Synthesis of OLED materials of several triarylamines by palladium catalysts and their light emitting property

Mingxin Yu[a,c]*, Meijun Wang[a], Xiaohang Chen[a], Bingbing Hong[b], Xiaoyan Zhang[b] and Chienhong Cheng[c]

[a]*Department of Chemistry, Zhejiang University, Hangzhou, 310027, China*

[b]*College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou, 310027, China*

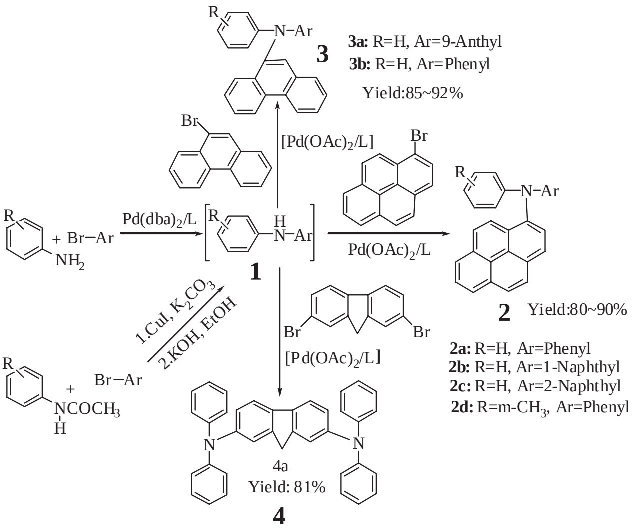
[c]*Department of Chemistry, Tsing Hua University, Taiwan, 30043*

Primary aryl amines reacted with aryl halides to give the secondary aryl amines by the catalysis of [Pd(dba)$_2$/P(*t*-Bu)$_3$] at 80 °C in toluene. Secondary aryl amines reacted with 1-bromo-pyrene and 9-bromo-phenanthrene and 2,7-dibromo-9H-fluorene to afford the OLED material of aminopyrene derivatives and aminophenanthrene derivatives and diamino-9H-fluorene type by the catalysis of [Pd(OAc)$_2$/P(*t*-Bu)$_3$] at 120 °C in *o*-xylene. The product structures were established by ^{1}H NMR, ^{13}C NMR, ^{13}C(DEPT), HRMS spectra. Physical properties were examined by UV-vis, PL and DSC spectra.

Keywords: palladium catalyst, triarylamine, light emitting property

Since the groundwork by Tang and co-workers,[1] OLED (organic light emitting devices) have continued to be a subject of great interest to researchers in various fields due to their potential application in flat panel displays.[2-5] Among the well-known light-emitting materials, Alq$_3$ is considered as the most commonly used green host emitter. The Alq$_3$-based devices have excellent properties in fabrication, lifetime, and brightness.[6-8] Several carbazole derivatives and diaminoanthracene derivatives have shown to be very efficient both as hole transporters and green emitters.[5,9] The synthesis of organic materials is very important for OLED. Triarylamines are standard hole transport materials,[10-12] many synthetic methods for the construction of an aryl-nitrogen bond have been reported. Aryl amines can be obtained either by copper-catalysed Ullmann condensation or palladium-catalysed cross-coupling reactions.[13-16] Ullmann reactions involve rather high temperatures and long reaction times and are limited to aryl iodides. Palladium-catalysed N-arylation reactions have opened up the possibility of producing a wide variety of aryl amines. We have synthesised some aryl amines and have reported the crystal structures of aryl amines and diaminoanthracene derivatives as high performance green host electroluminescent materials.[5,17-19] We now report synthesis of aminopyrene derivatives and aminophenanthrene derivatives and diamino-9H-fluorene as well as their light emitting properties. Reaction steps are outlined in Scheme 1.

The secondary aryl amines were acquired from primary aryl amines and aryl bromide to give a much higher yields by the catalysis of [Pd(dba)$_2$/P(*t*-Bu)$_3$] than by the catalysis of [Pd(OAc)$_2$/P(*t*-Bu)$_3$]. Aminopyrene derivatives and aminophenanthrene derivatives and diamino-9H-fluorene were successfully prepared in the presence of [Pd(OAc)$_2$/P(*t*-Bu)$_3$]. The palladium catalyst is very effective, giving the corresponding amino and diamino products in good yields with only a low amount of palladium catalyst (1%).



Scheme 1

All the product structures were demonstrated by ^{1}H NMR, ^{13}C NMR, ^{13}C(DEPT), HRMS spectra. Physical properties were examined by UV-vis, PL and DSC spectra, the results were summarised in Table 1. These compounds are probably carcinogens as they are triarylamines.

The lowest UV-vis absorption maximum in dichloromethane solution for aminopyrene derivatives appear in the narrow region 381–382 nm, that of aminophenanthrene derivatives and diamino-9H-fluorene appear at 348–421 nm and 366 nm. All these compounds emit light strongly in solution and in the solid state. The photoluminescent emission maximum of each compound in the solid state is bigger than that in solution except **3b** (Anthrancen-9-yl-phenanthren-9-yl-phenyl-amine).

Table 1 Physical properties of triarylamines

Entry	UV(CH_2Cl_2)	PL(CH_2Cl_2)	PL(Solid)	T_g/°C	T_c/°C	T_m/°C
2a	381, 300, 262, 245	467	484	54	133	183
2b	381, 326, 270, 246	468	475	91	No	227
2c	382, 318, 246	480	482	77	No	196
2d	382, 300, 274, 245	472	482	61	No	124
3a	421, 346, 252	504	522	54	No	160
3b	348, 294, 254	433	421	85	No	142
4a	366, 310, 239	412	425	No	No	227

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* Correspondent. E-mail: mingxinyu@css.zju.edu.cn

The emission maxima of these compounds fall in the range 412–480 nm in solution and 421–484 nm in the solid state. All of these compounds show melting points at 124–227 °C and exhibit glass transition points at 54–91°C. But there are no T_g for **4a** (N, N, N', N'-tetraphenyl-9H-fluorene-2,7-diamine) and no T_c except **2a** (diphenyl- pyren-1-yl-amine).

Experimental

All reactions were carried out under a nitrogen atmosphere in sealed reaction vessels and heated in an oil bath. Solvents were dried before use. Chemicals were purchased from Strem Chemical, Acros, or Lancaster as appropriate. Melting points were measured on a Fargo MP-2D melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Mercury 400 or Unity Inova 500 spectrometers. Mass spectra were obtained on a JEOL JMS-SX102A HRGC/LC/MS instrument operating in EI mode at 70 eV. UV-vis spectra were recorded on Hitachi U-3300 model. Photoluminescence (PL) spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer. The glass transition temperatures of compounds were determined by differential scanning calorimetry (DSC) under a helium atmosphere using a Seiko SII-EXSTAR 6000-DSC-6200 instrument.

General procedure for the synthesis of secondary aryl amines
Method A: 10 mmol of N-acetyl arylamine, 12 mmol of aryl bromide, 0.287g (1.5 mmol) of CuI, 0.138g (1 mmol) of K_2CO_3, and *o*-xylene (10 ml) were added to a 50 ml three-necked flask with stirring at room temperature. The reaction mixture was then stirred at 150° for 45 h. *o*-Xylene was removed by evaporation at reduced pressure. KOH 2.24g (40 mmol) and ethanol (20 ml) was added after cooling, and then the mixture was heated at reflux for 4h. The reaction mixture was quenched with cold water (10 ml) and extracted with diethyl ether (3 × 20 ml). The ethyl layer was separated. The diethyl ether solution was washed water (2 × 20 ml) and dried over $MgSO_4$. The solvent was removed by evaporation at reduced pressure. The crude product was purified by column chromatography on silica gel using acetic ether/ hexane as eluents: 40–60% yield.

Method B: 10 mmol of primary aryl amine, 12 mmol of aryl bromide, [Pd(dba)$_2$] (0.011 g, 0.12 mmol), [P(t-Bu)$_3$] (0.012 ml, 0.144 mmol), NaOBu-*t* (1.44g, 0.18mmol), toluene (15 ml) were added to a 50 ml three-neck flask with stirring at room temperature under dinitrogen. The reaction mixture was heated and stirred at 80 °C for an appropriate time until the reaction was complete. The reaction mixture was then cooled to room temperature, and water (20 ml) was added. The organic layer was separated. The toluene solution was washed water (2 × 20ml) and dried over $MgSO_4$. The solvent was removed by evaporation at reduced pressure. The crude product was purified by column chromatography on silica gel using acetic ether/ hexane as eluents: 81–90% yield.

General procedure for the synthesis of a few triarylamines
To a 25-ml sidearm flask in a dry nitrogen box were added aryl halide (1.25 mmol), diarylamine (1.25 mmol), [Pd(OAc)$_2$] (0.0125 mmol, Pd/Br=1%), tri-*tert*-butylphosphine (0.015 mmol), and sodium *tert*-butoxide (1.5 mmol). The flask was sealed with a septum and was then removed from the nitrogen box. To the flask was injected via a syringe *o*-xylene (10 ml). The reaction mixture was heated and stirred at 120° under dinitrogen for an appropriate time (10–16h). The reaction mixture was then cooled to room temperature, filtered through a Celite and silica gel pad, and washed with dichloromethane. The filtrate was washed with water and then dried with $MgSO_4$. Concentration of the filtrate on a rotary evaporator follow by washing of the solid material with methanol afforded the desired crude product. The crude product was the dried at 120 °C in a vacuum and was purified further by sublimation at $4–6 \times 10^{-3}$ Pa.

Diphenyl-pyren-1-yl-amine (**2a**): 90% yield; ^{1}H NMR (400, $CDCl_3$) δ_H: 8.15 (m, 6 H), 8.00 (m, 2 H), 7.88 (d, *J* = 8.0 Hz,1 H), 7.26 (m, 4 H), 7.17(d, *J* = 9.2Hz, 4 H), 6.99 (m, 2 H); ^{13}C NMR (500, $CDCl_3$) δ_C: 148.64 (C), 140.87 (C), 131.21 (C), 131.02 (C), 129.50 (C), 129.14 (CH), 128.17 (C),127.87 (CH), 127.65 (CH), 127.19 (CH), 127.08 (CH),126.32 (C), 126.17 (CH), 125.99 (CH), 125.17 (CH),125.08 (CH), 124.80 (C), 123.32 (CH), 122.05 (CH), 121.73 (CH). HRMS: *m/z*: calcd for $C_{28}H_{19}N$ 369.1517, found 369.1519.

Naphthalen-1-yl-phenyl-pyren-1-yl-amine (**2b**): 87% yield; ^{1}H NMR (400, $CDCl_3$) δ_H: 8.25 (d, *J* = 9.2Hz, 1 H), 8.06 (m, 7 H), 7.90 (dd, *J* = 5.6 Hz, *J* = 4.8 Hz 2 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, *J* = 7.6 Hz, 1 H), 7.35 (m, 2 H), 7.27(d, *J* = 6.0Hz, 1 H), 7.13 (t, *J* = 7.2 Hz, *J* = 7.6 Hz, 2 H), 6.89 (t, *J* = 7.2 Hz, *J* = 7.2 Hz, 1 H), 6.77(d, *J* = 7.6Hz, 2 H); ^{13}C NMR (500, $CDCl_3$) δ_C: 150.71 (C), 144.90 (C), 142.39 (C) 135.26 (C), 131.33 (C), 131.05 (C), 130.24 (C), 129.72 (C), 129.00 (CH), 128.92(C), 128.50 (CH), 127.70 (CH), 127.25 (CH), 126.78 (C), 126.68 (CH),126.30 (C), 126.25 (CH), 126.13 (CH), 126.02 (CH),125.78 (CH), 125.71 (CH), 125.66 (CH), 125.50 (CH), 125.07 (CH),124.94 (CH), 124.89 (CH), 124.46 (CH), 123.46 (CH), 120.69 (CH), 120.33 (CH). HRMS: *m/z*: calcd for $C_{32}H_{21}N$ 419.1674, found 419.1667.

Naphthalen-2-yl-phenyl-pyren-1-yl-amine (**2c**): 84% yield; ^{1}H NMR (400, $CDCl_3$) δ_H: 7.96 (m), 7.33 (m); ^{13}C NMR (500, $CDCl_3$) δ_C: 148.62 (C), 146.36 (C), 14086 (C) 134.44 (C), 131.21 (C), 131.03 (C), 129.73 (C), 129.59 (C), 129.50 (C), 129.23(CH), 128.84 (CH), 128.09 (C), 127.96 (CH), 127.66 (CH), 127.52 (CH),127.19 (CH), 127.13 (CH), 126.68 (CH), 126.35 (C),126.25 (CH), 126.21 (CH), 126.01 (CH), 125.21 (CH), 125.11 (CH),124.84 (C), 124.08 (CH), 123.29 (CH), 122.84 (CH), 122.40 (CH), 122.08 (CH). HRMS: *m/z*: calcd for $C_{32}H_{21}N$ 419.1674, found 419.1661.

Phenyl-pyren-1-yl-m-tolyl-amine (**2d**): 80% yield; ^{1}H NMR (400, $CDCl_3$) δ_H: 8.12 (m, 6 H), 7.97 (m, 2 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.20 (t, *J* = 8.4 Hz, *J* = 7.2 Hz 2 H), 7.08 (m, 3 H), 6.92 (q, 3 H), 6.78(d, *J* = 7.6Hz, 1 H), 2.21 (s, 3 H); ^{13}C NMR (500, $CDCl_3$) δ_C: 148.77 (C), 148.59 (C), 140.99 (C), 139.00 (C), 131.21 (C), 131.04 (C), 129.43 (C), 129.08 (CH), 128.92(CH), 128.19 (C), 127.81 (CH), 127.67 (CH), 127.19 (CH), 127.01 (CH),126.30 (C), 126.14 (CH), 125.96 (CH), 125.11 (CH),125.02 (CH), 124.80 (C), 123.38 (CH), 122.88 (CH), 122.75 (CH),121.92 (CH), 121.49 (CH), 119.43 (CH), 21.46 (CH_3). HRMS: *m/z*: calcd for $C_{29}H_{21}N$ 383.1674, found 383.1666.

Anthrancen-9-yl-phenanthren-9-yl-phenyl-amine (**3a**): 85% yield; ^{1}H NMR (500, $CDCl_3$) δ_H: 8.80 (d, *J* = 8.5 Hz, 1 H), 8.64 (d, *J* = 8.5 Hz, 1 H), 8.52 (s, 1 H), 8.39(d, *J* = 7.5 Hz, 1 H), 8.26 (d, *J* = 8.5 Hz, 2 H), 8.08 (d, *J* = 8.5 Hz, 2 H), 7.72 (t, *J* = 7.5 Hz, *J* = 7.0 Hz,1 H), 7.61 (t, *J* = 7.0 Hz, *J* = 7.0 Hz,1 H), 7.53–7.50 (m, 1 H), 7.44 (t, *J* = 7.0 Hz, *J* = 7.5 Hz, 2 H), 7.38 (d, *J* = 4.0 Hz, 2 H), 7.31 (t, *J* = 5.5 Hz, *J* = 9.5 Hz,3 H), 7.07(t, *J* = 8.5 Hz, *J* = 7.0 Hz, 2 H), 6.82 (t, *J* = 7.5Hz, *J* = 7.5 Hz, 1 H). 6.64 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (500, $CDCl_3$) δ_C: 150.49 (C), 141.18 (C), 139.66 (C), 132.79 (C), 132.37 (C), 132.09 (C), 130.71 (C), 128.98 (CH), 128.85(CH), 128.64 (C), 128.08 (C), 127.90 (CH), 126.62 (CH), 126.58 (CH),126.54 (CH), 126.51 (CH), 126.43 (CH), 126.38 (CH),125.75 (CH), 125.37 (CH), 124.56 (CH), 123.53 (CH), 122.82 (CH),122.33 (CH), 119.95 (CH), 118.82 (CH). HRMS: *m/z*: calcd for $C_{34}H_{23}N$ 445.1830, found 445.1825.

Phenanthren-9-yl-diphenyl-amine (**3b**): 92% yield; ^{1}H NMR (400, $CDCl_3$) δ_H: 8.69 (q, *J* = 8.0 Hz, *J* = 8.8 Hz, 2 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.73 (d, *J* = 7.6 Hz, 1 H), 7.54 (m, 5 H), 7.18 (t, *J* = 11.2 Hz, *J* = 8.4 Hz, 4 H), 7.10 (d, *J* = 7.6 Hz, 4 H), 6.93 (t, *J* = 7.2Hz, *J* = 7.2 Hz, 2 H); ^{13}C NMR (500, $CDCl_3$) δ_C: 148.24 (C), 142.08 (C), 132.44 (C), 132.12 (C), 130.45 (C), 129.38 (C), 129.11 (CH), 128.25(CH), 127.60 (CH), 126.94 (CH), 126.84 (CH), 126.48 (CH),125.07 (CH), 123.03 (CH), 122.57 (CH), 121.85 (CH),121.74 (CH). HRMS: *m/z*: calcd for $C_{26}H_{19}N$ 345.1517, found 345.1520.

N, N, N', N'-Tetraphenyl-9H-fluorene-2,7-diamine (**4a**): 81% yield; ^{1}H NMR (400, $CDCl_3$) δ_H: 7.57 (d, *J* = 7.6 Hz, 2 H), 7.11 (m, 24 H), 3.72 (s, 2 H); ^{13}C NMR (500, $CDCl_3$) δ_C: 148.00 (C), 146.24 (C), 146.51 (C), 136.76 (C), 129.16 (CH), 127.73 (CH), 123.75 (CH), 122.41 (CH), 121.44 (CH),119.90 (CH), 36.78 (CH_2). HRMS: *m/z*: calcd for $C_{37}H_{28}N_2$ 500.2252, found 500.2238.

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