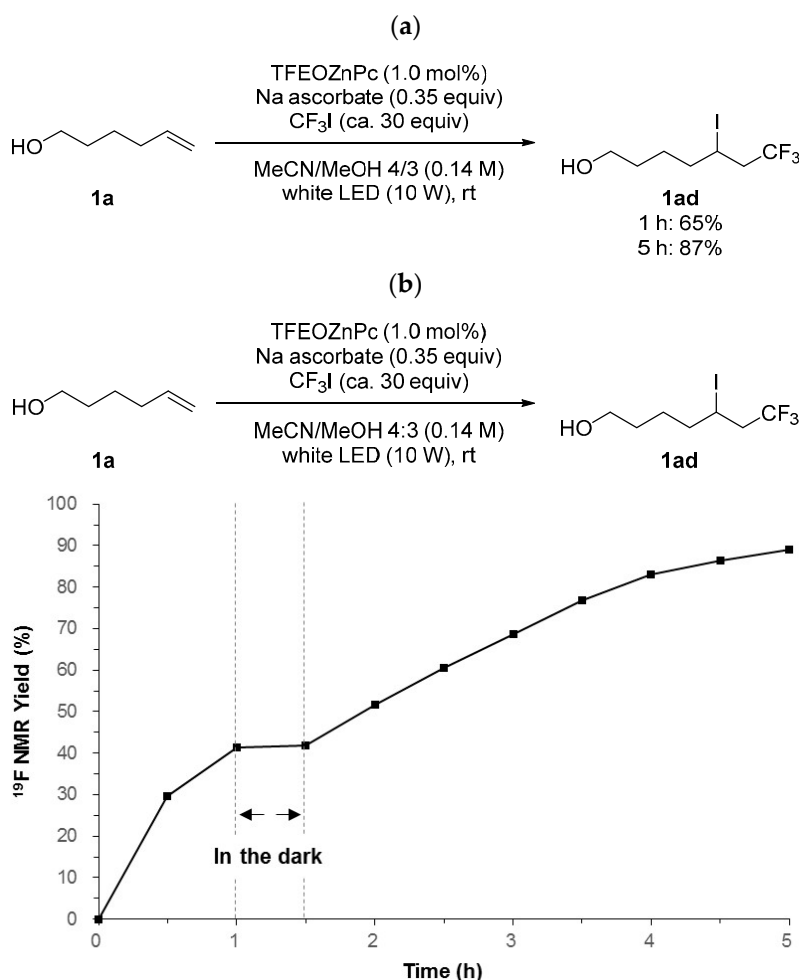
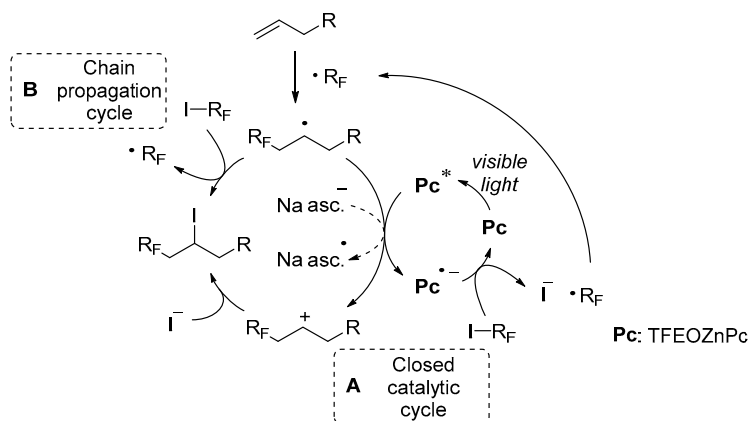


Figure 2. The time profile and light/dark experiment on trifluoromethylation of **1a** with TFEONPc under visible light irradiation: (a) Trifluoromethylation of **1a** with TFEONPc under optimized conditions for a reaction time of 1 h and 5 h; (b) Time profile and light/dark experiment on trifluoromethylation of **1a** with TFEONPc.

A plausible reaction mechanism shown in Scheme 1 is supported by previous reports [9] and by the light/dark experiment mentioned above. The reaction starts with the electron transfer from Na ascorbate to excited TFEONPc (Pc^*) by visible light to form the TFEONPc anion radical ($\text{Pc}^{\cdot-}$) and the anion radical reduces the perfluoroalkyl iodide ($\text{R}_\text{F}\text{I}$) to produce the perfluoroalkyl radical (R_F^\cdot). The radical reacts with an unsaturated moiety of the substrate to form an alkyl radical intermediate. Then, the alkyl radical may donate the electron to excited TFEONPc to reproduce the TFEONPc anion radical (Path A; Closed reaction cycle). Another possibility of this reaction is radical propagation

of the perfluoroalkyl radical intermediate with R_FI (Path B; Chain propagation cycle). The control experiment shows that both plausible reaction passes need an initial electron-transfer between Na ascorbate and TFEO-ZnPc and the experiment in Figure 1b shows that continuous light irradiation is essential for the production of a perfluoroalkylated product. From the previous study [46] and these results in this reaction, Path A and B may work concertedly in this transformation. Further studies are required to disclose the details of this mechanism.



Scheme 1. Plausible reaction mechanism of trifluoromethylation of alkenes with TFEO-ZnPc.

3. Materials and Methods

All reactions were performed in oven-dried glassware under the positive pressure of argon unless otherwise mentioned. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on a 0.25 mm Merck silica gel (60-F₂₅₄). TLC plates were visualized with UV light and KMnO₄ in water/heat. Column chromatography was carried out on columns packed with silica gel (60N spherical neutral size 63–210 μ m, Kanto Chemical Co., Inc., Tokyo, Japan). The ¹H-NMR (300 MHz), ¹⁹F-NMR (282 MHz), and ¹³C-NMR (125 MHz) spectra for solution in CDCl₃ were recorded on a Varian 300 (Agilent Technologies, Palo Alto, CA, USA) and a Bruker Avance 500 (Bruker, Billerica, MA, USA). Chemical shifts (δ) are expressed in ppm downfield from TMS (δ = 0.00) or C₆F₆ (δ = −162.2 (CDCl₃)) as an internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A (EI-MS) and Shimadzu LCMS-2020 (ESI-MS) (Shimadzu Corporation, Kyoto, Japan). Melting points were recorded on a Buchi M-565 (Büchi Labortechnik AG, Flawil, Switzerland). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer (Jasco Corporation, Tokyo, Japan). Chemicals were purchased and used without further purification unless otherwise noted. MeOH was dried and distilled before use.

All reactions were performed under irradiation by commercially available 10 W white LED (Panasonic Corporation, Osaka, Japan, DA10DGK60W, 810 lumens). The LEDs were placed at a distance of 3–4 cm.

3.1. Perfluoroalkylation of Alkenes and Alkynes with TFEOZnPc

A Schlenk tube equipped with a rubber septum and magnetic stir bar was charged with TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %) and Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv). The tube was degassed by vacuum evacuation and argon backfill ($\times 3$) before MeCN (1.0 mL), MeOH (0.75 mL), substrate (0.25 mmol, 1.0 equiv) and perfluoroalkyliodide (0.375 mmol, 1.5 equiv) were added. The mixture was degassed by the freeze-pump-thaw method ($\times 3$). The mixture was stirred for 1 h under irradiation by 10 W white LEDs. After the reaction was complete, the mixture was diluted by Et₂O and filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.

3.1.1. 5-Iodo-6-perfluorooctylhexane-1-ol (**2aa**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv) alkene **1a** (29.5 μ L, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 μ L, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give perfluoroalkylated product **2a** (150.2 mg, 93% yield) as a white solid.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [19].

MS (EI, *m/z*) 519 [(M – I)⁺]; ¹H-NMR (CDCl₃, 300 MHz): δ 4.40–4.30 (m, 1H), 3.70–3.66 (m, 2H), 3.00–2.70 (m, 2H), 1.90–1.50 (m, 7H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.2 (t, *J* = 9.0 Hz, 3F), –111.5–112.5 (m, 1F), –114.5–115.5 (m, 1F), –121.9 (br s, 2F), –122.3 (br s, 4F), –123.1 (br s, 2F), –123.9 (br s, 2F), –126.5 (br s, 2F).

3.1.2. 5-Iodo-6-perfluorohexylhexanol (**2ab**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv) alkene **1a** (29.5 μ L, 0.25 mmol, 1.0 equiv) and C₆F₁₃I (81.2 μ L, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give perfluoroalkylated product **2ab** (128.4 mg, 94% yield) as a white solid.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [19].

MS (EI, *m/z*) 419 [(M – I)⁺]; ¹H-NMR (CDCl₃, 300 MHz): δ 4.39–4.30 (m, 1H), 3.70–3.67 (m, 2H), 3.04–2.69 (m, 2H), 1.90–1.49 (m, 7H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.3 (t, *J* = 9.9 Hz, 3F), –111.7–112.7 (m, 1F), –114.7–115.7 (m, 1F), –122.3 (br s, 2F), –123.4 (br s, 2F), –124.1 (br s, 2F), –126.7 (br s, 2F).

3.1.3. 5-Iodo-6-perfluorobutylhexanol (**2ac**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv) alkene **1a** (29.5 μ L, 0.25 mmol, 1.0 equiv) and C₄F₉I (63.0 μ L, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give perfluoroalkylated product **2ac** (99.3 mg, 89% yield) as a white solid.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [50].

MS (EI, *m/z*) 319 [(M – I)⁺]; ¹H-NMR (CDCl₃, 300 MHz): δ 4.39–4.30 (m, 1H), 3.71–3.67 (m, 2H), 2.98–2.69 (m, 2H), 1.89–1.48 (m, 7H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.5 (t, *J* = 9.9 Hz, 3F), –111.9–112.9 (m, 1F), –115.1–116.0 (m, 1F), –125.1 (br s, 2F), –126.4 (br s, 2F).

3.1.4. 5-Iodo-6-trifluoromethylhexanol (**2ad**)

A Schlenk tube equipped with a rubber septum and a magnetic stir bar was charged with TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %) and Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv). The tube was degassed by vacuum evacuation and argon backfill ($\times 3$) before MeCN (1.0 mL), MeOH (0.75 mL) and alkene **1a** (29.5 μ L, 0.25 mmol, 1.0 equiv) were added. The mixture was degassed by the freeze-pump-thaw method ($\times 3$). CF₃I (1.45 g, 7.32 mmol, 29.3 equiv) in a balloon was then added to the tube via a needle then cooled to –78 °C in an ethanol bath. The mixture was warmed to room temperature and stirred for 5 h under irradiation by 10 W white LEDs. After the reaction was complete, the mixture was diluted by Et₂O and filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give desired product **2ad** (64.2 mg, 87% yield) as a white solid.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [51].

MS (EI, *m/z*) 169 [(M – I)⁺]; ¹H-NMR (CDCl₃, 300 MHz): δ 4.25–4.16 (m, 1H), 3.71–3.66 (m, 2H), 2.98–2.74 (m, 2H), 1.86–1.44 (m, 7H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ = –64.4 (t, *J* = 10.4 Hz, 3F).

3.1.5. 5-Iodo-6-perfluorooctylhexyl-4-methylbenzenesulfonate (**2b**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv) alkene **1b** (63.6 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give perfluoroalkylated product **2b** (184.3 mg, 92% yield) as a white solid.

m.p. = 54.3–55.3 °C; HRMS (EI) calcd. for C₂₁H₁₈F₁₇O₃S [(M – I)⁺]: 673.0705 found 673.0724; ¹H-NMR (300 MHz, CDCl₃): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.29–4.21 (m, 1H), 4.05 (t, *J* = 6.2 Hz, 2H), 2.92–2.66 (m, 2H), 2.45 (s, 3H), 1.73–1.46 (m, 6H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.2 (t, *J* = 9.4 Hz, 3F), –111.6––112.6 (m, 1F), –114.8––115.8 (m, 1F), –122.1 (br s, 2F), –122.4 (br s, 4F), –123.3 (br s, 2F), –124.1 (br s, 2F), –126.6 (br s, 2F); ¹³C NMR (CDCl₃, 125 MHz): δ = 144.8, 133.0, 130.0, 127.9, 120.0–108.8 (m, C₈F₁₇), 69.9, 41.6 (t, *J* = 20.7 Hz), 39.4 (apparent doublet, *J* = 1.3 Hz), 27.8, 25.8, 21.6, 19.7; IR (KBr) 2940, 2362, 1599, 1352, 1202, 957, 812, 660, 557 cm^{–1}.

3.1.6. 1-Bromo-5-iodo-6-perfluorooctylhexane (**2c**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1c** (40.8 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane) to give perfluoroalkylated product **2c** (160.3 mg, 90% yield) as yellow oil.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [19].

HRMS (EI) calcd. for C₁₄H₁₁BrF₁₇ [(M – I)⁺]: 580.9773 found 580.9785; ¹H-NMR (CDCl₃, 300 MHz): δ 4.37–4.28 (m, 1H), 3.42 (t, *J* = 6.6 Hz, 2H), 3.04–2.71 (m, 2H), 2.00–1.54 (m, 6H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.1 (t, *J* = 9.9 Hz, 3F), –111.2––112.3 (m, 1F), –114.2––115.2 (m, 1F), –121.7 (br s, 2F), –122.0 (br s, 4F), –122.9 (br s, 2F), –123.7 (br s, 2F), –126.3 (br s, 2F).

3.1.7. 1,5-Diiodo-6-perfluorooctylhexane (**2d**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1d** (52.5 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane) to give perfluoroalkylated product **2d** (178.3 mg, 94% yield) as yellow oil.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [19].

HRMS (EI) calcd. for C₁₄H₁₁F₁₇I₂ (M)⁺: 755.8679 found 755.8651; ¹H-NMR (CDCl₃, 300 MHz): δ 4.37–4.29 (m, 1H), 3.21–3.19 (m, 2H), 3.02–2.71 (m, 2H), 1.84–1.56 (m, 6H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.2 (t, *J* = 9.3 Hz, 3F), –111.4––112.3 (m, 1F), –114.5––115.5 (m, 1F), –121.9 (br s, 2F), –122.3 (br s, 4F), –123.1 (br s, 2F), –123.9 (br s, 2F), –126.5 (br s, 2F).

3.1.8. *tert*-Butyl (2-iodo-3-perfluorooctylpropyl)carbamate (**2e**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1e** (39.3 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give perfluoroalkylated product **2e** (163.6 mg, 83% yield) as a white solid.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [19].

MS (ESI, *m/z*) 726 [(M + Na)⁺]; ¹H-NMR (CDCl₃, 300 MHz): δ 5.09–4.99 (m, 1H), 4.43–4.35 (m, 1H), 3.58–3.50 (m, 2H), 2.93–4.73 (m, 2H), 1.45 (s, 9H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ –81.2 (t, *J* = 8.7 Hz, 3F), –112.1––114.7 (m, 2F), –121.9 (br s, 2F), –122.2 (br s, 4F), –123.1 (br s, 2F), –123.9 (br s, 2F), –126.5 (br s, 2F).

3.1.9. (3-Iodo-4-perfluorooctylbutyl)benzene (**2f**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1f** (33.0 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane) to give perfluoroalkylated product **2f** (145.4 mg, 86% yield) as a white solid.

The ¹H-NMR matched that reported in [52].

HRMS (EI) calcd. for C₁₈H₁₂F₁₇I (M)⁺: 677.9712 found 677.9713; ¹H-NMR (300 MHz, CDCl₃): δ 7.31 (d, *J* = 6.0 Hz, 2H), 7.26–7.20 (m, 3H), 4.31–4.22 (m, 1H), 2.93–2.70 (m, 4H), 2.16–2.08 (m, 2H). ¹⁹F-NMR (282 MHz, CDCl₃): δ −81.3 (t, *J* = 8.5 Hz, 3F), −111.3–112.3 (m, 1F), −114.6–115.6 (m, 1F), −122.1 (br s, 2F), −122.4 (br s, 4F), −123.2 (br s, 2F), −124.1 (br s, 2F), −126.6 (br s, 2F).

3.1.10. 3-Iodo-4-perfluorooctyldobut-3-en-1-ol (**2g**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkyne **1g** (17.5 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 8:2) to give perfluoroalkylated product **2g** (128.6 mg, 83% yield) as a white solid.

The ¹H-NMR, ¹⁹F-NMR spectrum matched that reported in [19].

HRMS (EI) calcd. for C₁₈H₁₂F₁₇I (M)⁺: 677.9712 found 677.9711; Data for major isomer of compound (**2g**); ¹H-NMR (CDCl₃, 300 MHz): δ 6.49 (t, *J* = 13.4 Hz, 1H), 3.89–3.85 (m, 2H), 2.97–2.92 (m, 2H), 1.70 (s, 1H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.2 (t, *J* = 9.4 Hz, 3F), −105.3–105.5 (m, 2F), −121.8 (br s, 2F), −122.3 (br s, 4F), −123.1 (br s, 2F), −123.4 (br s, 2F), −126.5 (br s, 2F). Data for minor isomer of compound (**2g**); ¹H-NMR (CDCl₃, 300 MHz): δ 6.41 (t, *J* = 12.1 Hz, 1H), 3.88–3.84 (m, 2H), 2.95–2.91 (m, 2H), 1.61 (s, 1H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.2 (t, *J* = 10.0 Hz, 3F), −109.1–109.2 (m, 2F), −121.8 (br s, 2F), −122.3 (br s, 4F), −123.2 (br s, 4F), −126.5 (br s, 2F).

3.1.11. 2-Iodo-1-perfluorooctyloctene (**2h**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1h** (28.0 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane) to give perfluoroalkylated product **2h** (160.2 mg, 97% yield) as colorless oil.

HRMS (EI) calcd. for C₁₆H₁₆F₁₇ [(M − I)⁺]: 531.0981 found 531.0997; ¹H-NMR (CDCl₃, 300 MHz): δ 4.38–4.30 (m, 1H), 3.03–2.68 (m, 2H), 1.87–1.75 (m, 2H), 1.55–1.52 (m, 8H), 0.91–0.90 (m, 3H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.3 (t, *J* = 9.4 Hz, 3F), −111.8–112.7 (m, 1F), −114.7–115.7 (m, 1F), −122.1 (br s, 2F), −122.3 (br s, 4F), −123.2 (br s, 2F), −124.1 (br s, 2F), −126.7 (br s, 2F); ¹³C NMR (CDCl₃, 125 MHz): δ = 106.4–120.8 (m, C₈F₁₇), 41.7 (t, *J* = 20.6 Hz), 40.3 (apparent doublet, *J* = 1.3 Hz), 31.4, 29.5, 28.2, 22.5, 20.9, 14.0 (apparent doublet, *J* = 5.0 Hz); IR (NaCl) 2932, 2860, 1468, 1434, 1368, 1206, 1151, 705, 657, 559 cm^{−1}.

3.1.12. 5-Iodo-6-perfluorooctylhexane-2-one (**2i**)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1i** (24.5 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 µL, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 9:1) to give perfluoroalkylated product **2i** (137.6 mg, 85% yield) as a white solid.

m.p. = 42.4–43.3 °C; HRMS (EI) calcd. for C₁₄H₁₀F₁₇O [(M − I)⁺]: 517.0460 found 517.0447; ¹H-NMR (CDCl₃, 300 MHz): δ 4.40–4.32 (m, 1H), 3.01–2.63 (m, 4H), 2.20–2.00 (m, 5H); ¹⁹F-NMR

(CDCl₃, 282 MHz): δ −81.2 (t, J = 8.5 Hz, 3F), −111.6—112.6 (m, 1F), −114.4—115.4 (m, 1F), −122.0 (br s, 2F), −122.3 (br s, 4F), −123.1 (br s, 2F), −124.0 (br s, 2F), −126.6 (br s, 2F).; ¹³C NMR (CDCl₃, 125 MHz): δ = 206.5, 120.1–106.0 (m, C₈F₁₇), 43.7, 41.9 (t, J = 20.6 Hz), 34.0, 30.1, 19.8; IR (KBr) 2924, 2370, 1714, 1434, 1250, 1146, 1034, 705, 659 cm^{−1}.

3.1.13. 1-Iodo-2-perfluorooctylcyclohexane (2j)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1j** (20.5 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 μ L, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane) to give perfluoroalkylated product **2j** (150.2 mg, 96% yield) as a white solid.

The ¹H-NMR spectrum matched that reported in [53].

HRMS (EI) calcd. for C₁₆H₁₆F₁₇ [(M − I)⁺]: 501.0511 found 501.0511; Data for major isomer of compound (**2j**); ¹H-NMR (CDCl₃, 300 MHz): δ 4.99–4.95 (m, 1H), 2.75–2.63 (m, 1H), 2.19–1.59 (m, 8H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.2 (t, J = 8.9 Hz, 3F), −108.6—109.6 (m, 1F), −110.3—111.3 (m, 1F), −121.0—121.3 (br s, 2F), −122.0—122.3 (m, 6F), −123.1 (br s, 2F), −126.5 (br s, 2F). Data for minor isomer of compound (**2j**); ¹H-NMR (CDCl₃, 300 MHz): δ 4.74–4.70 (m, 1H), 2.24–2.20 (m, 1H), 2.00–1.37 (m, 8H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.2 (t, J = 8.9 Hz, 3F), −118.0 (br s, 2F), −120.3—122.2 (m, 8F), −123.1 (br s, 2F), −126.5 (br s, 2F).

3.1.14. 2-Iodo-3-perfluorooctylnorbornane (2k)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1k** (23.5 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 μ L, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane) to give perfluoroalkylated product **2k** (69.8 mg, 44% yield) as a white solid.

The ¹H-NMR spectrum matched that reported in [53].

HRMS (EI) calcd. for C₁₅H₁₀F₁₇ [(M − I)⁺]: 513.0511 found 513.0497; ¹H-NMR (CDCl₃, 300 MHz): δ 4.33–4.31 (m, 1H), 2.50–2.31 (m, 3H), 1.93–1.30 (m, 6H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.3 (t, J = 9.3 Hz, 3F), −115.6–116.6 (m, 1F), −119.0—120.0 (m, 1F), −121.3 (br s, 2F), −122.2—122.5 (m, 6F), −123.2 (br s, 2F), −126.6 (br s, 2F).

3.1.15. 3-Iodo-4-(perfluorooctyl)butanenitrile (2l)

Following a general procedure, TFEO-ZnPc (5.4 mg, 0.0025 mmol, 1 mol %), Na ascorbate (17.3 mg, 0.0875 mmol, 0.35 equiv), alkene **1l** (17.8 mg, 0.25 mmol, 1.0 equiv) and C₈F₁₇I (99.0 μ L, 0.375 mmol, 1.5 equiv) were used in MeCN (1.0 mL) and MeOH (0.75 mL) at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (hexane/EtOAc = 9:1) to give perfluoroalkylated product **2l** (33.0 mg, 22% yield) as a yellow solid.

m.p. = 81.7–82.7 °C; HRMS (EI) calcd. for C₁₂H₅F₁₇NI [(M⁺)]: 612.9195 found 612.9209; ¹H-NMR (CDCl₃, 300 MHz): δ 4.49–4.41 (m, 1H), 3.34–3.16 (m, 2H), 3.03–2.88 (m, 2H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ −81.2 (t, J = 9.4 Hz, 3F), −111.8—112.7 (m, 1F), −114.9—115.9 (m, 1F), −122.1 (br s, 2F), −122.4 (br s, 4F), −123.2 (br s, 2F), −123.9 (br s, 2F), −126.6 (br s, 2F); ¹³C NMR (CDCl₃, 125 MHz): δ = 120.0–108.3 (m, C₈F₁₇), 116.4, 40.5 (t, J = 21.3 Hz), 30.3 (apparent doublet, J = 3.8 Hz), 5.34 (apparent doublet, J = 3.8 Hz); IR (KBr) 2958, 2920, 2366, 2258, 1371, 1203, 1149, 1117, 972, 657 cm^{−1}.

4. Conclusions

In summary, we disclose the first photo-induced radical perfluoroalkylation of alkenes and alkyne induced by trifluoroethoxy-coated zinc phthalocyanine as a catalyst. From the view of the ease of availability, lower cost, and the substantiality of phthalocyanines, this study will be a monumental work

of phthalocyanines as photocatalysts. Further studies to reveal the new potential of phthalocyanines are under investigation by our group [54].

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54. When we attempted the reaction of **1a** to **2aa** under the best conditions and in the presence of NaN_3 (3 equiv), the reaction was completely inhibited and the starting material was recovered. Further reactions will be investigated in the presence of a variety of nucleophiles

Sample Availability: Samples of the compounds TFEO-ZnPc and TFEO-SubPc are available from the authors.



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