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Accessing π-expanded heterocyclics beyond dibenzothiophene: Syntheses and properties of phenanthrothiophenes

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Abstract

A series of phenanthrothiophenes are designed and synthesized from polyarylthiophenes through regioselective Scholl reactions in one step using iron chloride as catalyst. The molecular structures of these heteroarenes displayed multiple twisted fjords, which perturb the shapes of the polycyclic frameworks to pack in slipped to near-perfect face-to-face styles in parallel or antiparallel packings. Field-effect transistor devices using single crystals of 6,12-difluorodiphenanthro[9,10-b:9′, 10′]thiophene gave a hole mobility of 0.22 $cm^2 V^{-1} s^{-1}$.

KEYWORDS

crystal packing, phenanthrothiophenes, scholl reactions, semiconducting molecules

1 | INTRODUCTION

In the past several decades, organic semiconducting materials have evolved into prominent materials due to their potential applications in flexible organic electronics, such as organic light-emitting diodes, organic field-effect transistors, photovoltaics, etc.[1] Yet, the availability of new organic semiconducting molecules, normally with an extended π-conjugation, are essential to the sustained progress of organic electronics.[2] The π-conjugated polycyclic aromatic hydrocarbons (PAHs) and polycyclic heteroarenes (PHs) have been excellent candidates due to their narrow bandgap, tunable absorption/emission properties, and possibly high charge mobility, which are the required properties in many electronic applications.[3] Mullen, Nuckolls, and others have studied PAHs extensively and demonstrated their potential applications in organic electronics.[4] In the presence of one or more heteroatoms, such as sulfur, selenium, nitrogen, phosphorus, and others in PHs, a great variety of new possibilities in molecular shape, packing, redox property, optical property, or charge mobility appears.[5] Among them, the sulfur-containing PHs, such as thiophene-incorporated polyaromatics, are of particular interest.[6] Fusion of benzene and thiophene units in linear and angular ways results in derivatives like dibenzothiophenes, benzonaphthothiophenes, and dinaphthothiophenes, which offer useful optical and semiconducting properties in these materials.[7] The framework expansion beyond planar dibenzothiophene into nonplanar frameworks is also interesting considering the possible co-facial packing motifs and thus greater electronic couplings expected between neighboring molecules for charge transfer.[8] Diphenanthro[9,10-b:9′,10′-d]thiophene (DPT), which

has a twisted framework due to several fjords in the molecule, was reported previously through a zinc-catalyzed reaction.[9] Nevertheless, there had been no report on the substituted derivatives, nor the properties such as crystal packing, photophysical, and redox properties. Recently, we reported a new series of benzo[3,4]phenanthro[1,2-b]benzo[3,4]phenanthro[2,1-b]thiophene derivatives, from which we observed that the substituents have much impact on the crystal packing and thus the charge mobility achievable with these materials.[10] Here, we wish to report the syntheses, characterization, and structural properties of substituted DPTs. In our previous reports on nitrogen-incorporated PHs, the phenanthrene- and tetracene-fused carbazoles were obtained from respective polyaryl-substituted carbazoles via simple Scholl reactions.[11] Similarly, phenanthrotriphenylenes were successfully prepared by performing Scholl reactions on tetraphenylbenzenes (Scheme 1).[12]

In this work, we report the designs and syntheses of a series of DPTs from respective polyarylthiophenes with the Scholl reactions as the key step, using iron chloride as the catalyst. Regioselective annulation reactions occurred, yielding twisted PHs. The crystal packing, photophysical, HOMO–LUMO energy levels, and other properties were measured and compared. Among them, the single-crystals of 6,12-difluorodiphenanthro[9,10-b:9′,10′-d]thiophene were used to fabricate single-crystal field-effect transistor devices, from which a hole mobility up to 0.22 $cm^2 V^{-1} s^{-1}$ was obtained.

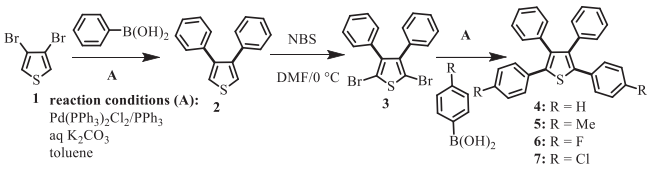
2 | RESULTS AND DISCUSSIONS

Schemes 2 and 3 show the preparations of polyarylthiophenes **4–7** and **9–13** precursors, while Schemes 4 and 5 present the syntheses of DPTs. Many catalysts have been reported to effect the Scholl reactions. These include iron chloride, copper salts, aluminum chloride, DDQ with acid, and a few others, although some complications may arise depending on the specific cases.[13]

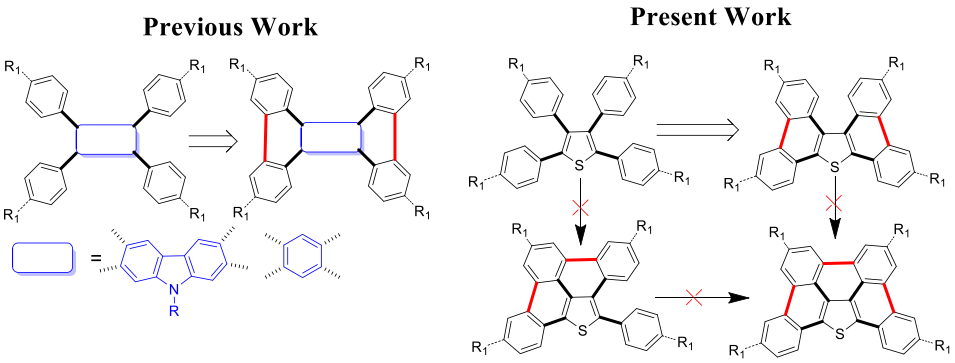
For the present conversions of polyarylthiophenes **4–7** and **9–13** to DPTs, we found that iron chloride was suitable catalyst, except in the case of parent DPT, where chlorination occurred at 6,12-positions. Nevertheless, the aluminum chloride served the purpose well to give the desired product, only after long reaction time (Scheme 4). The polyarylthiophenes **5–7**, with two R groups such as methyl, fluoro, and chloro groups, gave Me-DPT, Flu-DPT, and Cl-DPT, respectively, with iron chloride was the annulation agent (Scheme 4). With different R substituents, the time required for Scholl reaction varied from 0.5 h to 36 h, while reaction yields of annulated products were no lower than 90% (Table 1, entries **1–9**). A shorter reaction time was needed for the methyl-substituted polyarylthiophenes compared to the ones with chlorine, fluorine substituents, presumably due to the activating effect of methyl group versus others on the cationic intermediate involved (as shown in proposed mechanism in Scheme S1).

The Scholl reactions of polyarylthiophenes with four R groups are shown in Scheme 5. Polyarylthiophenes **9–11** gave Me-DPT1, Flu-DPT1, and Cl-DPT1 successfully, whereas **12–13**, in which eight fluorine atoms or four trifluoromethyl groups are involved, could not be annulated to give TFM-DPT and PFlu-DPT (Scheme 5, Table 1, entries **8–9**), again due to the deactivating effect of multiple electron-withdrawing groups.[14]

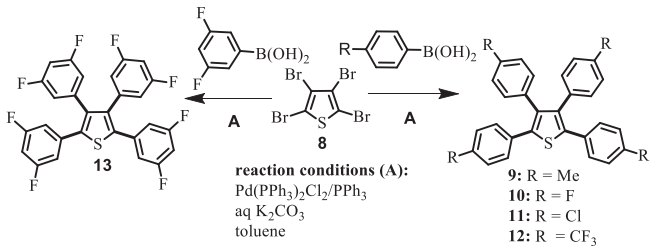
Although cyclization at the fjord at the top will give a six-membered ring of DBPT, this was not observed, possibly because of the strain involved at the fjord. Other annulated products such as Ph-BTT were not observed either, agreeing with the proposed reaction mechanism S1 (SI).



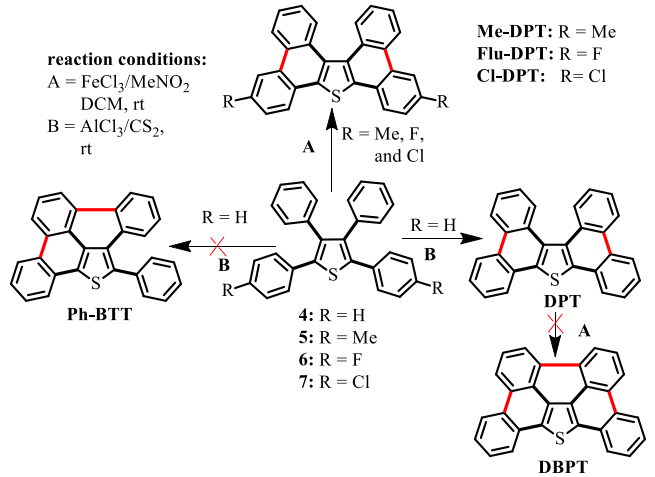
SCHEME 2 Preparation of polyarylthiophenes (**4–7**)



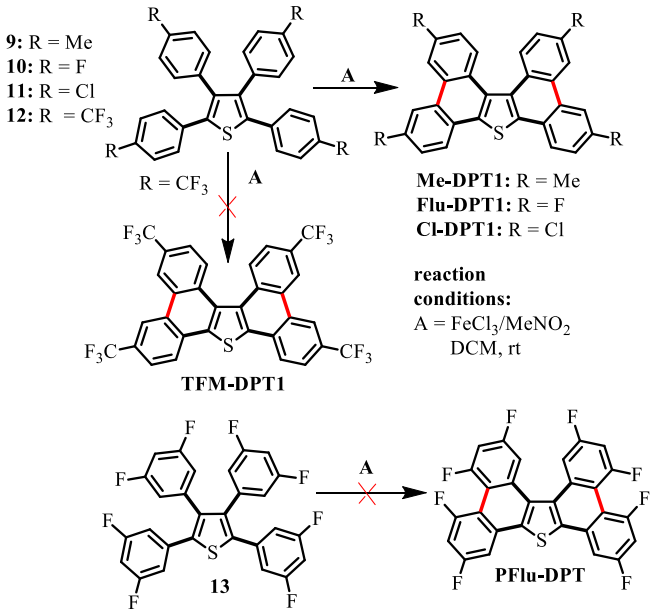
SCHEME 1 Representation of Scholl reactions successfully aimed by our group



SCHEME 3 Preparation of polyaryl thiophenes (**9–13**)



SCHEME 4 Preparation of disubstituted DPTs



SCHEME 5 Preparation of polysubstituted DPTs

2.1 | Single-crystal X-ray analyses

Single crystals of these thiophene derivatives were grown by the physical vapor transport (PVT) method.[15] Among them, crystal structures of three derivatives were successfully solved. Crystal structure analyses revealed that these DPTs contain three twisted fjords (bridges a, b and c) in their frameworks (Figure 1). The twist angle of the fjord varies from 19° to 23°. Smaller twist angles (~4° to ~10°) are observed for other two fjords.

The different twists in the fjords may contribute or perturb their cofacial packing (Figure 2). The introduction of heteroatom into the framework results in a molecular dipole (Table S1), which may also impact the packing motifs. In the case of DPT series, near cofacial packing and thus good π-π overlap of the frameworks for nearest neighbors was obtained for DPT and Cl-DPT, presumably due to geometric complementarity, and possibly the Cl...Cl interaction.[16]

Whereas the Flu-DPT adopts antiparallel packing for nearest neighbors, presumably because the molecular

TABLE 1 Conversions of polyarylthiophenes (**4–13**) to the annulated derivatives (DPTs) through iron/aluminum chloride-mediated annulation reactions

Entry	Reactant	Product	Yield (%)[a]	Time (hr)[a]
1	**4**	DPT[b]	90	18
2	**5**	Me-DPT	98	0.5
3	**6**	Flu-DPT	91	4
4	**7**	Cl-DPT	95	3
5	**9**	Me-DPT1	98	0.5
6	**10**	Flu-DPT1	92	14
7	**11**	Cl-DPT1	94	12
8	**12**	TFM-DPT[c]	—	36
9	**13**	PFlu[c]	—	36

[a]Yields and time are given for iron chloride-mediated Scholl reactions.
[b]Aluminum chloride-mediated annulation reaction.
[c]Unsuccessful Scholl reactions.

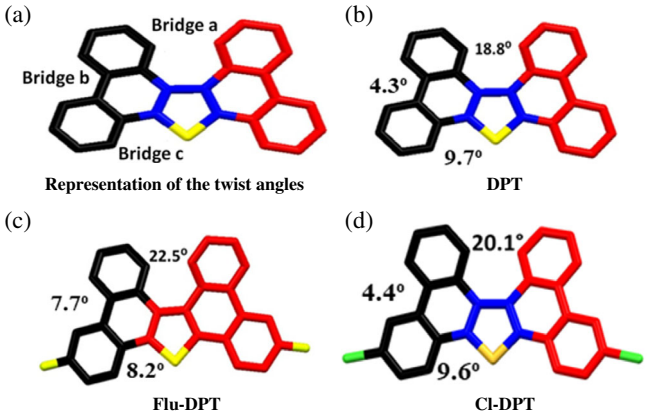


FIGURE 1 Molecular structures of DPT, Flu-DPT, and Cl-DPT, showing twist angles

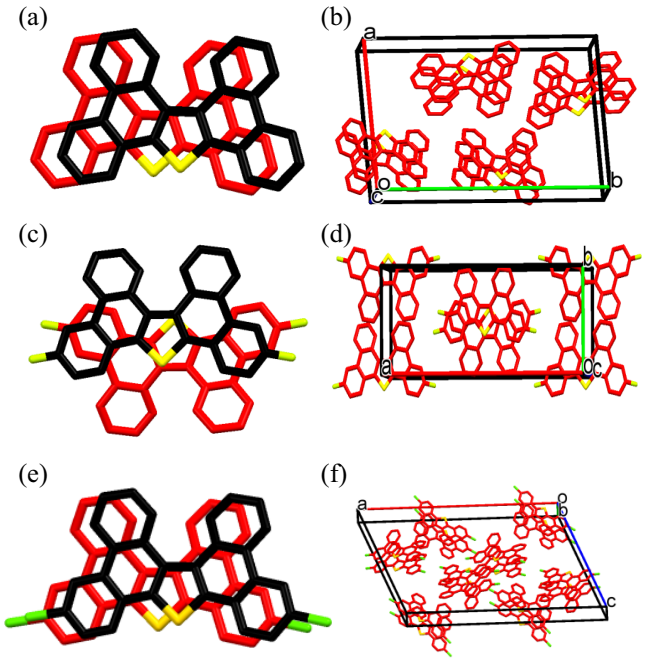


FIGURE 2 Packing motifs of (a,b) DPT, (c,d) Flu-DPT, and (e,f) Cl-DPT

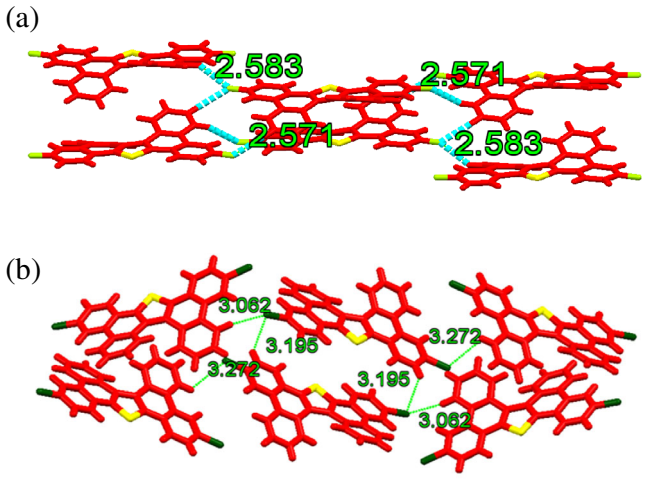


FIGURE 3 Packing motifs of (a) Flu-DPT and (b) Cl-DPT showing C-F...H-C and C-Cl...H-C interactions

dipole is dominating the packing so as to minimize the static repulsion. The twists in the molecule force the framework to shift in their packing, reducing their π-π overlaps. In their cofacial packing motifs, the π-π stacking distance, as measured between the two planes containing neighboring molecules, were found to be 3.62 Å to 3.72 Å. The packing motifs of DPTs were further examined to reveal interesting short contacts.[17] The fluoro- and chloro-substituted derivatives such as Flu-DPT and Cl-DPT, unlike the parent hydrocarbons, displayed C-H...

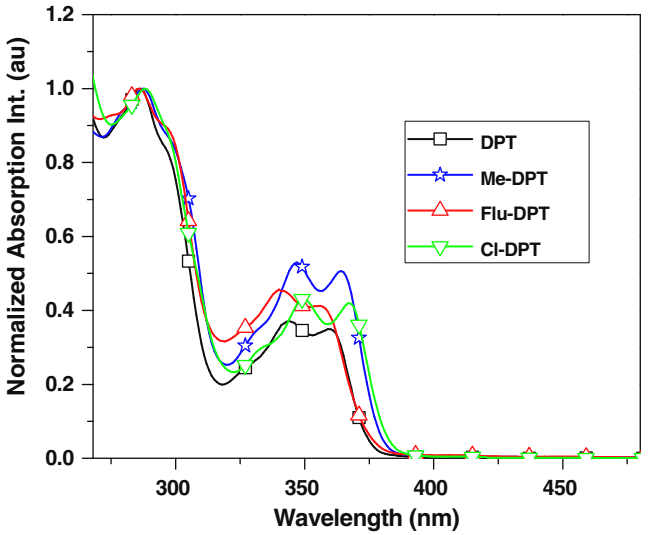


FIGURE 4 Normalized UV–Vis (in DCM) spectra of diphenanthrothiophenes (DPTs)

F-C (2.57 Å), C-H...Cl-C (3.06 Å) contacts (Figure 3), possibly because of the electronic effects two fluorines and chlorines on the respective polycyclic frameworks. The twisted geometries with cofacial packing of DPTs were expected to contribute to their photophysical properties as well.

2.2 | Photophysical, electrochemical, and thermal properties

The UV–Vis spectra of the DPTs are shown in Figure 4 and S39a, with pertinent values given in Table 2. As seen in Figure 4, the parent DPT gives three absorption bands centered at the wavelengths of 286, 344, and 359 nm respectively.

The absorption profile of this heteroarene was characteristic of that observed for the benzothiophene derivatives.[18] Bathochromic shift was noticed in its absorption profile compared to the dibenzothiophene. The absorption spectra of the substituted DPTs gave further shifts, depending on the electronic effects that methyl, fluorine, and chlorine substituents could exert on the parent DPT. These compounds showed deep blue emission in their dilute solutions (Figure S39b–c). Like the absorption, the substituted DPTs showed shifts in their emission profiles depending on the substituent. In addition to photophysical properties, other properties such as HOMO and LUMO of DPTs were determined both theoretically and experimentally (using AC–2). HOMO plots of DPTs indicate electron distribution over the thiophene portion and the linearly fused benzenes (Figure S40). The HOMO energy level is slightly altered by the substituents it

TABLE 2 Photophysical data and HOMO–LUMO energies and thermal decomposition temperatures of DPTs

Compd.	λ_{abs} (nm)	$\lambda_{em.}$ (nm)	E_{HOMO} (eV)[a]	E_{LUMO} (eV)[b]	E_g (eV)[c]	T_d (°C)[d]
DPT	359, 344, 286 (max)	402	5.66	2.37	3.29	316
Me-DPT	364, 346, 287 (max)	406	5.50	2.25	3.25	319
Flu-DPT	356, 340, 286 (max)	405	5.90	2.64	3.26	313
Cl-DPT	368, 348, 288 (max)	410	5.89	2.64	3.25	366
Me-DPT1	366, 348, 288 (max)	409	5.45	2.22	3.23	341
Flu-DPT1	354, 340, 282 (max)	412	—	—	3.25	311
Cl-DPT1	367, 349, 289 (max)	413	—	—	3.20	363

[a]E_{HOMO} was recorded by using photoelectron spectrometer.
[b]$E_{LUMO} = E_{HOMO} - E_g$.
[c]Optical bandgap, E_g, was determined from the intersections of normalized UV–Vis and emission spectra.
[d]Thermal decomposition temperatures measured at 5% weight loss.

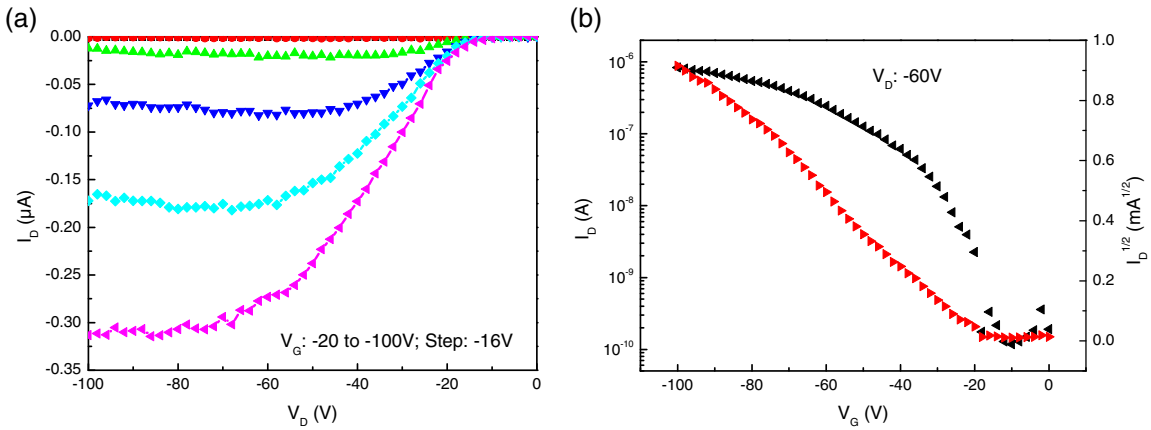


FIGURE 5 (a) Output characteristics of SCFET based on compound Flu-DPT. (b) transfer characteristics

carries, as shown in Table 2. These derivatives have good thermal stability, with their T_d values well above 300°C (-Figure S41, Table 2).

2.3 | SCFET performance

Single-crystal-based field-effect transistors (SCFETs) were attempted for these derivatives.[19] Nevertheless, except Flu-DPT, all other derivatives did not yield large enough crystals for device fabrication. Thus, Flu-DPT single crystal was used as the channel material in the fabrication of a top-contact, top-gate device on glass substrate, with painted colloidal graphite as the source, drain, and gate electrodes, respectively. A thin layer of parylene grown on the single crystal served as the dielectric material. The channel length, width, and parylene thickness were measured to be 1.0–0.5 mm, 0.25–0.20 mm, and 1.8–2.5 μm, respectively.

An average field-effect mobility of 0.14 $cm^2\ V^{-1}\ s^{-1}$ was obtained from the 17 devices made using Flu-DPT single-crystals. The maximum mobility was calculated to be 0.22 $cm^2\ V^{-1}\ s^{-1}$, while the on/off ratio was recorded as high as 2.86×10^4 (Figure 5, Table S2).

3 | CONCLUSIONS

In conclusion, we synthesized a series of substituted diphenanthrothiophenes from polyarylthiophenes. The Scholl reactions of these polyarylthiophenes were regioselective in the annulation step. The newly prepared DPTs were characterized by spectroscopic techniques including nuclear magnetic resonance (NMR), mass spectrometry, UV absorption, and further by single-crystal X-ray analyses for selected ones. The X-ray analyses show cofacial π-π stackings either in parallel or antiparallel fashion. The potential of these derivatives as semiconducting materials was demonstrated by the single-crystal field-effect transistors based on 6,12-difluoro diphenanthro[9,10:b]thiophene, which produced a maximum p–channel mobility of 0.22 $cm^2\ V^{-1}\ s^{-1}$ and an

average mobility of 0.16 $cm^2 V^{-1} s^{-1}$, with an on/off ratio more than 10^4.

4 | EXPERIMENTAL SECTION

The needed starting materials were directly purchased from the commercial sources. The starting materials such as 2,5-dibromo-3,4-diphenylthiophene (**3**),[20] 2,3,4,5-tetraphenylthiophene (**4**),[21] and 2,3,4,5-tetrakis (4-trifluoromethylphenyl) thiophene (**12**)[22] were synthesized according to literature reports. The coupling reactions such as Suzuki and Scholl reactions were carried out under inert atmosphere condition. The compounds were purified by column chromatography over silica gel (60–230 mesh). Solvents were distilled and dried before performing spectrophotometric and spectrofluorimetric analyses. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III-400 MHz spectrometer in $CDCl_3$. UV–Vis spectra were recorded by using U-3310 UV/VIS spectrophotometer and fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer. The HOMO energies were recorded using photoelectron spectrometer AC-2 (Riken Keiki). HOMO-LUMO plots were obtained from Spartan Pro program by the semiempirical method at the AM1 level.

4.1 | 2,5-dibromo-3,4-diphenylthiophene (3)[20]

In the absence of light, a DMF solution of N-bromosuccinamide (10.4 g, 58.4 mmol) was added dropwise to a solution of 3,4-diphenylthiophene (**2**) (6.70 g, 28.3 mmol) in DMF (45 mL) at 0°C. The reaction mixture was stirred at 0°C for 1 hr, followed by stirring for 15 hr at room temperature. The reaction was monitored using thin layer chromatography and after the starting material was consumed completely, water was added to the reaction mixture. The product was extracted with dichloromethane. Removal of dichloromethane by using a rotary evaporator gave the crude product, which was then recrystallized from ethanol to give the pure and colorless crystals. Yield: 10.2 g, 90%.

4.2 | General synthetic protocols for the preparation of polyaryl thiophenes (4–7 and 9–13)

General Suzuki C-C cross-coupling (protocol I): The preparation of polyarylthiophenes (**5–7**) was carried out in the following way using general Suzuki C-C cross-coupling reaction. A 250 ml round-bottom flask was charged with 3,4-diphenyl-2,5-dibromothiophene (**3**) (1.0 mmol), aryl boronic acid (2.1 mmol), $PdCl_2(PPh_3)_2$ (36 mg), triphenylphosphine (PPh_3) (26 mg) aq. potassium carbonate (1.39 g, 10.0 mmol, in 15 ml water), and toluene (50 ml) was added to it. This reaction, under an inert atmosphere, was conducted for 18 hr at 110°C. While the Suzuki coupling reaction progressed, the conversion of product was monitored by using thin layer chromatography. Cooling to room temperature led to two layers, from which the toluene layer was separated. Column chromatographic separation, using a mixture of dichloromethane and hexane, followed by solvent evaporation gave pure polyarylthiophenes.

General Suzuki C-C cross-coupling (protocol II): The preparation of polyarylthiophenes (**4** and **9–13**) was carried out in the following way using general Suzuki C-C cross-coupling reaction. A 250 ml round-bottom flask was charged with tetrabromothiophene (**8**) (1.0 mmol), aryl boronic acid (4.1 mmol), $PdCl_2(PPh_3)_2$ (72 mg), triphenylphosphine (PPh_3) (52 mg) aq. potassium carbonate (2.77 g, 20.0 mmol, in 30 ml water), and toluene (100 ml) was added to it. This reaction, under an inert atmosphere, was conducted for 24 hr at a temperature of 110°C. While the Suzuki coupling reaction progressed, the conversion of product was monitored by using thin layer chromatography. Cooling to room temperature gave two layers, from which toluene layer was separated. Column chromatographic separation, using a mixture of dichloromethane and hexane, followed by solvent removal gave pure polyarylthiophenes.

Preparation of 2,3,4,5-tetraphenylthiophene (4):[21] General Suzuki C-C cross-coupling (protocol **II**) was used to get compound **4**, by reacting tetrabromothiophene (**8**) with 4-phenylboronic acid (0.50 g, 4.1 mmol). Yield: 0.35 g, 89%. Spectroscopic characterization data of this compound are available in the ref. [21].

Preparation of 2,5-bis(4-methylphenyl)-3,4-diphenylthiophene (5): General Suzuki C-C cross-coupling (protocol **I**) was used to get compound **5**, by reacting 3,4-diphenyl-2,5-dibromothiophene (**3**) with 4-methylphenylboronic acid (0.29 g, 2.1 mmol). Yield: 0.38 g, 91%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.14–7.12 (m, 10H), 7.03–6.97 (m, 8H), 2.31 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 139.1, 138.3, 136.9, 136.7, 131.4, 130.9, 129.0, 127.8, 126.5, 21.1. HRMS [MALDI-TOF] m/z $\{M^+\}$ calcd for $C_{30}H_{24}S$ 416.1599; found 416.1595.

Preparation of 2,5-bis(4-fluorophenyl)-3,4-diphenylthiophene (6): General Suzuki C-C cross-coupling (protocol **I**) was used to get compound **6**, by reacting 3,4-diphenyl-2,5-dibromothiophene (**3**) with 4-fluorophenylboronic acid (0.30 g, 2.1 mmol). Yield: 0.40 g, 94%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.21–7.17 (m, 4H),

7.14–7.10 (m, 6H), 6.94–6.89 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.3, 160.9, 139.6, 137.3, 136.2, 130.9, 130.8, 130.8, 130.3, 127.9, 126.8, 115.4, 115.2. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{18}F_2S$ 424.1097; found 424.1092.

Preparation of 2,5-bis(4-chlorophenyl)-3,4-diphenylthiophene (7): General Suzuki C-C cross-coupling (protocol **I**) was used to get compound **7**, by reacting 3,4-diphenyl-2,5-dibromothiophene (**3**) with 4-chlorophenylboronic acid (0.33 g, 2.1 mmol). Yield: 0.42 g, 92%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.20–7.10 (m, 14H), 6.94 (d J = 7.6 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 140.1, 137.4, 136.0, 133.4, 132.6, 130.7, 130.4, 128.6, 128.1, 126.9. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{18}Cl_2S$ 456.0506; found 456.0504.

Synthesis of 2,3,4,5-tetrakis(4-methylphenyl)thiophene (9): General Suzuki C-C cross-coupling (protocol **II**) was used to get compound **9**, by reacting tetrabromothiophene (**8**) with 4-methylphenylboronic acid (0.56 g, 4.1 mmol). Yield: 0.40 g, 91%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.12 (d, J = 8.0 Hz, 4H), 7.02 (d, J = 8.0 Hz, 4H), 6.92 (d, J = 8.0 Hz, 4H), 6.84 (d, J = 8.0 Hz, 4H), 2.30 (m, 6H), 2.26 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 139.2, 138.0, 136.8, 135.9, 133.8, 131.7, 130.8, 129.1, 129.0, 128.6, 21.3, 21.2. HRMS [MALDI-TOF] m/z {M^+} for $C_{32}H_{28}S$ 444.1912; found 444.1912.

Preparation of 2,3,4,5-tetrakis(4-fluorophenyl)thiophene (10): General Suzuki C-C cross-coupling (protocol **II**) was used to get compound **10**, by reacting tetrabromothiophene (**8**) with 4-fluorophenylboronic acid (0.57 g, 4.1 mmol). Yield: 0.43 g, 93%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.20–7.16 (m, 4H), 6.96–6.82 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.4, 163.0, 161.0, 160.6, 138.3, 137.7, 132.4, 132.3, 132.0, 130.9, 130.8, 129.9, 115.6, 115.4, 115.3, 115.1. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{16}F_4S$ 460.0909; found 460.0911.

Preparation of 2,3,4,5-tetrakis(4-chlorophenyl)thiophene (11): General Suzuki C-C cross-coupling (protocol **II**) was used to get compound **11**, by reacting tetrabromothiophene (**8**) with 4-chlorophenylboronic acid (0.64 g, 4.1 mmol). Yield: 0.48 g, 92%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.22 (d, J = 8.4 Hz, 4H), 7.15–7.11 (m, 8H), 6.85 (d, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 138.3, 138.1, 134.1, 133.75, 133.2, 132.1, 132.0, 130.4, 128.8, 128.5. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{16}Cl_4S$ 523.9727; found 523.9721.

Preparation of 2,3,4,5-tetrakis(4-trifluoromethylphenyl) thiophene (12): General Suzuki C-C cross-coupling (protocol **II**) was used to get compound **12**, by reacting tetrabromothiophene (**8**) with 4-trifluoromethylphenyl boronic acid (0.78 g, 4.1 mmol). Yield: 0.54 g, 81%. Spectroscopic characterization data of this compound was available in the ref. [22].

Preparation of 2,3,4,5-tetrakis(3,5-difluorophenyl)thiophene (13): General Suzuki C-C cross-coupling (protocol **II**) was used to get compound **13**, by reacting tetrabromothiophene (**8**) with 3,5-difluorophenylboronic acid (0.65 g, 4.1 mmol). Yield: 0.32 g, 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.49–6.50 (m, 4H), 6.69–6.77 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.2, 164.1, 164.1, 164.0, 161.7, 161.7, 161.6, 161.5, 138.2, 138.0, 137.9, 137.8, 137.7, 135.7, 135.6, 135.5, 113.5, 113.4, 113.3, 113.2, 112.2, 112.1, 112.0, 111.9, 104.1, 103.9, 103.8, 103.6, 103.6, 103.4. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{12}F_8S$ 532.0532; found 532.0544.

Preparation of diphenanthro[9,10-b:9′,10′-d]thiophene (DPT): This compound was prepared by a cyclodehydrogenation protocol using compound **4** with a mixture of Cu(II)trifluoromethanesulfonate and aluminum(III)chloride. In a standard procedure, a 500 mL round-bottom flask was charged with 2,3,4,5-tetraphenylthiophene (**4**) (0.39 g, 1.0 mmol), Cu(II) trifluoromethanesulfonate (4.35 g, 12.0 mmol), and aluminum(III) chloride (1.6 g, 12.0 mmol), followed by the addition of CS_2 (200 mL). Stirring under nitrogen for 18 h and standing as such for 2 h afforded product as precipitates from the solution. The crude product was filtered and washed with aq. HCl, 10% ammonium hydroxide solution, and methanol to remove the copper and aluminum salts remained in the products. The dried solid was characterized to be the desired product. Yield: 0.35 g, 90%. Further sublimation at 320°C/270°C/220°C under vacuum (7.8×10^{-5} Torr) give 0.19 g pure product (Yield: 54%). Mp: 268–269°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.78–8.73 (m, 6H), 8.28–8.25 (m, 2H), 8.71–7.66 (m, 6H), 7.55 (t, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.4, 131.7, 130.1, 129.8, 129.2, 128.2, 127.5, 127.0, 126.9, 126.1, 125.3, 124.6, 123.8, 123.4. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{16}S$ 384.0973; found 384.0974.

4.3 | General method of Scholl reaction for the preparation of DPTs

The Scholl reaction between polyarylthiophenes and iron chloride afforded substituted DPTs. A general reaction procedure involves the reaction between polyarylthiophene (1.0 mmol) with iron chloride ($FeCl_3$) (2.92 g, 18.0 mmol) in DCM and nitromethane (12 mL). Thus, a solution of iron chloride in nitromethane was added to polythiophenene in dichloromethane under inert atmosphere. The dark reaction mixture obtained was stirred for different length of time of 0.5-36 h, depending on the substituent it carried. After the reaction was complete, as judged from TLC, the product was

precipitated by adding methanol to the reaction mixture. The product was isolated by filtration and the filtered solid product was washed with methanol and acetone.

Preparation of 6,12-dimethyldiphenanthro[9,10-b:9′,10′-d]thiophene (Me-DPT): A general Scholl reaction protocol was used to get the title compound, Me-DPT, by reacting 3,4-diphenyl-2,5-di-p-tolylthiophene (**5**) with iron chloride (Yield: 0.40 g, 98%). Further purification by temperature-gradient sublimation at 350°C/300°C/250°C (9.8×10^{-5} Torr) gave 0.38 g (Yield: 95%). Mp: 299°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.75–8.72 (m, 4H), 8.51 (s, 2H), 8.12 (d, J = 8.0 Hz, 2H), 7.66–7.63 (m, 2H), 7.55–7.50 (m, 4H), 2.66 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.1, 136.7, 131.1, 129.9, 129.8, 129.4, 129.0, 126.9, 126.1, 125.8, 125.1, 124.4, 123.8, 123.3, 22.1. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{30}H_{20}S$ 412.1286; found 412.1292.

Preparation of 6,12-difluorodiphenanthro[9,10-b:9′,10′-d]thiophene (Flu-DPT): A general Scholl reaction protocol was used to get pure title compound, Flu-DPT, by reacting 2,5-bis(4-fluorophenyl)-3,4-diphenyl thiophene (**6**) (0.43 g, 1.0 mmol) with iron chloride (Yield: 0.38 g, 91%). Further purification by temperature-gradient sublimation at 370°C/220°C/270°C (9.2×10^{-5} Torr) gave 0.34 g (Yield: 90%). Mp: 340°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.72 (d, J = 8.0 Hz, 2H), 8.61 (d, J = 8.4 Hz, 2H), 8.34 (dd, J = 13.2 Hz 3.2 Hz, 2H), 8.21–8.18 (m, 2H), 7.68 (t, J = 8.0 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.46–7.41 (m, 2H). Due to poor solubility, ^{13}C NMR of this compound was not recorded. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{14}F_2S$ 420.0784; found 420.0782.

Preparation of 6,12-dichlorodiphenanthro[9,10-b:9′,10′-d]thiophene (Cl-DPT) A general Scholl reaction protocol was used to get pure title compound, Cl-DPT, by reacting 2,5-bis(4-chlorophenyl)-3,4-diphenyl thiophene (**7**) (0.46 g, 1.0 mmol) with iron chloride (Yield: 0.43 g, 95%). Further purification by temperature-gradient sublimation at 380°C/3300°C/280°C (8.9×10^{-5} Torr) gave 0.38 g (Yield: 89%). Mp: >350°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.75–8.66 (m, 6H), 8.18 (d, J = 8.4 Hz, 2H), 7.72–7.65 (m, 4H), 7.61–7.57 (m, 2H). Due to poor solubility, ^{13}C NMR of this compound was not recorded. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{14}Cl_2S$ 452.0193; found 452.0200.

Preparation of 3,6,12,15-tetramethyldiphenanthro[9,10-b:9′,10′-d]thiophene (Me-DPT1) A general Scholl reaction protocol was used to get pure title compound, Me-DPT1, reacting 2,3,4,5-tetrakis(4-methyl phenyl)thiophene (**9**) (0.44 g, 1.0 mmol) with iron chloride (Yield: 0.43 g, 98%). Mp: 310°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.63 (d, J = 8.4 Hz, 2H), 8.50–8.49 (m, 4H), 8.10 (d, J = 8.0 Hz, 2H), 7.49–7.47 (m, 2H), 7.36–7.34 (m, 2H), 2.63 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.4, 136.2, 135.3, 131.1, 130.0, 129.5, 128.8, 127.3, 126.8, 126.5, 126.3, 124.4, 123.5, 123.2, 22.1, 21.9. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{32}H_{24}S$ 440.1599; found 440.1583.

Preparation of 3,6,12,15-tetrafluorodiphenanthro[9,10-b:9′,10′-d]thiophene (Flu-DPT1) A general Scholl reaction protocol was used to get pure title compound, Flu-DPT1, by reacting 2,3,4,5-tetrakis(4-fluoro phenyl)thiophene (**10**) (0.46 g, 1.0 mmol) with iron chloride (Yield: 0.40 g, 92%). Further purification by temperature-gradient sublimation at 370°C/320°C/270°C (9.5 × 10−5 Torr) gave 0.37 g (Yield: 90%). Mp: >350°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.70–8.66 (m, 2H), 8.25–8.22 (m, 6H), 7.49 (d, J = 10.0 Hz, 2H), 7.36–7.32 (m, 2H). Due to poor solubility, ^{13}C NMR of this compound was not recorded. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{12}F_4S$ 456.0596; found 456.0594.

Preparation of 3,6,12,15-tetrachlorodiphenanthro[9,10-b:9′,10′-d]thiophene (Cl-DPT1): A general Scholl reaction protocol was used to get pure title compound, Cl-DPT1, reacting 2,3,4,5-tetrakis(4-chlorophenyl)thiophene (**11**) (0.46 g, 1.0 mmol) with iron chloride (Yield: 0.49 g, 94%). Further purification by temperature-gradient sublimation at 410°C/360°C/310°C (9.2×10^{-5} Torr) gave 0.43 g (Yield: 87%). Mp: >350°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.60–8.57 (m, 6H), 8.16 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H). ^{13}C NMR of this compound could not be recorded due to poor solubility. HRMS [MALDI-TOF] m/z {M^+} calcd for $C_{28}H_{12}Cl_4S$ 519.9414; found 519.9408.

Preparation of 3,6,12,15-tetrakis(trifuoromethyl)diphenanthro[9,10-b:9′,10′-d]thiophene (TFM-DPT): According to the general Scholl reaction protocol, 2,3,4,5-tetrakis (4-trifluoromethylphenyl)thiophene (**12**) (0.66 g, 1.0 mmol) reacted with iron chloride but the reaction was not successful.

Preparation of 2,4,5,7,11,13,14,16-octafluorodiphenanthro[9,10-b:9′,10′-d]thiophene (PFlu-DPT): According to the general Scholl reaction protocol, 2,3,4,5-tetrakis(3,5-difluorophenyl)thiophene (**13**) (0.53 g, 1.0 mmol) reacted with iron chloride but the reaction was not successful.

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