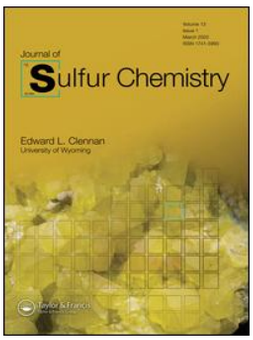

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Towards novel thieno-fused subporphyrazines via functionalized thiophene precursors

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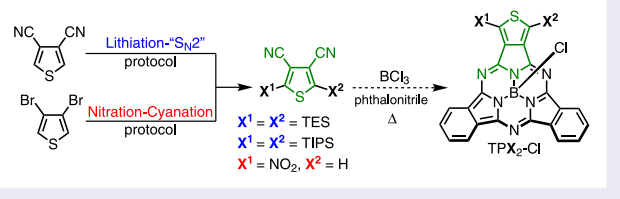
ABSTRACT

Thieno-fused subporphyrazines (TPs) containing a central and axially substituted boron atom are a class of compounds with interesting optical and redox properties. Here we present our efforts towards expanding this class of compounds using various thiophene substrates that were prepared by cyanation or nitration of 3,4-dibromothiophene. Moreover, we show that one TP derivative forms a 2:1 complex in the solid state with C_{70}.



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Cyanation; fullerene; nitration; subphthalocyanine; thiophene

Introduction

Boron subphthalocyanine with an axial chloride on the boron (**SubPc-Cl**; Figure 1) was first synthesized in 1972 by Meller and Ossko [1]. Throughout the years, its derivatives have gained attention due to promising applications in organic photovoltaics [2–5] as well as organic light-emitting diodes (OLEDs) [6,7]. The 14-π aromatic SubPc chromophore consists of three aza-linked isoindole moieties with an sp^3-hybridized boron metalloid center; giving rise to its unique concavo-convex shape [8–10].

As shown by Kobayashi and co-workers [11], extensive modifications of the SubPc core have been done by exchanging one isoindole unit with aromatic dicarbonitriles (*e.g.* 1,8-naphthalenedicarbonitrile, 2,2′-biphenyldicarbobonitrile, and 4,5-

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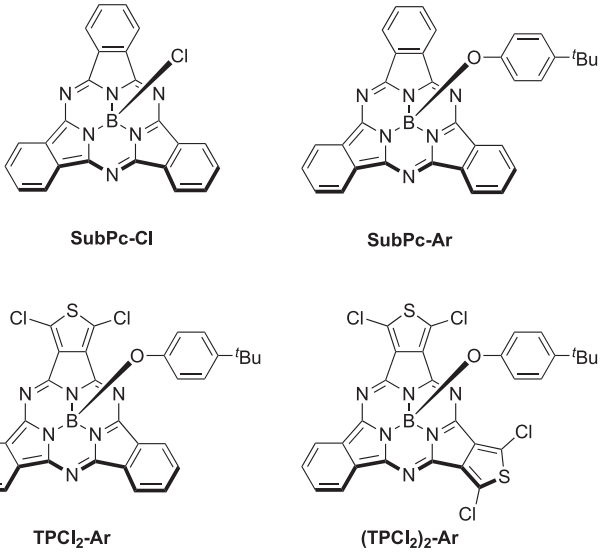
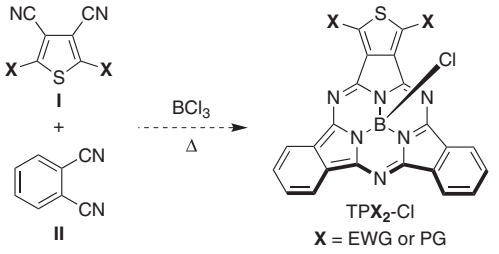


Figure 1. Boron subphthalocyanine chloride (**SubPc-Cl**), boron subphthalocyanine with axial aryl group (**SubPc-Ar**), and thieno-fused subporphyrazines **TPCl$_2$-Ar** and (**TPCl$_2$)$_2$-Ar**.

phenanthrenedicarbonitrile), yielding less symmetrical subporphyrazine (SubPz) scaffolds. Such reduction in symmetry (C_{3v} in SubPcs to C_s in SubPzs) leads to a characteristic splitting of the Q-band absorption for SubPzs originating from the breakdown of the degeneracy of the $S_0 \rightarrow S_1$ electronic transition. Recently, Nielsen and co-workers [12] introduced heterocyclic thiophene units onto the SubPz core, yielding thieno-fused subporphyrazines (**TPCl$_2$-Ar** and (**TPCl$_2$)$_2$-Ar**); (Figure 1). This new chromophore class (which we here generally name TP) exhibits desired photophysical properties regarding solar energy harvesting; namely redshift of Q-band absorption in addition to broadening of the Q-band without compromising the absorption intensity. Replacing benzene for thiophene units in the SubPc scaffold additionally enhances the capability of TPs to act as electron donors, reflected in the lowering of the oxidation potential [12]. Thiophene presents a versatile synthetic building block, which we thought to employ towards functionalizing the thiophene α-positions at the TP chromophore periphery. This modification poses an interest for further elucidation of the photophysical properties of the TP series and how these properties can be manipulated by substituent effects. For this reason, combined with the intrinsic property of enhanced donor strength of the TP core, we decided to work towards a **TPX$_2$-Cl** push–pull system (Scheme 1), by the installation of highly electron-withdrawing X = NO_2 groups (EWG) at the TP thiophene α-positions. Such targets would require suitably functionalized 3,4-dicyanothiophene precursors, which we set out to synthesize.

While push–pull systems of the TP class are still elusive, we herein report the synthesis of three nitro-substituted thiophene derivatives and one new silyl-functionalized TP derivative all en route towards the intriguing thieno-fused SubPz scaffolds with strongly electron-withdrawing groups.



Scheme 1. Synthetic strategy for formation of TP$\mathbf{X_2}$-Cl, **X** = EWG or PG. EWG = electron-withdrawing group; PG = protecting group.

Results and discussion

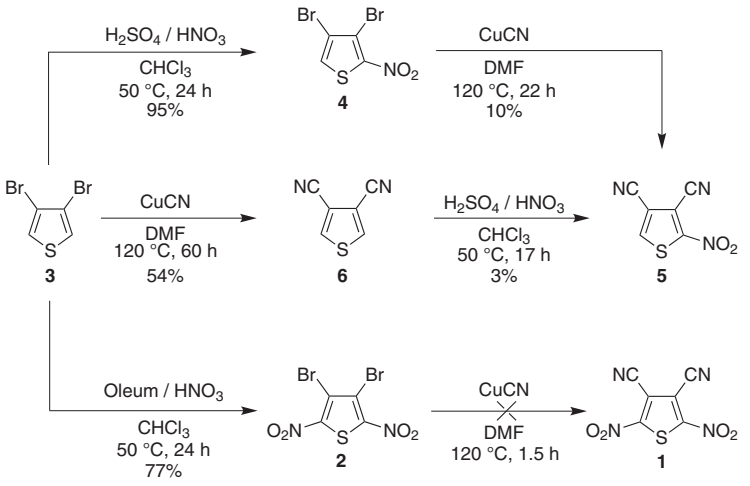
The synthetic approach for obtaining unsymmetrically substituted TP-scaffolds relies on a statistical cyclotrimerization reaction of suitable 1,2-dicyano derivatives (**I** and **II**) mediated by a strong Lewis acid, commonly BCl_3. During synthesis, chlorination poses a problem, as observed for both SubPc [13] and TP derivatives [12], likely occurring via electrophilic aromatic substitutions annotated to *in situ* generation of Cl_2 [14]. Thus, from the 3,4-dicyanothiophene substrate, only chlorinated TP products were isolated. Protection group (PG) functionalized TP derivatives, therefore, presented a potential way of avoiding chlorination at the α-positions while also providing the opportunity for functionalization at the same positions after the formation of the chromophore scaffold. The synthesis hereof demanded the preparation of suitable 3,4-dicyanothiophene derivatives **I** to be mixed with an excess of phthalonitrile **II** in the cyclotrimerization reaction (Scheme 1).

Synthesis of 3,4-dicyano derivatives

The initially targeted nitro-functionalized TP precursor **1** (Scheme 2) was to be synthesized by cyanation of thiophene derivative **2**, available from a patented nitration protocol of 3,4-dibromothiophene **3** [15]. However, in our hands, when those conditions were applied to **3**, only formation of the mono-nitrated thiophene derivative **4** was observed; nevertheless, in excellent yield (95%).

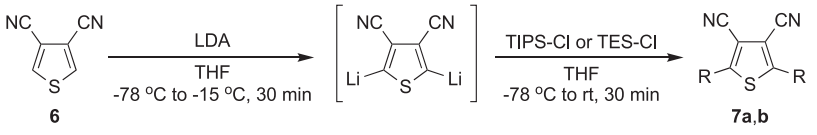
To obtain **2**, more forcing conditions had to be applied. Indeed, by use of 20% oleum instead of conc. sulfuric acid, the di-nitrated product **2** was obtained in 77% after recrystallization (Scheme 2). The following cyanation of **2** and **4**, respectively, under Rosenmund von-Braun conditions (using CuCN in DMF at elevated temperature), however, proved challenging. Only decomposition of the nitro-thiophene **2** was observed, while successful cyanation of **4** was achieved, after comprehensive temperature and solvent screening, giving the mono-nitrated TP precursor **5**, albeit only in a yield of 10%. As synthesis and purification of **5** proved tedious, a reverse functionalization protocol towards **5** was investigated via the dicyanothiophene **6** (easily obtained by cyanation of **3**). Nitration of **6** successfully gave **5**; however, in very poor yield upon full conversion of **6**. Nevertheless, a new potential precursor for TP formation was at hand.

As the formation of the TP scaffold ought to be performed under forcing conditions in presence of BCl_3 (*vide infra*), acid-resistant -SiR_3 groups posed as interesting candidates



Scheme 2. Synthesis of thiophene derivatives.

Table 1. Synthesis of α-functionalized 3,4-dicyano derivatives.



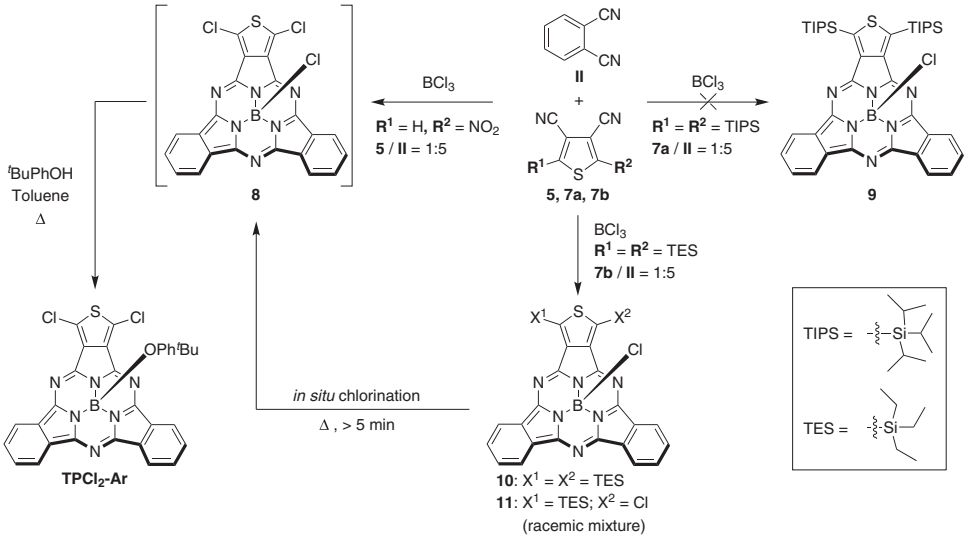
Starting compound	R	Product	Yield/%
6	TIPS	**7a**	53
6	TES	**7b**	61

for protection groups to avoid *in situ* chlorination of the thiophene α-positions. Additionally, a mild methodology for the removal of such silyl protection groups in the presence of the SubPc scaffold has already been developed within our group [16]. The protected TP precursors **7a**,**b** (Table 1) were afforded via a lithiation-substitution protocol of dicyanothiophene **6**, by treatment with lithium diisopropylamide (LDA) at −78°C, followed by addition of either triisopropylsilyl-(TIPS) or triethylsilyl-(TES) chloride.

Formation of thieno-fused subporphyrazine scaffolds

With the TP precursors **5**, **7a** and **7b** in hand, the formation of new TP derivatives was investigated (Table 2). Cyclotrimerization of the nitro-functionalized thiophene **5** and phthalonitrile in a 1:5 stoichiometry was initially attempted in a 1M BCl_3 solution in *p*-xylene. Unfortunately, upon heating towards reflux (137°C) only decomposition of the starting material **5** was observed. Changing the solvent to *o*-dichlorobenzene (*o*-DCB) and adding the BCl_3 (1M) in a hexane solution allowed a lower initial concentration of BCl_3. By initially distilling off the hexane as the temperature was slowly elevated towards the reflux point of *o*-DCB (180°C), a gradual concentration of the reaction mixture was

Table 2. Reaction conditions for formation of **$TPCl_2$-Ar** and **10**.



Thiophene substrate	R^1, R^2	Solvent[a]	Product	Yield/% (time/h)
5[b]	H, NO_2	*p*-xylene	–	—(0.5)
5	H, NO_2	*o*-DCB	**8**[c]	1 (0.5)
7a	TIPS, TIPS	*o*-DCB	n.r.	—(24)
7b	TES, TES	*o*-DCB	**10**	4 (0.5)
7b	TES, TES	*o*-DCB	**8**[c]	3 (2.5)

Note: n.r.: No reaction.
[a]Heated to reflux; bp: *p*-xylene (137°C), *o*-DCB (180°C).
[b]Decomposition of starting compound.
[c]Yield determined from the *p*-^{t}BuC$_6$H$_4$O-derivative **$TPCl_2$-Ar** (2 steps).

achieved. This approach successfully yielded a cyclotrimerization product without any apparent decomposition. TLC analysis only revealed one intensely purple-colored product eluting above parent **SubPc-Cl**. Surprisingly, high-resolution mass spectrometry (HRMS) revealed an intense peak at $m/z = 504.97603$ corresponding to the protonated species of the bis-chlorinated TP derivative **8**. This suggested two-fold α-chlorination of the thiophene moiety, implicating also that the nitro group in the 2-position of **5** had been replaced. The structure of **8** was decisively confirmed by replacement of the axial chloride with 4-*tert*-butylphenol in refluxing toluene (this replacement simplifies purification by chromatography), which gave the dark purple **$TPCl_2$-Ar** in 1% yield. Characterization of the isolated product was in complete agreement with data previously reported by Gotfredsen *et al.* [12].

The bulky TIPS-protected TP precursor **7a** presented an immediate solution to avoid the readily occurring chlorination of the thiophene α-position. However, upon treatment of **7a** even with large excess of BCl_3 at 180°C, no conversion or apparent degradation of **7a** was observed over the course of 24 h (neither in the presence nor in the absence of phthalonitrile). As **7a** proved stable and unreactive towards the given conditions, the less hindered TES-protected **7b** was investigated for possible TP formation. To our satisfaction, successful cyclotrimerization with phthalonitrile gave the dark pink TES-functionalized

TP chromophore **10**. From analysis by TLC of the reaction progress it was observed that upon reflux at 180°C, initially only formation of **10** occurred. This was shortly followed by formation of the light purple mono-chlorinated TES-TP **11** after only 5 min (supported by HRMS data), which was followed by formation of the dark purple bis-chlorinated TP **8** (confirmed by isolation as **$TPCl_2$-Ar**). This observation suggested a rapid stepwise chlorination of **10**, despite having TES-protection groups at the thiophene α-positions. The optimal reaction time for obtaining **10** versus the competing chlorination was concluded to be 30 min. By a parallel experiment with increased reaction time, full consumption of **10** and **11** was observed within 2.5 h. The only TP product formed, being the bis-chlorinated TP **8** (isolated as **$TPCl_2$-Ar**), was obtained in a surprisingly high yield of 3%; a 6-fold increase when compared to our previously reported synthesis of **$TPCl_2$-Ar**, from the non-chlorinated thiophene **3** [12]. As reflected in how readily the silyl-functionalized thiophene moiety of **10** and **11** underwent chemical transformation, both **10** and **11** proved to be unstable even when purified, stored at −18 ° under inert atmosphere. Nevertheless, a sufficiently pure sample could be obtained by utilizing size exclusion chromatography to allow confirmation of the structure. However, photo- and electrochemical properties remain unknown. On account of the sp^3-hybridized boron center and hence cone-shaped structure, compound **11** with two different substituents on one thiophene ring is chiral. As the starting materials are not chiral, this product has to be formed as a racemic mixture.

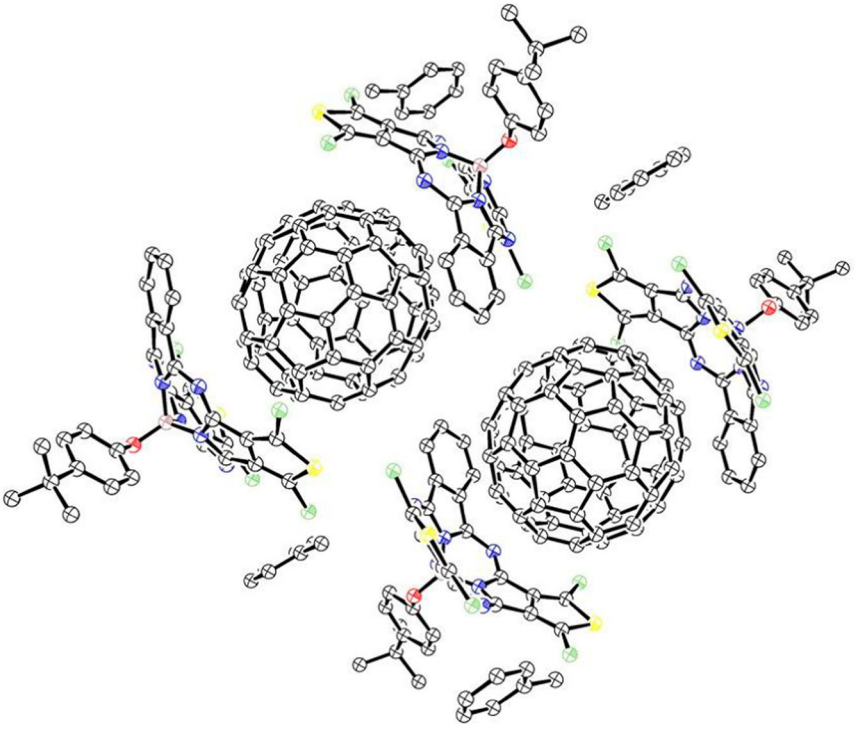


Figure 2. ORTEP diagram of 2:1 complex of **$(TPCl_2)_2$-Ar** and C_{70}. CCDC 1980090. Crystals were grown from a toluene/heptane bi-layer system. Thermal ellipsoids are displayed at 50%. Hydrogen atoms are omitted for clarity.

TP complex formation with c_{70} in the solid phase

The thieno-fused subporphyrazine **$(TPCl_2)_2$-Ar** was previously shown to co-crystalize with Buckminsterfullerene C_{60} in a 1:1 complex, promoted by π-π interactions [12], while **SubPc-Ar** formed 2:1 complexes with C_{60} as well as with C_{70} [10].[1] Crystallization of **$(TPCl_2)_2$-Ar** with the ellipsoid-shaped C_{70} yielded a 2:1 complex, which was determined by X-ray crystallographic analysis (Figure 2). The average distance between the convex (C_{70}) and concave (TP) π-systems is approximately 3.4 Å (see Supporting Information for details). The boron-boron distance between two **$(TPCl_2)_2$-Ar** molecules complexing the same C_{70} is 14.5 Å.

Conclusion

In this work we have presented two new synthetic protocols for thiophene functionalization, providing three new dicyanothiophene derivatives, designed to undergo cyclotrimerization reaction. All were investigated for reactivity towards cyclotrimerization with phthalonitrile, yielding one new silyl-functionalized thieno-fused subporphyrazine in addition to revealing two new synthetic pathways for obtaining a di-chlorinated thieno-fused subporphyrazine. Furthermore, a 2:1 packing motif of a chloro-thieno-subporphyrazine and fullerene C_{70} was observed in the solid state by X-ray crystallographic analysis. Synthesis of functionalized thieno-fused subporphyrazines is clearly a challenging task, and new strategies need to be explored in future work.

Experimental

General methods

All water sensitive reactions were carried out in flame-dried, and N_2- or Ar-flushed glassware. *o*-DCB was distilled prior to use from CaH_2. Diisopropylamine was distilled from NaH prior to use. Anhydrous DMF, toluene and THF were tapped from an Innovative Technology (IT) plant model PS-MD-05. Thin layer chromatography (TLC) aluminum sheets precoated with silica gel were used. Flash column chromatography was carried out using SiO_2 with particle size of 40–63 µm, whereas dry column vacuum chromatography was carried out with SiO_2 of 15–40 µm particle size. Size exclusion chromatography was carried out using Bio-Beads® S-X 8. Chemicals and solvents were purchased from the suppliers: Sigma Aldrich, Flourochem and VWR. A technical grade of petroleum ether was used with boiling point 40–65°C. Both ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz instrument with a non-inverse cryoprobe. As reference, the deuterated solvents were used: $CDCl_3$ (^{1}H NMR: $\delta = 7.26$ ppm, ^{13}C NMR: $\delta = 77.16$ ppm), CD_2Cl_2 (^{1}H NMR: $\delta = 5.32$ ppm, ^{13}C NMR: $\delta = 54.00$ ppm). HRMS was recorded on a Bruker SolariX XR MALDI-FT-ICR instrument with dithranol as matrix. All melting points are uncorrected. A Bruker FT-IR instrument using attenuated total reflectance (ATR) sampling technique was used for recording IR-spectra.

2,5-Dinitro-3,4-dibromothiophene (2)

A flask was charged with a solution of 3,4-dibromothiophene (3.00 g, 12.4 mmol) and HNO_3 (5 mL, 68%) in $CHCl_3$ (5 mL). Fuming H_2SO_4 (5 mL, 20% SO_3) was added dropwise

to the colorless reaction mixture over 5 min. The reaction mixture was heated to 50°C and stirred for 24 h, cooled to RT, diluted by addition of H_2O (20 mL) and extracted with CH_2Cl_2 (75 mL). The organic phase was washed with H_2O (3 × 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was recrystallized in a 1:2 boiling solution of CH_2Cl_2/petroleum ether, which yielded the title compound **2** (3.17 g, 77%) as bright yellow crystals. R_f(70% CH_2Cl_2/heptanes) = 0.69. M.p.: 128°C (Lit. [19]: 128°C from EtOH). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.28, 117.93 ppm. IR (ATR, neat): 1530, 1488, 1337, 1311, 1290, 1113, 907, 872, 834, 746, 615, 478 cm^{-1}. The title compound was not observed using the following methods: GC-MS, MALDI$^+$ or ESI$^+$.

2-Nitro-3,4-dibromothiophene (4)

A flask was charged with a solution of 3,4-dibromothiophene (3.00 g, 12.4 mmol) and HNO_3 (5 mL, 68%) in $CHCl_3$ (10 mL). H_2SO_4 (5 mL, 95%) was added dropwise to the colorless reaction mixture over 5 min. The reaction mixture was heated to 50°C and stirred for 24 h, cooled to RT, diluted by addition of H_2O (30 mL) and extracted with 1:4 CH_2Cl_2/petroleum ether (100 mL). The organic phase was washed with H_2O (3 × 30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was recrystallized in a 3:1 boiling solution of CH_2Cl_2/petroleum ether, which yielded the title compound **4** (3.39 g, 95%) as yellow crystals. R_f(70% CH_2Cl_2/heptanes) = 0.66. M.p.: 110–112°C (Lit. [19]: 115–116°C from EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 127.87, 117.93, 116.93, 116.82 ppm. IR (ATR, neat): 3094, 1529, 1489, 1386, 1311, 1291, 1113, 907, 833, 754, 746, 726 cm^{-1}. The title compound was not observed using the following methods: GC-MS, MALDI$^+$ or ESI$^+$.

2-Nitro-3,4-dicyanothiophene (5)

Method A: A flame-dried flask was charged with a mixture of **4** (10.0 g, 34.9 mmol), CuCN (12.4 g, 139 mmol) in anhydrous DMF (100 mL), heated to 120°C and stirred for 22 h. The reaction mixture was cooled to RT and filtered through a short silica plug (SiO_2, 15–40 μm) eluted with CH_2Cl_2 (combined fractions 800 mL). The filtrate was washed with sat. aqueous $Na_2S_2O_3$ (500 mL), sat. aq. $NaHCO_3$ (1000 mL) and water (1500 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2 and purified by dry column vacuum chromatography (SiO_2, 0–80% CH_2Cl_2/heptanes, 15% increment, 150 ml fractions), followed by flash column chromatography (SiO_2, 8% EtOAc/toluene) in addition to gravity column chromatography (SiO_2, 80% CH_2Cl_2/heptane) which afforded the title compound **5** (640 mg, 10%) as an off-white solid. R_f(80% CH_2Cl_2/heptanes) = 0.22. M.p.: 195°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.65, 138.62, 114.68, 111.79, 110.27, 108.64 ppm. IR (ATR, neat): 3113, 2246, 1546, 1519, 1451, 1339, 1174, 1060, 913, 871, 821, 780, 744, 536, 481, 452, 429, 409 cm^{-1}. The title compound was not observed using the following methods: GC-MS, MALDI$^+$ or ESI$^+$. Anal. Calcd (%) for $C_6HN_3O_2S$: C, 40.23; H, 0.56; N, 23.46; S,17.90. Found: C, 40.28; H, 0.69; N, 22.55; S, 17.76.

Method B: A flask was charged with a solution of **6** (200 mg, 1.49 mmol) and HNO_3 (5 mL, 68%) in $CHCl_3$ (10 mL). H_2SO_4 (5 mL, 95%) was added dropwise to the colorless reaction mixture over 5 min. The reaction mixture was heated to 50°C and stirred for 17 h, cooled to RT, diluted by addition of H_2O (30 mL) and extracted with CH_2Cl_2

(150 mL). The organic phase was washed with H_2O (3 × 30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by gravity column chromatography (SiO_2, 80% CH_2Cl_2/heptane) afforded the title compound **5** (8 mg, 3%) as an off-white solid. M.p, ^{1}H- and ^{13}C NMR spectroscopic data in accordance with data reported for compound obtained by method A.

3,4-Dicyanothiophene (6)

A flame-dried flask was charged with a mixture of 3,4-dibromothiophene (12.0 g, 49.6 mmol), CuCN (17.8 g, 198 mmol) and anhydrous DMF (100 mL), which was heated to 120°C and stirred for 60 h. The reaction mixture was cooled to RT and filtered through a short silica plug (SiO_2, 15–40 µm) then eluted with CH_2Cl_2 (combined fractions 800 mL). The filtrate was washed with sat. aq. $Na_2S_2O_3$ (500 mL), sat. aq. $NaHCO_3$ (500 mL) and water (500 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2 and purified by flash column chromatography (SiO_2, 70% CH_2Cl_2/heptanes), which afforded the title compound **6** (3.65 g, 54%) as a white solid. R_f(70% CH_2Cl_2/heptanes) = 0.13. M.p.: 170–171°C (Lit. [20]: 170–171.5°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.07, 113.29, 111.86 ppm. HRMS (MALDI$^+$, dithranol): m/z = 135.00223 [M + H$^+$], calcd. for [$C_6H_3N_2S^+$]: m/z = 135.00114. IR (ATR, neat): 3125, 3108, 2236, 1614, 1508 1450, 1169, 874, 832, 534, 476, 449, 432 cm^{-1}. Anal. Calcd (%) for $C_6H_2N_2S$: C, 53.72; H, 1.50; N, 20.88; S, 23.90. Found: C, 52.93; H, 1.45; N, 20.43; S, 23.93.

2,5-Bis(triisopropylsilyl)—3,4-dicyanothiophene (7a)

A flame-dried, argon-flushed flask was charged with a solution of freshly distilled diisopropylamine (1.26 mL, 8.94 mmol), anhydrous THF (20 mL) and cooled to −15°C. *n*-BuLi (5.6 mL, 9.0 mmol, 1.6 M in hexane) was added dropwise over 10 min while the reaction temperature was maintained at −15°C. The reaction mixture was stirred for an additional 30 min and cooled to −78°C. The prepared LDA solution was cannulated to a flame-dried, argon-flushed flask charged with a solution of **6** (200 mg, 1.49 mmol) in anhydrous THF (20 mL) at −78°C. The bronze reaction mixture was allowed to warm up to –15°C and stirred for 10 min. The now light green colored reaction mixture was cooled to −78°C, and chlorotriisopropylsilane (0.82 mL, 3.7 mmol, 97% w/v) was added. The reaction mixture was allowed to warm to RT. The reaction was quenched with H_2O (25 mL) and the organic phase was isolated and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 70% CH_2Cl_2/heptanes) afforded a crude yellow crystalline compound. The crude product was recrystallized in boiling methanol and charcoal, which yielded the title compound **7a** (352 mg, 53%) as a white crystalline solid. R_f(70% CH_2Cl_2/heptanes) = 0.47. M.p.: 114–115°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.62 (sep, J = 7.5 Hz, 6H), 1.14 (d, J = 7.5 Hz, 36H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.57, 121.48, 114.45, 18.56, 11.97 ppm. HRMS (MALDI$^+$, dithranol): m/z = 447.26859 [M + H$^+$], calcd. for [$C_{25}H_{43}N_2SSi_2^+$]: m/z = 447.26800. Anal. Calcd for $C_{24}H_{42}N_2SSi_2$: C, 64.51; H, 9.47; N, 6.27; S, 7.17. Found: C, 64.54; H, 9.62; N, 6.32; S, 6.75.

2,5-Bis(triethylsilyl)-3,4-dicyanothiophene (7b)

A flame-dried, argon-flushed flask was charged with a solution of freshly distilled diisopropylamine (6.31 mL, 44.7 mmol), anhydrous THF (25 mL) and cooled to −15°C. *n*-BuLi (28 mL, 45 mmol, 1.6 M in hexane) was added dropwise over 15 min while the reaction temperature was maintained at −15°C. The reaction mixture was stirred for an additional 30 min and cooled to −78°C. The prepared LDA solution was cannulated to a flame-dried, argon-flushed flask charged with a solution of **6** (1.00 g, 7.45 mmol) in dry THF (50 mL) at −78°C. The bronze reaction mixture was allowed to warm to −15°C and stirred for 10 min. The now light green colored reaction mixture was cooled to −78°C, and chlorotriethylsilane (3.22 mL, 18.7 mmol, 97% w/v) was added. The reaction mixture was allowed to warm up to −20°C. The reaction was quenched by dropwise addition of sat. aq. NH_4Cl (40 mL), and the organic phase was isolated and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 70% CH_2Cl_2/heptanes) afforded the title compound **7b** (1.65 g, 61%) as a bronze oil. R_f(70% CH_2Cl_2/heptanes) = 0.45. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02–0.98 (m, 30H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.64, 120.62, 113.94, 7.31, 3.74 ppm. HRMS: The title compound was not observed using the following methods: GC-MS, MALDI$^+$ or ESI$^+$. Anal. Calcd for $C_{18}H_{30}N_2SSi_2$: C, 59.61; H, 8.34; N, 7.72; S, 8.84. Found: C, 58.96; H, 8.39; N, 7.76; S, 8.03.

TP-TES$_2$-Cl (10)

A flame-dried flask was charged with **7b** (303 mg, 835 µmol) and phthalonitrile (535 mg, 4.18 mmol) in *o*-DCB (15 mL). A solution of BCl_3 (14.0 mL, 14.0 mmol, 1M in hexanes) was added to the reaction mixture, and it was heated to reflux (68°C) for 30 min. The hexanes were removed by distillation, and the reaction mixture was further refluxed (180°C) for 30 min. The reaction mixture was cooled to RT while applied with a N_2 stream and continued stirring to remove excess BCl_3. Following, the reaction mixture was concentrated to dryness *in vacuo*. The crude mixture was filtered through a short silica plug (SiO_2, 15–40 µm, 50% EtOAc/toluene) and concentrated to dryness *in vacuo*. Purification by gravity column chromatography (SiO_2, 1.5% EtOAc/toluene) yielded the crude **10** containing some **11** (while compound **8** has been removed; **8**: HRMS analysis (MALDI$^+$, dithranol): m/z = 504.97603 [M + H$^+$], calcd. For [$C_{22}H_9BCl_3N_6S^+$]: m/z = 504.97625). Extensive size exclusion column chromatography (S-X 8, toluene) afforded the title compound **10** (19 mg, 4%) as a pink solid, by removal of **11** (**11**: HRMS (MALDI$^+$, dithranol): m/z = 585.10198 [M + H$^+$], calcd. For [$C_{28}H_{24}BCl_2N_6SSi^+$]: m/z = 585.10170).

10: R_f(1.5% EtOAc/toluene) = 0.51. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.86–8.81 (m, 2H), 8.75–8.72 (m, 2H), 7.97–7.88 (m, 4H), 1.48–1.31 (m, 12H), 1.15–1.09 (m, 18H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 150.06, 149.24, 147.20, 146.84, 140.81, 131.66, 130.54, 130.33, 129.85, 122.46, 122.32, 7.95, 4.73 ppm. HRMS: (MALDI$^+$, dithranol): m/z = 665.22677 [M + H$^+$], calcd. For [$C_{34}H_{38}BCl_3N_6SSi^+$]: m/z = 665.22715

TPCl$_2$-Ar

Method A: A flame-dried flask was charged with **7b** (255 mg, 703 µmol) and phthalonitrile (450 mg, 3.52 mmol) in *o*-DCB (15 mL). A solution of BCl_3 (6.0 mL, 6.0 mmol, 1M in hexanes) was added to the reaction mixture, and it was heated to reflux (68°C) for 30 min. The hexanes were removed by distillation, and the reaction mixture was further refluxed

(180°C) for 2.5 h. The reaction mixture was cooled to RT while applied with a N_2 stream and continued stirring to remove excess BCl_3. The reaction mixture was concentrated to dryness *in vacuo* and transferred to a flask with 4-*tert*-butylphenol (430 mg, 2.86 mmol) in toluene (15 mL). The reaction mixture was heated to reflux for 48 h and concentrated *in vacuo*. The crude mixture was concentrated in *vacuo* and purified by gravity column chromatography (SiO_2, 1.5% EtOAc/toluene), followed by flash column chromatography (SiO_2, 12% EtOAc/heptanes), which afforded the title compound **TPCl$_2$-Ar** (11 mg, 3%) as a purple solid. R_f(1.5% EtOAc/toluene) = 0.39. M.p.: > 230°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.84–8.75 (m, 4H), 7.91–7.85 (m, 4H), 6.78 (d, J = 8.7 Hz, 2H), 5.37 (d, J = 8.7 Hz, 2H), 1.09 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.25, 150.11, 148.98, 145.96, 143.89, 134.04, 131.30, 130.18, 129.92, 129.56, 125.96, 122.41, 122.11, 121.11, 117.85, 33.99, 31.46 ppm. HRMS (MALDI$^+$, dithranol): m/z = 619.10386 [M + H$^+$], calcd. for [$C_{32}H_{22}BCl_2N_6OS^+$]: m/z = 619.10404.

Method B: A flame-dried flask was charged with **5** (250 mg, 1.40 mmol) and phthalonitrile (894 mg, 6.98 mmol) in *o*-DCB (15 mL). A solution of BCl_3 (24.0 mL, 24.0 mmol, 1M in hexanes) was added to the reaction mixture, and it was heated to reflux (68°C) for 30 min. The hexanes were removed by distillation, and the reaction mixture was further refluxed (180°C) for 30 min. The reaction mixture was cooled to RT while applied with a N_2 stream and continued stirring to remove excess BCl_3. The reaction mixture was concentrated to dryness *in vacuo* and transferred to a flask with 4-*tert*-butylphenol (850 mg, 5.59 mmol) and *N*,*N*-diisopropylethylamine (0.73 mL, 4.19 mmol) in toluene (15 mL). The reaction mixture was heated to reflux for 24 h and concentrated *in vacuo*. The crude mixture was filtered through a short silica plug (SiO_2, 15–40 µm, 50% EtOAc/toluene) and concentrated to dryness *in vacuo*. Purification by gravity column chromatography (SiO_2, 1.5% EtOAc/toluene) followed by gravity column chromatography (SiO_2, 25% EtOAc/heptane) afforded the title compound **TPCl$_2$-Ar** (8 mg, 1%).

Note

1. For other studies on subporphyrazine derivatives with fullerenes, see for example, [17,18].

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