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Comparative Syntheses of Arylamine Monomer with Styrylpyridyl Photo-Crosslinker of Polyarylamine for OLED Hole-Injection Material

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A new arylamine monomer with photo-crosslinkable styrylpyridinyl moiety of conjugated polyarylamine for OLED hole injection material was synthesized through two synthetic routes, BOC-amine protection/deprotection and nitro group reduction methods. Both synthetic routes yielded practically pure amine product by standard aqueous workup and crystallization in 61% overall yield from pyridinyl-vinylphenol **2**. *Their reaction efficiencies were comparatively studied in views of practicality and reaction scale. Also, the synthetic conditions of key compound of photo-crosslinker, pyridinylvinylphenol* **2** *was reinvestigated and established for the reproducible and reliable preparation.*

Keywords Conjugated polyarylamine; hole-injection material; organic light-emitting devise; photo-cross linker; styrylpyridine

Introduction

In the emerging field of organic electronics, such as OLED, PLED and organic photovoltaics, there is a significant need for improved organic conducting materials. Especially arylamines are widely used as itself for hole-injection molecules or as monomers for conjugated aromatic amine polymers [1–7]. Recently our group disclosed a conjugated arylamine polymer, poly(diotylfluorene-*alt*-biphenylamine) [8] prepared from the corresponding fluorene dibromide and biphenylamine by polymerization with Buchwald-Hartwig palladium-catalyzed aromatic amination [9]. The new arylamine polymer showed higher efficiency of hole-injection than the commonly used PEDOT:PSS did [10]. Most of recent OLED devises are fabricated by

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multi-layering polymeric materials with solution processing such as spin-coating or ink-jet printing techniques by which each layering component efficiently perform desired properties, such as EIL, ETL, EML, HTL and HIL. However, the new hole-injection polyarylamine was liphophilic unlike hydrophilic PEDOT:PSS which commonly used for hole-injection layer. Thus, practical solution processing of the new polyarylamine to prepare the multi-layered OLED devices was hampered because of the erosion of the subsequent layers of liphophilic organic solution. Thus, we devised crosslinkable polyarylamine polymers which could provide excellent solvent resistance after curing. An arylamine monomer with photo-crosslinkable styrylpyridyl group could be introduced into the conjugated polyarylamine polymers during copolymerization with arylamine monomers and countpart dihalide monomers by Buchwald-Hartwig palladium-catalyzed aromatic amination. The styrylpyridyl moiety is well known and used as photo-cross linkers on a number of polymers by [2 + 2] cycloaddition reaction [11–13].

In this work we report comparable synthetic methods and optimal reaction conditions of a new arylamine monomer with photo-crosslinkable styrylpyridyl moiety, which can be used as an amine monomer to synthesize conjugated poly aromatic amines, and also reinvestigated the optimized and reproducible preparation of styrylpyridine, the key component of [2 + 2] photo-cycloaddition.

Experimental

General remarks. All commercially obtained solvents and reagents were used as purchased. THF was freshly distilled from sodium–benzophenone under a nitrogen gas atmosphere. *N,N*-Dimethylformamide (DMF) was obtained as anhydrous, 99.8% grade. Methanol was obtained as reagent plus grade, 99.9+% and fresh methanol must be used for hydrogenation reaction. Lindlar catalyst was purchased from Aldrich. TLC analysis was performed using silica gel 60 F_{254} coated glass slides from Merck. Chromatographic purifications were performed by flash chromatography using silica gel (70–230 mesh). NMR data were obtained at 400 MHz for proton and at 100 MHz for carbon in the indicated solvent. Chemical shifts (δ) were recorded in ppm using either relative to TMS or residual undeuterated solvent and coupling constants in hertz (Hz). Melting points were measured on an opti melt automated melting point system and were uncorrected. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrometer. MS spectra were obtained in EI mode by a HP6890 Agilent 5973N gas chromatograph mass spectrometer. Elemental analyses were performed from Kyungpook center for scientific instruments.

Synthesis

4-[2-(2-Pyridinyl)ethenyl]phenyl acetate [14]. A mixture of 4-hydroxybenzaldehyde (12.2 g, 0.1 mol), 2-picoline (11.2 g, 0.12 mol), acetic anhydride (20.4 g, 0.2 mol) and acetic acid (1.2 g, 0.02 mol) in a round bottomed flask equipped with a condenser and an anhydrous $CaCl_2$ drying tube was vigorously heated under reflux with a heating mantle for 24 hrs. Volatile solvent was distilled out and the reaction residue was cooled. The residue was dissolved in CH_2Cl_2 (80 mL), washed with 20% $NaHCO_3$ aqueous solution (80 mL) and then with distilled water (50 mL × 2). The separated organic layer was dried over anhydrous $MgSO_4$, filtered, and

concentrated by a rotary evaporator. The solid was dissolved in hot EtOH (50 mL) and crystallized to give white crystalline product (14.7 g, 62%).

mp 109.6 – 110.8°C (109.2 – 110.3°C) [14]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (br dd, $J = 0.8$ and 4.8 Hz, 1 H), 7.66 (dt, $J = 1.6$ and 7.6 Hz, 1 H), 7.62 (d, $J = 16$ Hz, 1 H), 7.58 (d, $J = 8.4$ Hz, 2 H), 7.37 (br d, $J = 7.6$ Hz, 1 H), 7.15 (dd, $J = 0.8$ and 4.8 Hz, 1 H), 7.11 (d, $J = 16$ Hz, 1 H), 7.10 (d, $J = 8.4$ Hz, 2 H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 155.6, 150.7, 149.8, 136.7, 134.6, 131.8, 128.3, 128.2, 122.3, 122.2, 122.0, 21.3.

4-[2-(2-Pyridinyl)ethenyl]phenol (2) [14]. To a solution of 4-[2-(2-pyridinyl) ethenyl]phenyl acetate (9.57 g, 0.04 mol) in ethanol (70 mL) was added a 2 M KOH aqueous solution (10 mL). The mixture was heated at reflux for 12 hrs. To the warm yellow solution was added 1 M HCl solution (ca. 5 mL) to acidify to pH 5–6. The solid product was precipitated upon cooling to room temperature. The precipitate was collected by filtration, washed with distilled water and then dried under vacuum. The crude product was further crystallized from ethanol to give a white crystalline product (7.31 g, 93%).

mp 217.1 – 217.6°C (216.4 – 217.6°C) [14]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.69 (br s, 1 H), 8.52 (br dd, $J = 1.0$ and 4.8 Hz, 1H), 7.74 (dt, $J = 2.0$ and 7.6 Hz, 1H), 7.57 (d, $J = 16.1$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.45–7.49 (m, 1H), 7.19 (dd, $J = 7.6$ and 1.2 Hz, 1H), 7.07 (d, $J = 16.1$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.3, 155.9, 149.7, 137.1, 132.5, 129.0, 127.8, 125.1, 122.2, 122.1, 116.0.

2-(4-(6-Bromohexyloxy)styryl)pyridine (3). A mixture of 4-[2-(2-pyridinyl)ethenyl] phenol (1.98 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) in DMF (15 mL) was stirred at room temperature for 30 min and then added 1,6-dibromohexane (7.32 g, 30 mmol). The mixture was further stirred at room temperature overnight. The volatile solvent and excess dibromide was distilled out by vacuum distillation. The residue was suspended in CH_2Cl_2 and filtered through a short pad of silica gel. The filtrate was concentrated by a rotary evaporator. The solid residue was dissolved in hot hexane (20 mL × 3) and cooled in a refrigerator, and then the supernatant was taken out from precipitates by decantation. White crystals (2.90 g, 80%) were collected by filtration.

mp 82.5 – 82.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (br dd, $J = 0.8$ and 4.4 Hz, 1H), 7.64 (dt, $J = 1.6$ and 7.6 Hz, 1H), 7.58 (d, $J = 16.0$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 2H), 7.35 (d, $J = 7.9$ Hz, 1H), 7.11 (ddd, $J = 0.8$, 4.8 and 7.2 Hz, 1H), 7.04 (d, $J = 16.0$ Hz, 1H), 6.89 (d, $J = 8.7$ Hz, 2H), 3.99 (t, $J = 6.4$ Hz, 2H), 3.43 (t, $J = 6.8$ Hz, Hz, 2H), 1.90 (m, 2H), 1.81 (m, 2H), 1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 156.1, 149.7, 136.6, 132.5, 129.4, 128.6, 125.8, 121.9, 121.8, 114.8, 67.9, 34.0, 32.8, 29.2, 28.0, 25.4.

t-Butyl 4-hydroxyphenylcarbamate. A mixture of 4-aminophenol (1.456 g, 10 mmol), di-*tert*-butyl carbonate (2.400 g, 11 mmol), triethylamine (1.4 mL) and MeOH (15 mL) was stirred at room temperature overnight. The mixture was concentrated by a rotary evaporator. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with acidic water (30 mL) containing acetic acid (15 drops) and then with water (30 mL). The organic layer was separated, dried and concentrated by a rotary evaporator. The solid residue was recrystallized from toluene/hexane to afford white crystalline product (1.758 g, 84%). mp 142.8 – 143.3°C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.16 (d, $J = 8.4$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 6.35 (br s, 1H), 5.33 (br s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 152.4, 131.2, 121.8, 116.1, 80.9, 28.8.

t-Butyl 4-(6-(4-(2-(2-pyridinyl)vinyl)phenoxy)hexyloxy)phenylcarbamate (4). To a mixture of *t*-butyl 4-hydroxyphenylcarbamate (0.87 g, 4.2 mmol) and K_2CO_3 (0.58 g, 4.2 mmol) in DMF (10 mL) at room temperature was added 2-(4-(6-bromohexyloxy) styryl)pyridine (1.45 g, 4 mmol). The mixture was further stirred at room temperature overnight. The solvent was removed in vacuo. The residue was suspended in a mixture of CH_2Cl_2/water (2:1, 45 mL), filtered and washed with CH_2Cl_2 and then water. After drying under vacuum the white power (1.58 g, 80%) was obtained.

mp 185.4 – 186.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (br dd, $J = 0.8$ and 4.4 Hz, 1H), 7.64 (dt, $J = 1.6$ and 7.6 Hz, 1H), 7.58 (d, $J = 16.0$ Hz, 1H), 7.51 (d, $J = 8.8$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.12 (ddd, $J = 0.8$, 4.8 and 7.6 Hz, 1H), 7.04 (d, $J = 16.0$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 6.37 (br s, 1H), 4.00 (t, $J = 6.6$ Hz, 2H), 3.94 (t, $J = 6.4$ Hz, 2H), 1.81 (m, 4H), 1.54 (m, 4H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.6, 155.7, 153.4, 149.9, 136.4, 132.8, 131.8, 129.9, 128.6, 126.3, 121.7, 121.7, 121.1, 115.4, 115.2, 80.4, 68.7, 68.4, 29.5, 29.5, 28.6, 26.1 (double intensity).

1-(6-Bromohexyl)oxy-4-nitrobenzene (5). A mixture of 4-nitrophenol (1.39 g, 10 mmol) and K_2CO_3 (1.4 g, 10 mmol) in DMF (10 mL) was stirred at room temperature for 30 min and then added 1,6-dibromohexane (7.32 g, 30 mmol). The mixture was further stirred at room temperature for 20 hrs. The volatile solvent and excess dibromide was distilled out by vacuum distillation. The residue was suspended in CH_2Cl_2 and filtered through a short pad of silica gel. The filtrate was concentrated by a rotary evaporator. The oily residue was dissolved in hot hexane (10 mL) and cooled in a refrigerator, and then the supernatant above precipitates was taken by decantation. This process was performed three times and the combined supernatant was concentrated and filtered again through a short pad of silica gel with hexane. The filtrate was concentrated to give yellowish oily product (2.72 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, $J = 9.2$ Hz, 2H), 6.93 (d, $J = 9.2$ Hz, 2H), 4.05 (t, $J = 6.4$ Hz, 2H), 3.43 (t, $J = 6.8$ MHz, 2H), 1.90 (quin, $J = 6.8$ Hz, 2H), 1.84 (quin, $J = 6.8$ Hz, 2H), 1.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 141.5, 126.0, 114.5, 68.7, 33.9, 32.7, 28.9, 27.9, 25.3.

2-(4-(6-(4-Nitrophenoxy)hexyloxy)styryl)pyridine (6). A mixture of 4-[2-(2-pyridinyl)ethenyl]phenol (1.03 g, 5.2 mmol) and K_2CO_3 (0.73 g, 5.3 mmol) in DMF (15 mL) was stirred at room temperature for 30 min and then added 1-(6-bromohexyl) oxy-4-nitrobenzene (1.57 g, 5.2 mmol). The mixture was further stirred at room temperature for 20 hrs. The solvent was removed in vacuo and the solid residue was taken in CH_2Cl_2 (20 mL), and filtered through a short pad of silica gel. The filtrate was concentrated by a rotary evaporator. The solid residue was crystallized from ethanol to give white solid product (1.85 g, 85%).

mp 146.6 – 147.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (br d, $J = 4.8$ Hz, 1 H), 8.20 (d, $J = 9.2$ Hz, 2H), 7.65 (dt, $J = 2.0$ and 7.6 Hz, 1H), 7.58 (d, $J = 16.1$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.12 (dd, $J = 4.8$ and 7.2 Hz, 1H), 7.04 (d, $J = 16.1$ Hz, 1H), 6.94 (d, $J = 9.2$ MHz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.06 (t, $J = 6.4$ Hz, 2H), 4.01 (t, $J = 6.4$ Hz, 2H), 1.85 (m, 4H), 1.57 (m, 4H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 164.6, 159.8, 156.3, 150.0, 141.7, 136.9, 132.7, 129.7, 128.8, 126.3, 126.1, 122.2, 122.1, 115.1, 114.8, 69.1, 68.2, 29.5, 29.3, 26.2, 26.1.

4-(6-(4-(2-(2-Pyridinyl)vinyl)phenoxy)hexyloxy)aniline (1)

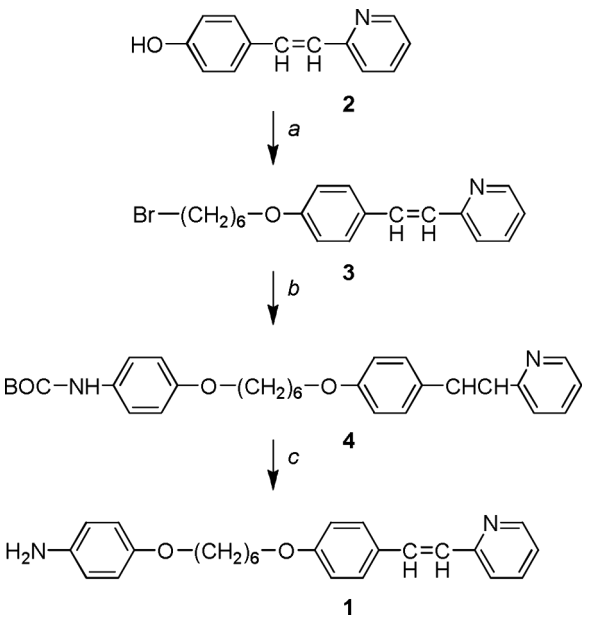
BOC-Protection/deprotection method. To a suspension of *t*-butyl 4-(6-(4-(2-(2--pyridinyl)vinyl)phenoxy)hexyloxy)phenylcarbamate (978 mg, 2 mmol) in CH_2Cl_2 (40 mL) was added trifluoroacetic acid (1.0 mL). The mixture was stirred at room temperature overnight. To the mixture was added NaOH aqueous solution (1 M, 20 mL) to basicify to be basic. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to give brownish solid product (677 mg, 87%).

Reduction method. A suspension of 2-(4-(6-(4-nitrophenoxy)hexyloxy)styryl) pyridine (293 mg, 0.7 mmol) in methanol (300 mL) was heated at reflux for 30 min. The resulting hot solution was cooled to room temperature under hydrogen gas. To the cooled suspension in methanol was added Lindlar catalyst (120 mg). The mixture was stirred at room temperature under atmospheric pressure of hydrogen gas in a rubber balloon. The hydrogenation reaction was monitored by TLC analysis (ca. 15 hrs). The suspension was filtered through a pad of celite to remove the catalyst. The filtrate was concentrated in vacuo and the oily residue was purified by a fresh column chromatography (silica gel, CH_2Cl_2/EtOAc, 9:1) to afford a yellowish solid product (220 mg, 80%).

mp 92.4 – 93.1°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (br dd, $J = 0.8$ and 4.8 Hz, 1H), 7.64 (dt, $J = 1.6$ and 7.6 Hz, 1H), 7.58 (d, $J = 16.0$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.11 (ddd, $J = 0.8$, 4.8 and 7.4 Hz, 1H), 7.04 (d, $J = 16.0$ Hz, 1H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.64 (d, $J = 8.8$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.90 (d, $J = 6.5$ Hz, 2H), 1.80 (m, 4H), 1.53 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.5, 156.1, 152.4, 149.7, 140.0, 136.6, 132.5, 129.3, 128.5, 125.7, 121.9, 121.8, 116.5, 115.8, 114.8, 68.6, 68.0, 29.5, 29.3, 26.0 (double intensity); IR (KBr) 3425, 3390, 3040, 2940, 2860, 1605, 1582, 1512, 1474, 1250, 1170 cm^{-1}; MS (EI, relative intensity) m/z 390 (M + 2, 15), 389 (M + 1, 55), 388 (M^+, 100), 387 (84), 280 (80), 196 (83), 167 (26), 109 (97); Anal. Calcd for $C_{25}H_{28}N_2O_2$: C, 77.29; H, 7.26; N, 7.21. Found: C, 76.93; H, 7.12; N, 7.52.

Results and Discussion

The devised new arylamine monomer **1** with photo-crosslinkable group has aniline and styrylpyridine moieties which are linked together through 1,6-hexylene bridge. A flexible hexylene bridging linker is chosen for two rigid styrylpyridine moieties which are freely aligned in head-to-tail fashion during [2 + 2] photo-cycloaddion reaction. Reasonable synthetic approach might be through ether functional connections two phenolic nucleophiles, 4-aminophenol and 4-[2-(2-pyridinyl)ethenyl]phenol **2**, with 1,6-dihalohexane (Scheme 1). Amino group of *p*-aminophenol was protected with di-*t*-butyl carbonate in a polar methanol solvent because of insolubility of Zwitterionic *p*-aminophenol in conventional ethereal solvents. Pyridinylvinylphenol **2** as styrylpyridine moiety was alkylated with excess 1,6-dibromohexane to yield mono-alkylated product styrylpyridinyl bromohexyl ether **3** in reasonably good yield. The styrylpyridinyl bromohexyl ether **3** was further reacted with the other phenolic countpart, *t*-butyl 4-hydroxyphenylcarbamate to afford diether **4** in a good



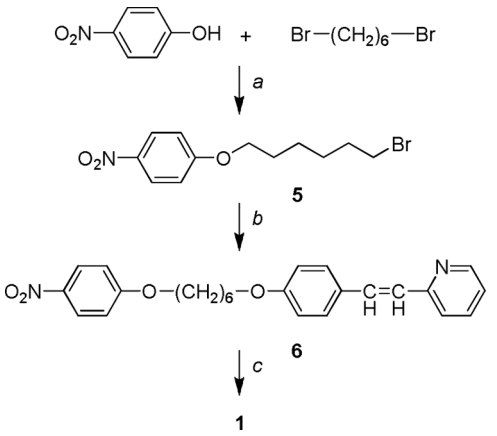
Scheme 1. Crosslinkable arylamine monomer **1** by BOC-protection/deprotection method; Reagents and conditions: (*a*) 1,6-dibromohexane, K_2CO_3, DMF, rt, 82%; (*b*) *t*-butyl 4-hydroxyphenylcarbamate, K_2CO_3, DMF, rt, 85%; (*c*) CF_3COOH, CH_2Cl_2, rt, 88%.

yield. BOC group on aniline moiety of diether **4** was deprotected with trifluoroacetic acid to the aniline-styrylpyridine diether **1** after basicifying the protonated product.

In this synthetic route all adapted reaction conditions are simple alkylation reactions and protection/deprotection in DMF solvent, and all synthetic intermediates were solid which could be isolated by crystallization. It is practically useful for large scale synthesis. Without difficulties, the reactions could be scaled up to gram scale. Three reaction steps and a protection of aminophenol resulted to give in 61% overall yield. However, relatively expensive di-*tert*-butyl carbonate did not allow large reaction scales.

It is worth to reinvestigate the preparation of the known key compound **2** because this simple reaction was not reproducible or produced only low yield of product, 4-[2-(2-pyridinyl)ethenyl]phenyl acetate when a mixture of hydroxybenzaldehyde and 2-picoline in acetic anhydride was heated at reflux. Rationalized reaction mechanism suggests that the limiting species of rate determining reaction is probably 2-methylene-1,2-dihydropyridine, a tautomer formed from 2-picoline which react with aldehyde countpart as aldol condensation fashion. Formation of the non-aromatic tautomer is apparently high energy process because overcoming resonance energy of aromatic pyridine moiety is required. When the reaction mixture was vigorously heated on a heating mantle rather than oil bath, reasonable yield of the desired product was formed reproducibly. Using excess 2-picoline balanced with the corresponding amount of acetic acid the reaction was optimized and reproducible. The detailed reaction condition is described in the experimental section.

Nitro group was often used as amine precursor and equivalent to amino protection functional group. Introducing *p*-nitorophenol instead of aminophenol could reduce the number of reaction steps (Scheme 2).



Scheme 2. Crosslinkable arylamine monomer **1** by nitro-to-amine reduction method; Reagents and conditions: (*a*) K_2CO_3, DMF, rt, 90%; (*b*) pyridinylvinylphenol **2**, K_2CO_3, DMF, rt, 85%; (*c*) H_2 (1 atm), Lindlar catalyst, rt, 80%.

Two starting alkylation reactions were easily performed and gave high yields of products by aqueous workup and crystallization methods. The selective reductions of nitro group of **6** to aniline product **1** were performed with common reduction conditions such as with metal hydrides, with metals. These reduction conditions were not practical to isolate the desired pure product without contamination or decomposition. However, catalytic hydrogenations in the presence of Pd and Pt catalysts were apparently practical to isolate the pure product. Both Pt and Pd catalysts fully reduced nitro and vinyl groups non-selectively even under atmospheric pressure of hydrogen. Lindlar catalyst showed some selectivity for the desired product **1** over the over hydrogenated product in methanol at room temperature. The starting material, nitrophenyl pyridinylvinylphenlyl diether **6** were nearly soluble in methanol (10 mg/30 mL) but the reduced amine product **1** was freely soluble. At the elevated temperature to solubilize the starting material **6** the reduction was retarded and finally ceased probably due to low solubility of hydrogen gas under atmospheric pressure and deactivation of catalyst in prolonged reaction time. In other non-protic solvents such as toluene, THF and dioxane under the same reaction condition only over hydrogenated product was obtained without any selectivity. It was found that moisture in the methanol caused deactivation of catalyst but also lose selectivity. The balanced amount of the starting material over Lindlar catalyst in the dried methanol was important factor to get selective reduction to the product **1** with complete reduction of the starting material without over-hydrogenation. To avoid over-hydrogenation the reaction in a flask was monitored at room temperature and under atmospheric pressure of hydrogen. Complete and selective reduction to the product **1** could be achieved, but it was hardly reproducible and unavoidable to isolate and purify the product using chromatographic method.

With BOC protection/deprotection of amino group, the product was straightforwardly obtained by aqueous workup and crystallization without laborious chromatographic isolation of product, and reactions could be scaled up. However, the extra protection step and expensive di-*tert*-butyl carbonate hampered large scale reactions. With catalytic hydrogenation of nitro group, the protection step with expensive

protection reagent was unnecessary and easy workup of filtration to get rid of catalyst and concentration allowed to access the catalytic hydrogenation. However, it also has drawback on reproducibility, but it has advantage to scale up without any limiting factors if reactions were carefully monitored to avoid over-hydrogenation.

Summary

An arylamine monomer **1** with styrylpydine moiety devised for hole-injection conjugated polyarylamine in OLED was efficiently synthesized. Two reaction approaches, protection/deprotection of amine group and catalytic hydrogenation of nitro precursor were comparatively performed. Both synthetic routes afforded reasonable yields of the arylamine product **1** in three consecutive reaction steps, ether formations of phenolic nucleophile with hexylene dibromide and deprotection of BOC-protected precursor or reduction of nitro precursor. BOC-Protection synthetic route is useful to obtain pure product in small reaction scale, but catalytic hydrogenation approach are economically viable from the precisely controlling complete hydrogention of selective reduction with Lindlar catalyst. An optimized and reproducible preparation of a valuable photo-cross linking moiety of styrylpyridine was also reestablished based on the rationalized reaction mechanism.

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