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Synthesis of New *N,N*-Bis(5-acetylpyridin-2-yl)-phenylamine Derivatives and Their Solvatochromic Effects

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Abstract : A group of new *N,N*-bis(5-acetylpyridin-2-yl)phenylamine derivatives was synthesized in good yield applying an optimized Buchwald-Hartwig amination protocol. The synthesized compounds showed UV absorption maxima in the range of 320-360 nm, and showed good luminescence at dilute concentrations in the blue region of the spectra (in the range of 480-497 nm). They showed also a bathochromic shift associating the increase in solvent polarity. The synthesized compounds could be investigated for use in OLEDs or as potential monomers for PLEDs.

Keywords : Pyridine, triarylamine, photoinduced charge transfer, photoluminescence.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted great attention in recent years with their potential to form the next generation of flat-panel displays, due to their low-voltage operation, wide-viewing angle, excellent color quality, high contrast and mechanical flexibility[1-2]. More recently, intense efforts have been made for more improvements of OLEDs, by developing new materials with better required properties, such as high emission quantum yield[3], high thermal and photochemical stability[4], high photoemission[5], and good color purity[6].

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Triphenylamine is a common group in both OLEDs and PLEDs because of its excellent hole-injection ability and good UV-light harvesting properties[7-9]. Herein, we report the synthesis and photoluminescent properties of triarylamine analogues. These analogues were designed in such a way that an electron donating phenylamine part and an electron deficient acetyl pyridine part are present together within the same molecule as shown in Figure 1. By this design, photoinduced charge transfer (PICT) could be initiated in the excited state [10-11]. Furthermore, the presence of two acetyl groups in all the molecules makes them to be potential precursors for polymerization with suitable polymerizing agents, such as biscarboxaldehydes[12-13], for application in PLEDs. Although the synthesis of this typical

scaffold is new, the synthesis of *N,N*-bis(pyridin-2-yl)phenylamine has been reported before[14-15]. However, in these reported procedures the target triarylamines was obtained in low yields, specially for derivatives substituted by electron withdrawing groups[14]. A high yield synthesis was also successfully achieved, but by using specially designed Pd catalyst that's not available commercially[15], while in this work, we succeeded in the preparation of the target triarylamines in good yields using commercially available Pd catalyst.

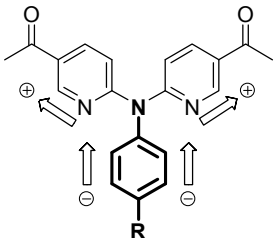


Figure 1. The dipolar design of the target compounds

2. Experimental

2.1 General

^{1}H-NMR (300 MHz) and ^{13}C-NMR(75 MHz) were recorded on a Bruker Avance 300 spectrometer with TMS as an internal reference. Melting points were taken on a Thomas-Hoover capillary melting apparatus and were uncorrected. UV-visible spectra and luminescence spectra were recorded on S-2130 spectroscopy and RF-5301-PC luminescent spectroscopy, respectively. Column chromatography was performed on Merck silica gel 60 (230 - 400 mesh). TLC was carried out using glass sheets precoated with silica gel 60 F254 prepared by E. Merck. All the commercially available reagents were obtained from Aldrich and Tokyo Kasei Chemical and generally used without further purification.

2.2. 5-Acetyl-2-bromopyridine (1)

Under N_2 atmosphere, *n*-BuLi (8.1 mL, 13 mmol, 1.6 M in hexane) was added to a mixture of 2,5-dibromopyridine (3.1 g, 13 mmol) and anhydrous diethyl ether (50 mL) at -78 °C. The reaction mixture was stirred for 30 minutes and then *N,N*-dimethylacetamide (1.4 mL, 15 mmol) was added and stirred at -78 °C to ambient temperature within 1 hour. The whole mixture was poured into saturated NH_4Cl solution and then extracted with diethyl ether (150 mL x 3). The combined organic layer was washed with brine, dried, and concentrated. The crude product was purified by column chromatography (silica gel, hexane:EtOAc = 7.5:1) to give **1** as a yellowish white solid (1.3 g, 51 %). mp 124-128 °C (124-128 °C [16]); ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3H, CH_3), 7.61 (d, J = 8.2 Hz, 1H, H_3), 8.07 (d, J = 7.6 Hz, 1H, H_4), 8.89 (s, 1H, H_6); ^{13}C NMR ($CDCl_3$): δ 26.79 (CH_3), 128.44 (C_3), 131.41 (C_5), 137.70 (C_4), 146.96 (C_2), 150.42 (C_6), 195.65 (C=O).

2.3. General procedure for the preparation of compounds 2a-g

A mixture of dichlorobis (triphenylphosphine)palladium(II) (27 mg, 0.038 mmol), Xantphos (4,5-bis (diphenylphosphino)-9,9-dimethylxanthene) (22 mg, 0.038 mmol) and 18-crown-6 (20 mg, 0.076 mmol) in toluene (1 mL) was stirred at 60 °C under N_2 atmosphere for 30 minutes. A mixture of 5-acetyl-2-bromopyridine (155 mg, 0.76 mmol), the appropriate aniline derivative (0.38 mmol) and NaO*t*-Bu in toluene (2 mL) was added to this slurry. The reaction mixture was refluxed under N_2 atmosphere for the specified reaction time. The reaction mixture was evaporated under vacuum, and the residue was triturated with water (20 mL) and extracted with dichloromethane (50 mL x 3). The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated under vacuum. The

crude product was purified by column chromatography (silica gel, hexane:EtOAc = 4:1) to give the pure products.

2.3.1. *N,N*-Bis(5-acetylpyridin-2-yl) -*N*-phenylamine (2a)

It was obtained as yellow powder (78 mg, 62 % yield). mp 145–146 °C; ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 6H, $2CH_3$), 7.12 (d, *J* = 8.7 Hz, 2H, Pyr-H_3), 7.23-7.28 (m, 2H, Ar-H), 7.38–7.42 (m, 1H, Ar-H), 7.46–7.51 (m, 2H, Ar-H), 8.14 (dd, *J* = 2.2, 6.6 Hz, 2H, Pyr-H_4), 8.92 (d, *J* = 1.6 Hz, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.50 ($2CH_3$), 116.16, 127.69, 128.29, 130.35, 137.24, 143.12, 149.80, 159.83, 195.45 (2C=O).

2.3.2. *N,N*-Bis(5-acetylpyridin-2-yl) -*N*-(4-methoxyphenyl)amine (2b)

It was obtained as brown powder (76 mg, 55 % yield). mp 94–95 °C; ^{1}H NMR ($CDCl_3$): δ 2.59 (s, 6H, $2CH_3$), 3.87 (s, 3H, OCH_3), 7.03 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.8 Hz, 2H, Pyr-H_3), 7.17 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.15 (dd, *J* = 2.3, 6.5 Hz, 2H, Pyr-H_4), 8.98 (s, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.40 ($2CH_3$), 55.52 (OCH_3), 103.28, 103.43, 115.63, 115.81, 127.52, 129.67, 137.14, 149.60, 158.94, 159.81, 195.31 (2C=O).

2.3.3. *N,N*-Bis(5-acetylpyridin-2-yl) -*N*-(4-dimethylaminophenyl)amine (2c)

It was obtained as dark brown powder (85 mg, 60 % yield). mp 133–134 °C; ^{1}H NMR ($CDCl_3$): δ 2.57 (s, 6H, $2CH_3$), 3.02 (s, 6H, $2NCH_3$), 6.79 (d, *J* = 8.6 Hz, 2H, Pyr-H_3), 7.07–7.12 (m, 4H, Ar-H), 8.12 (d, *J* = 8.7 Hz, 2H, Pyr-H_4), 8.89 (s, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.37 ($2CH_3$), 40.53 ($2NCH_3$), 99.99, 113.50, 115.86, 127.27, 129.18, 136.90, 149.79, 160.28, 195.45 (2C=O).

2.3.4. *N,N*-Bis(5-acetylpyridin-2-yl) -*N*-(4-cyanophenyl)amine (2d)

It was obtained as yellow powder (92 mg, 68 % yield). mp 202–203 °C; ^{1}H NMR ($CDCl_3$): δ 2.61 (s, 6H, $2CH_3$), 7.14 (d, *J* = 8.7 Hz, 2H, Pyr-H_3), 7.29 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.73 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.21 (dd, *J* = 2.2, 6.5 Hz, 2H, Pyr-H_4), 8.91 (s, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.53 ($2CH_3$), 116.76, 127.89, 128.69, 133.86, 137.77, 149.94, 159.16, 195.17 (2C=O).

2.3.5. N,N-Bis(5-acetylpyridin-2-yl) -N-(4-phenoxyphenyl)amine (2e)

It was obtained as yellow powder (117 mg, 73 % yield). mp 55–56 °C; ^{1}H NMR ($CDCl_3$): δ 2.59 (s, 6H, $2CH_3$), 7.11–7.28 (m, 9H, Ar-H), 7.41 (d, *J* = 7.1 Hz, 2H, Ar-H), 8.17 (dd, *J* = 2.0, 6.3 Hz, 2H, Pyr-H_4), 8.95 (s, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.43 ($2CH_3$), 103.15, 115.93, 119.67, 119.79, 124.19, 127.72, 129.77, 129.97, 137.42, 149.52, 195.23 (2C=O).

2.3.6. *N,N*-Bis(5-acetylpyridin-2-yl) -*N*-(4′-biphenyl)amine (2f)

It was obtained as orange powder (110 mg, 71 % yield). mp 103–104 °C; ^{1}H NMR ($CDCl_3$): δ 2.61 (s, 6H, $2CH_3$), 7.15 (d, *J* = 8.8 Hz, 2H, Pyr-H_3), 7.18 – 7.51 (m, 5H, Ar-H), 7.63 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.71 (d, *J* = 8.3 Hz, 2H, Ar-H), 8.19 (dd, *J* = 2.1, 6.7 Hz, 2H, Pyr-H_4), 8.98 (d, *J* = 1.6 Hz, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.48 ($2CH_3$), 116.27, 127.13, 127.77, 127.88, 128.42, 128.93, 129.07, 137.57, 139.93, 141.88, 149.56, 159.44, 195.23 (2C=O).

2.3.7. 1-(4′-(N,N-Bis(5-acetylpyridin -2-yl)amino)biphenyl-4-yl) ethanone (2g)

It was obtained as yellowish orange powder (80 mg, 47% yield). mp 165–166 °C; ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 6H, $2CH_3$), 2.66 (s, 3H, C_1-CH_3) 7.19 (d, *J* = 8.7 Hz, 2H, Pyr-H_3), 7.72 (d, *J* = 6.3 Hz, 4H, Ar-H), 8.06 (d, *J* = 8.1 Hz, 2H, Ar-H), 8.18 (dd, *J* = 1.5, 7.2 Hz, 2H, Pyr-H_4), 8.92 (s, 2H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.47 ($2CH_3$),

26.71 (C_1-CH_3), 101.99, 116.35, 127.19, 127.95, 128.50, 129.04, 136.13, 137.30, 138.82, 143.35, 149.92, 159.79, 195.38 (2C=O), 206.44 (C_1-C=O).

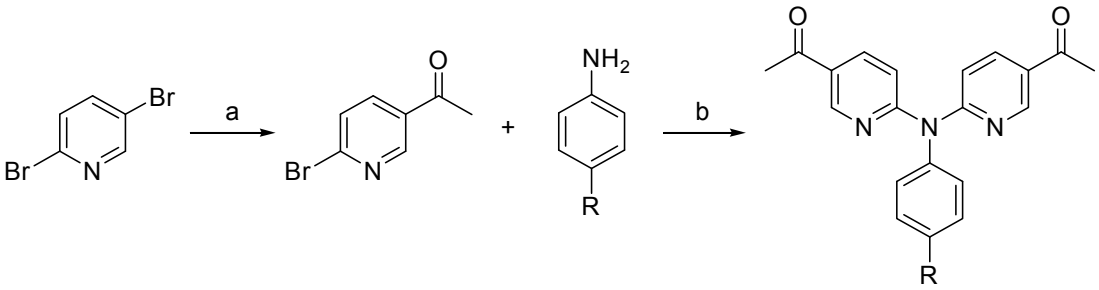
2.4. 1-(6-(Phenylamino)pyridin-3-yl) ethanone

A mixture of dichlorobis (triphenylphosphine)Palladium(II) (27 mg, 0.038 mmol) and Xantphos (22 mg, 0.038 mmol) in toluene (1 mL) was stirred at 60 °C under N_2 atmosphere for 30 minutes. A mixture of 5-acetyl-2-bromopyridine (155 mg, 0.76 mmol), aniline (35 mg, 0.38 mmol) and NaO*t*-Bu in toluene (2 mL) was added to this slurry. The reaction mixture was refluxed under N_2 atmosphere for 24 h. The reaction mixture was evaporated under vacuum, and the residue was triturated with water (20 mL) and extracted with dichloromethane (50 mL x 3). The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated under vacuum. The crude product was purified by column chromatography (silica gel, hexane:EtOAc = 4:1) to give **3** as a yellow powder (45 mg, 56 % yield). mp 126-127 °C; ^{1}H NMR ($CDCl_3$): δ2.53 (s, 3H, CH_3), 6.85 (d, *J* = 8.9 Hz, 1H, Pyr-H_3), 7.14-7.20 (m, 1H, Ar-H), 7.39 (d, *J* = 4.3 Hz, 4H, Ar-H), 7.97 (s, 1H, NH), 8.04 (dd, *J* = 2.1, 6.8 Hz, 1H, Pyr-H_4), 8.79 (d, *J* = 1.7 Hz, 1H, Pyr-H_6); ^{13}C NMR ($CDCl_3$): δ 26.12 (CH_3), 107.19, 121.96, 124.55, 124.63, 129.52, 137.65, 138.96, 150.98, 159.02, 195.37 (C=O).

3. Results and discussion

As shown in Scheme 1, the synthesis of the target compounds started with the preparation of 5-acetyl-2-bromopyridine (**1**) in 51% yield, by lithiation of 2,5-dibromopyridine in diethyl ether at -78 °C

Scheme 1.



Reaction conditions: a) i) *n*-BuLi, Et_2O, -78 °C, ii) *N*,*N*-dimethylacetamide, b) $Pd(PPh_3)_2Cl_2$ (10 mol%), Xantphos (10 mol%), 18-crown-6 (10 mol%), NaO*t*-Bu, toluene, 110 °C.

Compound No.	2a	2b	2c	2d	2e	2f	2g
R	H	-OCH_3	-$N(CH_3)_2$	-CN	-OPh	-Ph	-(Ph)-4-Ac
Reaction time (h)	6	4	6	10	6	6	8
Yield (%)*	62	55	60	68	73	71	47

*Yield is for product of reaction step b after purification with column chromatography.

under nitrogen atmosphere, followed by acetylation at 5-position by *N,N*-dimethylacetamide[16].

5-Acetyl-2-bromopyridine (**1**) was allowed to react with 4-substituted anilines in order to obtain the target *N,N*-bis(5-acetylpyridin-2-yl)phenylamine derivatives (**2a-g**). The reaction was carried out in boiling toluene, under nitrogen atmosphere, following an optimized Buchwald-Hartwig *N*-arylation protocol [17], using dichlorobis triphenylphosphine)palladium(II) as a catalyst, Xantphos as a phosphine ligand, and sodium *tert*-butoxide as a base.

en these typical conditions were applied for the reaction, only the mono-*N*-arylaniline product, 1-(6-(phenylamino)pyridin3-yl) thanone, was obtained in the reaction of 5-acetyl-2-bromopyridine (**1**) with aniline. The reason that only 1-(6-(phenylamino) yridin-3-yl)ethanone was obtained under these conditions is that the highly acidic NH proton of the *N*-arylaniline generated at the first step of the reaction undergoes a rapid exchange with the Na^+ ion species of sodium *tert*-butoxide, forming a stable sodium amide that is too polar to keep inside the reaction phase[18].

Table 1. The λ_{max} values for compounds **2a-2g**

Compound	λ_{max} (nm)		FWHM[d] (nm)
	UV[a]	PL[b,c]	
2a	355	480	99
2b	357	494	133
2c	320	446	119
2d	341	448	135
2e	355	494	91
2f	355	497	100
2g	349	485	99

[a]In CH_2Cl_2 solution on 50 μM, [b]In CH_2Cl_2 solution on 100 nM, [c]PL spectra recorded by single beam excitation at UV λ_{max}, [d]The full widths at half maximum value of PL spectra.

In order to solve this problem, a phase transferring agent such as crown ethers (e.g. 18-crown-6) or quaternary ammonium salts (e.g. tetrabutylammonium bromide) was used. The use of quaternary ammonium salts, however, was found to be ineffective, producing only minute amount of the desired product, while the yields obtained by using crown ether were much more convenient as shown in Scheme 1.

The absorption and photoluminescence (PL) spectra of compounds **2a-g** were recorded in dichloromethane using UV-vis and luminescence spectroscopy, respectively. The results are shown in Table 1 and the typical spectra are shown in Figure 2.

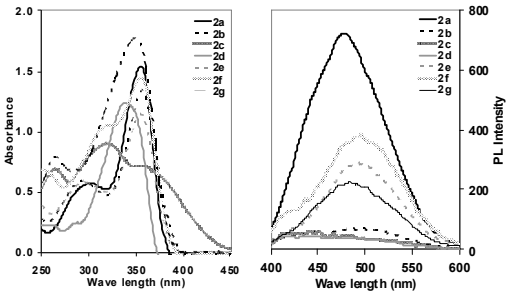


Figure 2. UV (left) and PL (right) spectra for compounds **2a-2g.**

As shown in Figure 2, the UV spectra of all the recorded compounds showed absorption maxima in the range of (340 - 360 nm) except for compound **2c** which shows maximum absorption at 320 nm, and extended absorption until 450 nm.

Excitation of these compounds by a single beam UV light at the λ_{max} of their absorption spectra resulted in an intense emission at the range of (480 - 500 nm) in compounds **2a** and **2e-2f,** while compounds **2b-2d** showed only weak emissions at 100 nM concentration.

By comparing the PL intensities of the tested compounds, it was revealed that the most intense luminescence was produced by compounds **2a** and **2f**. Consequently, the

photoluminescence of these two compounds was measured in various solvents, and the intensities as a percent of PL relative to dichloromethane were calculated. The results are shown in Table 2 and the typical spectra are shown in Figure 3.

Table 2. Solvatochromic effect on the compounds **2a** and **2f** in various solvents.

Solvent	λ_{max} (nm)[a]		RI[b] (%)	
	2a	**2f**	**2a**	**2f**
Toluene	436	450	123	144
Diethyl ether	450	447	74	147
THF	450	478	41	124
CH_2Cl_2	480	497	100	100
DMSO	505	513	94	144

[a]All readings were made at 100nM, [b]RI = Relative intensity of PL as a percent of PL in CH_2Cl_2.

The emission peaks showed a stepwise red-shift with increasing solvent polarity, from (436 – 450 nm) in toluene to (505 – 513 nm) in DMSO. This effect proves that photoinduced charge transfer (PICT) occurs in the excited state, and that the excited state is highly polarized and hence, stabilized by solvation with the polar solvent after photoexcitation[6].

4. Conclusion

We have synthesized a group of new *N,N*-bis(5-acetylpyridin-2-yl)phenylamines **2a**-**2g** having good luminescence, at dilute concentration, in the blue region of the spectra. The synthesized compounds showed bathochromic shift associating the increase in solvent polarity, which indicates that photoinduced charge transfer (PICT) occurs in the excited state. The synthesized compounds could be used in OLEDs or as potential monomers for PLEDs.

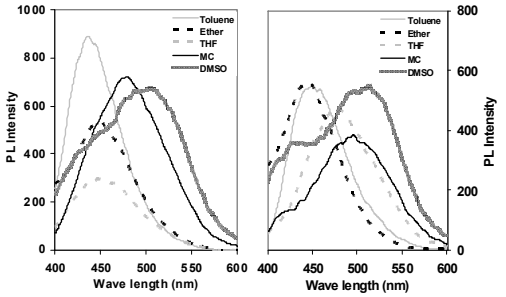


Figure 3. Solvatochromic effect on **2a** (left) and **2f** (right).

Acknowledgements

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