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Synthesis of SF_5-Substituted Tetrapyrroles, Metalloporphyrins, BODIPYs, and Their Dipyrrane Precursors

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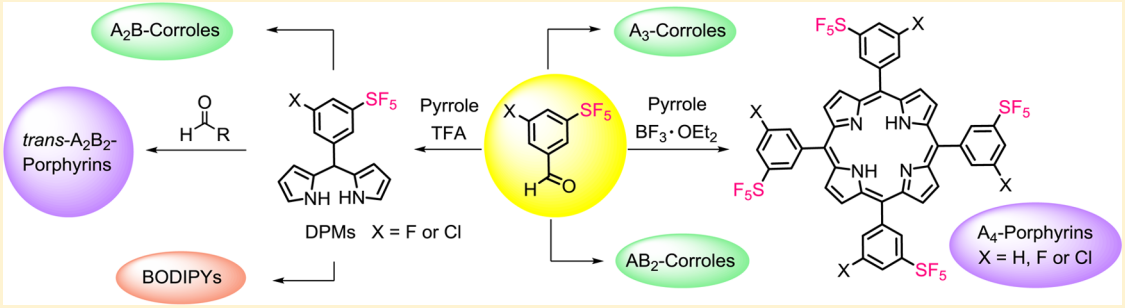
Supporting Information



ABSTRACT: The synthesis of novel pentafluorosulfanyl (SF_5)-substituted A_4-type porphyrins, their corresponding Zn^{II}– and Pd^{II}–metal complexes, A_3-, A_2B- and AB_2-type corroles, BODIPYs, and their dipyrrane precursors was studied utilizing commercially available SF_5-substituted aryl aldehydes. In addition, the functionalization of SF_5-substituted tetrapyrroles was investigated by applying the concept of the nucleophilic aromatic substitution (S_NAr) with alcohols and sodium azide onto the pentafluorophenyl moiety of a *trans*-A_2B_2-porphyrin and two corrole derivatives with a mixed substitution pattern involving the SF_5 group. This allows a fine-tuning of the properties of these macrocycles through a selective and mild introduction of functional groups, giving access to multifunctionalized SF_5-substituted porphyrinoids. As an example, one functionalized corrole was further reacted with an azido-substituted BODIPY via the copper(I)-catalyzed 1,3-dipolar cycloaddition yielding the first corrole-BODIPY heterodimer involving the pentafluorosulfanyl group.

INTRODUCTION

Aromatic compounds with a pentafluorosulfanyl group also known as the pentafluorothio (SF_5) group were described for the first time by Sheppard et al. around 50 years ago.[1] The SF_5 group was declared as the "substituent of the future" due to its unique and impressive properties: high chemical and thermal resistance,[2] high lipophilicity,[3] steric bulkiness,[4] and strong electron-withdrawing effect. Within the last decades, various SF_5-substituted aromatic compounds have been prepared, with possible applications as pesticides,[5] liquid crystals,[6] or enzyme inhibitors.[7]

Our group is focused on the synthesis and functionalization of tetrapyrroles,[8] the remarkable class of macrocycles found inter alia in the heme protein, chlorophyll, or cobalamin as the molecular backbone. Such systems containing the SF_5 substituent are not known to date; therefore, we decided to explore their synthesis in more detail. For this aim, aldehydes bearing the SF_5 motif, e.g., the commercially available compounds **1a–c**, are of essential use (see Table 1 and Scheme 1). Such aldehydes should allow access to SF_5-substituted tetrapyrroles via the classical condensation with pyrrole. Moreover, SF_5-substituted aldehydes, in particular those carrying additional halogen atoms like **1b** and **1c**, because of the increased overall electron deficiency of the aryl substituent, should form dipyrranes or dipyrromethanes (DPMs) exhibiting a high resistance to "scrambling" (acid-catalyzed recombination of the DPM) or polymerization.[9] This effect is well-known for pentafluorophenyl-substituted systems, i.e., pentafluorophenyl dipyrromethane (PFP-DPM), which compared to 5-alkyl-substituted DPMs hardly undergo scrambling or decomposition.[8e,9a]

RESULTS AND DISCUSSION

Following Lindsey's method for porphyrin synthesis,[9a,10] pyrrole was condensed first with SF_5-substituted aldehydes **1a–c** in DCM under acid catalysis (Table 1). When the acid catalyst ($BF_3{\cdot}OEt_2$ or TFA) and its loading were varied, best results were achieved with $BF_3{\cdot}OEt_2$ and 25 mol % loading (entries 1, 4, and 9). An increase of catalyst loading decreased the yield in the case of BF_3 catalysis, while with TFA a slight increase was observed. In general, TFA-catalyzed condensations resulted in the corresponding products with lower yield. This is in accordance with literature observations where electron-deficient aldehydes like pentafluorobenzaldehyde usually give higher yields under BF_3 catalysis.[9b] The resulting SF_5-

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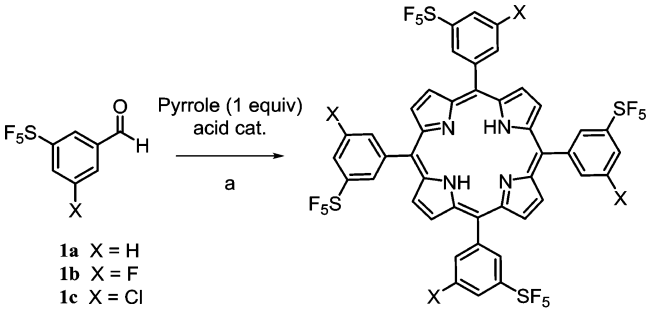
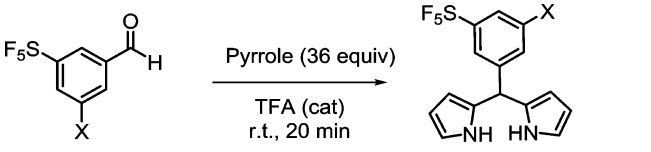
Table 1. Optimization of the A_4-Porphyrin Condensation



entry	X	acid catalyst	mol %	product	yield[b] (%)
1	H	$BF_3{\cdot}OEt_2$	25	**2a**	36
2	H	$BF_3{\cdot}OEt_2$	50	**2a**	18
3	H	$BF_3{\cdot}OEt_2$	100	**2a**	10
4	F	$BF_3{\cdot}OEt_2$	25	**2b**	39
5	F	$BF_3{\cdot}OEt_2$	50	**2b**	17
6	F	$BF_3{\cdot}OEt_2$	100	**2b**	8
7	F	TFA	25	**2b**	4
8	F	TFA	50	**2b**	6
9	Cl	$BF_3{\cdot}OEt_2$	25	**2c**	30
10	Cl	$BF_3{\cdot}OEt_2$	50	**2c**	11
11	Cl	TFA	50	**2c**	6

[a]Reaction conditions: (1) DCM, argon atmosphere, rt, 24 h; (2) DDQ, rt, 4 h. [b]Yield of purified product.

Scheme 1. Synthesis of SF_5-Substituted Dipyrromethanes

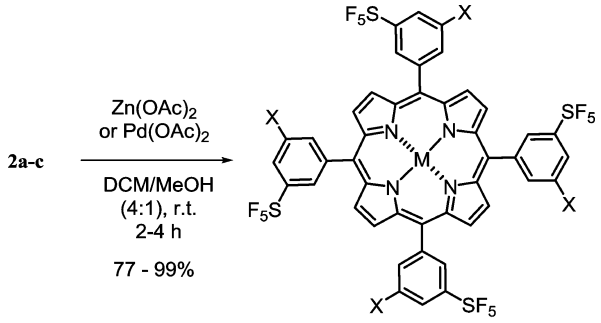


substituted porphyrins could easily be converted into their corresponding metal complexes by reaction of the free-base porphyrins **2a–c** with zinc acetate or palladium acetate, respectively, in a DCM/MeOH 4:1 mixture within 2–4 h (Table 2), providing the metalloporphyrin in high yields. Such metal complexes of highly electron-deficient porphyrins have found application as oxidation catalysts.[11]

Dipyrromethanes (DPMs) are important building blocks for the synthesis of polypyrrolic macrocycles such as dipyrrins, *trans*-porphyrins, corroles, or calixpyrroles.[12] The synthesis of simple *meso*-functionalized DPMs without additional α- or β-substituents can be carried out by condensation of aldehydes with an excess of pyrrole under acid catalysis. Hence, condensation of aldehydes **1a–c** under these conditions using TFA as catalyst afforded the corresponding SF_5-substituted DPMs **5a–c** in good yields (Scheme 1).

Using these DPMs as precursors for porphyrins allows a selective access to *trans*-substituted A_2B_2 porphyrins. Therefore, we investigated the condensation of SF_5–DPMs **5a–c** with pentafluorobenzaldehyde and 3-acetoxybenzaldehyde. The A_2B_2 porphyrins **6** and **7** carrying the two different substituents

Table 2. Metalation of A_4-Type SF_5-Substituted Porphyrins by Zn^{II} and Pd^{II} Coordination



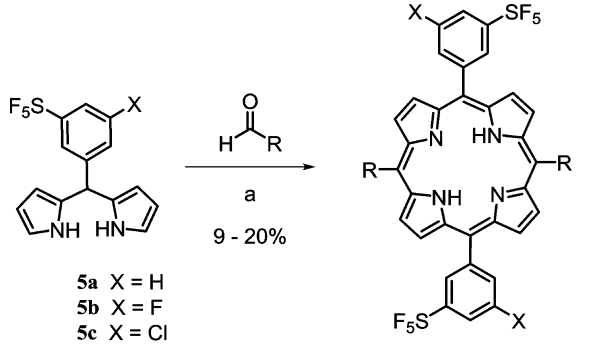
entry	X	M	product	yield[a] (%)
1	H	Zn	**3a**	99
2	F	Zn	**3b**	99
3	Cl	Zn	**3c**	99
4	H	Pd	**4a**	77
5	F	Pd	**4b**	96
6	Cl	Pd	**4c**	81

[a]Yield of purified product.

in a defined arrangement were obtained in yields typical for such dipyrromethane condensations (Table 3).

These porphyrins bear the potential of further modifications: Deprotection of the acetoxy residue would yield amphiphilic compounds and the pentafluorophenyl group (PFP) allows

Table 3. Synthesis of SF_5-Substituted A_2B_2 *trans*-Porphyrins



entry	X	R	product	yield (%)[b]
1	H		**6a**	20
2	F		**6b**	9
3	Cl		**6c**	11
4	F		**7a**	9
5	Cl		**7b**	18

[a]Reaction conditions: (1) TFA, DCM, argon atmosphere, rt, 24 h; (2) DDQ, rt, 4 h. [b]Yield of purified product.

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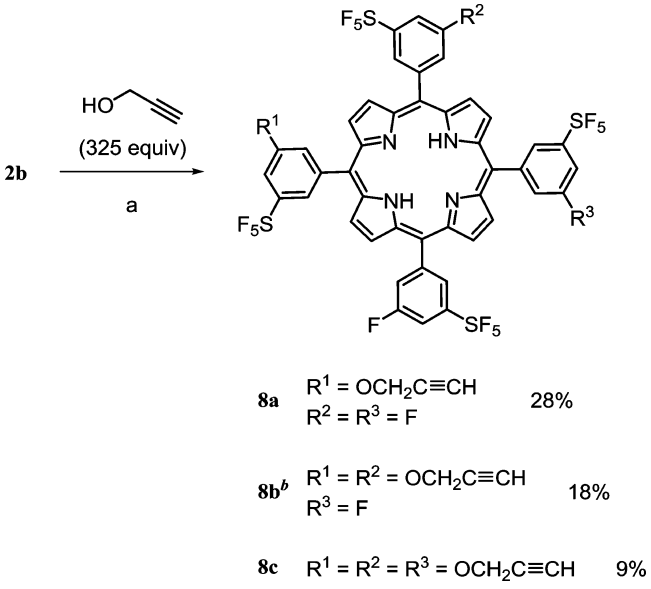
nucleophilic substitution reactions (see below and refs 8d and 13).

However, not only the PFP substituent is prone to undergo a reaction with nucleophiles. It is conceivable that systems with an additional fluorine atom in the vicinity of the SF_5 group (i.e., **2b**) may undergo side reactions at this position if treated with nucleophiles due to the strong electron-withdrawing nature of the SF_5 group, which may facilitate a nucleophilic attack on the aryl core. Moreover, even the SF_5 group itself could react with strong nucleophiles. Therefore, porphyrin **2b** was treated with propargyl alcohol under reaction conditions we recently used for the functionalization of PFP-substituted porphyrins and dipyrromethanes (Scheme 2) to test the resistance of the SF_5 group to a nucleophilic attack under these conditions.[8d,e]

Scheme 2. Functionalization of A_4-Porphyrin 2b with Propargyl Alcohol



8a $R^1 = OCH_2C{\equiv}CH$, $R^2 = R^3 = F$ 28%

8b[b] $R^1 = R^2 = OCH_2C{\equiv}CH$, $R^3 = F$ 18%

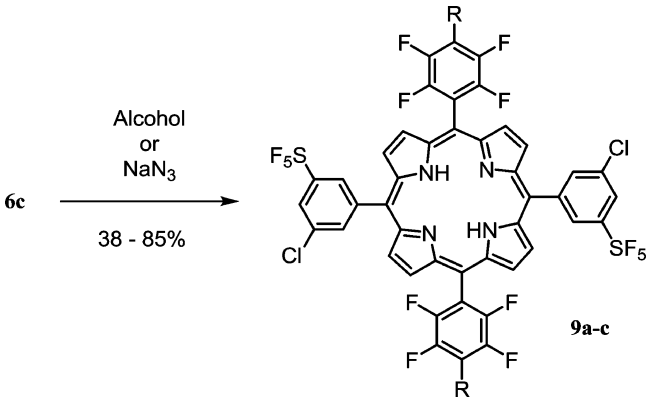
8c $R^1 = R^2 = R^3 = OCH_2C{\equiv}CH$ 9%

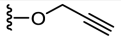
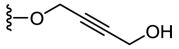
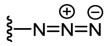
[a]Reaction conditions: KOH (65 equiv), THF, 60 °C, 24 h. [b]Isolated as a mixture (*cis*/*trans*-substituted A_2B_2 porphyrins).

As a result, the substitution of the *meta*-fluorine atom in **2b** took place, but after far longer reaction time and under more harsh conditions. No reactivity toward the alkoxide was observed at room temperature; even after 96 h in THF and 24 h in DMSO, respectively, only trace amounts of **8a** were detected. Increasing the temperature to 60 °C enhanced the reaction in THF which after 24 h resulted mostly in a mixture of mono-, di-, and trialkoxy-substituted porphyrins **8a**–**c** with a preference for the monosubstituted compound **8a**. Porphyrins **2a** and **2c**, respectively, showed no reactivity and high resistance against a nucleophilic attack either by hydroxide or alkoxides on the SF_5 substituent itself, the benzene ring, or the chlorine substituent (for **2c**).

Hence, systems carrying both the PFP- and SF_5/halogen aryl substituents can undergo a selective alkoxy functionalization with strong preference for the PFP moiety. This type of functionalization was exemplified first on *trans*-porphyrin **6c** with alcohols and sodium azide (Table 4). The substitution reactions toward **9a** and **9b** were carried out with an excess of alcohol (50 equiv) and powdered KOH (to increase the surface area, 25 equiv). In both cases, the reaction proceeded within 20 min without formation of side products. In analogy, the direct

Table 4. Functionalization of an SF_5-Substituted *trans*-Porphyrin with Alcohols and Sodium Azide by Nucleophilic Aromatic Substitution[a]



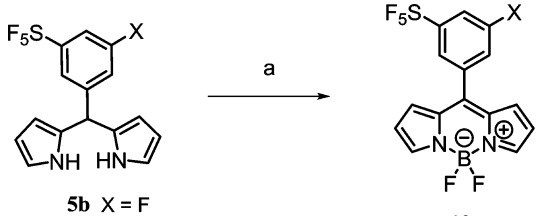
Entry	R	conditions[a]	9	Yield (%)[b]
1		KOH, DMSO, r.t., 20 min	**9a**	68
2		KOH, DMSO, r.t., 20 min	**9b**	47
3		DMF, 50 °C 2.5 h	**9c**	38

[a]Substitution reactions with alcohols were carried out under argon atmosphere. [b]Yield of isolated product after purification.

azidation with sodium azide resulted in porphyrin **9c** with acceptable yield.

Difluoroboraindacenes, also known as BODIPYs, constitute a remarkable class of fluorescent dyes with various applications inter alia for cell imaging or OLED technology.[14] The synthesis of *meso*-functionalized BODIPYs can be carried out directly starting from the DPM precursor. In accordance with the general three-step, one-pot approach[14] involving (i) DDQ oxidation to the dipyrromethene, (ii) proton abstraction with DIPEA, and (iii) boron complexation with $BF_3{\cdot}OEt_2$ the DPMs **5b**,**c** were transformed into their corresponding boron complexes **10a**,**b** (Scheme 3).

Scheme 3. Synthesis of SF_5-Substituted BODIPYs



5b X = F
5c X = Cl

10a X = F 52%
10b X = Cl 33%

[a]Reaction conditions: (1) DCM, DDQ, rt, 5 min; (2) DIPEA, rt, 20 min; (3) $BF_3{\cdot}OEt_2$, rt, 15 min.

In close analogy to the above-described SF_5–porphyrins, we also briefly explored the synthesis of SF_5-substituted corroles. Depending on the desired substitution pattern, these can be prepared either by a direct condensation reaction of pyrrole and an aldehyde for A_3-type systems or a DPM building block with an aldehyde to obtain A_2B-type systems.[15] Gryko et al. achieved

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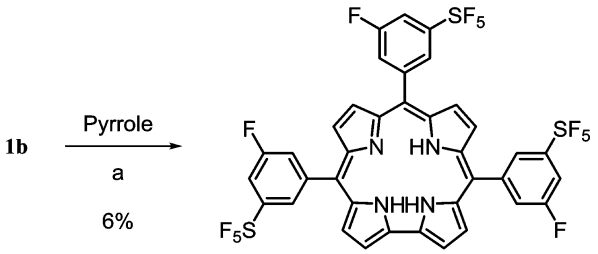
a breakthrough in corrole synthesis by exchanging halogenated solvents by a methanol/water mixture, which in result led to quick transformations combined with high product yields.[15b] In accordance with this methodology, we tried first the synthesis of an A_3-type corrole by condensing aldehyde **1b** with pyrrole, resulting in the desired SF_5–corrole **11** (Scheme 4).

Scheme 4. Synthesis of an SF_5-Substituted Corrole

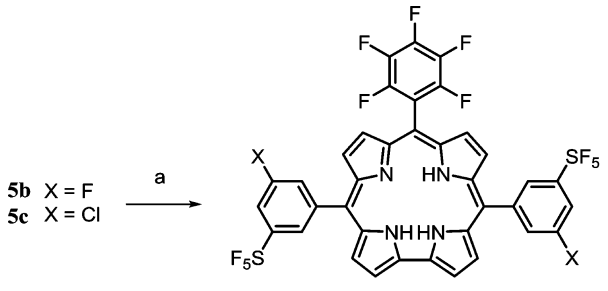


11

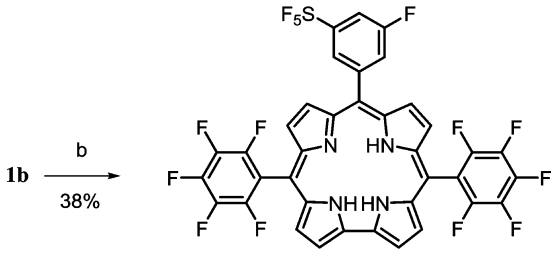
[a]Reaction conditions: (1) HCl (37%), MeOH/H_2O = 1:1 (v/v), rt, 3 h; (2) DDQ, rt, 1 h.

Then, the synthesis of A_2B- and AB_2-type corroles was carried out starting with DPM building blocks (Scheme 5). For A_2B-type corroles DPMs **5b,c** were condensed with pentafluorobenzaldehyde (PFBA). After DDQ oxidation, corroles **12a** and **12b** were obtained with 13% and 12% yield, respectively. In analogy, the condensation of SF_5-substituted aldehyde **1b** with PFP-DPM led to the AB_2-type corrole **13**. PFP-DPM was obtained according to the literature by condensation of PFBA with an excess of pyrrole under TFA catalysis.[9a]

Scheme 5. Synthesis of SF_5-Substituted A_2B- and AB_2-Corroles



12a X = F 13%
12b X = Cl 12%

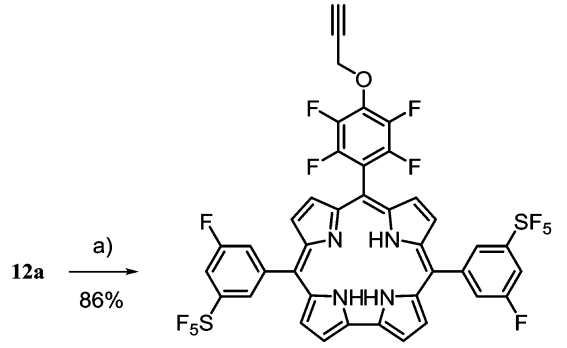


13

[a]Reaction conditions: (1) pentafluorobenzaldehyde (1 equiv), HCl (37%), MeOH/H_2O = 1:1 (v/v), rt, 1 h; (2) DDQ, rt, 1 h. [b](1) PFP-DPM (1 equiv), HCl (37%), MeOH/H_2O = 1:1 (v/v), rt, 1 h; (2) DDQ, rt, 3 h.

Corroles **12a** and **13** were functionalized with propargyl alcohol,[8d] extending the scope for further reactions, i.e., 1,3-dipolar cycloadditions of the terminal alkyne moiety (Scheme 6; see also below Scheme 7). The substitution reactions

Scheme 6. Reaction of SF_5-Substituted Corroles with Propargyl Alcohol



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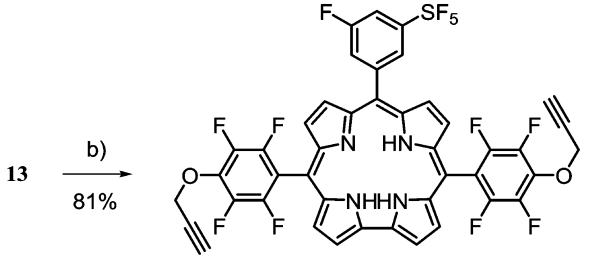

15

[a]Reaction conditions: KOH, DMSO, argon atmosphere, rt, 30 min. [b]KOH, DMSO, argon atmosphere, rt, 60 min.

afforded only the desired products **14** and **15**, respectively, again without any evidence of a *m*-fluorine exchange at the SF_5/F aryl group.

Corroles like **14** or **15** can be used in the construction of multichromophoric systems by coupling them to other (azido-substituted) chromophores via the copper(I)-catalyzed 1,3-dipolar cycloaddition. Such systems are of interest, e.g., in light-harvesting and other optical applications.[16] To principally elucidate this possibility, we investigated the reaction of alkynyl-substituted corrole **14** with the azido-substituted BODIPY **16** (8-(4-azido-2,3,5,6-pentafluorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene).[8e] Reacting **14** with a 1.5-fold excess of **16** in the presence of the copper catalyst and sodium ascorbate yielded within 15 min the corrole–BODIPY heterodimer **17** in acceptable yield. Copper(II) sulfate pentahydrate had to be used in excess as part of the copper is complexed by the corrole in the course of the reaction. The heterodimer **17** is a diamagnetic copper(III) complex[17] which could fully be characterized by NMR spectroscopy.

CONCLUSION

In summary, starting with SF_5-substituted aryl aldehydes, the first synthesis of porphyrinoids, BODIPYs, and their building block precursor DPMs containing the SF_5-group is presented.

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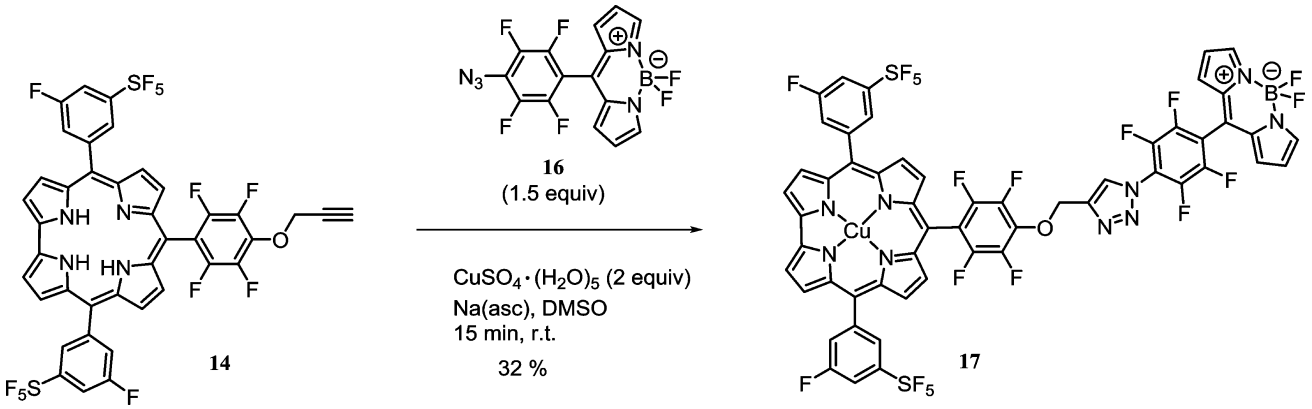
Scheme 7. Synthesis of a BODIPY−Cu(III)corrole Array via 1,3-Dipolar Cycloaddition



An additional functionalization of the resulting tetrapyrroles by the nucleophilic aromatic substitution protocol with alcohols and sodium azide, respectively, allows an efficient access to amphiphilic and multifunctional systems containing the SF_5 group. In these reactions, the SF_5 group exhibited a high chemical resistance giving access to corroles and porphyrins (and their metal complexes) carrying this strongly lipophilic and electron-withdrawing group. These products offer options for further functionalizations and applications in photomedicine, catalysis, and photophysics.[18]

EXPERIMENTAL SECTION

General Methods. Nomenclature and numbering (^{13}C NMR) are in accordance to IUPAC recommendations. Reactions were performed in oven-dried flasks and under inert argon atmosphere if not mentioned otherwise. Solvents were distilled and dried by standard procedures. THF and DMSO were kept over molecular sieves. All liquid reagents were added by syringe. Purchased reagents were used as received without further purification. All reactions were monitored by thin-layer chromatography (TLC) analysis, and detection was done by a variable UV detector (λ = 254/366 nm). Purification was carried out by column chromatography on silica gel (60 M, 40−63 μm). Recrystallization of the porphyrinoids was performed by dissolving the product in a minimum amount of solvent (e.g., DCM) and layering it with a 3-fold excess of the antisolvent (e.g., methanol/water = 9:1, v/v). On slow evaporation of the solvent the crystalline product was obtained. Yields refer to analytically pure samples. NMR spectra were recorded on 250, 400, 500, and 700 MHz instruments. Chemical shifts are reported relative to TMS (^1H: δ = 0.00 ppm), $CHCl_3$ (^1H: δ = 7.26 ppm), and $CDCl_3$ (^{13}C: δ = 77.0 ppm) in acetone-d_6 or DMSO-d_6 solution. Integrals are in accordance with assignments; coupling constants are given in hertz. All ^{13}C NMR spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quintet), m (multiplet), m_c (centered multiplet), dd (doublet of doublets), br s (broad singlet). For detailed peak assignments, 2D spectra were measured (COSY $^1H-^1H$, HMQC $^1H-^{13}C$, and HMBC $^1H-^{13}C$ correlation experiments). The UV−vis spectra were measured using acetone, DCM, or methanol as solvent and quartz cuvettes of 1 cm length. Fluorescence emission spectra were recorded using quartz cuvettes of 1 cm length and acetone as solvent. HRMS analyses were performed by ESI-TOF, the solvent flow rate was adjusted to 4 μL/min, and spray voltage was set to 4 kV. Drying gas flow rate was set to 15 psi (1 bar). All other parameters were adjusted for a maximum abundance of the respective $[M + H]^+$. (ESI-TOF = electrospray ionization − time-of-flight, MALDI-TOF = matrix-assisted laser desorption ionization − time-of-flight). Compound **16** was synthesized according to the literature.[8e]

Synthesis of 5,10,15,20-Tetrakis[5-(pentafluorothio)phenyl]-porphyrin (2a). Dry dichloromethane (450 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After pyrrole (0.29 mL, 4.30 mmol) and 3-(pentafluorothio)-benzaldehyde (**1a**) (1.00 g, 4.30 mmol) were added, the flask was shielded from ambient light, $BF_3{\cdot}OEt_2$ (0.14 mL, 1.20 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then DDQ (0.97 g, 4.30 mmol) was added, the mixture was stirred for additional 2 h and after cooling to room temperature filtered over silica gel, and the solvent was evaporated. After column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallization [DCM/(methanol/water = 95:5)] the product was obtained as purple crystals (0.43 g, 36%). Mp > 300 °C. ^1H NMR (500 MHz, $CDCl_3$): δ −2.87 (s, 2H), 7.91 (t, J = 8.2 Hz, 4H), 8.23 (ddd, J = 8.6, 2.2, 0.9 Hz, 4H), 8.34−8.42 (m, 4H), 8.62−8.68 (m, 4H), 8.85 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 118.5, 125.7, 127.3, 131.4, 137.1, 142.8, 152.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.47 (d, $^2J_{F-F}$ = 149.6 Hz, 16F), 84.13 (quin, t, $^2J_{F-F}$ = 152.6, $^4J_{H-F}$ = 26.8 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{27}F_{20}N_4S_4$ $[M + H]^+$ 1119.0799, found 1119.0815. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 414 (5.33), 507 (4.09), 584 (3.41), 655 (1.51) nm.

Synthesis of 5,10,15,20-Tetrakis[3-fluoro-5-(pentafluoro-thio)phenyl]porphyrin (2b). Dry dichloromethane (1500 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After pyrrole (0.85 mL, 12.7 mmol) and 3-fluoro-5-(pentafluorothio)benzaldehyde (**1b**) (3.17 g, 12.7 mmol) were added, the flask was shielded from ambient light, $BF_3{\cdot}OEt_2$ (0.45 mL, 3.60 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then DDQ (2.90 g, 12.8 mmol) suspended in dry dichloromethane (100 mL) was added, the mixture was refluxed for 2 h and after cooling to room temperature filtered over silica gel, and the solvent was evaporated. After column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallization (DCM/methanol) the product was obtained as purple crystals (1.45 g, 39%). Mp: 279 °C. ^1H NMR (500 MHz, $CDCl_3$): δ −2.92 (s, 2H), 8.02 (dt, J = 8.7, 1.8 Hz, 4H), 8.16 (d, J = 8.0 Hz, 4H), 8.49 (s, 4H), 8.91 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 114.2 (d, quin, $^{2,3}J_{C-F}$ = 26.6, 5.9 Hz), 117.5, 124.6 (d, $^2J_{C-F}$ = 22.2 Hz), 127.6 (d, $^3J_{C-F}$ = 7.7 Hz), 131.4, 144.1, 153.1 (td, $^{2,3}J_{C-F}$ = 18.3, 7.0 Hz), 160.3 (d, $^2J_{C-F}$ = 252.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.64 (d, $^2J_{F-F}$ = 150.0 Hz, 16F), 82.71 (q, $^2J_{F-F}$ = 150.8 Hz, 4F), −111.17 (t, $^3J_{H-F}$ = 10.2 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{23}F_{24}N_4S_4$ $[M + H]^+$ 1191.0422, found 1191.0462. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 414.5 (5.29), 506.5 (3.98), 583.5 (3.39), 655 (1.48) nm.

Synthesis of 5,10,15,20-Tetrakis[3-chloro-5-(pentafluoro-thio)phenyl]porphyrin (2c). Dry dichloromethane (440 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After pyrrole (0.25 mL, 3.70 mmol) and 3-chloro-5-(5-pentafluorothio)benzaldehyde (**1c**) (1.00 g, 3.70 mmol) were added, the flask was shielded from ambient light, $BF_3{\cdot}OEt_2$ (0.13 mL, 1.00 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then, DDQ (0.84 g, 3.70 mmol) suspended in dry dichloromethane (100 mL) was added, the mixture was refluxed for 2 h and after cooling to room temperature filtered over silica gel, and the solvent was evaporated. After column chromatography (silica

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gel, DCM/*n*-hexane = 1:1) and recrystallization (DCM/methanol) the product was obtained as purple crystals (0.35 g, 30%). Mp: 289 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −2.95 (s, 2H), 8.25 (t, J = 2.0 Hz, 4H), 8.36−8.39 (m, 4H), 8.51−8.54 (m, 4H), 8.87 (s, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 117.4, 126.2, 129.6, 133.4, 136.9, 143.6, 152.9 (q, $^2J_{C-F}$ = 16.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.71 (d, $^2J_{F-F}$ = 151.0 Hz, 16F), 82.51 (qt, $^2J_{F-F}$ = 147.7, $^4J_{H-F}$ = 13.2 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{23}Cl_4F_{20}N_4S_4$ [M + H]$^+$ 1254.9240, found 1254.9075. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 415 (5.40), 507 (4.12), 584 (3.42), 656 (1.59) nm.

Synthesis of [5,10,15,20-Tetrakis[5-(pentafluorothio)-phenyl]porphyrinato]zinc(II) (3a). 5,10,15,20-Tetrakis[5-(pentafluorothio)phenyl]porphyrin (**2a**) (121 mg, 108 μmol) was placed in a round-bottom flask and dissolved with 15 mL of a DCM/methanol (4:1, v/v) mixture. Zinc(II) acetate (5.06 g, 23.0 mmol) and sodium acetate (0.26 g, 3.17 mmol) were added, and the mixture was stirred at room temperature for 6 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallization [DCM/(methanol/water = 9:1)] to obtain pink crystals (127 mg, 99%). Mp > 300 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.90−7.97 (m, 4H), 8.26 (ddd, J = 8.6, 2.3, 1.0 Hz, 4H), 8.40−8.45 (m, 4H), 8.66−8.69 (m, 4H), 8.96−9.00 (m, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 119.4, 125.4, 127.1, 131.3, 132.4, 136.9, 143.2, 150.1, 152.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 61.92 (d, $^2J_{F-F}$ = 149.6 Hz, 16F), 82.71 (qt, $^2J_{F-F}$ = 144.8, $^4J_{H-F}$ = 22.5 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{24}F_{20}N_4S_4Zn$ [M]$^+$ 1179.9856, found 1179.9884, calcd for $C_{44}H_{25}F_{20}N_4S_4Zn$ [M + H]$^+$ 1180.9929, found 1180.9915. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 424 (5.51), 556 (4.21) nm.

Synthesis of [5,10,15,20-Tetrakis[3-fluoro-5-(pentafluorothio)phenyl]porphyrinato]zinc(II) (3b). 5,10,15,20-Tetrakis[3-fluoro-5-(pentafluorothio)phenyl]porphyrin (**2b**) (208 mg, 174 μmol) was placed in a round-bottom flask and dissolved with 15 mL of a DCM/methanol (4:1, v/v) mixture. Zinc(II) acetate (5.06 g, 23.0 mmol) and sodium acetate (0.26 g, 3.17 mmol) were added, and the mixture was stirred at room temperature for 6 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallization [DCM/(methanol/water = 9:1)] to obtain pink crystals (210 mg, 99%). Mp > 300 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.03 (dt, J = 8.8, 2.2 Hz, 4H), 8.17 (d, J = 7.8 Hz, 4H), 8.49 (t, J = 1.7 Hz, 4H), 9.01−9.03 (m, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 113.8 (d, $^2J_{C-F}$ = 26.6 Hz), 118.4, 124.3, 127.4 (d, $^3J_{C-F}$ = 7.7 Hz), 132.5, 144.7, 149.9, 152.8, 160.1 (d, $^2J_{C-F}$ = 251.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.06 (d, $^2J_{F-F}$ = 149.9 Hz, 4F), 81.07 (q, $^2J_{F-F}$ = 149.8 Hz, 1F), −112.41 to −112.77 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{20}F_{24}N_4S_4Zn$ [M]$^+$ 1251.9479, found 1251.9399. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 422 (5.42), 555.5 (4.03) nm.

Synthesis of [5,10,15,20-Tetrakis[3-chloro-5-(pentafluorothio)phenyl]porphyrinato]zinc(II) (3c). 5,10,15,20-Tetrakis[3-chloro-5-(pentafluorothio)phenyl]porphyrin (**2c**) (114 mg, 90.9 μmol) was placed in a round-bottom flask and dissolved with 15 mL of a DCM/methanol (4:1, v/v) mixture. Zinc(II) acetate (5.06 g, 23.0 mmol) and sodium acetate (0.26 g, 3.17 mmol) were added, and the mixture was stirred at room temperature for 6 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallization [DCM/(methanol/water = 9:1)] to obtain pink crystals (117 mg, 99%). Mp > 300 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.28 (t, J = 1.9 Hz, 4H), 8.41−8.44 (m, 4H), 8.57 (dt, $^4J_{H-F}$ = 3.8, $^4J_{H-H}$ = 1.8 Hz, 4H), 9.01 (s, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 118.3, 126.0, 129.5, 132.5, 133.1, 136.8, 144.4, 150.0, 152.8 (q, $^2J_{C-F}$ = 19.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 61.92 (d, $^2J_{F-F}$ = 149.6 Hz, 16F), 82.71 (qt, $^2J_{F-F}$ = 145.0, $^4J_{H-F}$ = 22.5 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{21}Cl_4F_{20}N_4S_4Zn$ [M + H]$^+$ 1319.8374, found 1319.8301. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 423 (5.01), 555 (3.97) nm.

Synthesis of [5,10,15,20-Tetrakis[5-(pentafluorothio)-phenyl]porphyrinato]palladium(II) (4a). 5,10,15,20-Tetrakis[5-(pentafluorothio)phenyl]porphyrin (**2a**) (100 mg, 89.3 μmol) was placed in a round-bottom flask and dissolved with 16 mL of a DCM/methanol (7:1, v/v) mixture. Palladium(II) acetate (180 mg, 0.80 mmol) and sodium acetate (30 mg, 0.37 mmol) were added, and the mixture was stirred at room temperature for 24 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:2) and recrystallization [DCM/(methanol/water = 9:1)] to obtain pink crystals (89 mg, 77%). Mp > 300 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.89−7.94 (m, 4H), 8.25 (ddd, J = 8.7, 2.3, 0.9 Hz, 4H), 8.34−8.39 (m, 4H), 8.61−8.64 (m, 4H), 8.81−8.85 (m, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ = 120.1, 125.7, 127.3, 131.0, 131.4, 136.6, 141.5, 142.2, 152.7 (q, $^2J_{C-F}$ = 19.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.46 (d, $^2J_{F-F}$ = 150.9 Hz, 16F), 84.11 (q, $^2J_{F-F}$ = 150.9 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{24}F_{20}N_4PdS_4$ [M]$^+$ 1223.9603, found 1223.9676. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 422 (4.76), 554.5 (3.53) nm.

Synthesis of [5,10,15,20-Tetrakis[3-fluoro-5-(pentafluorothio)phenyl]porphyrinato]palladium(II) (4b). 5,10,15,20-Tetrakis-[3-fluoro-5-(pentafluorothio)phenyl]porphyrin (**2b**) (105 mg, 88.2 μmol) was placed in a round-bottom flask and dissolved with 15 mL of a DCM/methanol (4:1, v/v) mixture. Palladium(II) acetate (180 mg, 0.80 mmol) and sodium acetate (30 mg, 0.37 mmol) were added, and the mixture was stirred at room temperature for 6 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:2) and recrystallization [DCM/(methanol/water = 9:1)] to obtain pink crystals (110 mg, 96%). Mp > 300 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.03 (dt, J = 8.8, 2.2 Hz, 4H), 8.13 (d, J = 7.4 Hz, 4H), 8.43−8.47 (m, 4H), 8.88 (s, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 114.2 (d, $^2J_{C-F}$ = 26.6 Hz), 119.1, 124.1, 127.1, 131.5, 141.4, 143.6, 143.7, 153.0, 160.2 (d, $^2J_{C-F}$ = 252.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.61 (d, $^2J_{F-F}$ = 151.1 Hz, 16F) 84.13 (q, $^2J_{F-F}$ = 151.1, 4F), −110.39 to −110.75 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{19}F_{24}N_4PdS_4$ [M + H]$^+$: 1292.9133, found 1292.9262. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 422.5 (5.02), 556 (4.11) nm.

Synthesis of [5,10,15,20-Tetrakis[3-chloro-5-(pentafluorothio)phenyl]porphyrinato]palladium(II) (4c). 5,10,15,20-Tetrakis-[3-chloro-5-(pentafluorothio)phenyl]porphyrin (**2c**) (105 mg, 83.7 μmol) was placed in a round-bottom flask and dissolved with 15 mL of a DCM/methanol (9:1, v/v) mixture. Palladium(II) acetate (180 mg, 0.80 mmol) and sodium acetate (30 mg, 0.37 mmol) were added, and the mixture was stirred at room temperature for 24 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was purified by column chromatography (silica gel, DCM/*n*-hexane = 1:2) and recrystallization [DCM/(methanol/water = 9:1)] to obtain pink crystals (93 mg, 81%). Mp > 300 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.27 (t, J = 1.9 Hz, 4H), 8.35−8.40 (m, 4H), 8.51−8.54 (m, 4H), 8.87 (s, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 119.0, 126.3, 129.2, 131.5, 133.5, 136.5, 141.4, 143.3, 152.9 (q, $^2J_{C-F}$ = 18.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.70 (d, $^2J_{F-F}$ = 150.9 Hz, 16F), 82.49 (q, $^2J_{F-F}$ = 152.5 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{19}Cl_4F_{20}N_4PdS_4$ [M + H]$^+$ 1356.7962, found 1356.8046. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 423 (4.83), 554.5 (3.79) nm.

Synthesis of 5-[3-(Pentafluorothio)phenyl]dipyrromethane (5a). A 50 mL, two-necked, round-bottom flask was loaded under argon atmosphere with pyrrole (21.8 mL, 0.31 mol) and 5-(pentafluorothio)benzaldehyde (**1a**) (2.00 g, 8.61 mmol). After 15 min, BF_3·OEt_2 (57 μL, 0.74 mmol) was added and the mixture stirred for 20 min at room temperature. Afterward, the excess pyrrole was evaporated under reduced pressure at 60 °C and the resulting dark oil purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) to obtain a bright yellow, viscous oil (1.86 g, 62%). Mp: 110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.51 (s, 1H), 5.88−5.90 (m, 2H), 6.18−6.21 (m, 2H), 6.71−6.72 (m, 2H), 7.34 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.64−7.68 (m, 2H), 7.91 (br s, 2H). ^{13}C NMR (128 MHz, $CDCl_3$): δ 43.96, 107.8, 108.7, 118.0, 124.6 (q, $^3J_{C-F}$ = 4.0 Hz),

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125.9 (q, $^{3}J_{C-F}$ = 4.3 Hz), 128.8, 131.3, 131.6, 143.5, 154.2 (q, $^{2}J_{C-F}$ = 17.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.97 (d, $^{2}J_{F-F}$ = 148.6 Hz, 4F), 84.67 (q, $^{2}J_{F-F}$ = 149.9 Hz, 1F). HRMS (ESI-TOF): m/z calcd for $C_{15}H_{14}F_5N_2S$ $[M + H]^+$ 349.0792, found 349.0692. Anal. calcd for $C_{15}H_{13}F_5N_2S$ (348.0): C, 51.72; H, 3.76; N, 8.04; S, 9.20. Found: C, 51.70; H, 3.75; N, 8.03; S, 9.20.

Synthesis of 5-[3-Fluoro-5-(pentafluorothio)phenyl]-dipyrromethane (5b). A 100 mL, two-necked, round-bottom flask was loaded under argon atmosphere with pyrrole (20 mL, 0.29 mol) and 3-fluoro-5-(pentafluorothio)benzaldehyde (**1b**) (2.00 g, 7.99 mmol). After 15 min, TFA (57 μL, 0.74 mmol) was added and the mixture stirred for 20 min at room temperature. Afterward, the excess pyrrole was evaporated under reduced pressure at 60 °C and the resulting dark oil purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallyzation (DCM/*n*-pentane) to obtain a pale white-yellow solid (2.10 g, 72%). Mp: 123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.51 (s, 1H), 5.88−5.90 (m, 2H), 6.18−6.21 (m, 2H), 6.72−6.74 (m, 2H), 7.06 (t, J = 1.8 Hz, 1H), 7.39 (t, J = 2.2 Hz, 1H), 7.46 (t, J = 1.7 Hz, 1H), 7.91 (br s, 2H). ^{13}C NMR (128 MHz, $CDCl_3$): δ 43.7, 107.8, 108.8, 112.6 (dq, $^{2,3}J_{C-F}$ = 26.7, 4.5 Hz), 118.1, 118.7 (d, $^{2}J_{C-F}$ = 21.7 Hz), 121.6−121.9, 130.5, 145.7, 154.4 (qd, $^{2,3}J_{C-F}$ = 18.8, 8.4 Hz), 161.7 (d, $^{1}J_{C-F}$ = 250.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.08 (d, $^{2}J_{F-F}$ = 150.0 Hz, 4F), 83.11 (q, $^{2}J_{F-F}$ = 150.5, 1F), −109.28 (t, $^{3}J_{H-F}$ = 8.7 Hz, 1F). HRMS (ESI-TOF): m/z calcd for $C_{15}H_{11}F_6N_2S$ $[M - H]^+$ 365.0542, found 365.0547. Anal. calcd for $C_{15}H_{12}F_6N_2S$ (366.0): C, 49.18; H, 3.30; N, 7.65; S, 8.75. Found: C, 49.16; H, 3.27; N, 7.64; S, 8.72.

Synthesis of 5-[3-Chloro-5-(pentafluorothio)phenyl]dipyrromethane (5c). A 100 mL, two-necked, round-bottom flask was loaded under argon atmosphere with pyrrole (19.0 mL, 0.27 mol) and 3-chloro-5-(pentafluorothio)benzaldehyde (**1c**) (2.00 g, 7.50 mmol). After 15 min, TFA (57 μL, 0.74 mmol) was added and the mixture stirred for 20 min at room temperature. Afterward, the excess pyrrole was evaporated under reduced pressure at 60 °C and the resulting dark oil purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallyzation (DCM/*n*-pentane) to obtain a pale white-yellow solid (2.28 g, 80%). Mp: 117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.49 (s, 1H), 5.88−5.90 (m, 2H), 6.18−6.21 (m, 2H), 6.72−6.74 (m, 2H), 7.32 (t, J = 1.7 Hz, 1H), 7.53 (t, J = 1.8 Hz, 1H), 7.66 (t, J = 2.0 Hz, 1H), 7.90 (br s, 2H). ^{13}C NMR (128 MHz, $CDCl_3$): δ 43.7, 108.1, 108.9, 118.3, 124.3 (q, $^{3}J_{C-F}$ = 4.9 Hz), 145.2, 154.4 (q, $^{2}J_{C-F}$ = 17.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.71 (d, $^{2}J_{F-F}$ = 150.3 Hz, 4F), 82.50 (qt, $^{2}J_{F-F}$ = 148.2, $^{4}J_{H-F}$ = 12.7 Hz, 1F). HRMS (ESI-TOF): m/z calcd for $C_{15}H_{10}ClF_5N_2S$ $[M - 2H]^+$ 381.0246, found 381.0208. Anal. calcd for $C_{15}H_{13}ClF_5N_2S$ (383.7): C, 46.94; H, 3.41; N, 7.30; S, 8.35. Found: C, 47.00; H, 3.24; N, 7.09; S, 8.35.

Synthesis of 5,15-Bis(pentafluorophenyl)-10,20-bis[3-(pentafluorothio)phenyl)]porphyrin (6a). Dry dichloromethane (500 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After pentafluorobenzaldehyde (0.24 mL, 2.00 mmol) and 5-(pentafluorothio)phenyldipyrromethane (**5a**) (696 mg, 2.00 mmol) were added, the flask was shielded from ambient light. $BF_3{\cdot}OEt_2$ (0.12 mL, 1.00 mmol) was added and the reaction mixture stirred at room temperature for 18 h. Then, DDQ (0.70 g, 0.30 mmol) suspended in dry dichloromethane (50 mL) was added and the mixture stirred for 2 h, filtered over silica gel, and evaporated to dryness. After column chromatography (silica gel, DCM/*n*-hexane = 1:3) and recrystallization (DCM/MeOH:H_2O = 95:5) the product was obtained as purple crystals (220 mg, 20%). Mp: 228 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −2.80 (s, 2H), 7.94 (t, J = 7.9 Hz, 2H), 8.28 (ddd, J = 8.6, 2.3, 1.0 Hz, 2H), 8.39 (d, J = 7.4 Hz, 2H), 8.69 (t, J = 1.9 Hz, 2H), 8.84−8.97 (m, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 102.1, 115.8 (t, J = 19.8 Hz), 120.0, 125.9, 127.3, 131.1, 137.1, 137.57 (dt, $^{1,2}J_{C-F}$ = 252.9, 14.5 Hz), 142.0 (d, $^{1}J_{C-F}$ = 258.5 Hz), 142.1, 146.5 (d, $^{1}J_{C-F}$ = 250.1 Hz), 152.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.49 (d, $^{2}J_{F-F}$ = 149.8 Hz, 8F), 82.45 (q, $^{2}J_{F-F}$ = 150.3 Hz, 2F), −136.19 to −136.89 (m, 4F), −151.55 (t, J = 20.8 Hz, 2F), −161.08 to −161.66 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{19}F_{20}N_4S_2$ $[M + H]^+$ 1047.0726, found 1047.0724. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 416.5 (5.25), 510 (4.21), 584 (3.54), 650 (2.58) nm.

Synthesis of 5,15-Bis(pentafluorophenyl)-10,20-bis[3-fluoro-5-(pentafluorothio)phenyl)]porphyrin (6b). Dry dichloromethane (500 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After PFBA (0.25 mL, 2.00 mmol) and 5-[3-fluoro-5-(pentafluorothio)phenyl]dipyrromethane (**5b**) (732 mg, 2.00 mmol) were added, the flask was shielded from ambient light. $BF_3{\cdot}OEt_2$ (0.24 mL, 2.00 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then, DDQ (0.70 g, 0.30 mmol) suspended in dry dichloromethane (50 mL) was added, and the mixture was stirred for 2 h. The mixture filtered over silica and the solvent evaporated. After column chromatography (silica gel, DCM/*n*-hexane = 1:2) and recrystallization (DCM/MeOH:H_2O = 95:5) the product was obtained as purple crystals (81 mg, 9%). Mp 207 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −2.93 (s, 2H), 8.00 (dt, $^{3}J_{H-F}$ = 8.8 Hz, $^{4}J_{H-H}$ = 2.2 Hz, 2H), 8.13 (d, $^{3}J_{H-F}$ = 8.2 Hz, 2H), 8.46 (dt, $^{4}J_{H-F}$ = 5.2 Hz, $^{4}J_{H-H}$ = 1.7 Hz), 8.89 (br s). ^{13}C NMR: (176 MHz, $CDCl_3$): δ 103.3, 114.2 (d, $^{2}J_{C-F}$ = 25.3 Hz), 115.8, 117.6, 124.5 (d, $^{2}J_{C-F}$ = 21.3 Hz), 127.4, 137.5 (d, $^{1}J_{C-F}$ = 255.0 Hz), 142.2 (d, $^{1}J_{C-F}$ = 253.1 Hz), 143.74 (d, $^{3}J_{C-F}$ = 7.4 H), 146.5 (d, $^{1}J_{C-F}$ = 253.9 Hz), 153.0, 160.2 (d, $^{1}J_{C-F}$ = 252.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.62 (d, $^{2}J_{F-F}$ = 150.0 Hz, 8F), 82.43 (q, $^{2}J_{F-F}$ = 150.7 Hz, 2F), −110.50 to −110.66 (m, 2F), −136.45 to −136.88 (m, 2F), −151.26 (t, J = 20.9 Hz, 2F), −161.12 to −161.45 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{17}F_{22}N_4S_2$ $[M + H]^+$ 1083.0543, found 1083.0503. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 417 (5.11), 509 (4.15), 585 (3.39), 652 (2.49) nm.

Synthesis of 5,15-Bis(pentafluorophenyl)-10,20-bis[3-chloro-5-(pentafluorothio)phenyl)]porphyrin (6c). Dry dichloromethane (500 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After PFBA (0.25 mL, 2.00 mmol) and 5-[3-chloro-5-(pentafluorothio)phenyl]dipyrromethane (**5c**) (765 mg, 2.00 mmol) were added, the flask was shielded from ambient light. $BF_3{\cdot}OEt_2$ (0.24 mL, 2.00 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then, DDQ (0.70 g, 0.30 mmol) suspended in dry dichloromethane (50 mL) was added, and the mixture was stirred for 2 h. The mixture filtered over silica gel and the solvent evaporated. After column chromatography (silica gel, DCM/*n*-hexane = 1:3) and recrystallization (DCM/MeOH:H_2O = 95:5), the product was obtained as purple crystals (123 mg, 11%). Mp: 211 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −2.89 (s, 2H), 8.29 (t, J = 1.9 Hz, 2H), 8.42 (dt, $^{4}J_{H-F}$ = 7.4 Hz, $^{4}J_{H-H}$ = 1.7 Hz, 2H), 8.58 (dt, $^{4}J_{H-F}$ = 8.7 Hz, $^{4}J_{H-H}$ = 1.8 Hz, 2H), 8.93 (s, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 103.4, 115.8 (t, J = 19.7 Hz), 117.5, 126.2, 129.6, 133.5, 136.9 (d, $^{3}J_{C-F}$ = 3.6 Hz), 137.5 (d, $^{1}J_{C-F}$ = 253.2 Hz), 142.2 (d, $^{1}J_{C-F}$ = 251.2 Hz), 143.3, 146.5 (d, $^{1}J_{C-F}$ = 251.2 Hz), 152.9 (q, $^{2}J_{C-F}$ = 19.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.71 (d, $^{2}J_{F-F}$ = 150.3 Hz, 8F), 82.45 (q, $^{2}J_{F-F}$ = 150.5 Hz, 2F), −136.44 to −136.89 (m, 4F), −151.22 (t, J = 20.7 Hz, 2F), −161.09 to −161.46 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{17}Cl_2F_{20}N_4S_2$ $[M + H]^+$ 1114.9947, found 1114.9956. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 416.5 (5.22), 511 (4.26), 584 (3.43), 654 (2.68) nm.

Synthesis of 5,15-Bis(3-acetoxyphenyl)-10,20-bis[3-fluoro-5-(pentafluorothio)phenyl)]porphyrin (7a). Dry dichloromethane (500 mL) was placed in a 1 L, three-necked flask equipped with a magnetic stirrer and argon gas inlet. After 3-acetoxybenzaldehyde (0.28 mL, 2.00 mmol) and [3-fluoro-5-(pentafluorothio)phenyl]-dipyrromethane (**5b**) (732 mg, 2.00 mmol) were added, the flask was shielded from ambient light. Trifluoroacetic acid (0.17 mL, 2.00 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then, DDQ (0.70 g, 0.30 mmol) suspended in dry dichloromethane (50 mL) was added, and the mixture was stirred for 2 h. Triethylamine (0.27 mL, 2.00 mmol) was added, after 15 min, the mixture filtered over silica gel, and the solvent was evaporated. After column chromatography (silica gel, DCM/*n*-hexane = 1:1) and recrystallization (DCM/MeOH:H_2O = 95:5) the product was obtained as purple crystals (90 mg, 9%). Mp: 189 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −2.90 (s, 2H), 2.39 (s, 6H), 7.55−7.59 (m, 2H), 7.77−7.81 (m, 2H), 7.96 (t, J = 2.1 Hz, 1H), 7.97 (m, 3H), 8.06−8.09 (m, 2H), 8.09−8.15 (m, 2H), 8.42−8.49 (m, 2H), 8.78−8.48 (m, 4H), 8.96−9.03 (m, 4H). ^{13}C NMR (176 MHz, $CDCl_3$): δ

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21.2, 113.7 (d, $^2J_{C-F}$ = 25.8 Hz), 116.6, 119.9, 121.3, 124.5 (d, $^2J_{C-F}$ = 21.1 Hz), 127.5, 127.8, 128.0, 132.1, 142.7, 144.6, 149.3, 152.8, 160.1 (d, $^1J_{C-F}$ = 251.9 Hz), 169.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.64 (d, $^2J_{F-F}$ = 150.0 Hz, 8F), 82.71 (q, $^2J_{F-F}$ = 150.7 Hz, 2F), −111.04 − −111.26 (m, 2F). HRMS (ESI-TOF): m/z calcd for $C_{48}H_{31}F_{12}N_4O_4S_2$ $[M + H]^+$: 1019.1595, found: 1019.1553. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1} · cm^{-1})]: 417 (5.47), 512 (4.35), 585 (3.61), 655 (2.52) nm.

Synthesis of 5,15-Bis(3-acetoxyphenyl)-10,20-bis[3-chloro-5-(pentafluorothio)phenyl)]porphyrin (7b). Dry dichloromethane (500 mL) was placed in a three-necked flask equipped with a magnetic stirrer and argon gas inlet. After 3-acetoxybenzaldehyde (0.28 mL, 2.00 mmol) and 5-[3-chloro-5-(pentafluorothio)]dipyrromethane (**5c**) (0.76 g, 2.00 mmol) were added, the flask was shielded from ambient light. Trifluoroacetic acid (0.33 mL, 4.00 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. Then, DDQ (0.70 g, 0.30 mmol) suspended in dry dichloromethane (50 mL) was added, and the mixture was stirred for 2 h. Triethylamine (1.0 mL, 7.00 mmol) was added, after 15 min, the mixture was filtered over silica gel, and the solvent was evaporated. After column chromatography (silica gel, DCM/*n*-hexane = 1:2) and recrystallization (DCM/methanol), the product was obtained as purple crystals (94 mg, 18%). Mp: 196 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −2.91 (s, 2H), 2.39 (s, 6H), 7.54−7.59 (m, 2H), 7.78 (t, J = 7.9 Hz, 2H), 7.97 (t, J = 2.0 Hz, 2H), 8.06−8.11 (m, 2H), 8.22 (t, J = 1.9 Hz, 2H), 8.35−8.40 (m, 2H), 8.51−8.56 (m, 2H), 8.80 (s, 4H), 8.99 (s, 4H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 21.2, 116.5, 119.9, 121.3, 125.9, 127.8, 128.0, 129.6, 132.1, 133.2, 137.0, 142.7, 144.2, 149.3, 152.8 (q, $^2J_{C-F}$ = 18.3 Hz), 169.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.72 (d, $^2J_{F-F}$ = 150.1 Hz, 8F), 82.72 (q, $^2J_{F-F}$ = 150.8 Hz, $^4J_{H-F}$ = 13.2 Hz, 2F). HRMS (ESI-TOF): m/z calcd for $C_{48}H_{31}Cl_2F_{10}N_4O_4S_2$ $[M + H]^+$: 1051.1004, found: 1051.0954. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}· cm^{-1})]: 417 (5.38), 510 (4.31), 585.5 (3.23), 655 (2.44) nm.

Synthesis of 5,10,15-Tris[3-fluoro-5-(pentafluorothio)-phenyl]-20-[3-(2-propyn-1-oxy)-5-pentafluorothio)phenyl]-porphyrin (8a), Bis[3-fluoro-5-(pentafluorothio)phenyl]bis[3-(2-propyn-1-oxy)-5-pentafluorothio)phenyl]porphyrins (8b), and 5-[3-Fluoro-5-(pentafluorothio)phenyl]-10,15,20-tris[3-(2-propyn-1-oxy)-5-pentafluorothio)phenyl]porphyrin (8c). Under argon atmosphere 5,10,15,20-tetrakis[3-fluoro-5-(pentafluorothio)-phenyl]porphyrin (**2b**) (63.4 mg, 53.2 μmol) was dissolved with 2.0 mL of dry THF in a 50 mL, two-necked, round-bottom flask. Propargyl alcohol (1.0 mL, 17.3 mmol) and KOH (200 mg, 3.50 mmol) were added, and the reaction mixture was stirred at 60 °C for 24 h. Water was added after cooling to room temperature. After aqueous workup, drying over sodium sulfate, purification by column chromatography (silica gel, DCM/*n*-hexane = 1:1), and recrystallization (DCM/methanol), three fractions were obtained as purple crystals (**8a**, 18 mg, 28%; **8b**, 12 mg, 18%; **8c**, 6 mg, 9%).

Characterization Data of ***8a***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.92 (s, 2H), 2.66 (t, J = 2.7 Hz, 1H), 4.96 (d, J = 2.3 Hz, 2H), 7.89 (t, J = 2.2 Hz, 1H), 8.01 (dt, $^3J_{H-F}$ = 8.7, $^4J_{H-H}$ = 2.2 Hz, 3H), 8.04 (br s, 1H), 8.12−8.18 (m, 3H), 8.29 (br s, 1H), 8.48 (br s, 3H), 8.83−9.03 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 56.7, 77.4, 113.6, 114.0, 114.2, 117.3, 117.4, 119.0, 123.9, 124.5, 124.6, 125.1, 127.6, 131.6, 143.1, 144.2, 153.1, 153.2, 155.7, 160.2 (d, $^2J_{C-F}$ = 251.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.50 (d, $^2J_{F-F}$ = 150.0 Hz, 4F), 63.62 (d, $^2J_{F-F}$ = 150.6 Hz, 12F), 82.52 (q, $^2J_{F-F}$ = 150.6 Hz, 3F), 83.73 (q, $^2J_{F-F}$ = 151.7 Hz, 1F), −110.53 to −111.01 (m, 3F). HRMS (ESI-TOF): m/z calcd for $C_{47}H_{26}F_{23}N_4OS_4$ $[M + H]^+$ 1227.0617, found 1227.0621. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 414 (5.21), 507 (3.77), 582 (3.21), 650 (1.82) nm.

Characterization Data of ***8b***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.91 (s, 2H), 2.66 (t, J = 3.0 Hz, 2H), 4.93−4.97 (m, 4H), 7.88 (t, J = 2.2 Hz, 2H), 8.00 (dt, $^3J_{H-F}$ = 8.7, $^4J_{H-H}$ = 2.2 Hz, 2H), 8.03 (br s, 2H), 8.11−8.18 (m, 2H), 8.28 (br s, 2H), 8.47 (br s, 2H), 8.82−9.00 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 56.7, 77.4, 113.6, 113.9, 114.1, 117.1, 117.2, 118.7, 118.8, 123.9, 124.5, 124.6, 125.1, 127.6, 131.6, 143.2, 144.2, 153.1, 153.2, 155.7, 160.2 (d, $^2J_{C-F}$ = 252.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.50 (d, $^2J_{F-F}$ = 150.0 Hz, 8F), 63.62 (d, $^2J_{F-F}$ = 150.5 Hz, 8F), 81.64−84.77 (m, 4F), −110.53 to −111.01 (m, 2F). HRMS (ESI-TOF): m/z calcd for $C_{50}H_{29}F_{22}N_4O_2S_4$ $[M + H]^+$ 1263.0817, found 1263.0820. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}· cm^{-1})]: 414 (5.17), 507.5 (3.64), 582 (3.15), 650 (1.78) nm.

Characterization Data of ***8c***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.91 (s, 2H), 2.63−2.67 (m, 3H), 4.94 (br s, 6H), 7.86 (t, J = 2.2 Hz, 3H), 7.98 (dt, $^3J_{H-F}$ = 8.7, $^4J_{H-H}$ = 2.2 Hz, 1H), 8.02 (br s, 3H), 8.09−8.17 (m, 1H), 8.27 (br s, 3H), 8.46 (br s, 1H), 8.79−8.99 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 56.6, 77.4, 113.5, 114.0, 116.8, 116.8, 118.4, 123.8, 124.5, 125.0, 127.5, 143.1, 144.3, 153.1, 155.6, 160.1 (d, $^2J_{C-F}$ = 250.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.49 (d, $^2J_{F-F}$ = 150.0 Hz, 12F), 63.62 (d, $^2J_{F-F}$ = 150.4 Hz, 4F), 81.71−84.90 (m, 4F), −110.56 to −111.15 (m, 1F). HRMS (ESI-TOF): m/z calcd for $C_{53}H_{32}F_{21}N_4O_3S_4$ $[M + H]^+$ 1299.1016, found 1299.0995. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 414.5 (5.19), 507 (3.71), 582 (3.03), 651 (1.45) nm.

Synthesis of 5,15-Bis[4-(2-propyne-1-oxy)-2,3,5,6-tetrafluorophenyl]-10,20-bis[3-chloro-5-(pentafluorothio)phenyl]-porphyrin (9a). 5,15-Bis(pentafluorophenyl)-10,20-bis[3-chloro-5-(pentafluorothio)phenyl]porphyrin (**6c**) (28.0 mg, 25.1 μmol) was dissolved in dry DMSO (1.5 mL) under argon atmosphere, KOH (36.6 mg, 0.65 mmol), and propargyl alcohol (68.0 μL, 1.26 mmol) were added, and the reaction mixture was stirred at room temperature for 20 min. After aqueous workup, extraction with ethyl acetate, and drying over sodium sulfate, the crude product was evaporated to dryness, purified by column chromatography (DCM/*n*-hexane = 1:2) and recrystallized (silica gel, DCM/*n*-hexane) to obtain purple crystals (22 mg, 68%). Mp: 276 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.91 (s, 2H), 2.81 (t, J = 2.4 Hz, 2H), 5.22 (d, J = 2.4 Hz, 4H), 8.25 (t, J = 2.0 Hz, 2H), 8.42 (dt, $^4J_{H-F}$ = 5.7 Hz, $^4J_{H-H}$ = 1.6 Hz, 2H), 8.58 (dt, $^4J_{H-F}$ = 6.6 Hz, $^4J_{H-H}$ = 1.7 Hz, 2H), 8.85−9.00 (m, 8H). ^{13}C NMR (176 MHz, $CDCl_3$): 62.0 (t, $^3J_{C-F}$ = 3.8 Hz), 77.2, 77.8, 104.3, 115.3, 117.4, 126.3, 129.7, 133.5, 137.1, 143.6, 153.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.71 (d, $^2J_{F-F}$ = 150.6 Hz, 8F), 81.95−83.42 (m, 2F), −138.18 to −138.74 (m, 4F), −155.22 to −155.82 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{50}H_{23}Cl_2F_{18}N_4O_2S_2$ $[M + H]^+$ 1186.0274, mass could not be detected. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}· cm^{-1})]: 416 (4.97), 509 (3.21), 581 (2.89), 654 (1.15) nm.

Synthesis of 5,15-Bis[4-(1-oxybut-2-yne-4-ol)-2,3,5,6-tetrafluorophenyl]-10,20-bis[3-chloro-5-(pentafluorothio)phenyl]-porphyrin (9b). 5,15-Bis(pentafluorophenyl)-10,20-bis[3-chloro-5-(pentafluorothio)phenyl]porphyrin (**6c**) (28.0 mg, 25.1 μmol) was dissolved in dry DMSO (2.0 mL) under argon atmosphere, KOH (34.0 mg, 0.60 mmol) and 1,4-butynediol (104 mg, 1.21 mmol) were added, and the reaction mixture was stirred at room temperature for 20 min. After aqueous workup, extraction with ethyl acetate, and drying over sodium sulfate, the crude product was evaporated to dryness, purified by column chromatography (silica gel, acetone/*n*-hexane = 1:1), and recrystallized (DCM/*n*-hexane) to obtain purple crystals (24 mg, 47%). Mp: 281 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = −2.90 (s, 2H), 4.49 (dt, J = 5.5, 1.9 Hz, 4H), 5.26 (t, J = 1.8 Hz, 4H), 8.29 (t, J = 2.0 Hz, 2H), 8.42 (dt, $^4J_{H-F}$ = 5.3 Hz, $^4J_{H-H}$ = 1.6 Hz, 2H), 8.58 (dt, $^4J_{H-F}$ = 6.2 Hz, $^4J_{H-H}$ = 1.7 Hz, 2H), 8.85−9.03 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 51.2, 62.4 (t, $^4J_{C-F}$ = 3.8 Hz), 79.4, 88.1, 104.3, 115.3 (t, J = 19.3 Hz), 117.4, 126.3, 129.7, 133.5, 137.1 (d, $^3J_{C-F}$ = 2.0 Hz), 141.5 (d, $^1J_{C-F}$ = 253.3 Hz), 143.6, 146.5 (d, $^1J_{C-F}$ = 243.8 Hz), 153.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.71 (d, $^2J_{F-F}$ = 150.2 Hz, 8F), 81.80−83.28 (m, 2F), −138.13 to −138.67 (m, 4F), −155.38 to −155.93 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{52}H_{27}Cl_2F_{18}N_4O_4S_2$ $[M + H]^+$ 1247.0558, found 1247.0544. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 416.5 (5.01), 508.5 (3.49), 581 (3.14), 654 (1.62) nm.

Synthesis of 5,15-Bis(4-azidotetrafluorophenyl)-10,20-bis[3-chloro-5-(pentafluorothio)phenyl)]porphyrin (9c). Dry DMF (1.3 mL) was placed under argon atmosphere in a 25 mL, two-necked flask equipped with a magnetic stirrer. 5,15-Bis-(pentafluorophenyl)-10,20-bis[3-chloro-5-(pentafluorothio)phenyl)]-porphyrin (**6c**) (32.0 mg, 28.7 μmol) and sodium azide (4.50 mg, 68.9 μmol) were added, and the reaction mixture was stirred at 50 °C for 2.5 h. After aqueous workup, extraction with ethyl acetate, purification

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by column chromatography (silica gel, DCM/*n*-hexane = 1:2), and recrystallization (DCM/MeOH:H_2O = 95:5) the product was obtained as purple crystals (13 mg, 38%). Mp: 231 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.91 (s, 2H), 8.27 (t, J = 1.9 Hz, 2H), 8.38−8.42 (m, 2H), 8.54−8.58 (m, 2H), 8.87−8.97 (s, 8H). ^{13}C NMR (128 MHz, $CDCl_3$): δ 103.9, 117.5, 126.4, 129.7, 133.6, 137.0, 140.5 (d, $^1J_{C-F}$ = 252.9 Hz), 143.5, 146.5 (d, $^1J_{C-F}$ = 249.6 Hz), 153.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.72 (d, $^2J_{F-F}$ = 150.3 Hz, 8F), 81.80-83−19 (m, 2F), −137.08 to −137.50 (m, 4F), −151.39 to −151.67 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{44}H_{17}Cl_2F_{18}N_{10}S_2$ [M + H]$^+$ 1161.0163, found 1161.0207. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 418 (5.31), 508.5 (3.98), 584 (3.24), 650 (1.93) nm. IR (substance): ν = 2125 (N_3) cm^{-1}.

Synthesis of 8-[3-Fluoro-5-pentafluorothio)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (10a). 5-[3-Fluoro-5-(pentafluorothio)phenyl]dipyrromethane (**5b**) (100 mg, 0.27 mmol) was dissolved with DCM (5 mL) in a 100 mL round-bottom flask. After addition of DDQ (61.7 mg, 0.27 mmol), the reaction mixture was stirred for 5 min at room temperature followed by addition of DIPEA (0.33 mL, 1.91 mmol) and stirring for 3 min. Then BF_3·OEt_2 (0.37 mL, 3.00 mmol) was added, and the mixture stirred further for 35 min. After aqueous workup and extraction with DCM, the organic phase was washed twice with water, dried over sodium sulfate, and evaporated to dryness. The crude reaction mixture was purified by column chromatography (silica gel, DCM/*n*-hexane = 3:1) to obtain the BODIPY **10a** (58 mg, 52%) as a red-green solid. Mp: 277 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62−6.65 (m, 2H), 6.89−6.91 (m, 2H), 7.49−7.52 (m, 1H), 7.80−7.83 (m, 1H), 8.00−8.01 (m, 1H) 8.00 (br s, 2 H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 119.6, 120.6 (d, $^2J_{C-F}$ = 23.0 Hz), 123.6−123.7, 127.9, 131.0, 134.4, 142.4, 145.2, 145.8, 154.5, 161.3 (d, $^1J_{C-F}$ = 253.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.12 (d, $^2J_{F-F}$ = 151.1 Hz, 4F), 80.44−82.66 (m, 1F), −107.74 (t, J = 8.1 Hz, 1F), −144.55 to −145.10 (m, 2F). HRMS (ESI-TOF): m/z calcd for $C_{15}H_9BF_8N_2NaS$ [M + Na]$^+$ 435.0349, found 435.0352. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 490 (4.13), 519.5 (4.41) nm. Fluorescence emission (acetone): λ_{max} = 560 nm at $\lambda_{excitation}$ = 470 nm.

Synthesis of 8-[3-Chloro-5-(pentafluorothio)phenyl]-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (10b). 5-[3-Chloro-5-(pentafluorothio)phenyl]dipyrromethane (**5c**) (600 mg, 1.59 mmol) was dissolved with DCM (30 mL) in a 100 mL round-bottom flask. After addition of DDQ (359 mg, 1.59 mmol) the reaction mixture was stirred for 5 min at room temperature followed by addition of DIPEA (1.94 mL, 11.2 mmol) and stirring for 3 min. Then BF_3·OEt_2 (2.17 mL, 17.5 mmol) was added and the mixture stirred further for 35 min. After aqueous workup and extraction with DCM, the organic phase was washed twice with water, dried over sodium sulfate, and evaporated to dryness. The crude reaction mixture was purified by column chromatography (silica gel, DCM/*n*-hexane = 3:2) to obtain the BODIPY **10b** (226 mg, 33%) as a red-green solid. Mp: 263 °C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.62−6.65 (m, 2H), 6.88−6.91 (m, 2H), 7.75 (t, J = 1.7 Hz, 1H), 7.89 (dd, J = 2.0, 1.7 Hz, 1H), 8.00 (t, J = 1.9 Hz, 1H), 8.01−8.04 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 119.6, 125.9, 128.2, 131.0, 133.0, 134.4, 135.1, 135.7, 142.2, 145.8, 154.2 (q, $^2J_{C-F}$ = 19.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.24 (d, $^2J_{F-F}$ = 151.8 Hz, 4F), 81.60 (q, $^2J_{F-F}$ = 151.4, 149.6 Hz, 1F), −144.78 (dd, J = 57.0, 28.7 Hz, 2F). HRMS (ESI-TOF): m/z calcd for $C_{15}H_9BClF_7N_2NaS$ [M + Na]$^+$ 451.0054, found 451.0062. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 490 (4.21), 519 (4.38) nm. Fluorescence emission (acetone): λ_{max} = 565 nm at $\lambda_{Excitation}$ = 470 nm.

Synthesis of 5,10,15-Tris[3-fluoro-5-(pentafluorothio)-phenyl)]corrole (11). A single-necked, 500 mL flask was loaded with methanol (200 mL), and 3-fluoro-5-(pentafluorothio)-benzaldehyde (**1b**) (1.00 g, 3.99 mmol) and pyrrole (0.55 mL, 8.00 mmol) were added. Subsequently, a solution of aqueous HCl (36%, 16 mL) in 200 mL of water was added and the reaction mixture stirred at room temperature for 3 h. After extraction of the bilayer with DCM and drying by sodium sulfate, the DCM-containing solution was diluted to 300 mL with DCM, DDQ (0.90 g, 4.00 mmol) was added, and the reaction mixture stirred for 1 h at room temperature. After filtration over silica gel, purification over column chromatography (silica gel, DCM/*n*-hexane = 1:2) and recrystallization [DCM/(methanol/water = 9:1)] the corrole was obtained as a purple solid (80 mg, 6%). Mp: 228 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.23−8.34 (m, 3H), 8.35−8.77 (m, 8H), 8.77−8.99 (m, 3H) 9.08−9.34 (m, 3H). ^{13}C NMR: a meaningful interpretation was not possible (see Figure S102, Supporting Information); adequately resolved ^{13}C NMR spectra could not be obtained regardless which solvent or spectrometer (126 and 176 MHz) was used. ^{19}F NMR (376 MHz, acetone-d_6): δ 63.69 (d, $^2J_{F-F}$ = 147.4 Hz, 12F), 82.98 (q, $^2J_{F-F}$ = 151.6 Hz, 3F), 109.89 (s, 3F). HRMS (ESI-TOF): m/z calcd for $C_{37}H_{19}F_{18}N_4S_3$ [M − H]$^-$ 957.0490, found 957.0471. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 414 (4.21), 507 (3.95), 583 (3.51) nm.

Synthesis of 5,15-Bis[3-fluoro-5-(pentafluorothio)phenyl)]-10-(pentafluorophenyl)corrole (12a). A single-necked, 500 mL flask was loaded with methanol (200 mL), 3-fluoro-5-(pentafluorothio)dipyrromethane (**5b**) (1.46 g, 3.99 mmol), and pentafluorobenzaldehyde (0.24 mL, 2.00 mmol). Subsequently, a solution of HCl (36%, 10 mL) in 200 mL of water was added and the reaction mixture stirred at room temperature for 1 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the DCM-containing solution was concentrated to 1000 mL, DDQ (676 mg, 3.00 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature. After filtration over silica gel, purification by column chromatography (silica gel, DCM/*n*-hexane = 1:2), and recrystallization [DCM/(methanol/water = 9:1)], the corrole was obtained as a purple solid (237 mg, 13%). Mp: 205 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ −3.30 (s, 1H), −1.75 (s, 2H), 8.12−8.24 (m, 2H), 8.33−9.38 (m, 12H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 92.4, 112.8 (d, $^2J_{C-F}$ = 27.5 Hz), 116.5, 125.0, 127.9, 137.9 (d, $^1J_{C-F}$ = 256.5 Hz), 141.1, 142.6, 146.9 (d, $^1J_{C-F}$ = 242.5 Hz), 153.6, 161.5 (d, $^1J_{C-F}$ = 247.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.99 (d, $^2J_{F-F}$ = 149.2 Hz, 8F), 82.88 (q, $^2J_{F-F}$ = 149.1 Hz, 2F), −110.78 to −111.74 (m, 2F), −139.46 to −140.41 (m, 2F), −156.61 to −157.20 (m, 1F), −164.62−165.52 (m, 2F). HRMS (ESI-TOF): m/z calcd for $C_{37}H_{16}F_{17}N_4S_2$ [M + H]$^+$ 903.0550, found 903.0525. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 413 (4.06), 507 (3.88), 583 (3.43) nm.

Synthesis of 5,15-Bis[3-chloro-5-(pentafluorothio)phenyl)]-10-(pentafluorophenyl)corrole (12b). A single-necked 500 mL flask was loaded with methanol (200 mL), 3-chloro-5-(pentafluorothio)dipyrromethane (**5c**) (1.53 g, 3.99 mmol), and (pentafluoro)benzaldehyde (0.24 mL, 2.00 mmol). Subsequently, a solution of HCl (36%, 10 mL) in 200 mL of water was added and the reaction mixture stirred at room temperature for 1 h. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the DCM-containing solution was concentrated to 1000 mL, DDQ (676 mg, 3.00 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature. After filtration over silica gel, purification by column chromatography (silica gel, DCM/*n*-hexane = 1:2), and recrystallization [DCM/(methanol/water = 9:1)] the corrole was obtained as a purple solid (228 mg, 12%). Mp: 201 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.93−9.45 (m, 14H). ^{13}C NMR (176 MHz, $CDCl_3$): a meaningful interpretation was not possible (see Figure S110, Supporting Information); adequately resolved ^{13}C NMR spectra could not be obtained regardless of which solvent or spectrometer (126 and 176 MHz) was used. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.57 (d, $^2J_{F-F}$ = 150.3 Hz, 8F), 82.90 (q, $^2J_{F-F}$ = 150.5 Hz, 2F), −137.17 (s, 2F), −152.54 (s, 1F), −161.06 (s, 2F). HRMS (ESI-TOF): m/z calcd for $C_{37}H_{18}Cl_2F_{15}N_4S_2$ [M + H]$^+$ 937.0105, found 937.0102. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 413.5 (4.15), 506.5 (3.73), 582 (3.31) nm.

Synthesis of 5,15-Bis(pentafluorophenyl)-10-[3-fluoro-5-(pentafluorothio)phenyl)]corrole (13). A single-necked, 1000 mL flask was loaded with methanol (400 mL), 5-(pentafluorophenyl)-dipyrromethane (2.50 g, 7.99 mmol), and 3-fluoro-5-(pentafluorothio)benzaldehyde (**1b**) (1.00 g, 3.99 mmol). Subsequently, a solution of HCl (36%, 20 mL) in 400 mL of water was added and the reaction mixture stirred at room temperature for 1 h. After extraction of the bilane with DCM and drying over sodium sulfate, the DCM-containing solution was diluted to 1800 mL with

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DCM, DDQ (2.70 g, 12.0 mmol) was added, and the reaction mixture was stirred for 3 h at room temperature. After filtration over silica gel, purification by column chromatography (silica gel, DCM/*n*-hexane = 1:2), and recrystallization [DCM/(methanol/water = 9:1)] the corrole was obtained as a purple solid (1.30 g, 38%). Mp: 223 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.96 (dt, $^{3}J_{H-F}$ = 8.7 Hz, $^{4}J_{H-H}$ = 2.2 Hz, 1H), 8.12 (d, $^{3}J_{H-F}$ = 8.1 Hz, 1H), 8.48 (s, 1H), 8.63 (br s, 4H), 8.69 (d, J = 4.6 Hz, 2H), 8.81 (d, J = 4.6 Hz, 2H), 9.17 (d, J = 4.1 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 109.6, 113.5 (d, $^{2}J_{C-F}$ = 27.3 Hz), 113.7 (t, $^{2}J_{C-F}$ = 17.4 Hz), 117.7, 124.7 (d, $^{2}J_{C-F}$ = 20.8 Hz), 126.6, 127.0, 127.7, 137.9 (d, $^{1}J_{C-F}$ = 255.0 Hz), 141.9 (d, $^{1}J_{C-F}$ = 254.3 Hz), 144.2 (d, $^{3}J_{C-F}$ = 7.4 Hz), 146.1 (d, $^{1}J_{C-F}$ = 249.3 Hz), 153.3, 160.5 (d, $^{1}J_{C-F}$ = 251.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.60 (d, $^{2}J_{F-F}$ = 149.8 Hz, 4F), 82.90 (q, $^{2}J_{F-F}$ = 150.7 Hz, 1F), −110.94 (s, 1F), −137.71 (ddd, J = 53.1, 24.1, 8.4 Hz, 4F), −152.14 (t, J = 20.9 Hz, 2F), −161.33 (dd, J = 22.8, 8.5 Hz, 4F). HRMS (ESI-TOF): m/z calcd for $C_{37}H_{13}F_{16}N_4S$ $[M - H]^-$ 849.0611, found 849.0677. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 415 (4.21), 508 (3.96), 585 (3.32) nm.

Synthesis of 5,15-Bis[3-fluoro-5-(pentafluorothio)phenyl)]-10-[4-(2-propyn-1-oxy)-2,3,5,6-tetrafluorophenyl]corrole (14). 5,15-Bis[3-fluoro-5-(pentafluorothio)phenyl)]-10-(pentafluorophenyl)corrole (**12a**) (143 mg, 0.15 mmol) was dissolved in dry DMSO (3.0 mL) under argon atmosphere, KOH (70.0 mg, 1.24 mmol) and propargyl alcohol (0.50 mL, 8.65 mmol) were added, and the reaction mixture was stirred at room temperature for 30 min. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was evaporated to dryness, purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1), and recrystallized (acetone/*n*-hexane) to obtain a black-purple solid (122 mg, 86%). Mp: 188 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 2.84 (t, J = 2.4 Hz, 1H), 5.23 (d, J = 2.4 Hz, 2H), 7.52−9.58 (br m, 14H). ^{13}C NMR (176 MHz, $CDCl_3$) signals could not be detected. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.49 (d, $^{2}J_{F-F}$ = 150.0 Hz, 8F), 82.94 (q, $^{2}J_{F-F}$ = 150.7 Hz, 2F), −109.98 (s, 2F), −138.65 (br s, 2F), −155.56 (br s, 2F). HRMS (ESI-TOF): m/z calcd for $C_{40}H_{19}F_{16}N_4OS_2$ $[M - H]^-$ 939.0750, found 939.0714. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 415 (4.09), 508 (3.79), 584 (3.21) nm.

Synthesis of 5,15-Bis[4-(2-propyn-1-oxy)-2,3,5,6-tetrafluorophenyl]-10-[3-fluoro-5-(pentafluorothio)phenyl)]corrole (15). 5,15-Bis(pentafluorophenyl)-10-[3-fluoro-5-(pentafluorothio)-phenyl)]corrole (**13**) (320 mg, 0.37 mmol) was dissolved in dry DMSO (8.0 mL) under argon atmosphere, KOH (90.0 mg, 1.60 mmol) and propargyl alcohol (1.0 mL, 17.2 mmol) were added, and the reaction mixture was stirred at room temperature for 30 min. After aqueous workup, extraction with DCM, and drying over sodium sulfate, the crude product was evaporated to dryness, purified by column chromatography (silica gel, DCM/*n*-hexane = 1:1), and recrystallized (acetone/*n*-hexane) to obtain a black-purple solid (283 mg, 81%). Mp: 197 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 2.82 (t, J = 2.4 Hz, 2H), 5.21 (d, J = 2.4 Hz, 4H), 7.95 (d, $^{3}J_{H-F}$ = 8.7 Hz, 1H), 8.12 (d, $^{3}J_{H-F}$ = 8.1 Hz, 1H), 8.48 (s, 1H), 8.60−8.73 (m, 4H), 8.84 (d, J = 3.8 Hz, 2H), 9.12−9.20 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 61.9 (t, $^{4}J_{C-F}$ = 3.6 Hz), 77.6, 109.3, 113.4, 113.4, 117.4, 124.7 (d, $^{2}J_{C-F}$ = 21.1 Hz), 126.7, 126.9, 127.7, 136.4, 141.8 (d, $^{1}J_{C-F}$ = 249.8 Hz), 144.4 (d, $^{3}J_{C-F}$ = 7.4 Hz), 146.1 (d, $^{1}J_{C-F}$ = 249.8 Hz), 153.2, 160.5 (d, $^{1}J_{C-F}$ = 252.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.61 (d, $^{2}J_{F-F}$ = 149.8 Hz, 4F), 82.99 (q, $^{2}J_{F-F}$ = 150.7 Hz, 1F), −110.98 to −11.14 (m, 1F), −138.98 (m, 4F), −154.92 to −155.65 (m, 4F). HRMS (ESI-TOF): m/z calcd for $C_{43}H_{19}F_{14}N_4O_2S$ $[M - H]^-$ 921.1011, found 921.1057. UV−vis (DCM), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 414 (3.98), 505 (3.44), 582.5 (3.11) nm.

Synthesis of BODIPY−Cu(III)−Corrole Array (17). $CuSO_4 \cdot (H_2O)5$ (20.0 mg, 0.12 mmol), sodium ascorbate (75.0 mg, 0.38 mmol), 8-(4-azido-tetrafluorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (**16**) (36.0 mg, 95.6 μmol), and 5,15-bis[3-fluoro-5-(pentafluorothio)phenyl)]-10-[4-(2-propyn-1-oxy)tetrafluorophenyl]-corrole (**14**) (60.0 mg, 63.7 μmol) were suspended in 2 mL of DMSO, and the mixture was stirred for 15 min at room temperature. After aqueous workup, extraction with ethyl acetate, and drying over sodium sulfate, the crude product was evaporated to dryness, purified by column chromatography (DCM), and recrystallized (DCM/(MeOH/H_2O = 9:1)] to obtain array **17** as a brown solid (28 mg, 32%). Mp: 244 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ 5.71, 6.62−6.67 (m, 2H), 6.88−6.93 (m, 2H), 7.19 (m$_c$, 2H), 7.34 (m$_c$, 2H), 7.53 (m$_c$, 2H), 7.58 (m$_c$, 2H), 7.71 (d, $^{3}J_{H-F}$ = 8.1 Hz, 1H), 7.91−7.95 (m, 2H), 7.95−8.00 (m, 2H), 8.05 (s, 2H), 8.25 (s, 1H). ^{13}C NMR (176 MHz, $CDCl_3$): δ 67.3, 111.2, 114.5, 120.1, 120.4, 122.8, 123.6, 125.7, 127.7, 128.5, 130.3, 133.3, 134.5, 143.7, 147.1, 149.9, 160.8, 162.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ 63.16 (d, $^{2}J_{F-F}$ = 150.3 Hz, 8F), 82.50 (q, $^{2}J_{F-F}$ = 151.1 Hz, 2F), −109.18 (m$_c$, 2F), −134.19 to −134.42 (m, 2F), −138.41 to −139.00 (m, 2F), −144.68 (dd, J = 55.8, 28.1 Hz, 2F, BF_2), −143.86 to −144.02 (m, 2F), −154.76 to −155.04 (m, 2F). HRMS (ESI-TOF): m/z calcd for $C_{55}H_{23}BCuF_{22}N_9OS_2$ $[M]^-$ 1381.0505, found 1381.0450. UV−vis (acetone), λ_{max} [log ε (L·mol^{-1}·cm^{-1})]: 406 (5.26), 514.5 (4.65) nm. Fluorescence emission (acetone): λ_{max} = 546 nm at λ_{Excit} = 350 and 500 nm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR and HRMS spectra of the described new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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