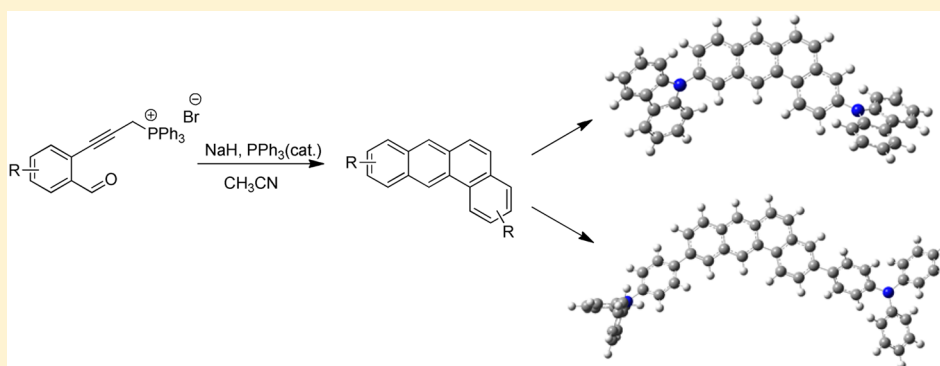


One-Pot Synthesis of Tetraphene and Construction of Expanded Conjugated Aromatics

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S Supporting Information



ABSTRACT: Acene derivatives as a class of polycyclic aromatic hydrocarbons have attracted considerable interest because of their outstanding semiconductor properties. We developed a one-pot synthesis for fully conjugated tetraphene via a sequence of propargyl-allenyl isomerization, phosphine addition, intramolecular Wittig reactions, and Diels–Alder cyclization reactions. The derivative-conjugated aromatic compounds including carbazole or triphenylamine have been constructed via Pd-catalyzed coupling reaction with dibromotetraphene. These compounds show superior photophysical and electrochemical properties, which make them possible candidates for optoelectronic conjugated materials.

Over the past two decades, polycyclic aromatic hydrocarbons (PAHs) have attracted considerable interest as organic electronic materials because of their photophysical and electrochemical properties, and their applicability in organic field-effect transistors (OFETs), photovoltaic (OPV) cells, and organic light-emitting diodes (OLEDs).¹ Among those polycyclic systems, PAHs such as tetracene, pentacene, and its derivatives play an important role in semiconducting materials for device applications.² The extended conjugated PAHs could exhibit good performance in devices; however, these systems beyond five rings are susceptible to oxidation, photodegradation, and Diels–Alder reactions.³ To improve the stability of these higher acenes, some strategies, including the incorporation of heteroatoms,⁴ the addition of protecting bulky substituents,⁵ and the introduction of two-dimensional acene analogues,⁶ were adopted in construction of these compounds, which could lead to acene synthesis being more difficult and could affect charge transport to some extent. On the other hand, PAHs with fewer than five rings such as pyrene,⁷ chrysene,⁸ and tetraphene⁹ also have been reported and applied as organic electronic materials. To the best of our knowledge, the simple synthesis and modification of tetraphene have not been well-documented; as a result, the application of tetraphene is rarer than that of pyrene in organic functional materials. Therefore, the development of efficient synthesis routes for four-ring aromatics remains interesting and challenging for chemists.

Since Wittig olefination was reported in 1953, intramolecular Wittig reactions have been applied in the synthesis of cyclic compounds through the classic strategy, in which a carbonyl group and suitable phosphorus ylide were constructed in the same substrate.¹⁰ On the basis of our previous research, base-catalyzed propargyl-allenyl isomerization could generate in situ functionalized allene intermediates.¹¹ We envisioned that the allenylphosphonium including the carbonyl group might produce a cyclic intermediate in the presence of phosphine and then undergo the intramolecular Wittig reactions and Diels–Alder cyclization reactions to give conjugated aromatic compounds. Herein, we report the novel synthesis of tetraphene by using simple propargylphosphonium salts as starting materials.

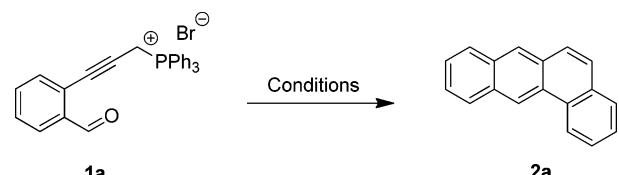
Stimulated by this proposal, we chose propargylphosphonium salt (**1a**) as the starting material, which could be synthesized readily via the treatment of 2-(3-bromoprop-1-yn-1-yl)benzaldehyde with triphenylphosphine in toluene. We initiated our reaction by using compound **1a** and screened the optimal conditions, such as base, solvent, and temperature. *t*-BuOK was widely used as the base in Wittig reaction; thus, we first examined the reaction with *t*-BuOK as the base and CH₃CN as the solvent. Fortunately, the desired product **2a** was

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obtained in 23% yield (Table 1, entry 1), which was confirmed by NMR and MS spectra. Replacing *t*-BuOK with NaH

Table 1. Optimization of the Reaction Conditions^a



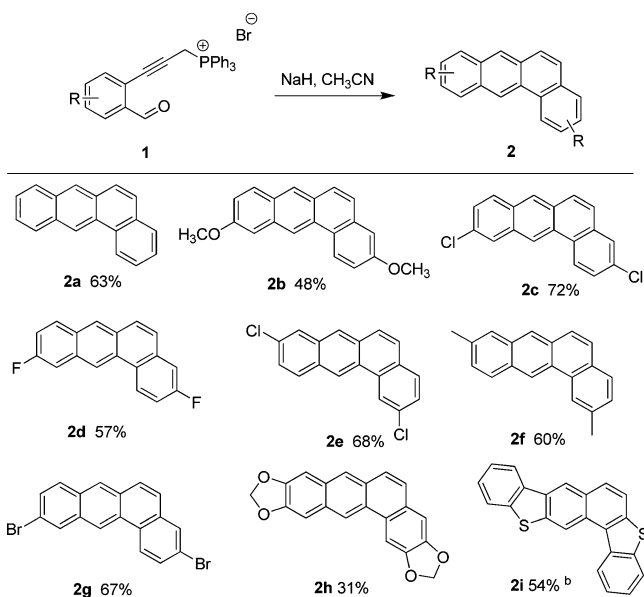
entry	base	solvent	T (°C)	yield (%)
1	<i>t</i> -BuOK	CH ₃ CN	40	23
2	NaH	CH ₃ CN	40	63
3	Et ₃ N	CH ₃ CN	40	8
4	DBU	CH ₃ CN	40	6
5	NaH	toluene	40	11
6	NaH	THF	40	45
7	NaH	CH ₃ CN	rt	48
8	NaH	CH ₃ CN	60	40

^aThe reaction was conducted using **1a** (0.5 mmol), base (0.6 mmol), and triphenylphosphine (5 μmol) in solvent (3 mL) under Ar.

produced the best result as the yield was improved to 63%, while an organic base (Et₃N and DBU) produced low yields. Subsequent screening showed that the use of other common solvents such as toluene and THF did not improve the yield (entries 5 and 6).

With the optimal condition in hand, the scope of this reaction was further investigated. As shown in Table 2, this reaction was successfully used to construct the disubstituted tetraphene compounds in one pot. Among those compounds, naphthobisbenzo[*b*]thiophene (**2i**) was easily synthesized with our method, which was obtained using multistep synthetic

Table 2. Synthesis of Disubstituted Tetraphene and Naphthobisbenzo[*b*]thiophenes^a



^aCondition: **1** (0.5 mmol) and NaH (0.6 mmol) in CH₃CN (3 mL) at 40 °C for 12 h under Ar. ^bCompound **2i** was obtained by using 2-carbaldehydebenzo[*b*]thiophene-3-propargylphosphonium salt as the starting material.

routes and exhibited excellent OFET characteristics in the previous report.^{4d} Furthermore, 3,10-dibromotetraphene (**2g**) was afforded and unequivocally confirmed by the X-ray single-crystal analysis (Figure S1).¹²

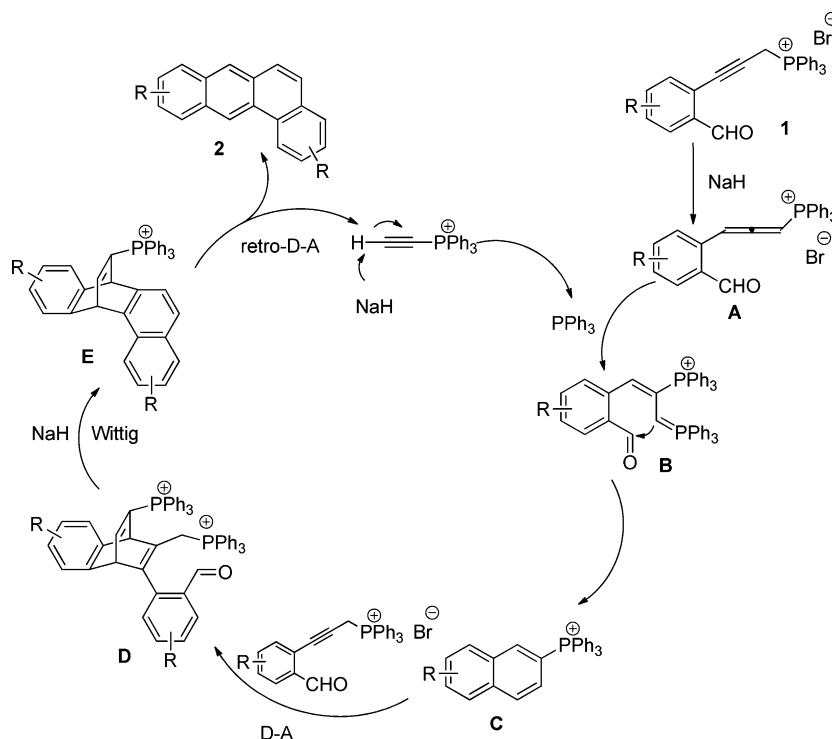
On the basis of the result described above, we propose a possible reaction pathway as shown in Scheme 1. The starting materials **1**, via the propargyl–allenyl isomerization in the presence of NaH, form phosphonium salts **A**¹³ attacked by trace nucleophiles PPh₃ to afford **B**.¹⁴ Then, intermediate **B** experiences its first intramolecular Wittig reaction, producing **C**, which undergoes Diels–Alder reaction with another molecule of **1** to offer intermediate **D**.¹⁵ The second Wittig reaction gives intermediate **E**, which undergoes the retro-Diels–Alder reaction to offer the final compound **2**. The ethynephosphonium salts may release PPh₃ in the presence of NaH, which recycles the reaction.

Bromo-modified acenes have attracted a great deal of attention in the organic electronics community for designing and constructing novel organic semiconducting functional materials.^{7,8} Therefore, with intermediate **2g** in hand, the expended conjugated aromatic compounds could be synthesized via Pd-catalyzed coupling reaction. As shown in Scheme 2, Buchwald coupling of **2g** with carbazole afforded compound **3a** in 46% yield, and Suzuki coupling of **2g** with 4-(diphenylamino)phenylboronic acid gave compound **3b** in 62% yield.

The absorption and fluorescence spectra of **3a** and **3b** in dichloromethane are shown in Figure 2, and the data are listed in Table 3. Compounds **3a** and **3b** display absorption peaks at 345 and 368 nm, respectively, which are attributed to the HOMO–LUMO transition of these molecules. These peaks reflect the extent of conjugation between the tetraphene core and the electron donor (carbazole or triphenylamine). As shown in Figure 1 and Table 3, compound **3a** in dichloromethane shows the maximal emission peaks at 434 nm and gives a sky blue color under an UV lamp. Because of the large extent of conjugation compared with that of **3a**, compound **3b** displays emission peaks around at 488 nm with an obvious red-shift, which can be observed as green color. The fluorescence quantum yields of **3a** and **3b** in dichloromethane have been measured to be 0.71 and 0.82, respectively, using quinine sulfate ($\Phi_F = 0.546$ in 1 N H₂SO₄) as a reference.¹⁶

The electrochemical characteristics of **3a** and **3b** were investigated by cyclic voltammetry using a standard three-electrode cell in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in dichloromethane. The working electrode is glassy carbon; the counter electrode is a platinum wire, and the reference electrode is a Ag/AgCl electrode. As shown in Figure 2, compounds **3a** and **3b** show two oxidation peaks and one oxidation peak, respectively, which are well-defined reversible oxidation waves. The half-wave oxidation potentials ($E_{1/2}$) for **3a** and **3b** are 0.55 and 0.47 V, respectively, which were measured relative to Fc⁺/Fc used as an internal standard. The oxidation potential decreases show that **3a** with triphenylamine increases the level of conjugation more than **3b** does. On the basis of the half-wave oxidation potentials, the highest occupied molecular orbital (HOMO) energy levels of **3a** and **3b** are -5.35 and -5.27 eV, respectively (HOMO = $E_{1/2} + 4.8$ eV), and the lowest unoccupied molecular orbital (LUMO) energy levels are -2.35 and -2.49 eV, respectively, estimated from the HOMO and energy band gap (E_g) based on the absorption thresholds from absorption spectra.

Scheme 1. Proposed Pathway



Scheme 2. Synthetic Route of Compounds 3a and 3b

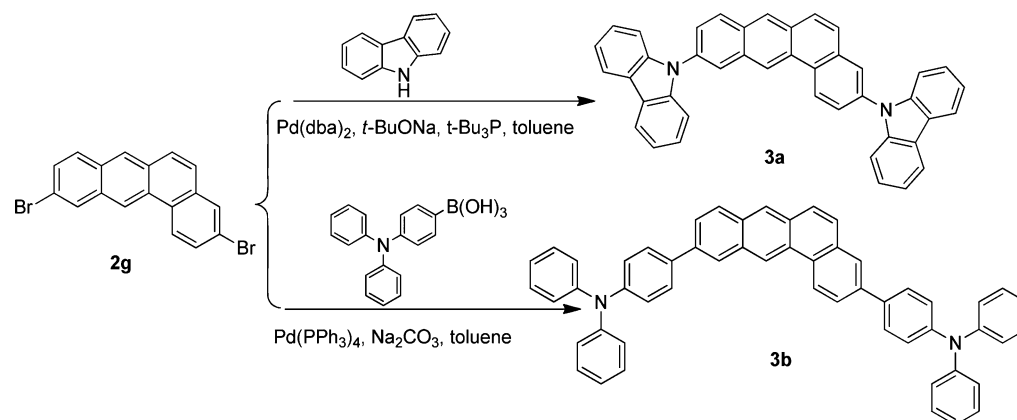


Table 3. Photophysical and Electrochemical Properties of 3a and 3b

compd	λ_{abs}^a (nm)	λ_{em}^a (nm)	Φ_{F}	$E_{1/2}^b$ (V)	HOMO/LUMO ^c (eV)
3a	345 (2.34 ^d)	434	0.71	0.55	-5.35/-2.35
3b	368 (5.3 ^d)	488	0.82	0.47	-5.27/-2.49

^aCH₂Cl₂ solution. ^bHalf-wave oxidation potentials vs Fc⁺/Fc. ^cHOMO values calculated on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV): LUMO = HOMO + E_{g} . ^dThe values in parentheses are molar extinction coefficients (10⁴ M⁻¹cm⁻¹).

To determine the electronic structures and the frontier orbitals, density functional theory (DFT) calculations of 3a and 3b were conducted at the B3LYP/6-31G(d) level (Table 3). Charge distributions are listed in Table 4. At the HOMO level, electrons are fully delocalized over the whole aromatics, including the electron donor (carbazole or triphenylamine) and tetraphene cores, whereas they are located most prevalently

on the tetraphene cores at the LUMO level. This electron density is redistributed, which indicates that an intramolecular charge transfer process from the electron donor to the tetraphene core occurs.

In summary, we have developed a simple and efficient method for fully accessing conjugated tetraphene derivatives through a sequence of propargyl–allenyl isomerization, phosphine addition, intramolecular Wittig reactions, and Diels–Alder reactions. This reaction brings about the breaking of synthesis of four-fused ring aromatic compounds. On the basis of the key intermediate 3,10-dibromotetraphene, the extended conjugated aromatics including carbazole or triphenylamine have been constructed. These aromatics display high fluorescence quantum yields and excellent electrochemical properties, which could greatly enhance their application as optoelectronic conjugated materials.

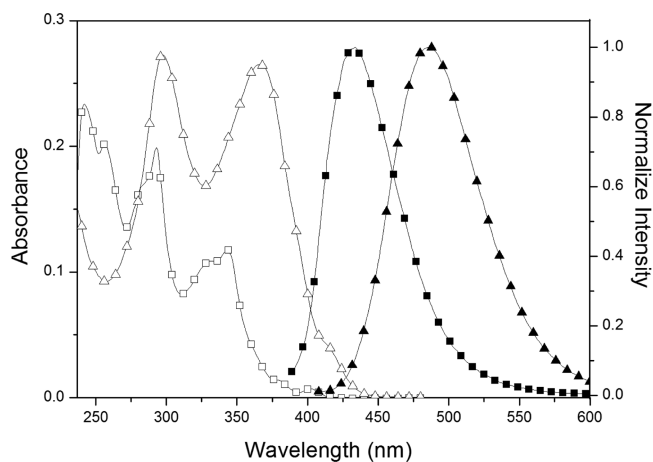


Figure 1. Absorption spectra (empty) (5.0 μM) and normalized fluorescence emission spectra (filled) of compounds **3a** (squares) and **3b** (triangles) in dichloromethane solutions.

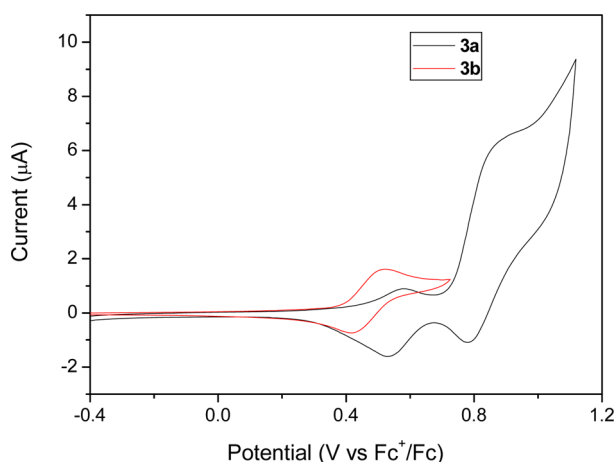


Figure 2. Cyclic voltammetry of **3a** and **3b** in dichloromethane.

Table 4. Frontier Molecular Orbitals of **3a and **3b** Calculated at the B3LYP/6-31G(d) Level**

Compd	HOMO	LUMO
3a		
3b		

EXPERIMENTAL SECTION

General. THF and toluene were dried with sodium and distilled freshly before being used. CH_3CN was dried with CaH_2 and distilled freshly before being used. Other materials and solvents were purchased from commercial suppliers and used without additional purification. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 at 400 and 100 MHz, respectively, and chemical shifts are reported in parts per million using tetramethylsilane (TMS) as an internal standard. Mass spectroscopy data of the products were collected with an HRMS-TOF instrument. UV-vis absorption and fluorescence emission spectra were recorded at room temperature. Cyclic voltammetry was performed at room temperature using an Electrochemical Workstation. The working electrode was a glassy carbon electrode. The

counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) was used as the supporting electrolyte, with ferrocene/ferrocenium (Fc/Fc^+) as an external reference. The scan rate used was 100 mV s^{-1} .

Typical Procedure for the Synthesis of **2a.** To a solution of **1a** (243 mg, 0.5 mmol) and triphenylphosphine (1.3 mg, 5 μmol)¹⁷ in dry CH_3CN (3.0 mL) at room temperature was added NaH (24 mg, 0.6 mmol, 60%) in 3.0 mL under N_2 . The reaction mixture was stirred at 40 $^\circ\text{C}$ for 12 h. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution, and the mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4 . After evaporation, chromatography on silica gel (50:1 petroleum ether/ethyl acetate) of the reaction mixture afforded **2a** as a white solid (36 mg, 63%).

Tetraphene (2a**).**^{18a} White solid (36 mg, 63%): mp 158–159 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.18 (s, 1H), 8.84 (d, $J = 8.4$ Hz, 1H), 8.38 (s, 1H), 8.13 (d, $J = 6.0$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 9.2$ Hz, 1H), 7.66–7.69 (m, 1H), 7.60–7.63 (m, 2H), 7.55–7.58 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.9, 128.6, 128.4, 127.7, 127.3, 127.1, 126.8, 126.7, 125.7, 122.9, 121.5; HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{12}$ 228.0939, found 228.0938.

3,10-Dimethoxytetraphene (2b**).**^{18b} White amorphous solid (35 mg, 48%): mp 178–179 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.18 (s, 1H), 8.71 (d, $J = 8.8$ Hz, 1H), 8.27 (s, 1H), 7.91 (d, $J = 9.2$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.34 (d, $J = 2.0$ Hz, 1H), 7.26–7.29 (m, 2H), 7.20 (dd, $J = 8.2, 2.4$ Hz, 1H), 4.00 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 157.5, 133.6, 133.2, 129.4, 128.4, 128.0, 127.6, 126.8, 125.8, 124.5, 124.2, 119.7, 119.0, 116.1, 109.6, 104.6, 55.4, 55.3; HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2$ 288.1150, found 288.1153.

3,10-Dichlorotetraphene (2c**).** White amorphous solid (53 mg, 72%): mp 192–193 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.94 (s, 1H), 8.66 (d, $J = 8.8$ Hz, 1H), 8.31 (s, 1H), 8.06 (s, 1H), 7.95 (d, $J = 9.2$ Hz, 1H), 7.76–7.81 (m, 2H), 7.61 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.53 (d, $J = 9.2$ Hz, 1H), 7.47 (dd, $J = 8.8, 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.2, 133.1, 132.3, 131.7, 130.4, 130.1, 129.4, 129.0, 128.5, 128.4, 127.7, 127.3, 127.1, 126.7, 126.2, 124.5, 120.6; HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{10}\text{Cl}_2$ 296.0160, found 296.0164.

3,10-Difluorotetraphene (2d**).** White amorphous solid (38 mg, 57%): mp 196–197 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.98 (s, 1H), 8.76 (dd, $J = 8.8, 5.2$ Hz, 1H), 8.35 (s, 1H), 8.03 (dd, $J = 8.8, 5.6$ Hz, 1H), 7.80 (d, $J = 9.2$ Hz, 1H), 7.68 (dd, $J = 9.6, 1.2$ Hz, 1H), 7.55 (d, $J = 9.2$ Hz, 1H), 7.49 (dd, $J = 9.2, 2.4$ Hz, 1H), 7.35–7.41 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.8 (d, $^1J_{\text{C-F}} = 246.2$ Hz), 160.6 (d, $^1J_{\text{C-F}} = 246.1$ Hz), 133.7, 132.5, 130.5, 129.5, 129.2, 128.9, 128.5, 127.3, 126.5, 126.1, 125.2, 120.4, 117.1, 115.2, 113.2, 110.4; HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{10}\text{F}_2$ 264.0751, found 264.0749.

2,9-Dichlorotetraphene (2e**).** White amorphous solid (50 mg, 68%): mp 181–182 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.04 (s, 1H), 8.74 (d, $J = 1.6$ Hz, 1H), 8.26 (s, 1H), 8.06 (d, $J = 8.8$ Hz, 1H), 8.02 (d, $J = 1.6$ Hz, 1H), 7.76–7.79 (m, 2H), 7.63 (s, 1H), 7.56–7.60 (m, 1H), 7.50 (dd, $J = 8.8, 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.0, 132.5, 132.0, 131.6, 131.2, 130.2, 130.1, 129.9, 129.9, 127.9, 127.6, 127.3, 127.1, 126.9, 126.1, 126.0, 122.7, 121.9; HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{10}\text{Cl}_2$ 296.0160, found 296.0161.

2,9-Dimethyltetraphene (2f**).** White amorphous solid (38 mg, 60%): mp 165–166 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 1H), 8.60 (s, 1H), 8.23 (s, 1H), 8.02 (d, $J = 8.8$ Hz, 1H), 7.78 (s, 1H), 7.71 (t, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 9.2$ Hz, 1H), 7.37–7.43 (m, 2H), 2.65 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 135.4, 132.2, 130.9, 130.6, 130.3, 129.6, 128.4, 128.3, 128.3, 128.2, 128.1, 126.8, 126.4, 126.2, 125.8, 122.8, 121.2, 22.1, 21.9; HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{16}$ 256.1252, found 256.1254.

3,10-Dibromotetraphene (2g**).** White amorphous solid (65 mg, 67%): mp 172–173 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1H), 8.59 (d, $J = 8.8$ Hz, 1H), 8.30 (s, 1H), 8.26 (s, 1H), 7.97 (d, $J = 2.0$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 1H), 7.75–7.78 (m, 2H), 7.60 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.6, 132.8, 130.9, 130.5, 130.2, 130.1, 129.9, 129.5, 129.4,

129.0, 128.9, 128.4, 127.2, 126.2, 124.7, 121.4, 120.6, 120.0; HRMS (EI-TOF) calcd for $C_{18}H_{10}Br_2$ 383.9149, found 383.9148.

Tetrapheno[2,3-d:9,10-d']bis([1,3]dioxole) (2h). White amorphous solid (25 mg, 31%): mp 187–188 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.15 (s, 1H), 8.13 (s, 1H), 7.66 (d, $J = 9.2$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 1H), 7.32 (s, 1H), 7.25 (s, 1H), 7.21 (s, 1H), 6.12 (s, 2H), 6.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.7, 147.9, 131.1, 129.5, 125.9, 125.6, 125.3, 119.8, 106.3, 103.1, 102.5, 101.4, 101.3, 101.1; HRMS (EI-TOF) calcd for $C_{20}H_{12}O_4$ 316.0736, found 316.0740.

Naphthobisbenzo[b]thiophenes (2i).^{4d} White amorphous solid (46 mg, 54%): mp 224–225 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.93 (d, $J = 8.4$ Hz, 1H), 8.75 (s, 1H), 8.29–8.31 (m, 1H), 8.02–8.07 (m, 2H), 7.88–7.93 (m, 2H), 7.65–7.68 (m, 1H), 7.50–7.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.9, 136.6, 135.0, 133.7, 132.1, 129.5, 129.4, 128.4, 127.9, 127.5, 125.2, 125.0, 124.7, 124.4, 123.3, 122.9, 121.8, 121.5, 120.5, 115.2; HRMS (EI-TOF) calcd for $C_{22}H_{12}S_2$ 340.0380, found 340.0377.

Synthesis of 3a. A mixture of **2g** (78 mg, 0.2 mmol), carbazole (84 mg, 0.5 mmol), $Pd(dba)_2$ (8 mg, 0.014 mmol), $t-Bu_3P\cdot HBF_4$ (4 mg, 0.014 mmol), and $t-BuONa$ (58 mg, 0.6 mmol) in dry toluene (8 mL) was stirred at 100 °C for 4 h under Ar. After completion of the reaction, it was quenched with a saturated aqueous NH_4Cl solution, and the mixture was extracted with ethyl acetate. The organic layers were dried Na_2SO_4 , filtered, and evaporated. The residue was purified by silica gel column chromatography (10:1 petroleum ether/ethyl acetate) to give compound **3a** (52 mg, 46%) as a pale white solid: mp 190–191 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 9.05 (d, $J = 8.8$ Hz, 1H), 8.56 (s, 1H), 8.37 (s, 1H), 8.31 (d, $J = 8.8$ Hz, 1H), 8.20–8.23 (m, 4H), 8.09 (d, $J = 2.0$ Hz, 1H), 7.96 (d, $J = 9.2$ Hz, 1H), 7.90 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.79 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.74 (d, $J = 9.2$ Hz, 1H), 7.55–7.60 (m, 4H), 7.44–7.49 (m, 4H), 7.33–7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.9, 136.8, 135.3, 133.4, 132.5, 131.0, 130.9, 129.9, 129.2, 129.2, 128.4, 127.4, 127.0, 126.2, 126.1, 126.0, 125.7, 125.6, 125.4, 124.9, 123.6, 123.5, 121.7, 120.4, 120.4, 120.2, 120.1, 109.9, 109.8; HRMS (EI-TOF) calcd for $C_{42}H_{26}N_2$ 558.2096, found 558.2092.

Synthesis of 3b. A mixture of **2g** (78 mg, 0.2 mmol), 4-(diphenylamino)phenylboronic acid (146 mg, 0.5 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), and K_2CO_3 (84 mg, 0.6 mmol) in a toluene (8 mL)/water (1 mL) solvent was stirred at 90 °C for 10 h under Ar. After completion of the reaction, it was quenched with a saturated aqueous NH_4Cl solution, and the mixture was extracted with ethyl acetate. The organic layers were dried with Na_2SO_4 , filtered, and evaporated. The residue was purified by silica gel column chromatography (10:1 petroleum ether/ethyl acetate) to give compound **3b** (89 mg, 62%) as a pale yellow solid: mp 170–171 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.86 (d, $J = 8.8$ Hz, 1H), 8.36 (s, 1H), 8.30 (s, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 8.03 (d, $J = 1.6$ Hz, 1H), 7.91 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.81 (dd, $J = 8.8, 2.0$ Hz, 2H), 7.66–7.71 (m, 5H), 7.28–7.33 (m, 8H), 7.17–7.24 (m, 12H), 7.05–7.09 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.4, 147.3, 139.2, 137.7, 134.8, 134.5, 132.4, 132.3, 130.9, 130.6, 129.3, 129.1, 129.1, 129.0, 128.3, 128.0, 127.9, 127.7, 127.2, 126.6, 126.1, 125.5, 125.1, 124.5, 124.4, 123.9, 123.9, 123.5, 123.0, 123.0, 121.6; HRMS (EI-TOF) calcd for $C_{54}H_{38}N_2$ 714.3035, found 714.3032.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00890.

1H and ^{13}C NMR spectra of all new compounds and crystal structure of **2g** (PDF)
Crystallographic data of **2g** (CIF)

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Notes

The authors declare no competing financial interest.

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