Scientific paper

Synthesis and Characterization of Tetraarylphenazine and Tetraaryldibenzo[*b,i*]phenazine

Liang-Hong Hu and Qian-Cai Liu*

School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China

** Corresponding author: E-mail: qcliu@chem.ecnu.edu.cn*

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Abstract

Phenazine and 6,13-diazapentacene are nitrogen-containing linear heterocycles that have attracted significant attention in the fields of organic electronics, and materials science. A straightforward strategy has been developed to construct 1,4,6,9-tetraarylphenazines and 5,7,12,14-tetraaryl-6,13-diazapentacenes with 1,4,6,9-tetrabromophenazine and 5,6,12,14-tetrabromo-6,13-dihydrodibenzo[*b*,*i*]phenazine as the key intermediates, which were obtained easily from the bromination of phenazine and 6,13-dihydrodibenzo[*b*,*i*]phenazine, respectively. While the Pd(amphos)Cl$_2$ catalyzed ligand-free Suzuki couplings between above described intermediates and various arylboronic acids were performed to afford directly tetraarylphenazines or tetraaryl-6,13-diazapentacenes by subsequent oxidations. All of the new compounds are fully characterized by spectroscopy.

Keywords: Palladium, Suzuki coupling, Tetraarylphenazine, Tetraaryl-6,13-diazapentacene, Diazacenes.

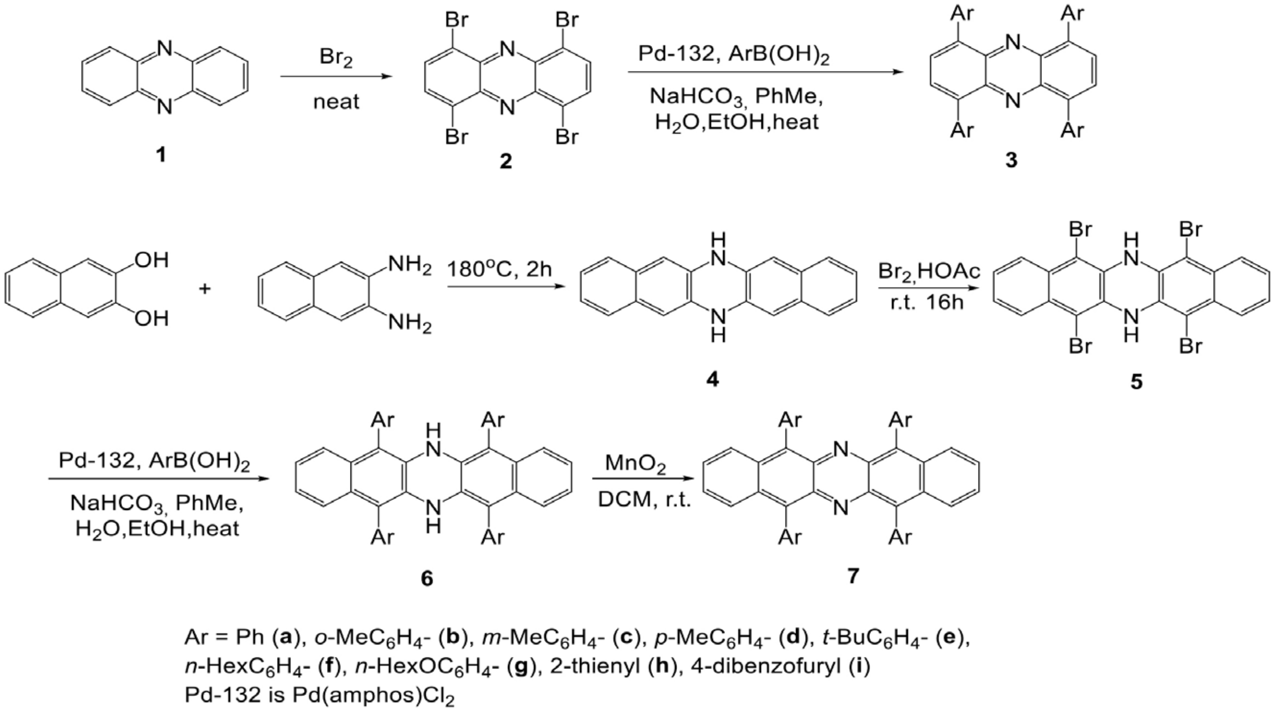
1. Introduction

Polycyclic aromatic hydrocarbons are of particular interest in the field of organic electronics, where they are studied for their potential applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaics (OPVs) in both academic and industrial spheres as part of an ongoing pursuit for the development of energy-saving and high-quality display technologies.[1–2] Nitrogen-containing polycyclic aromatic hydrocarbons (N-PAHs) are a class of organic compounds that combine the stability and electronic properties of PAHs with the versatile reactivity of nitrogen atoms.[3] Azaacenes have attracted great interest due to their potential applications in opto-material areas.[4–10] Phenazine and 6,13-diazapentacene are two prominent examples of N-PAHs, each exhibiting distinct chemical and physical properties. Phenazine has been widely studied for its biological activity and as a building block for more complex molecules. On the other hand, 6,13-diazapentacene, a larger PAH with two nitrogen atoms, has emerged as a key material in organic electronics due to its excellent charge transport properties and tunable electronic structure.[11–13] Tetraarylphenazine and tetraaryl-6,13-diazapentacene are two classes of nitrogen-containing polycyclic aromatic hydrocarbons (N-PAHs) that have garnered significant attention in recent years due to their unique electronic, optical, and structural properties. These compounds are characterized by their extended π-conjugated systems and the presence of nitrogen atoms, which impart distinct electronic properties and make them suitable for applications in organic electronics, photovoltaics, and sensing. The examples of higher substituted azaacenes with phenazine or 6,13-diazapentacene as central cores are rare, which might be due to the synthetic barriers of suitable precursors compared to their carbo-congeners.[14–18] Shao *et al.* reported several examples based on 1,4,6,9-tetraarylphenazine core during their investigation of organic photovoltaic property and structural relationship of non-fullerene small molecule acceptors from the combination of tetraarylphenazine motif and perylene diimide.[19] While very few examples on tetraaryl-6,13-diazapentacenes as BN heterosuperbenzenes or as n-channel semiconductor have been reported, which were evaluated in organic field effect transistors by Pei and Bunz individually.[20–21] Herein, we decorate the 5,10-diazaanthracene and diazapentacene framework by Pd(amphos)Cl$_2$ catalyzed fourfold Suzuki–Miyaura coupling using the method developed by us before.[22] This research will offer quick approach to multifunctionalized diazaanthracenes and diazapentacenes with a wide range of scope emphasizing their significance in both fundamental research and practical applications (Scheme 1).

2. Experimental

Materials and Instruments

All reagents and chemicals were reagent grade, commercially available, and used directly for the reaction. The palladium catalyst bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II) (Pd(amphos)Cl_2) was purchased from Energy-chemical, China. NMR spectra were recorded on Bruker AV-500 (500 and 125 MHz, respectively) and Bruker AV-600 (600 and 150 MHz, respectively). Melting point was measured on an X-4 micrographic melting point apparatus. UV-VIS spectroscopy was performed on a computer-controlled Agilent Cary 60 spectrophotometer UV-VIS spectrometer. The photoluminescence characteristics were studied on the Hitachi F-7000 spectro-fluorometer. Mass spectra were measured on Thermo Fisher Q-Exactive or Bruker maXis Impact.



Ar = Ph (**a**), *o*-MeC_6H_4- (**b**), *m*-MeC_6H_4- (**c**), *p*-MeC_6H_4- (**d**), *t*-BuC_6H_4- (**e**), *n*-$HexC_6H_4$- (**f**), *n*-$HexOC_6H_4$- (**g**), 2-thienyl (**h**), 4-dibenzofuryl (**i**)
Pd-132 is Pd(amphos)Cl_2

Scheme 1. Synthetic route of the targeted phenazines and diazapentacenes

Syntheses of 1,4,6,9-Tetrabromophenazine and 6,13-Dihydro-6,13-diazapentacene

Synthesis of 1,4,6,9-Tetrabromophenazine (2)[19]

A RB flask was charged phenazine (**1**) (3.0 g, 16.6 mmol, 1.0 eq.) and liquid bromine 30 mL (585 mmol, 35.0 eq) was added dropwise. The stirring was continued until the cease of HBr. The mixture was diluted with MeOH and filtered. The yellow solid was washed with MeOH before recrystallized from mesitylene to afford yellow to yellow-green crystals **2** (6.80 g, 13.72 mmol, 82.39%). M.p. > 300 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.26 (s, 4H).

Synthesis of 5,6,12,14-Tetrabromo-6,13-dihydrodibenzo[*b,i*]phenazine (5)[20]

(a) A mixture of 2,3-dihydroxynaphthalene (1.0 g, 6.24 mmol) and 2,3-diaminonaphthalene (1.0 g, 6.32 mmol) in RB flask (50 mL) was heated at 180 °C under nitrogen for 1 h before it was cooled to room temperature. Then acetone was introduced into the mixture and it was refluxing with stirring for 1 h and filtered. The solid was washed with acetone and diethyl ether and dried to obtain a gray-yellow powder **4** (1.41 g, 4.99 mmol, 80.0%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (s, 2H), 7.28 (dd, J = 6.0, 3.3 Hz, 4H), 6.98 (dt, J = 6.1, 3.4 Hz, 4H), 6.48 (s, 4H).

(b) To a suspension of 6,13-dihydrodibenzo[*b,i*]phenazine (1.0 g, 3.54 mmol) in glacial acetic acid (100 mL) was added bromine (0.80 mL, 2.51 g, 15.68 mmol) slowly. The mixture was stirred at room temperature for 16 h before it was filtered. The crude material was suspended in EtOH (50 mL) with stirring for 2 h and filtered to obtain a green solid **5** (1.72 g, 2.88 mmol, 81.22%). No ^{1}H NMR could be obtained due to the low solubilities in common solvents such as $CHCl_3$, THF, toluene, *ortho*-dichlorobenzene, 1,2,4-trichlorobenzene, DMF and DMSO, etc. m.p. > 300 °C. HRMS (APCI) *m/z* calcd. for $C_{20}H_9N_2Br_4$ $[M+H]^+$: 592.7505, found: 592.7521.

Synthesis of 1,4,6,9-Tetraarylphenazines and 5,7,12,14-Tetraaryl-6,13-diazapentacenes (3a–3i and 7a–i)

Synthesis of 1,4,6,9-tetraarylphenazine

*General procedure (**3a** as example)*

Under N_2 a two neck 100 mL Schlenk flask was charged 1,4,6,9-tetrabromophenazine (**2**, 1.0 g, 2.02 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 1.5%), $NaHCO_3$ (1.36 g, 16.14 mmol, 8.0 eq.) and a mixture of PhMe-H_2O (40 mL, v:v = 1:1). The mixture was heated at 75 °C in an oil bath. The heating was stopped before a solution of phenylboronic acid (1.48 g, 12.10 mmol, 6.0 eq.) in EtOH (15 mL) was added via syringe. After addition, the stirring was conducted at 75 °C for further 8 h before it was cooled to room temperature and filtered. The solid was washed with water and petroleum ether before it was dried to afford yellow powder, which was further recrystallized in toluene to obtain yellow crystals **3a** (802 mg, 1.65 mmol, 82.05%). M.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 4H), 7.79 (dd, *J* = 6.4, 3.2 Hz, 8H), 7.39 (dd, *J* = 5.0, 1.7 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.79, 140.27, 138.18, 131.04, 130.10, 127.80, 127.32. HRMS (ESI) *m/z* calcd. for $C_{36}H_{24}N_2$ $[M+H]^+$: 485.2012. Found: 485.1957.

Synthesis of 3b; general procedure of **3a** with **2** (1.0 g, 2.02 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 1.5%), $NaHCO_3$ (1.36 g, 16.14 mmol, 8.0 eq.) and PhMe-H_2O (40 mL, v:v = 1:1) as well as 2-methylphenylboronic acid (1.65 g, 12.10 mmol, 6.0 eq.) in EtOH (15 mL) to afford a yellow powder **3b** (856 mg, 1.58 mmol, 78.49%). M.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 4H), 7.28–7.26 (m, 2H), 7.24 (d, *J* = 2.1 Hz, 2H), 7.20–7.13 (m, 8H), 7.04 (d, *J* = 7.6 Hz, 4H), 1.78 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.59, 140.65, 138.35, 137.66, 130.52, 129.91, 129.57, 127.17, 124.73; HRMS (ESI) *m/z* calcd. for $C_{40}H_{32}N_2$ $[M+H]^+$: 541.2638. Found: 541.2583.

Synthesis of 3c; general procedure of **3a** with **2** (1.0 g, 2.02 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 1.5%), $NaHCO_3$ (1.36 g, 16.14 mmol, 8.0 eq.) and PhMe-H_2O (40 mL, v:v = 1:1) as well as 3-methylphenylboronic acid (1.65 g, 12.10 mmol, 6.0 eq.) in EtOH (15 mL) to afford a yellow powder **3c** (875 mg, 1.62 mmol, 80.23%). M.p. 284.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 4H), 7.61 (d, *J* = 7.6 Hz, 4H), 7.54 (s, 4H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.20 (d, *J* = 7.5 Hz, 4H), 2.26 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.79, 140.23, 138.18, 137.05, 131.99, 129.96, 128.07, 128.00, 127.62; HRMS (ESI) *m/z* calcd. for $C_{36}H_{24}N_2$ $[M+H]^+$: 541.2638. Found: 541.2563.

Synthesis of 3d; general procedure of **3a** with **2** (1.0 g, 2.02 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 1.5%), $NaHCO_3$ (1.36 g, 16.14 mmol, 8.0 eq.) and PhMe-H_2O (40 mL, v:v = 1:1) as well as 4-methylphenylboronic acid (1.65 g, 12.10 mmol, 6.0 eq.) in EtOH (15 mL) to afford a yellow powder **3d** (792 mg, 1.46 mmol, 72.62%). M.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 4H), 7.68 (d, *J* = 8.0 Hz, 8H), 7.19 (d, *J* = 8.0 Hz, 8H), 2.47 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.84, 139.98, 136.84, 135.41, 130.94, 129.61, 128.49, 21.31. HRMS (ESI) *m/z* calcd. for $C_{36}H_{24}N_2$ $[M+H]^+$: 541.2638. Found: 541.2567.

Synthesis of 3e; general procedure of **3a** with **2** (1.0 g, 2.02 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 1.5%), $NaHCO_3$ (1.36 g, 16.14 mmol, 8.0 eq.) and PhMe-H_2O (40 mL, v:v = 1:1) as well as 4-*tert*-butylphenylboronic acid (2.15 g, 12.10 mmol, 6.0 eq.) in EtOH (15 mL) to afford a yellow powder **3e** (1.26 g, 1.78 mmol, 88.11%). M.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 4H), 7.89–7.84 (m, 8H), 7.49–7.44 (m, 8H), 1.43 (s, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.25, 140.83, 139.63, 135.58, 130.83, 130.46, 124.79, 34.63, 31.56. HRMS (APCI) *m/z* calcd. for $C_{36}H_{24}N_2$ $[M+H]^+$: 709.4516. Found: 709.4519.

Synthesis of 3f; general procedure of **3a** with **2** (1.0 g, 2.02 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 1.5%), $NaHCO_3$ (1.36 g, 16.14 mmol, 8.0 eq.) and PhMe-H_2O (40 mL, v:v = 1:1) as well as 4-*n*-hexylphenylboronic acid (2.49 g, 12.10 mmol, 6.0 eq.) in EtOH (15 mL) to afford yellow crystals **3f** (1.36 g, 1.66 mmol, 82.1%). M.p. 225.6–227.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 4H), 7.75–7.71 (m, 8H), 7.22–7.19 (m, 8H), 2.73–2.67 (m, 8H), 1.78–1.70 (m, 8H), 1.50–1.43 (m, 8H), 1.39 (tq, *J* = 6.0, 2.9, 2.5 Hz, 16H), 0.94 (td, *J* = 5.9, 4.8, 2.3 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.97, 140.82, 139.89, 135.60, 131.01, 129.80, 127.85, 35.99, 31.91, 31.80, 29.38, 22.74, 14.18. HRMS (APCI) *m/z* calcd. for $C_{60}H_{72}N_2$ $[M+H]^+$: 821.5768. Found: 821.5777.

Synthesis of 3g; general procedure of **3a** with **2** (300 mg, 605.09 μmol), Pd(amphos)Cl_2 (10 mg, 14.08 μmol, 2%), $NaHCO_3$ (406.6 mg, 4.84 mmol, 8.0 eq.), and PhMe-H_2O (20 mL, v:v = 1:1) as well as 4-*n*-hexyloxyphenylboronic acid (806.31 mg, 3.63 mmol, 6.0 eq.) in EtOH (10 mL) to afford an orange solid **3g** (470 mg, 530.9 μmol, 87.74%). M.p. 217.5–220.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 4H), 7.75 (d, *J* = 8.7 Hz, 8H), 6.93 (d, *J* = 8.7 Hz, 8H), 4.05 (t, *J* = 6.6 Hz, 8H), 1.88-1.83 (m, 8H), 1.52 (s, 8H), 1.40 (q, *J* = 5.3, 3.7 Hz, 16H), 0.95 (d, *J* = 7.0 Hz, 12H). HRMS (APCI) *m/z* calcd. for $C_{60}H_{72}N_2O_4$ $[M+H]^+$: 885.5565. Found: 885.5561.

Synthesis of 3h; general procedure of **3a** with **2** (300 mg, 605.09 μmol), Pd(amphos)Cl_2 (10 mg, 14.08 μmol, 2%), $NaHCO_3$ (407 mg, 4.8 mmol, 8.0 eq.), PhMe-H_2O (20 mL, v:v = 1:1) as well as 2-thienylboronic acid (464 mg, 3.63 mmol, 6.0 eq.) in EtOH (8 mL) at 75 °C for 8 h to afford purple-red powder **3h** (256 mg, 0.5 mmol, 83.17%). M.p. > 300 °C. (R_f = 0.45, PE/DCM = 6/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 4H), 7.88 (d, *J* = 3.5 Hz, 4H), 7.45 (d, *J* = 5.5 Hz, 4H), 7.17 (dd, *J* = 5.3, 3.2 Hz, 4H). HRMS (APCI) *m/z* calcd. for $C_{28}H_{17}N_2S_4$ $[M+H]^+$: 509.0269. Found: 509.0265.

Synthesis of 3i; general procedure of **3a** with **2** (300 mg, 605.09 µmol), Pd(amphos)Cl_2 (10 mg, 14.08 µmol, 2%), $NaHCO_3$ (407 mg, 4.8 mmol, 8.0 eq.), PhMe-H_2O (20 mL, v:v = 1:1) as well as 4-dibenzofurylboronic acid (770 mg, 3.63 mmol, 6.0 eq.) in EtOH(8 mL) at 75 °C for 8 h to afford yellow powder **3i** (384 mg, 454.5 mmol, 75.11%). M.p. > 300 °C. R_f = 0.5 (PE/DCM = 3/1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 4H), 7.94 (d, *J* = 7.6 Hz, 4H), 7.63–7.58 (m, 4H), 7.51–7.47 (m, 4H), 7.36–7.32 (m, 4H), 7.26–7.20 (m, 8H), 6.80 (t, *J* = 7.6 Hz, 4H). HRMS (APCI) *m/z* calcd. for $C_{60}H_{33}N_2O_4$ [M+H]+: 845.2435. Found: 845.2421.

General Synthesis of 5,7,12,14-Tetraaryl-6,13-dihyro-6,13-diazapentacenes 7a–i (7a as example)

A two-necked RB flask was charged 5,7,12,14-tetrabromo-6,13-dihyro-6,13-diazapentacene (**5**, 500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 ***µmol***, 3%), $NaHCO_3$ (702.5 mg, 8.36 mmol, 10.0 eq.) and a mixture of PhMe-H_2O (30 mL v:v = 1:1). The mixture was heated to 75 °C and the heating was stopped before a solution of phenylboronic acid (620 mg, 5.08 mmol, 6.0 eq.) in EtOH (10 mL) was added dropwise. The mixture was heated at 75 °C for 10 h before it was cooled to room temperature. The solid was filtered and washed with water and petroleum ether and dried to afford a green solid **6a** (352 mg, 0.60 mmol, 71.74%). M.p. > 300 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.26 (m, 12H), 7.14 (dd, *J* = 7.7, 1.5 Hz, 8H), 7.03 (dd, *J* = 6.4, 3.3 Hz, 4H), 6.94 (dd, *J* = 6.4, 3.3 Hz, 4H), 5.65 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.80, 130.40, 129.61, 129.30, 128.19, 127.57, 124.17, 123.39, 117.89.

The Oxidation of 5,7,12,14-Tetraaryl-6,13-dihydro-6,13-diazapentacenes to 5,7,12,14-Tetraaryl-6,13-diazapentacenes (6a to 7a as general procedure)

A 100 mL RB flask was charged 5,7,12,14-tetraphenyl-6,13-dihydro-6,13-diazapentacene (**6a**, 200 mg, 0.31 mmol), MnO_2 (892 mg, 10.26 mmol, 30.0 eq.) and dichloromethane (20 mL). The mixture was stirred overnight at room temperature (TLC monitoring at 365 nm with color changing from blue to khaki fluorescence). It was filtered, the filtrate was evaporated and washed with petroleum ether to obtain a dark-green solid **7a** (120 mg, 0.21 mmol, 60.12%). M.p. 297.9–299.5 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.02–7.94 (m, 4H), 7.45–7.40 (m, 9H), 7.39–7.34 (m, 9H), 7.29 (d, *J* = 3.2 Hz, 2H), 7.27 (d, *J* = 3.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.39, 138.32, 136.83, 132.60, 132.16, 127.61, 127.45, 126.79, 126.03, 77.27, 77.02, 76.76.

Synthesis of 6b and 7b; compound **6b** was obtained the same as **6a** by employing **5** (500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 µmol, 3%), $NaHCO_3$ (704 mg, 8.38 mmol, 10.0eq.), PhMe-H_2O (30 mL, v:v = 1:1) as well as 2-methylphenylboronic acid (686 mg, 5.05 mmol, 6.0 eq) in EtOH (10 mL) at 75 °C for 10 h to afford green solid (306 mg) which was used directly. This crude material (200 mg) was mixed with MnO_2 (820 mg, 9.43 mmol, 30.0 eq.) in dichloromethane (20 mL). The mixture was stirred at room temperature overnight before it was filtered. The filtrate was evaporated to remove volatiles, and the solid was mixed with petroleum ether with stirring and filtered and dried to obtain a dark-green solid **7b** (115 mg, 0.18 mmol, 57.68%). M.p. > 300 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.85–7.67 (m, 4H), 7.27 (s, 4H), 7.26–7.17 (m, 8H), 7.17–7.01 (m, 8H), 1.85–1.64 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.54, 138.47, 138.43, 138.38, 138.32, 138.23, 138.11, 137.89, 137.59, 137.49, 137.41, 136.90, 136.87, 136.79, 136.73, 132.94, 132.81, 132.77, 132.67, 132.59, 131.29, 131.20, 131.15, 131.12, 131.04, 129.80, 129.69, 129.33, 129.25, 127.57, 127.53, 127.48, 127.43, 127.22, 127.18, 127.15, 127.11, 126.09, 126.06, 125.97, 124.78, 124.73, 124.69, 124.48, 20.40, 20.36, 20.32, 20.29. HRMS (ESI) *m/z* calcd. for $C_{48}H_{36}N_2$ $[M+H]^+$: 641.2951. Found: 641.2881.

Synthesis of 6c and 7c; compound **6c** was obtained the same as **6a** by employing **5** (500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 µmol, 3%), $NaHCO_3$ (702.5 mg, 8.36 mmol, 10.0 eq.) and a mixture of PhMe-H_2O (30 mL v:v = 1:1) as well as 3-phenylboronic acid (689 mg, 5.07 mmol, 6.0 eq.) in EtOH (10 mL) at 75 °C for 10 h to afford a yellow powder **6c** (350 mg, 0.54 mmol, 65.11%). M.p. 261.5–263.9 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 2.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.19 (tt, *J* = 7.5, 1.4 Hz, 2H), 7.10 (t, *J* = 6.8 Hz, 4H), 7.04 (ddq, *J* = 7.1, 3.7, 2.0 Hz, 4H), 7.00–6.85 (m, 12H), 5.63 (s, 2H), 2.27 (dd, *J* = 10.3, 2.1 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.84, 138.74, 134.86, 134.82, 130.91, 130.88, 130.66, 129.62, 129.17, 128.83, 128.28, 128.24, 127.50, 127.24, 124.18, 123.21, 117.82, 21.50, 21.44.

7c was obtained the same as **7a** by employing of **6c** (200 mg, 0.31 mmol) and MnO_2 (830 mg, 9.55 mmol, 30.0 eq.) in dichloromethane (20 mL). The crude solid was chromatographed with silica gel (PE/DCM = 6/1) to obtained a dark-green solid **7c** (85 mg, 0.13 mmol, 42.63%). M.p. 265.3–269.2 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.2, 3.2 Hz, 4H), 7.33–7.29 (m, 2H), 7.27 (d, *J* = 3.2 Hz, 4H), 7.24 (d, *J* = 5.5 Hz, 4H), 7.20 (d, *J* = 7.5 Hz, 8H), 7.16 (s, 2H), 2.31 (d, *J* = 13.8 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.49, 138.41, 136.83, 136.62, 136.54, 133.16, 132.59, 129.44, 128.87, 127.68, 127.63, 127.58, 127.25, 127.06, 125.86, 21.59, 21.51. HRMS (APCI) *m/z* calcd. for $C_{48}H_{36}N_2$ $[M+H]^+$: 641.2951. Found: 641.2958.

Synthesis of 6d and 7d; compound **6d** was obtained the same as **6a** by employing **5** (500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 µmol, 3%), $NaHCO_3$ (704 mg, 8.38 mmol, 10.0 eq.) and a mixture of PhMe-H_2O (30 mL, v:v = 1:1) as well as 4-methylphenylboronic acid (689 mg, 5.07 mmol, 6.0 eq.) in EtOH (10 mL) at 75 °C for 10 h to afford green solid (389 mg) which was used directly. The above crude **6d** (200 mg) was mixed with MnO_2 (845 mg, 9.72 mmol, 30.0 eq.) in dichloromethane (20 mL). The mixture was stirred at room temperature overnight before it was filtered. The filtrate was evaporated to remove volatiles, and the solid was mixed with petroleum ether with stirring and filtered and dried to obtain a dark-green solid **7d** (101 mg, 0.16 mol, 50.66%). M.p. > 300 °C. ^{1}H NMR (500 MHz, CDCl3) δ 8.03 (dd, *J* = 7.0, 3.2 Hz, 4H), 7.35–7.29 (m, 8H), 7.27 (t, *J* = 2.9 Hz, 4H), 7.18 (d, *J* = 7.6 Hz, 8H), 2.54 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.50, 138.17, 136.09, 133.93, 132.52, 132.17, 128.08, 127.69, 125.81, 21.46. HRMS (APCI) *m/z* calcd. for $C_{48}H_{36}N_2$ $[M+H]^+$: 641.2951. Found: 641.2956.

Synthesis of 6e and 7e; compound **6e** was obtained the same as **6a** by employing **5** (500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 3%), $NaHCO_3$ (704 mg, 8.38 mmol, 10.0 eq.), PhMe-H_2O (30 mL, v:v = 1:1). It was then added 4-*tert*-buthylphenylboronic acid (902 mg, 5.07 mmol, 6.0 eq.) in EtOH (10 mL) at 75 °C for 10 h to obtain a crude solid, which was washed with water and petroleum ether and dried to afford green solid **6e** (498 mg, 0.61 mmol, 73.42%). M.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.39 (m, 8H), 7.20–7.15 (m, 8H), 6.91 (dd, *J* = 6.5, 3.3 Hz, 4H), 6.86 (dt, *J* = 6.5, 3.3 Hz, 4H), 6.15 (s, 2H), 1.40 (s, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.42, 131.80, 130.43, 130.34, 128.10, 125.78, 124.26, 123.15, 117.52, 34.64, 31.52. HRMS (APCI) *m/z* calcd. for $C_{60}H_{62}N_2$ $[M+H]^+$: 811.4986. Found: 811.4990.

7e was obtained the same as **7a** by employing of **6e** (200 mg, 0.25 mmol), MnO_2 (650 mg, 7.48 mmol, 30.0 eq.), and dichloromethane (20 mL) at room temperature (TLC monitoring at 365 nm with color changing from blue to khaki fluorescence). It was filtered, the filtrate was evaporated. The residue was purified with column chromatography on silica gel (PE/DCM = 10/1) with petroleum ether to obtain a dark-green solid **7e** (97 mg, 0.12 mmol, 48.62%). M.p. > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.1, 3.2 Hz, 4H), 7.50 (d, *J* = 8.1 Hz, 8H), 7.44 (d, *J* = 8.3 Hz, 8H), 7.23 (dd, *J* = 7.2, 3.0 Hz, 4H), 1.48 (s, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.70, 137.98, 137.64, 133.94, 133.24, 132.43, 127.82, 125.78, 124.22, 34.70, 31.70. HRMS (APCI) *m/z* calcd. for $C_{60}H_{60}N_2$ $[M+H]^+$: 809.4829. Found: 809.4836.

Synthesis of 6f and 7f; compound **6f** was obtained the same as **6a** by employing **5** (500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 3%), $NaHCO_3$ (704 mg, 8.38 mmol, 10.0 eq.) and a mixture of PhMe-H_2O (30 mL, v:v = 1:1). It was then heated at 75 °C before a solution of 4-*n*-hexylphenylboronic acid (1.03 g, 5.02 mmol, 6.0 eq.) in EtOH (10 mL) was added dropwise via syringe. The resulting mixture was stirred at 75 °C for additional 10 h. It was filtered and the solid was washed with water and petroleum ether and dried to afford green solid **6f** (520 mg, 0.56 mmol, 67.34%). M.p. 232.5–235.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.8 Hz, 8H), 7.08–7.01 (m, 12H), 6.92 (d, *J* = 7.4 Hz, 4H), 5.86 (s, 2H), 2.69–2.59 (m, 8H), 1.70 (p, *J* = 8.0, 7.6 Hz, 8H), 1.41 (ddtd, *J* = 16.8, 13.4, 10.0, 9.4, 4.1 Hz, 24H), 0.99–0.90 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.03, 131.95, 130.29, 129.88, 129.04, 128.92, 124.25, 123.17, 117.64, 35.97, 31.86, 31.42, 29.45, 22.74, 14.16. HRMS (APCI) *m/z* calcd. for $C_{68}H_{78}N_2$ $[M+H]^+$: 923.6238. Found: 923.6230.

7f was obtained the same as **7a** by employing of **6f** (200 mg, 0.22 mmol), MnO_2 (570 mg, 6.56 mmol, 30.0 eq.) in dichloromethane (20 mL) at room temperature (TLC monitoring at 365 nm with color changing from blue to khaki fluorescence). The filtrate was evaporated and washed with petroleum ether to obtain a dark-green solid **7f** (102 mg, 0.11 mmol, 55.11%). M.p. 235.2–237.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–7.95 (m, 4H), 7.37 (d, *J* = 7.5 Hz, 8H), 7.26 (s, 2H), 7.24 (d, *J* = 3.0 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 8H), 2.76 (t, *J* = 8.0 Hz, 8H), 1.79 (p, *J* = 7.9, 7.4 Hz, 8H), 1.50 (s, 8H), 1.48–1.35 (m, 16H), 0.97 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.25, 138.37, 138.10, 134.08, 132.72, 132.31, 127.78, 127.34, 125.76, 36.15, 31.96, 31.68, 29.57, 22.80, 14.20. HRMS (ESI) *m/z* calcd. for $C_{68}H_{76}N_2$ $[M+H]^+$: 921.6081. Found: 921.5464.

Synthesis of 6g and 7g; compound **6g** was obtained the same as **6a** by employing **5** (500 mg, 0.84 mmol), Pd(amphos)Cl_2 (21 mg, 29.6 μmol, 3%), $NaHCO_3$ (704 mg, 8.38 mmol, 10.0 eq.) and a mixture of PhMe-H_2O (30 mL, v:v = 1:1) as well as 4-*n*-hexyloxyphenylboronic acid (1.11 g, 5.02 mmol, 6.0 eq.) in EtOH (10 mL) at 75 °C for 10 h. The filtered solid was washed with water and petroleum ether and dried to afford green solid **6g** (520 mg, 0.56 mmol, 67.34%). M.p. 246.7–249.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11–7.03 (m, 12H), 6.93 (s, 4H), 6.89–6.81 (m, 8H), 5.88 (s, 2H), 4.00 (t, *J* = 6.7 Hz, 8H), 1.86 (p, *J* = 6.8 Hz, 8H), 1.56 (d, *J* = 8.0 Hz, 6H), 1.52 (d, *J* = 6.9 Hz, 2H), 1.41 (tt, *J* = 6.5, 2.9 Hz, 16H), 0.96 (td, *J* = 5.8, 4.7, 2.3 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.56, 131.51, 129.99, 126.52, 124.25, 123.15, 117.38, 115.23, 68.07, 31.81, 29.52, 25.86, 22.70, 14.11. HRMS (APCI) *m/z* calcd. for $C_{68}H_{78}N_2O_4$ $[M+H]^+$: 987.6034. Found: 987.6041.

7g was obtained the same as **7a** by employing of **6g** (200 mg, 0.20 mmol), MnO_2 (530 mg, 6.10 mmol, 30.0 eq.) in dichloromethane (20 mL) at room temperature (TLC monitoring at 365 nm with color changing from blue to khaki fluorescence). The filtrate was evaporated and washed with petroleum ether to obtain a dark-green solid **7g** (110 mg, 0.11 mmol, 55.11%). M.p. 262.5–265.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.1, 3.2 Hz, 4H), 7.37 (d, *J* = 8.5 Hz, 8H), 7.27 (s, 2H), 7.25 (s, 2H), 6.93 (d, *J* = 8.6 Hz, 8H), 4.11 (t, *J* = 6.6 Hz, 8H), 1.95–1.81 (m, 8H), 1.63–1.56 (m, 8H), 1.50–1.39 (m, 16H), 0.98 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.30, 138.47, 137.64, 133.54, 132.68, 128.96, 127.75, 125.73, 113.55, 68.06, 31.86, 29.67, 25.97, 22.74, 14.14. HRMS (ESI) *m/z* calcd. for $C_{68}H_{76}N_2O_4$ $[M+H]^+$: 985.5878. Found: 985.5784.

Synthesis of 6h and 7h; compound **6h** was obtained the same as **6a** by employing **5** (600 mg, 1.0 mmol), Pd(amphos)Cl_2 (35 mg, 50.2 μmol, 5%), $NaHCO_3$ (674 mg, 8.0 mmol, 10.0 eq.), PhMe-H_2O (30 mL, v:v = 1:1) as well as 2-thienylboronic acid (620 mg, 5.08 mmol, 6.0 eq.) in EtOH (10 mL) at 75 °C for 10 h. The filtered solid was washed with water and petroleum ether and dried to green solid **6h** (480 mg, 0.78 mmol,78.31%). M.p. > 300 °C. R_f = 0.4 (PE/DCM = 6/1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.2, 1.1 Hz, 4H), 7.24 (dt, *J* = 7.3, 3.7 Hz, 4H), 7.09–7.00 (m, 8H), 6.88 (dd, *J* = 3.4, 1.1 Hz, 4H), 6.16 (s, 2H). HRMS (APCI) *m/z* calcd. for $C_{36}H_{23}N_2S_4$ $[M+H]^+$: 611.0739. Found: 611.0731.

7h was obtained essentially the same as that of **7a** by employing of **6h** (100 mg, 0.16 mmol), MnO_2 (427 mg, 4.9 mmol, 30.0 eq.), in dichloromethane (20 mL) at room temperature (TLC monitoring at 365 nm with color changing from blue to khaki fluorescence). The filtrate was evaporated and washed with petroleum ether to obtain dark-green solid **7h** (61 mg, 0.10 mmol, 61.20%). M.p. > 300 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.2, 3.2 Hz, 2H), 7.58 (d, *J* = 5.6 Hz, 2H), 7.52–7.35 (m, 4H), 7.34–7.29 (m, 2H), 7.23 (dd, *J* = 5.2, 3.5 Hz, 4H), 7.20–7.09 (m, 2H), 7.09–7.02 (m, 2H). HRMS (APCI) *m/z* calcd. for $C_{36}H_{21}N_2S_4$ $[M+H]^+$: 609.0582. Found: 609.0574.

Synthesis of 6i and 7i; compound **6i** was obtained the same as **6a** by employing **5** (600 mg, 1.0 mmol), Pd(amphos)Cl_2 (35 mg, 50.2 μmol, 5%), $NaHCO_3$ (674 mg, 8.0 mmol, 10.0 eq.), PhMe-H_2O (30 mL, v:v = 1:1) as well as 4-dibenzofurylboronic acid (620 mg, 5.08 mmol, 6.0 eq.) in EtOH (10 mL) at 75 °C for 10 h. The filtered solid was washed with H_2O and PE and dried to afford a green solid **6i** (562 mg, 0.59 mmol, 59.34%). M.p. > 300 °C. R_f = 0.4 (PE/DCM = 5/1). ^1H NMR (600 MHz, DMSO) δ 7.99 (t, *J* = 4.3 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 4.7 Hz, 2H), 7.30–7.12 (m, 6H), 7.03 (t, *J* = 8.1 Hz, 2H), 6.94–6.87 (m, 2H), 6.84–6.76 (m, 2H), 5.82 (s, 1H). HRMS (APCI) *m/z* calcd. for $C_{68}H_{39}N_2O_4$ $[M+H]^+$: 947.2904. Found: 947.2882.

7i was obtained the same as **7a** by employing of **6i** (100 mg, 0.11 mmol), MnO_2 (275 mg, 4.9 mmol, 30.0 eq.) in dichloromethane (20 mL) at room temperature overnight (TLC monitoring at 365 nm with color changing from blue to khaki fluorescence). The filtrate was evaporated and washed with petroleum ether to obtain dark-green solid **7i** (40 mg, 0.04 mmol, 40.1%). M.p. > 300 °C. R_f = 0.4 (PE/DCM = 3/1). ^1H NMR (600 MHz, DMSO) δ 8.27 (d, *J* = 7.5 Hz, 1H), 8.12–7.84 (m, 2H), 7.73 (s, 1H), 7.51–7.43 (m, 1H), 7.39 (d, *J* = 12.5 Hz, 1H), 7.13 (d, *J* = 28.0 Hz, 1H), 6.92 (s, 1H), 6.52 (d, *J* = 7.4 Hz, 1H). HRMS (APCI) *m/z* calcd. for $C_{68}H_{37}N_2O_4$ $[M+H]^+$: 945.2748. Found: 945.2740.

3. Results and Discussion

The most challenging derivatives to synthesize among the linear aza-acenes are ones that have their *ortho* positions of nitrogen atoms on the aromatic rings functionalized due to the synthetic difficulties of the suitable precursors. The parent phenazine (**1**) and 6,13-dihydro-6,13-diazapentacene (**4**) are either commercially available or easily generated through a condensation between the readily available 2,3-dihydroxynaphthalene and 2,3-diaminonaphthalene.

The tetrabromo derivatives of **1** or **4** are difficult to prepare by direct condensation due to the lack of mild and efficient methods for aromatization and annulation. As a part of our ongoing research on palladium-catalyzed coupling project, we are interested in the exploration of quick and efficient syntheses of 1,4,6,9-tetraarylphenazine and 5,7,12,14-tetraaryl-6,13-diazapentacene. This has not emerged on 1,4,6,9-tetraaryl-phenazines until a recent excellent research on a pair of perylene diimide (PDI) non-fullerene small molecular acceptors based on a phenazine core with aryl linkers were reported. In this report *Shao* and co-workers revealed the highly practical synthetic detail on the synthesis of 1,4,6,9-tetrabromophenazine (**2**) by the reaction of phenazine and elemental bromine at room temperature, and the bromine atoms in compound **2** have been confirmed to be reactive towards Suzuki–Miyaura and Stille couplings in this report.[18] Furthermore, the pioneering studies on 5,6,12,14-tetrafunctionalized-6,13-dihydrodibenzo[*b,i*]phenazine as reported individually by Bunz and Pei offered us to obtain the tetraaryl derivatives of 6,13-diazapentacene. The fourfold Suzuki–Miyaura couplings between 5,6,12,14-tetrabromo-6,13-dihydrodibenzo[*b,i*]phenazine (**5**) and different boronic acids under standard palladium catalysis conditions were quite time-consuming (according to Bunz's procedure generally completed within 4 days). While 5,6,12,14-tetrafunctionalized-6,13-dihydrodibenzo[*b,i*] phenazines were obtained by the fourfold Stille couplings between compound **5** and tributyl(5-alkylthiophen-2-yl) stannanes in about 12 h at quite high temperature (170 °C) with toxic stannanes. These shortcomings prompted us to explore the tetraaryl-phenazines with different (hetero)aromatic substituents from a more convenient and efficient method as reported before.[22]

Initially compound **2** was efficiently achieved from the reaction of phenazine in neat bromine as reported by Shao,[18] while 6,13-dihydro-6,13-diazapentacene (**4**) was easily accessed through simple thermo-condensation between a 2,3-naphthalenediamine and 2,3-naphthalenediol, which was further regioselectively brominated with Br_2 to form compound **5**. Then the fourfold Suzuki–Miyaura couplings between **2** and different boronic acids (carbo-aromatic or heteroaromatic) with catalyst loading ranging from 1.5% to 5% (*ca.* 0.4–1.25% per bromide) were performed to afford compounds **3a–i** in the yields of 72–88%. While the dihydro-diazapentacene analogs were generally obtained between **5** and different boronic acids in the same manner to form **6a–i**, with the yields ranging from 40% to 80%, which were oxidized by MnO_2 in dichloromethane to diazapentacenes **7a–i** easily by following the procedure as developed by Bunz.[22]

It is noted that all of the coupling concerning compounds **2** and **5** with (hetero)arylboronic acids can be finished under mild conditions (75 °C) in no more than 10 h, which are less than those reported before.[18–22] The photophysical properties of all compounds **3a–i** and **7a–i** were investigated (Figures 1–4).

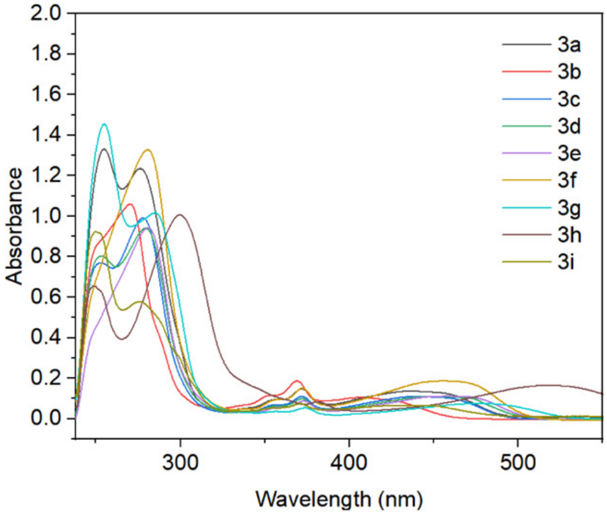


Figure 1. The UV-Vis spectra of **3a**–**i** in chloroform (1 · 10^{-5} M).

The UV-Vis spectra of **3a–i** are shown in Figure 1. The absorption spectra of **3a–i** are basically three bands. The strongest absorption band is at 235–320 nm, which is the π→π* transition of the benzene ring and belongs to the E band. The absorption band at 320–390 nm is the n→π* transition of the lone pair of electrons on N and the lone pair of electrons conjugated with the benzene ring, belonging to the R band. The wide absorption band at 390–550 nm is the π→π* transition in the conjugated system and belongs to the B band, which is caused by the overlapping of the fine structure vibrations of the benzene ring. The peak shapes of all compounds are basically the same with different substituents. Among the electron-donating alkyl-substituted phenyl groups, the **3b** with an *ortho*-methyl group on phenyl ring shows a significant blue shift (6 nm) compared to the unsubstituted **3a**, while the other alky-substituted **3c–f** show slight red shifts (2–5 nm), with the exception of **3e** with the maximum red shift (5 nm). The alkyl group of **3f** activates the conjugated double bond, resulting in an increase in the B band absorption. While the decreased absorption of **3g** with a significant red shift (9 nm) compared to that of **3f** might be due to oxygen atoms on substituents. The absorption **3h** with also a significant red shift (*ca.* 24 nm) with the decreased due to the lone pair of electrons on S of thienyl group. The absorption of **3i** decrease with a slight blue shift (*ca.* 1 nm) compared to **3a** might be attributed to the more conjugated dibenzofuran group.

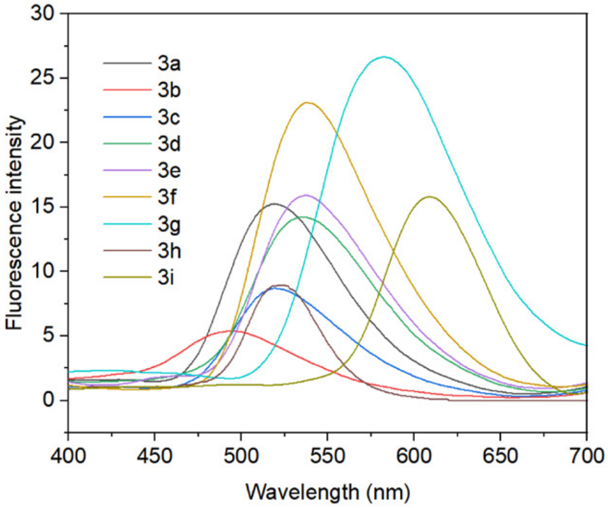


Figure 2. Fluorescence spectra of of **3a**–**i** in chloroform (1 · 10^{-5} M).

From the fluorescence emission spectra, the emission of **3a** appears at 519 nm. The emission of **3b** with *ortho*-methyl on phenyl is weakened with a significant blue shift, while those of **3c** and **3d** (with *meta*- or *para*-methyl) are also weakened but with red shift. The fluorescence emissions of those with *para*-substituents (**3e**–**g**) are enhanced all with significant red shifts, among which **3g** is the one with maximum emission at 582 nm with a red shift of 63 nm compared to that of **3a**. For **3h** with thienyl group, there is a significant red shift (4 nm compared to **3a**) with no significant change in intensity, while the one with conjugated dibenzofuryl groups (**3i**) only displays a slight blue shift.

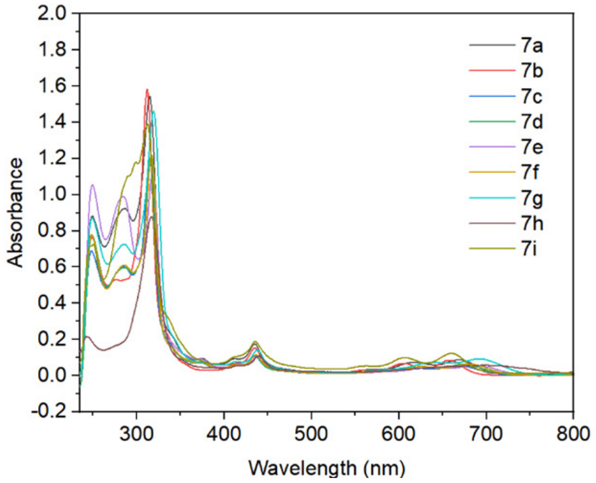


Figure 3. The UV-Vis spectra of **7a**–**i** in chloroform (1 · 10^{-5} M).

From the Figure 3, the absorption bands and ranges of **7a**–**i** are nearly the same as those of **3a**–**i** with strongest absorption band also around 235–320 nm. The substituents imply slight impacts on absorptions compared to those of **3a**–**i**.

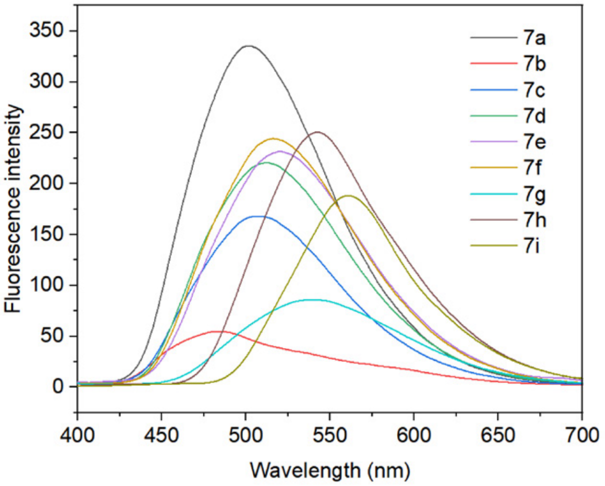


Figure 4. Fluorescence spectra of **7a**–**i** chloroform ($1 \cdot 10^{-5}$ M).

The fluorescence of **7a** displays at 501 nm the strongest emission. That of **7b** with *ortho*-methyl on phenyl group is weakened with a significant blue shift compared to **7a**. Those of **7c** and **7d** with *meta*- or *para*-methyl groups are decreased with some red shifts. While the emission of compounds with *para*-*tert*-butyl, *n*-hexyl or *n*-hexyloxy groups (**7e**–**g**) are also accordingly decreased but with red shifts (*ca.* 15 nm to 39 nm) compared to**7a**, among which **7g** owned the max red shift (39 nm). For the **7h**, there is a significant red shift (41 nm), while the higher red shift (60 nm) was found for **7i** both compared to **7a**.

4. Conclusion

Phenazine and 6,13-diazapentacene represent two important classes of N-PAHs with diverse applications in chemistry, biology, and materials science. Their unique electronic and structural properties make them invaluable in the development of organic semiconductors, fluorescent probes, and bioactive molecules. As research in this field progresses, these compounds are likely to play an increasingly important role in advancing technology and improving our understanding of organic materials. In this paper, a quick and practical synthetic approach towards tetra(hetero)aryl phenazines and 6,13-diazapentacene via a ligand-free palladium catalyzed fourfold Suzuki couplings under mild conditions and a wide scope of substituents is developed, which offers an alternative method to conduct potential investigations on multifunctionalized diazacenes. The primary spectra investigations indicated that those compounds were potential blue emitting emitters for opto-materials .

Supplementary Materials & Data Availability

All of ^{1}H NMR and ^{13}C NMR as well as Mass spectra data are available in Supporting information online.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Povzetek

Phenazine and 6,13-diazapentacene are nitrogen-containing linear heterocycles that have attracted significant attention in the fields of organic electronics, and materials science. A straightforward strategy has been developed to construct 1,4,6,9-tetraarylphenazines and 5,7,12,14-tetraaryl-6,13-diazapentacenes with 1,4,6,9-tetrabromophenazine and 5,6,12,14-tetrabromo-6,13-dihydrodibenzo[b,i]phenazine as the key intermediates, which were obtained easily from the bromination of phenazine and 6,13-dihydrodibenzo[*b*,*i*]phenazine, respectively. While the Pd(amphos)Cl_2 catalyzed ligand-free Suzuki couplings between above described intermediates and various arylboronic acids were performed to afford directly tetraarylphenazines or tetraaryl-6,13-diazapentacenes by subsequent oxidations. All of the new compounds are fully characterized by spectroscopy.