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Non-linear Polyfused Aromatics with Extended π–Conjugation from Phenanthrotriphenylene, Tetracene and Pentacene: Syntheses, Crystal Packings, and Properties

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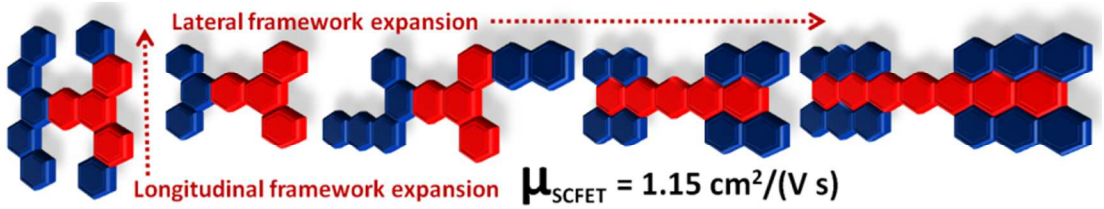
Supporting Information (**SI**) Placeholder



Abstract New classes of non-linear polyaromatics with extended conjugation at lateral and longitudinal directions from triphenylene, tetracene and pentacene backbones are reported. These planar and twisted polyfused aromatics are obtained through specific and selective multifold Scholl reactions from pre-designed polyaryls. These derivatives displayed shifted to perfect cofacial packing motifs. Single-crystals of one derivative, phenanthro[9,10:*b*]triphenylene, were used as p–channel materials in fabricating transistor devices, which exhibited an average mobility of 0.38 $cm^2V^{-1}s^{-1}$ and a maximum mobility reaching 1.15 $cm^2V^{-1}s^{-1}$

Introduction

The polycyclic aromatic hydrocarbons (PAHs), with variable modes of ring fusion, molecular shapes and geometry, have always attracted researchers' attention because the rich properties they possess, which find wide applications in many electronic and optoelectronic devices.[1] The packing motifs of a PAH in the solid or film state is crucial to its properties, such as photoluminescence, electronic coupling, and charge mobility.[2]

Depending on the π–electron distribution and geometric requirement, the polyaromatics may adopt cofacial, herringbone, or shifted π–stacking arrangement, each with different impact on their π–π electronic couplings and thus charge transport rate.[3] Extended conjugation system is generally favored for greater chance of π–π stacking and narrower band gap. Linear acenes such as anthracene, tetracene, pentacene, and hexacene are typical examples with the electronic coupling and thus charge mobility scales with the dimension of conjugation.[4]

Linear acenes are known to crystallize in herringbone arrangements.[5] Expanding the conjugation from the linear acenes in other dimensions is of interest in that new packing motifs and new intermolecular interactions may develop and lead to new or different possibilities in many physical or electronic properties.[6] To access these extended acenes, Bergmann and others were successful in synthesizing the parent phenanthrotriphenylene from respective polyaryl and other substrates.[7] Recently, we reported the syntheses of some polyaromatics with π–conjugation expanded/extended from coronene, perylene and pyrene core frameworks and some of them were shown to exhibit good hole carrier mobility in field-effect transistor configuration.[8]

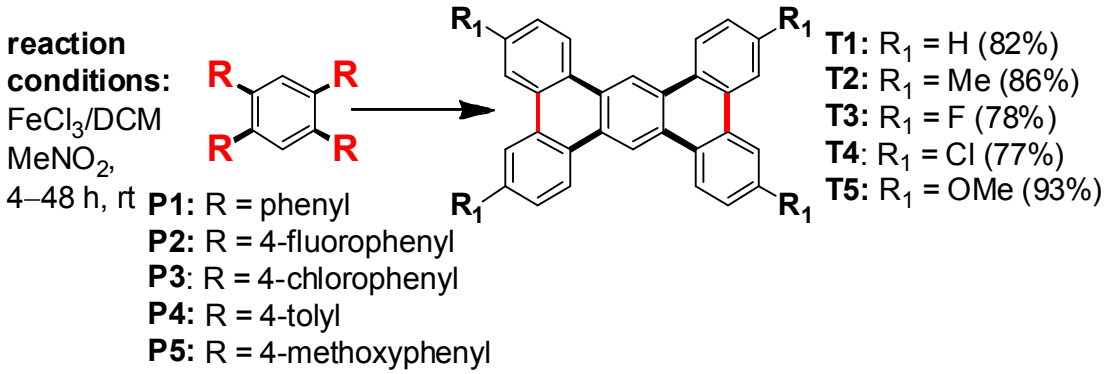
In this work, we demonstrate the synthesis and characterization of a series of twisted or planar PAHs extended from phenanthrotriphenylene, tetracene and pentacene frameworks. These derivatives were obtained by carrying out Scholl reactions on respective 1,2,4,5-tetraaryl substituted benzenes. The Scholl reactions of these polyaryls incorporating larger aromatic units such as 1-naphthyl, 2-naphthyl, 2-anthracenyl groups exhibited different reactivity and regioselectivity in the annulation steps. The resultant PAHs display a range of crystal packings, from exactly cofacial to shifted π-stacking, to herringbone arrangements, depending on the substitution and shape of the molecule. Single crystal-based field-effect transistor device with one of them, phenanthro[9,10:*b*]triphenylene, gave

a maximum hole mobility of 1.15 $cm^2V^{-1}s^{-1}$and an average mobility of 0.38 $cm^2V^{-1}s^{-1}$, which was higher than that measured for known triphenylenes and phenanthrotriphenylenes,[9] demonstrating the potential of these molecules as semiconducting materials.

Results and Discussions

Syntheses

The syntheses of the PAHs (**T1–T16**) reported here all started from the tetraaryl-substituted benzene derivatives and are illustrated in the Schemes **1–4**, with the preparation of starting polyaryls **P1–16** shown in the Schemes **S1-S4** (Supporting Information, **SI**). The polaryls of this type have been interesting scaffolds to undergo Scholl reaction and other cyclodehydrogenation reactions, furnishing polyaromatic hydrocarbons with graphene-type architectures.[10] With appropriate aryl substitution, expansion of conjugation in longitudinal or lateral direction of acenes can be envisaged. Various reagents, such as $FeCl_3$, DDQ, $MoCl_5$, $AlCl_3$, and $AlBr_3$ are known to be used in effecting cyclodehydrogenations.[11] Among these, we used $FeCl_3$ as the catalyst in the Scholl reactions presented here.

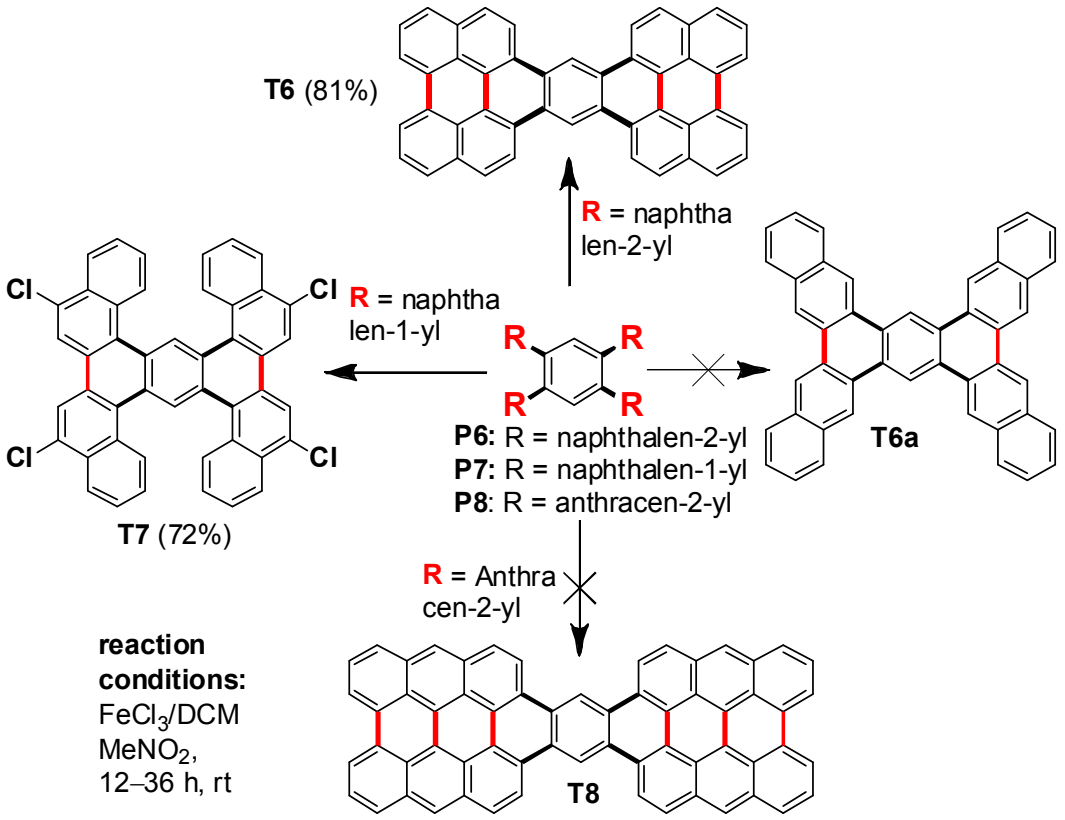


Scheme 1. Synthesis of substituted phenanthrotriphenylenes **(T1–T5)**.

Scheme 1 shows the Scholl reactions of benzene with 1,2,4,5-positions substituted with the same four groups of *para*-substituted phenyls, which is the most studied scaffolds.

Thus the polyaryls **P1–P5**, carrying different *para*-substituents, exhibited different reactivity (reaction time from 4 h to 48 h), resulted in different yields (72% to 93%). Here, the *para*-fluoro and *para*-chlorophenyl-substituted polyaryls had lower reactivity than that of the unsubstituted and *para*-methoxy-substituted ones, presumably because the oxidative formation of cation radical in the reaction mechanism is disfavored by electron-withdrawing groups.

Scheme 2 shows the Scholl reactions of polyaryls with the same yet larger naphthyl or anthracenyl units at all four positions. These polyaryls in general showed higher reactivity than with substituted phenyls (except for methoxy-substituted one), possibly because these involved more stable reaction intermediates, according to the reported reaction mechanism.[12] However, with different R groups of 2-naphthyl, 1-naphthyl and 2-anthracenyl, the annulating pattern varied. With 1-naphthyl unit, the only possible position of annulation would be the nearby 2-position, which was indeed the observed reaction site.[13] However, as shown in **Scheme 2**, the annulation occurred together with chlorination at 4-position to give the derivative **T7**. No parent compound was found.

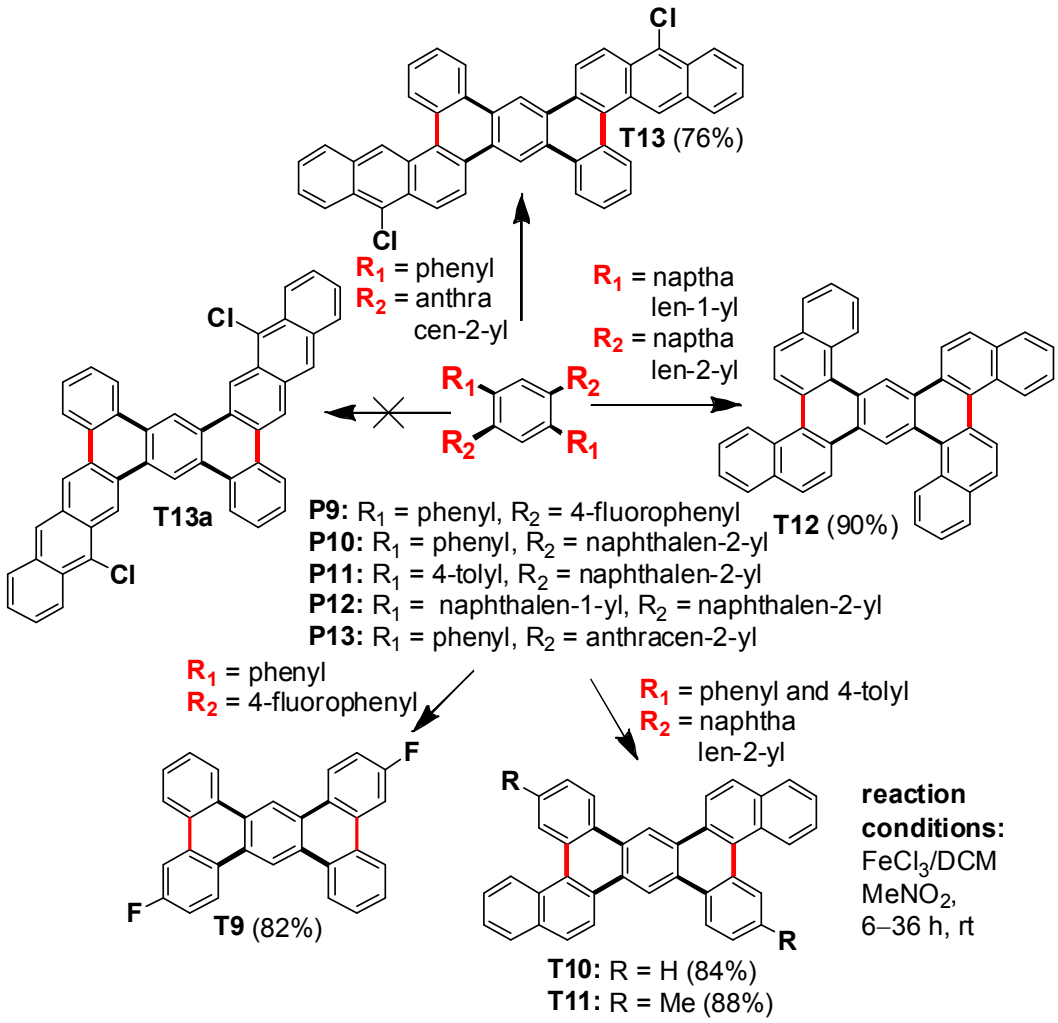


Scheme 2. Synthesis of tetranaphtho pentacenes (**T6**) and tetrabenzo phenanthrotriphenylene (**T7**).

This led to extension in the longitudinal direction from the phenanthrotriphenylene framework. With 2-naphtyl groups, the annulation occurred selectively at the 1-position of the naphthyl units, followed by further annulation at the 8-position to give **T6**, which has a pentacene-cored framework. The other mode of annulation at the 3-position was not observed. The regioselectivity is presumably due to the stability of a benzylic cation involved in the reaction mechanism (**Scheme S5, SI**). For 2-anthracenyl-substituted one, the precursor was sparingly soluble and no expected annulation product **T8** was isolated, although the annulation at the 1-position seems plausible.

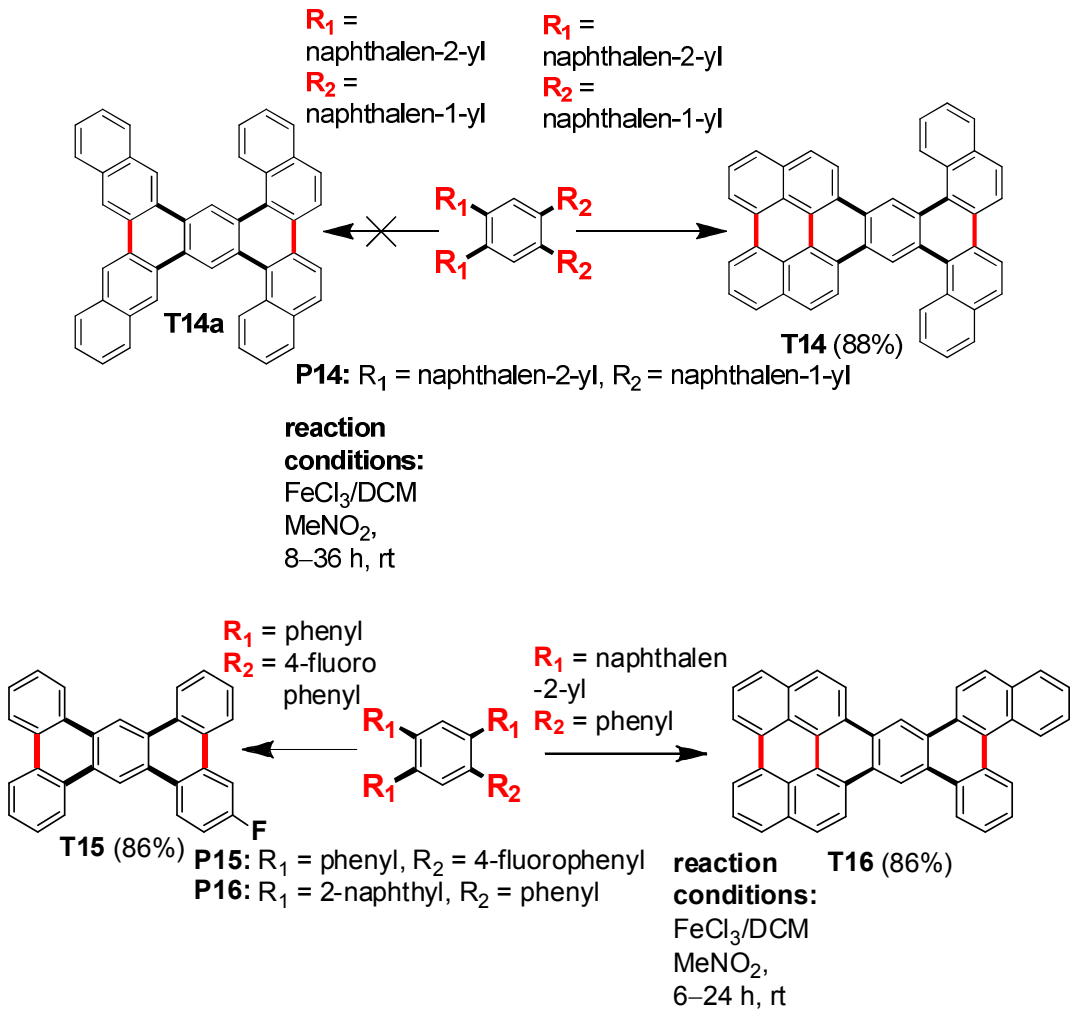
Scheme 3 shows the Scholl reactions with benzene substituted with two types of groups, from phenyl, naphthyl, and anthracenyl groups substituted unsymmetrically around benzene ring. Again, whenever 1-naphthyl group or phenyl group was involved, the neighboring 2-position was where the annulation occurred. While with 2-naphthyl group

or 2-anthracenyl group involved, the 1-position was where the annulation occurred. Thus regioselective formation of **T9–T13** was obtained (**Scheme 3**), with chlorination occurred on the 10-position of anthracene unit in **T13**. The observed regioselectivities for **T7** and **T13** are rationalized by the electronic effect on the stability of the intermediates involved (**Schemes S6** and **S7, SI**).



Scheme 3. Synthesis of phenanthrotriphenylenes **(T9–T13).**

Scheme 4 shows additional reactions for benzene substituted with different aryl groups on each side of the benzene ring. In cases where 2-naphthyl substituent was involved, multifold oxidative annulations at the 1,8-positions, yielding **T14**, **T16** (**Scheme 4**), were obtained. These are derivatives with a π–expansion from tetracene framework.



Scheme 4. Synthesis of phenanthrotriphenylenes and tetracenes derivatives (**T14–T16**).

Single-crystal X-ray analyses

To obtain the information about the packing motif, single-crystals of these PAHs were grown by physical vapor transport method (PVT). PVT method produced colorless, light-yellow to yellow and red-colored single-crystals of phenanthrotriphenylenes, tetracenes and pentacenes derivatives, with which the single-crystal X–ray measurements were performed (Figure **S63, SI**). Crystal packing of polyaromatics has been widely studied and broadly classified into categories such as herringbone, sandwich, γ, and β types, according to their balance of C···C and C···H interactions.[14] Of the seven crystals shown in Figure **1**, **T1** and **T6**, which were planar molecules, adopting γ type packing, with the neighboring molecules parallel, yet shifted (glided) to each other.

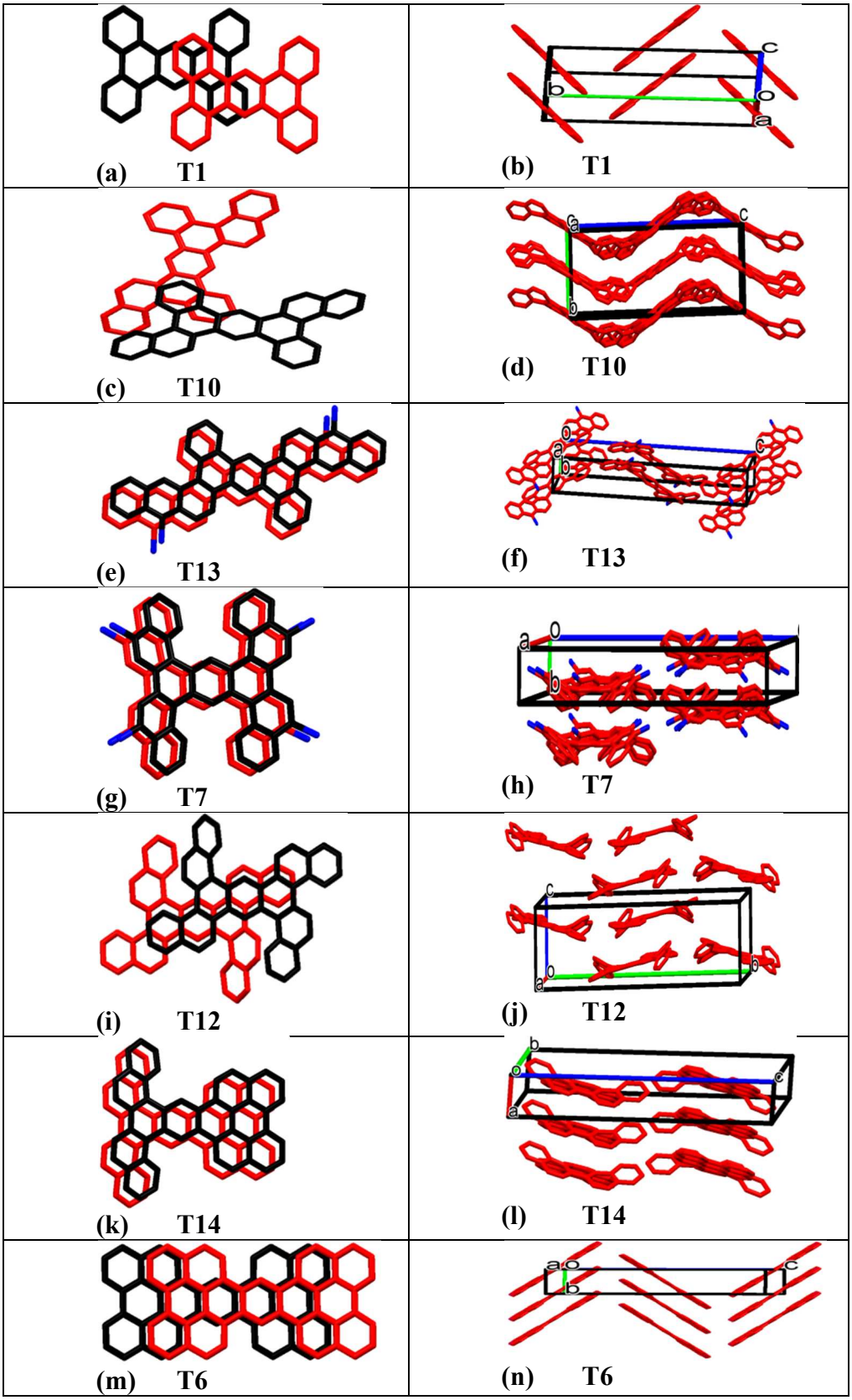


Figure 1. π–π stacks and packing motif of designed PAHs.

The two columns of cofacially π-stacked layers were separated by another layer, whose π-face made an angle with the π-faces of neighboring layers (with a dihedral angles of 62°

and 65° in **T1** and **T6**, respectively). The triphenylene and tetranaphthopentacene units had a π–π coupling distance of ~3.4 Å between the neighboring ring planes (Figure **1a** and **1m**). The rest of the molecules are contorted, with various extent of twist of the molecules. In the slightly twisted **T10**, the packing motif was somewhat perturbed to one with poorer π–π cofacial overlap and longer coupling distance of 3.7 Å in the triphenylene units of neighbouring molecules. The much twisted and chlorinated derivatives **T7** and **T13** exhibit nearly perfectly cofacial overlap, from which a stronger electronic coupling can be expected. In contrast to **T10**, the multiple chlorine atoms in these two molecules may have strong Cl···Cl interactions[15] and draw the neighbouring molecules face to face to have more C···C (~3.4 Å) and CCl···HC (2.8 Å to 2.9 Å) contacts (Figure **S65**, **SI**). The polyfused frameworks of **T14** (a twist angle of 35° between the naphthyl moiety and the central tetracene unit) and **T12** (twist angles 12° and 33° between the two naphthyls and the central anthracene unit) were more twisted compared to other derivatives, they also had good face-to-face overlap (β type), in which two cofacial layers were separated by 3.3 Å. In derivative **T14**, π–π stacked molecular layers were also nearly cofacial with each other. The diverse geometry of these PAHs, as it affected their packing, could contribute to their optical profiles as well.

Photophysical studies

These PAHs exhibited white (substituted phenanthrotriphenylenes), light-yellow to yellow (phenanthrotriphenylenes with larger frameworks), brown to red colors (benzo and naphthotetracenes and pentacenes) in their solid states. The electronic absorption spectra of the phenanthrotriphenylenes and naphthopentacenes are sketched in the Figures **2** and **S66 (SI)**, while the related data is enclosed in Table **S1** (**SI**). The electronic absorption of triphenylene framework was shown to be in the region of 200 to 280 nm.[16]

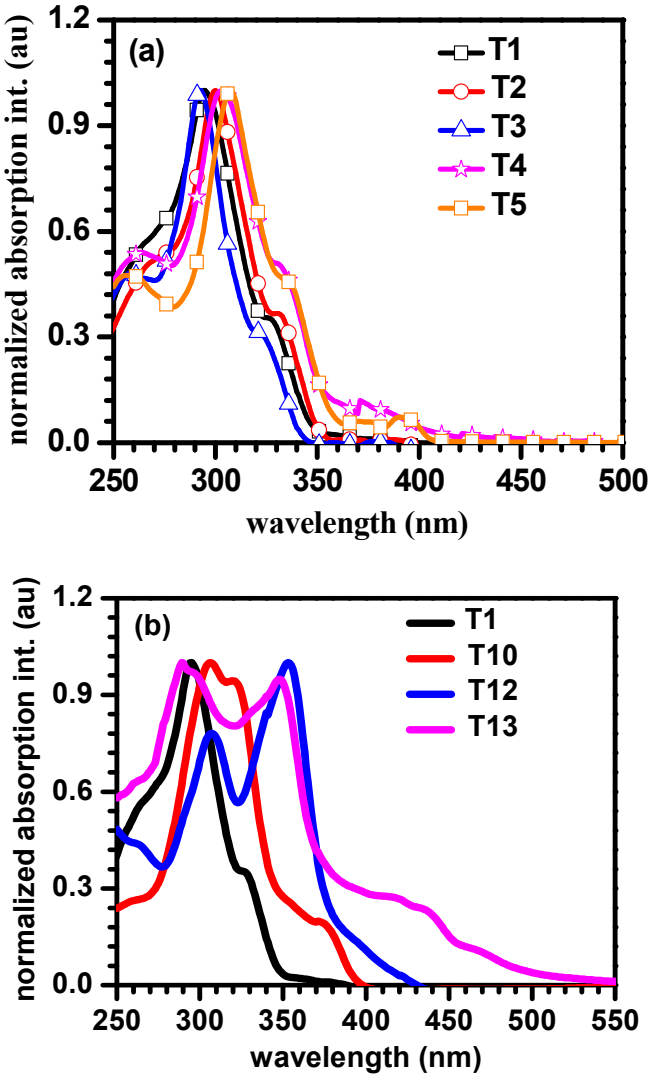


Figure 2. Normalized absorption spectra of phenanthrotriphenylenes as recorded in dichloromethane.

As theoretically suggested from the Clar's rule,[17] the absorption bands of phenanthrotriphenylenes were expected to be derived from triphenylene portion. The absorption features of parent phenanthrotriphenylenes followed the similar pattern for triphenylenes. The absorption bands of substituted phenanthrotriphenylenes such as **T2–T5** were found to arrange in the order of the electronic effects mediated by methoxy, methyl groups, fluorine and chlorine atoms. With their effective π–conjugating ability, the large phenanthrotriphenylenes such as **T10**, **T12**, **T7** and **T13** shifted their absorption maxima to longer wavelength. The tetracene derivatives **T14** and **T16** showed

characteristic absorption pattern of tetracene unit,[18] although there was a bathochromic shift in their absorption profiles (Figure **S66**, **SI**).

HOMO-LUMO Energies

The energies of highest occupied molecular orbitals (E_{HOMO}) for selected PAHs were measured by photoelectron spectrometry (AC-2) from the solid samples of PAHs. The optical band gaps of these PAHs were estimated from the absorption edges of their UV−visible spectra and the energies of lowest unoccupied molecular orbitals (E_{LUMO}) were calculated by subtracting the optical band gap from the HOMO energies. The HOMO and LUMO energies are given in the Table **1**.

The HOMO energies of substituted phenanthrotriphenylenes were found to be depending on the electronic effects of methyl, fluoro functional groups and change in π–conjugation on fusing extra benzenes with parent **T1**. For example, methyl-substituted **T2** and fluorine substituted **T10** (the derivative with two fluorine atoms) raised and lowered their HOMO energy levels with respect to parent **T1,** respectively. The phenanthrotriphenylenes **T3** and **T4** with multiple fluorine and chlorine atoms could not oxidize as to give their HOMO energy levels in AC2 measurements. Interestingly, adding four extra benzenes in **T1** raised the HOMO energy of **T13,** in agreement with the notion that electron removal could be easy from a more π–conjugated system. Also, based on the similar fact, tetracene derivative had higher-lying HOMO level with respect to the triphenylenes. The optical band gaps of **T10**, **T12** and **T14**, which had more π–extended polyfused frameworks, were lower compared to other derivatives.

Table 1. HOMO−LUMO energies of PAHs.

Compd.	[a] E_{HOMO} **(eV)**	[b] E_{LUMO} **(eV)**	[c] E_g **(eV)**

T1	5.80	2.13	3.67
T2	5.55	1.92	3.63
T3	-[d]	-	3.73
T4	-[d]	-	3.55
T9	5.91	2.21	3.70
T10	5.83	2.62	3.21
T12	5.56	2.50	3.06
T14	5.27	2.60	2.67

[a]E_{HOMO} was measured by photoelectron spectrometer (AC2). [b]$E_{LUMO} = E_{HOMO} - E_g$. [c]Optical band gap, E_g, was obtained from the absorption edge. [d]Compound samples were not measurable in AC-2 experiment.

Single crystal field-effect transistor performance

To demonstrate the capability of these PAHs to be used as semiconductor, single crystals of one of the derivatives, phenanthro[9,10:*b*]triphenylene (**T1**) were used as the channel material in the fabrication of single crystal field-effect transistor (SCFET) device. Carefully chosen single crystals were placed on a glass substrate, with both ends painted with colloidal graphite as the source and drain electrodes. After growing a thin layer of parylene on top of the crystal as the dielectric, colloidal graphite was painted on top to constitute a top-contact, top-gate transistor device.[19] The channel length, width and parylene thickness were measured for each to be in the range of 1.0–0.5 mm, 0.25–0.20 mm, and 1.8–2.5 μm, respectively (Figure **S67**, **SI**). Based on the data from 11 transistors, an average hole mobility of 0.38 $cm^2V^{-1}s^{-1}$ was calculated and a maximum mobility of 1.15 $cm^2V^{-1}s^{-1}$ was observed, with an on/off ratio of ~10^4 (Table **S2**, **SI**).

Conclusions

In conclusion, we have successfully synthesized and characterized new series of PAHs with extended conjugation from the phenanthrotriphenylene, tetracene and pentacene backbones laterally or longitudinally. All new derivatives were characterized by NMR and

high-resolution mass spectroscopy, while single-crystal X–ray analyses were also carried out for selected derivatives. The planar PAHs derivatives adopt γ type packing motif, where the π faces stack parallel and shifted from each other. The non-planar PAHs show a strong tendency to pack face-to-face for complementarity in shape. Those with multiple chlorine atoms may also favor cofacial π–π stacking due to Cl···Cl interactions. One of the derivatives, phenanthro[9,10:*b*]triphenylene was used to fabricate single crystal field-effect transistor and produced a maximum p–channel mobility of 1.15 $cm^2/V^{-1}s^{-1}$, with an on-off ratio of ~10^4.

Experimental Section

The required starting materials were purchased from commercial sources and used without further purification. Solvents were distilled and dried before performing spectrophotometric, and spectrofluorimetric analyses. The coupling reactions such as Suzuki coupling and Scholl reactions were carried out in nitrogen atmosphere. 1,4-Dibromo-2,5-diphenylbenzene (**3**)[20] and 1,2-dibromo-4,5-diphenylbenzene (**7**)[21] were prepared according to known protocols. The purification of the compounds was carried out by column chromatography using silica gel with 60-230 mesh size as the stationary phase. Nuclear magnetic resonance spectra were recorded on a Bruker AMX400 O FT-NMR spectrometer in chloroform-d_1 with tetramethylsilane (TMS) as the internal standard. V-550JASCOUV/VIS spectrophotometer was used to carry out absorption measurements using dichloromethane as solvent. Single crystals were grown in a temperature-gradient copper tube by vapor phase transfer method with Argon as the carrier gas. The X-ray diffraction was carried out on a Bruker X8APEX X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å) and the structure was solved by SHELX 97 program. The HOMO energies (E_{HOMO}) of selected samples were measured by a photoelectron spectrometer AC-2 (Riken Keiki).

Preparation of 1-bromo-2,4,5-triiodobenzene (**9**) 1-bromo-4-iodobenzene (2.83 g, 10.0 mmol), iodine (3.56 g, 14.0 mmol) and KIO_3 (1.50 g, 7.0 mmol) were dissolved in a mixture of acetic acid (50 ml) and sulfuric acid (10 ml). The reaction mixture was heated at 80 °C for 6 h. On completion of reaction, the mixture was cooled and poured into ice water. The precipitated solid was filtered, washed with water and methanol to afford a white solid. Yield: 3.96 g, 74%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (s, 1H), 8.05 (s, 1H). ^{13}C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_6H_2BrI_3$ 533.6474; found 533.6464.

General procedure of Suzuki coupling on bromo/iodo benzenes The Suzuki coupling reactions of bromo/iodo benzenes were performed with different mole ratio of aryl boronic acids and $Pd(PPh_3)_2Cl_2$ and PPh_3. In four-fold Suzuki coupling reactions of 1,2,4,5-tetrabromobenzene (**1**), the compound (5.0 mmol) was mixed with aryl boronic acid (21.0 mmol), $Pd(PPh_3)_2Cl_2$ (144 mg), PPh_3 (104 mg) in a mixture of toluene (60 ml) and water (20 ml). In two-fold Suzuki coupling reactions of 1,4-dibromo-2,5-diiodobenzene (**2**), 1,4-dibromo-2,5-diarylbenzene (**3**–**5**), 1,2-dibromo-4,5-diiodobenzene (**6**), 1,2-dibromo-4,5-diarylbenzene (**7**–**8**), these derivatives (5.0 mmol) were mixed with aryl boronic acid (11.0 mmol), $Pd(PPh_3)_2Cl_2$ (72 mg), PPh_3 (52 mg) in a mixture of toluene (60 ml) and water (20 ml). In three-fold Suzuki coupling reactions of 1-bromo-2,4,5-triiodobenzene (**9**), the compound (5.0 mmol) was mixed with aryl boronic acid (16.0 mmol), $Pd(PPh_3)_2Cl_2$ (108 mg), PPh_3 (78 mg) in toluene (60 ml) and water (20 ml) mixture. In one-fold Suzuki coupling reactions of 1-bromo-2,4,5-triarylbenzene (**10**–**11**), the compound (5.0 mmol) was mixed with aryl boronic acid (6.0 mmol), $Pd(PPh_3)_2Cl_2$ (36 mg), PPh_3 (26 mg) in toluene (60 ml) and water (20 ml) mixture.

The reaction mixture was heated to reflux for 24 h in nitrogen atmosphere. On completion of the reaction, the product solution was cooled and the toluene layer was separated.

Toluene was removed by rotary evaporator. The product was purified by column chromatography using dichloromethane–hexane as the eluent to give a white powder.

Preparation of 1,4-dibromo-2,5-bis(naphthalene-2-yl)benzene (4) Following the general procedure, 1,4-dibromo-2,5-diiodobenzene (**2**) (2.44 g, 5.0 mmol) and naphthalene-2-boronic acid (1.89 g, 11.0 mmol) were reacted to give the product as white powder. Yield: 1.71 g, 70%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96-7.92 (m, 8H), 7.80 (s, 2H), 7.64-7.61 (m, 2H), 7.58-7.54 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0, 137.0, 135.5, 133.1, 132.9, 128.4, 128.3, 127.8, 127.7, 127.2, 126.6, 121.6. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{26}H_{16}Br_2$ 485.9619; found 485.9637.

Preparation of 1,2-dibromo-4,5-bis(naphthalene-1-yl)benzene (5) Following the general procedure, 1,4-dibromo-2,5-diiodobenzene (**2**) (2.44 g, 5.0 mmol) and naphthalene-1-boronic acid (1.89 g, 11.0 mmol) were reacted to give the product as powder. Yield: 1.66 g, 68%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99-7.95 (m, 4H), 7.77 (s, 2H), 7.68-7.47 (m, 10H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.3, 137.6, 135.5, 133.5, 131.4, 129.0, 128.8, 128.8, 128.2, 127.2, 126.5, 126.2, 125.8, 125.2, 123.1. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{26}H_{16}Br_2$ 485.9619; found 485.9620.

Preparation of 1,2-dibromo-4,5-bis(naphthalene-2-yl)benzene (8) Following the general reaction procedure, 1,2-dibromo-4,5-diiodobenzene (**6**) (2.44 g, 5.0 mmol) and naphthalene-2-boronic acid (1.89 g, 11.0 mmol) were reacted to give the product as white powder. Yield: 1.81 g, 74%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (s, 2H), 7.78-7.72 (m, 6H), 7.54 (d, *J* = 8.8 Hz 2H), 7.46-7.44 (m, 4H), 7.08-7.05 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.2, 136.8, 135.7, 133.3, 132.4, 128.4, 128.1, 127.6, 126.3, 123.9. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{26}H_{16}Br_2$ 485.9619; found 485.9623.

Preparation of 1-bromo-2,4,5-triphenylbenzene (10) Following the general procedure, 1-bromo-2,4,5-diiodobenzene (**9**) (2.67 g, 5.0 mmol) and phenylboronic acid (1.95 g, 16.0 mmol) were reacted to give the product as white powder. Yield: 1.25 g, 65%. ^{1}H NMR

($CDCl_3$, 400 MHz) δ7.77 (s, 1H), 7.54-7.40 (m, 6H), 7.26-7.15 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.5, 141.1, 140.6, 140.2, 139.9, 139.8, 134.9, 133.3, 129.7, 129.4, 128.2, 128.1, 128.0, 127.7, 127.0, 126.9, 121.4. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{24}H_{17}Br$ 384.0514; found 384.0523.

Preparation of 1-bromo-2,4,5-tris(naphthalene-2-yl)benzene (11) Following the general reaction procedure, 1-bromo-2,4,5-diiodobenzene (**9**) (2.67 g, 5.0 mmol) and naphthalene-2-boronic acid (2.75 g, 16.0mmol) were reacted to give the product as white powder. Yield: 1.85 g, 69%. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.01 (s, 1H), 7.96-7.89 (m, 5H), 7.85 (s, 1H), 7.80-7.70 (m, 5H), 7.66 (s, 1H), 7.59-7.52 (m, 4H), 7.48-7.42 (m, 4H), 7.19-7.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.8, 141.2, 139.9, 138.1, 137.9, 137.5, 135.4, 134.1, 133.4, 133.2, 132.8, 132.4, 132.3, 128.5, 128.4, 128.3, 127.8, 127.6, 126.4, 126.2, 126.1, 121.9. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{36}H_{23}Br$ 534.0983; found 534.0975.

General procedure for the preparation of 1,2,4,5-tetraphenylbenzene (P1) Following general reaction procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and phenylboronic acid (2.56 g, 21.0 mmol) were reacted to give product as white powder. Yield: 1.76 g, 92%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.54 (s, 2H), 7.25-7.23 (m, 20H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.0, 139.4, 139.6, 133.0, 129.9, 128.0, 126.6. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{30}H_{22}$ 382.1722; found 382.1726.

Preparation of 1,2,4,5-tetrakis(4-methylphenyl)benzene (P2) Following the general procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and *para*-tolylboronic acid (2.86 g, 21.0 mmol) were reacted to give the product as white powder. Yield: 1.93 g, 88%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.48 (s, 2H), 7.12 (t, J = 6.0 Hz, 8H), 7.06 (d, J = 8.0 Hz, 8H), 2.34 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.3, 138.2, 136.1, 133.0, 129.7, 128.7, 21.1.HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{34}H_{30}$ 438.2348; found 438.2359.

Preparation of 1,2,4,5-tetrakis(4-fluorophenyl)benzene (P3) Following the general procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and 4-fluorophenylboronic acid (2.94 g, 21.0 mmol) were reacted to give the product as white powder. Yield: 1.95 g, 86%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (s, 2H), 7.19-7.14 (m, 8H), 6.99-6.93 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.2, 160.7, 138.8, 136.5, 132.8, 131.4, 131.3, 115.2, 115.0. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{30}H_{18}F_4$ 454.1345; found 454.1348.

Preparation of 1,2,4,5-tetrakis(4-chlorophenyl)benzene (P4) Following the general procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and 4-chlorophenylboronic acid (3.28 g, 21.0 mmol) were reacted to give the product as white powder. Yield: 2.08 g, 80%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (s, 2H), 7.24 (d, J = 8.4 Hz, 8H), 7.12 (d, J = 8.4 Hz, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.8, 138.7, 133.2, 132.7, 131.0, 128.5. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{30}H_{18}Cl_4$ 518.0163; found 518.0154.

Preparation of 1,2,4,5-tetrakis(4-methoxyphenyl)benzene (P5) Following the general procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and 4-methoxyphenylboronic acid (3.19 g, 21.0 mmol) were reacted to give the product as white powder. Yield: 2.06 g, 82%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (s, 2H), 7.15 (t, J = 6.8 Hz, 8H), 6.80 (d, J = 8.4 Hz, 8H), 3.80 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.3, 138.8, 133.6, 132.8, 129.0, 128.2, 113.4, 55.1.HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{34}H_{30}O_4$ 502.2144; found 502.2148.

Preparation of 1,2,4,5-tetra(naphthalen-2-yl)benzene (P6) Following the general procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and 2-naphthaleneboronic acid (3.61 g, 21.0 mmol) were reacted to give the product as white powder. Yield: 2.04 g, 70%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (s, 4H), 7.94 (s, 2H), 7.91-7.72 (m, 8H), 7.65-7.59 (m, 4H), 7.57-7.27 (m, 12H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.4, 133.8, 132.7, 128.5, 128.2, 127.7, 126.3, 126.1, 126.0, 125.7. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{30}$ 582.2348; found 582.2344.

Preparation of 1,2,4,5-tetra(naphthalen-1-yl)benzene (P7) Following the general reaction procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and 1-naphthaleneboronic acid (3.61 g, 21.0 mmol) were reacted to give the product as white powder. Yield: 2.21 g, 76%. Compound was partially soluble in most of the solvents and it could not be purified to get good ^{1}Hand ^{13}CNMR spectra. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{30}$ 582.2348; found 582.2342.

Preparation of 1,2,4,5-tetra(anthracen-2-yl)benzene (P8) Following the general procedure, 1,2,4,5-tetrabromobenzene (**1**) (1.97 g, 5.0 mmol) and 2-anthraceneboronic acid (4.66 g, 21.0 mmol) were reacted to give the product as white powder. The compound was almost insoluble in most of the solvents and it could not be purified to get good ^{1}H and ^{13}CNMR spectra. Yield: 3.13 g, 80%. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{62}H_{38}$ 782.2974; found 782.2984.

Preparation of 1,4-diphenyl-2,5-bis(4-fluorophenyl)benzene (P9) Following the general procedure, 1,4-dibromo-2,5-diphenylbenzene (**3**) (1.94 g, 5.0 mmol) and 4-fluorophenylboronic acid (1.54 g, 11.0 mmol) were reacted to give the product as white powder. Yield: 1.67 g, 80%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (s, 2H), 7.29-7.16 (m, 14H), 6.97-6.92 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.1, 160.7, 140.7, 139.8, 138.7, 136.8, 132.8, 131.4, 129.8, 128.1, 126.8, 115.1, 114.8. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{30}H_{20}F_2$ 418.1533; found 418.1546.

Preparation of 1,4-diphenyl-2,5-bis(naphthalene-2-yl)benzene (P10) Following the general procedure, 1,4-dibromo-2,5-diphenylbenzene (**3**) (1.94 g, 5.0 mmol) and naphthalene-2-boronic acid (1.89 g, 11.0 mmol) were reacted to give product as white powder. Yield: 1.88 g, 78%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ7.89 (s, 2H), 7.81-7.78 (m, 4H), 7.71 (s, 2H), 7.48-7.46 (m, 4H), 7.32-7.30 (m, 4H), 7.26-7.22 (m, 8H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 139.9, 139.6, 138.7, 133.4, 132.2, 129.9, 128.5, 128.3, 128.1,

128.0, 127.6, 127.2, 126.8, 126.0, 125.9. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{38}H_{26}$ 482.2035; found 482.2041.

Preparation of 1,4-bis(*para*-tolyl)-2,5-bis(naphthalene-2-yl)benzene (P11) Following general reaction procedure, 1,4-dibromo-2,5-bis(naphthalene-2-yl)benzene (**4**) (2.44 g, 5.0 mmol) and *para*-tolueneboronic acid (1.50 g, 11.0 mmol) were reacted to give product as white powder. Yield: 2.14 g, 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ7.89 (s, 2H), 7.82-7.79 (m, 4H), 7.66 (d, *J* = 8.8 Hz 4H), 7.48-7.46 (m, 4H), 7.27-7.17 (m, 6H), 7.03 (d, *J* = 8.0 Hz 4H), 2.31 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.6, 139.5, 139.0, 137.9, 136.4, 133.5, 132.2, 129.8, 128.8, 128.4, 128.0, 127.6, 127.1, 125.9, 125.8, 21.1. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{40}H_{30}$ 510.2348; found 510.2360.

Preparation of 1,4-bis(naphthalene-1-yl)-2,5-bis(naphthalene-2-yl)benzene (P12) Following the general reaction procedure, 1,4-dibromo-2,5-bis(naphthalene-2-yl)benzene (**4**) (2.44 g, 5.0 mmol) and naphthalene-1-boronic acid (1.89 g, 11.0 mmol) were reacted to give the product as white powder. Yield: 2.39 g, 82%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08-8.01 (m, 2H), 7.87-7.78 (m, 8H), 7.66-7.59 (m, 4H), 7.47-7.34 (m, 12H), 7.19-7.16 (m, 4H). ^{13}C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{30}$ 582.2348; found 582.2363.

Preparation of 1,4-diphenyl-2,5-bis(anthracene-2-yl)benzene (P13) Following the general reaction procedure, 1,4-dibromo-2,5-diphenylbenzene (**3**) (1.94 g, 5.0 mmol) andanthracene-2-boronic acid (2.44 g, 11.0 mmol) were reacted to give product as white powder. Yield: 2.33 g, 80%. The compound was partially soluble in most of the solvents and was used directly for next reaction. ^{1}H and ^{13}C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{30}$ 582.2348; found 582.2352.

Preparation of 1,2-bis(naphthalene-1-yl)-4,5-bis(naphthalene-2-yl)benzene (P14) Following the general reaction procedure, 1,2-dibromo-4,5-bis(naphthalene-2-yl)benzene

(**8**) (2.44 g, 5.0 mmol) and naphthalene-1-boronic acid (1.89 g, 11.0 mmol) were reacted to give the product as white powder. Yield: 2.51 g, 86%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, J = 8.0 Hz, 1H), 8.01-7.96 (m, 3H), 7.84-7.73 (m, 7H), 7.67-7.59 (m, 5H), 7.51-7.41 (m, 6H), 7.34-7.24 (m, 5H), 7.18-7.06 (m, 3H). ^{13}C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{46}H_{30}$ 582.2348; found 582.2357.

Preparation of 1-(4-fluorophenyl)-2,4,5-triphenylbenzene (P15) Following the general reaction procedure, 1-dibromo-2,4,5-triphenylbenzene (**10**) (1.93 g, 5.0 mmol) and 4-fluorophenylboronic acid (0.84 g, 6.0 mmol) were reacted to give the product as white powder. Yield: 1.66 g, 83%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (s, 1H), 7.50 (s, 1H), 7.29-7.17 (m, 17H), 6.96-6.92 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.1, 160.6, 143.1, 140.9, 140.8, 139.8, 139.7, 138.6, 136.9, 133.0, 132.8, 131.4, 129.9, 128.1, 128.0, 126.7, 115.0, 114.8. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{21}F$ 400.1627; found 400.1638.

Preparation of 1-(phenyl)-2,4,5-tris(naphthalene-2-yl)benzene (P16) Following the general reaction procedure, 1-dibromo-2,4,5-tris(naphthalene-2-yl)benzene (**11**) (2.68 g, 5.0 mmol) and phenylboronic acid (0.73 g, 6.0 mmol) were reacted to give the product as white powder. Yield: 2.40 g, 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 2H), 7.90 (s, 1H), 7.81-7.74 (m, 8H), 7.66 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.47-7.43 (m, 6H), 7.33-7.31 (m, 2H), 7.27-7.23 (m, 6H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 140.1, 139.8, 138.7, 133.9, 133.6, 133.5, 132.2, 130.0, 128.5, 128.4, 128.2, 128.1, 127.6, 127.4, 127.3, 126.8, 126.0, 125.9. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{42}H_{28}$ 532.2191; found 532.2198.

General procedure for preparation of extensive π–conjugates of phenanthrotriphenylene, tetracene and pentacene hydrocarbons 1,2,4,5-tetraaryl benzene (**P1–P16**) (1.0 mmol) was dissolved in anhydrous dichloromethane (60 ml). Iron

chloride (3.24 g, 20.0 mmol), as dissolved in nitromethane (10 ml), was added via syringe to the polyaryl solution. In case of **P14** and **P16** (4.86 g, 30.0 mmol), **P6** (6.48 g, 40.0 mmol) and **P8** (9.72 g, 60.0 mmol) different mole ratio of iron chloride was used.

The reaction mixture was stirred for 4–36 h at room temperature in nitrogen atmosphere. On completion of reaction, the product was precipitated by adding methanol. The precipitated product was washed with methanol and acetone, successively. The product exhibited white to red color, depending on the conjugation in polyaromatic hydrocarbon.

Preparation of phenanthro[9,10:*b*]triphenylene (T1) Following the general procedure, 1,2,4,5-tetraphenylbenzene (**P1**) (0.38 g, 1.0 mmol) and iron chloride were reacted for 18 h to give the product as white solid. Yield: 0.31 g, 82%. The product was further purified by vacuum sublimation in a temperature gradient oven at 440 °C/390 °C/350 °C ($4.1*10^{-5}$ Torr) to give 0.24 g (Yield: 78%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.94 (s, 2H), 8.98 (d, J = 8.0 Hz, 4H), 8.71 (d, J = 7.6 Hz, 4H), 7.80-7.71 (m, 8H).^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{18}$ 378.1403; found 378.1407.

Preparation of 3,6,12,15-tetramethylphenanthro[9,10:*b*]triphenylene (T2) Following the general procedure, 1,2,4,5-tetrakis(4-methylphenyl)benzene (**P2**) (0.44 g, 1.0 mmol) and iron chloride were reacted for 12 h to give the product as white solid. Yield: 0.37 g, 86%. The product was further purified by vacuum sublimation in a temperature gradient oven at 450 °C/400 °C/350 °C ($4.3*10^{-5}$ Torr) to give 0.27 g (Yield: 72%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.77 (s, 2H), 8.81 (d, J = 8.4 Hz, 4H), 8.46 (s, 4H), 7.55 (d, J = 8.0 Hz, 4H), 2.66 (s, 12H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{34}H_{26}$ 434.2029; found 434.2027.

Preparation of 3,6,12,15-tetrafluorophenanthro[9,10:*b*]triphenylene (T3) Following the general reaction procedure, 1,2,4,5-tetrakis(4-fluorophenyl)benzene (**P3**) (0.45 g, 1.0

mmol) and iron chloride were reacted for 24 h to give the product as white solid. Yield: 0.35 g, 78%. The product was further purified by vacuum sublimation in a temperature gradient oven at 480 °C/430 °C/380 °C ($4.2*10^{-5}$ Torr) to give 0.25 g (Yield: 70%). Mp: >300 °C. ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz) δ 9.69 (s, 2H), 8.93-8.90 (m, 4H), 8.19 (d, J = 10.4 Hz, 4H), 7.57-7.52 (m, 4H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{30}H_{14}F_4$ 450.1026; found 450.1015.

Preparation of 3,6,12,15-tetrachlorophenanthro[9,10:*b*]triphenylene (T4) Following the general procedure, 1,2,4,5-tetrakis(4-chlorophenyl)benzene (**P4**) (0.52 g, 1.0 mmol) and iron chloride were reacted for 48 h to give the product as white solid. Yield: 0.40 g, 77%. The product was further purified by vacuum sublimation in a temperature gradient oven at 480 °C/430 °C/380 °C ($6.3*10^{-5}$ Torr) to give 0.27 g (Yield: 68%). Mp: >300 °C. ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz) δ 9.69 (s, 2H), 8.82 (d, J = 8.8 Hz, 4H), 8.55 (s, 4H), 7.76 (d, J = 7.6 Hz, 4H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (EI) m/z: $[M]^+$ calcd for $C_{30}H_{14}Cl_4$ 513.9850; found 513.9855.

Preparation of 3,6,12,15-tetramethoxyphenanthro[9,10:*b*]triphenylene (T5) Following the general procedure, 1,2,4,5-tetrakis(4-methoxyphenyl)benzene (**P5**) (0.50 g, 1.0 mmol) and iron chloride were reacted for 4 h to give the product as white solid. Yield: 0.46 g, 93%. The product was further purified by vacuum sublimation in a temperature gradient oven at 420 °C/380 °C/330 °C ($9.6*10^{-5}$ Torr) to give 0.28 g (Yield: 60%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.57 (s, 2H), 8.80 (d, J = 8.8 Hz, 4H), 7.98 (s, 4H), 7.34 (d, J = 8.0 Hz, 4H), 4.07 (s, 12H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{34}H_{26}O_4$ 498.1826; found 498.1832.

Preparation of tetranaphtho[8,1,2-*cde*:2',1',8'-*jkl*:8'',1'',2''-*nop*:2''',1''',8'''-*uva*]pentacene (T6) Following the general procedure, 1,2,4,5-tetra(naphthalen-2-

yl)benzene (**P6**) (0.58 g, 1.0 mmol) and iron chloride were reacted for 12 h to give the product as red solid. Yield: 0.47 g, 81%. The product was further purified by vacuum sublimation in a temperature gradient oven at 560 °C/510 °C/460 °C ($6.4*10^{-5}$ Torr) to give 0.20 g (Yield: 47%). Mp: >300 °C. ^{1}H NMR and ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{22}$ 574.1716; found 574.1708. The crystal structure was solved by X-ray diffraction.

Preparation of 5-chloro tetrabenzo phenanthrotriphenylene (T7) Following the general procedure, 1,2,4,5-tetra(naphthalen-1-yl)benzene (**P7**) (0.58 g, 1.0 mmol) and iron chloride were reacted for 12 h to give the product as yellow solid. Yield: 0.52 g, 72%. The product was further purified by vacuum sublimation in a temperature gradient oven at 520 °C/470 °C/420 °C ($8.1*10^{-5}$ Torr) to give 0.23 g (Yield: 44%). Mp: >300 °C. ^{1}H NMR and ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{22}Cl_4$ 714.0476; found 714.0467.

Attempted preparation of tetraanthraceno hexacene (T8) Following the general procedure, 1,2,4,5-tetra(anthracen-2-yl)benzene (**P8**) (0.78 g, 1.0 mmol) and iron chloride were reacted for 36 h to give partially annulated products. This reaction did not lead to the formation of completely annulated **T9**. MALDI-TOF mass of mixture containing partially annulated derivatives was recorded.

Preparation of 3,12-difluorophenanthro[9,10:*b*]triphenylene (T9) Following the general procedure, 1,4-diphenyl-2,5-bis(4-fluorophenyl)benzene (**P9**) (0.42 g, 1.0 mmol) and iron chloride were reacted for 36 h to give the product as yellow-white solid. Yield: 0.34 g, 82%. The product was further purified by vacuum sublimation in a temperature gradient oven at 480 °C/430 °C/380 °C ($9.3*10^{-5}$ Torr) to give 0.27 g (Yield: 80%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.83 (s, 2H), 8.96-8.92 (m, 4H), 8.57 (d, *J* = 7.6 Hz, 2H), 8.32 (d, *J* = 11.6 Hz, 2H), 7.82-7.72 (m, 4H), 7.52-7.47 (m, 2H). ^{13}C NMR could

not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{30}H_{16}F_2$ 414.1215; found 414.1223.

Preparation of dibenzo phenanthrotriphenylene (T10) Following the general procedure, 1,4-diphenyl-2,5-bis(naphthalene-2-yl)benzene (**P10**) (0.48 g, 1.0 mmol) and iron chloride were reacted for 12 h to give the product as white-yellow solid. Yield: 0.42 g, 84%. The product was further purified by vacuum sublimation in a temperature gradient oven at 460 °C/410 °C/360 °C ($7.4*10^{-5}$ Torr) to give 0.28 g (Yield: 66%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.96 (s, 2H), 9.06-8.93 (s, 8H), 8.15-8.07 (m, 4H), 7.83-7.64 (m, 8H).^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{38}H_{22}$ 478.1719; found 478.1719.

Preparation of 3-methyl-dibenzophenanthrotriphenylene (T11) Following the general procedure, 1,4-bis(*para*-tolyl)-2,5-bis(naphthalene-2-yl)benzene (**P11**) (0.51 g, 1.0 mmol) and iron chloride were reacted for 6 h to give the product as white-yellow solid. Yield: 0.45 g, 88%. Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.80 (s, 2H), 8.97-8.86 (m, 6H), 8.69 (s, 2H), 8.07 (s, 4H), 7.64-7.59 (m, 6H), 2.64 (s, 6H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{40}H_{26}$ 506.2029; found 506.2034.

Preparation of tetrabenzophenanthrotriphenylene (T12) Following the general procedure,1,4-bis(naphthalene-2-yl)-2,5-bis(naphthalene-1-yl)benzene (**P12**) (0.51 g, 1.0 mmol) and iron chloride were reacted for 8 h to give the product as yellow solid. Yield: 0.52 g, 90%. The product was further purified by vacuum sublimation in a temperature gradient oven at 520 °C/480 °C/420 °C ($6.4*10^{-5}$ Torr) to give 0.29 g (Yield: 56%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ10.33 (s, 2H), 9.45 (d, J = 7.6 Hz, 2H), 8.99-8.84 (s, 6H), 8.18-8.07 (m, 8H), 7.88 (t, J = 6.8 Hz, 2H), 7.77 (t, J = 7.2 Hz, 2H), 7.69-7.64 (m, 4H). ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{26}$ 578.2029; found 578.2037.

Preparation of 3-chloro-dinaphthophenanthrotriphenylene (T13) Following the general procedure, 1,4-diphenyl-2,5-bis(anthracen-2-yl)benzene (**P13**) (0.51 g, 1.0 mmol) and iron chloride were reacted for 24 h to give the product as yellow solid. Yield: 0.49 g, 76%. The product was further purified by vacuum sublimation in a temperature gradient oven at 520 °C/470 °C/420 °C ($6.3*10^{-5}$ Torr) to give 0.20 g (Yield: 40%). Mp: >300 °C. ^{1}H NMR and ^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{24}Cl_2$ 646.1255; found 646.1262. The crystal structure was solved by x-ray diffraction.

Preparation of tetranaphtho tetracene (T14) Following the general procedure, 1,2-bis(naphthalene-2-yl)-4,5-bis(naphthalene-1-yl)benzene (**P14**) (0.51 g, 1.0 mmol) and iron chloride were reacted for 8 h to give the product as orange color solid. Yield: 0.51 g, 88%. The product was further purified by vacuum sublimation in a temperature gradient oven at 520 °C/480 °C/430 °C ($6.3*10^{-5}$ Torr) to give 0.21 g (Yield: 42%). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.53 (s, 2H), 9.43 (d, *J* = 8.4 Hz, 2H), 9.01 (d, *J* = 8.8 Hz, 2H), 8.79 (d, *J* = 7.6 Hz, 2H), 8.70 (d, *J* = 8.8 Hz, 2H), 8.22-8.09 (m, 8H), 7.93-7.75 (m, 6H).^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{24}$ 576.1873; found 576.1879.

Preparation of 3-fluorophenanthro[9,10:*b*]triphenylene (T15) Following the general procedure, 1-(4-fluorophenyl)-2,4,5-triphenylbenzene (**P15**) (0.40 g, 1.0 mmol) and iron chloride were reacted for 24 h to give the product as white solid. Yield: 0.36 g, 86%. Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.89 (s, 1H), 9.80 (s, 1H), 8.95-8.85 (m, 4H), 8.69 (d, *J* = 7.6 Hz, 2H), 8.55 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 6.8 Hz, 1H), 7.81-7.71 (m, 6H), 7.59-7.50 (m, 1H).^{13}C NMR could not be recorded due to poor solubility of the derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{30}H_{17}F$ 396.1314; found 396.1322.

Preparation of tetranaphthobenzotetracene (T16) Following the general procedure, 1-(phenyl)-2,4,5-tris(naphthalene-2-yl)benzene **(P16)** (0.53 g, 1.0 mmol) and iron chloride

were reacted for 12 h to give product as brown solid. Yield: 0.45 g, 86%. Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.93 (s, 1H), 9.84 (s, 1H), 8.97 (d, *J* = 8.8 Hz, 1H), 8.93-8.85 (m, 4H), 8.79 (d, *J* = 8.8 Hz, 1H), 8.61 (d, *J* = 7.6 Hz, 2H), 8.08-7.98 (m, 6H),7.79-7.63 (m, 6H).^{13}C NMR could not be recorded due to poor solubility of this derivative. HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{42}H_{22}$ 526.1722; found 526.1725.

ASSOCIATED CONTENT

Supporting Information

The Supporting information including X-ray crystallography data, additional mass spectra, ^{1}H and ^{13}C NMR spectra, absorption spectra, and photophysical data for complete spectroscopic analysis is available free of charge on the ACS Publications website.

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