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Facile Synthesis of 5,10-Diaryl-5,10-dihydrophenazines and Application to EL Devices

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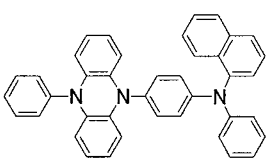
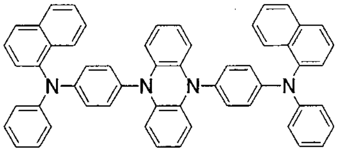
ABSTRACT



1k



3c

An efficient method for the synthesis of 5,10-diaryldihydrophenazine was developed using a recently developed Pd(0)-mediated cross-coupling reaction. The products 1k and 3c showed excellent properties as hole injection materials in electroluminescent (EL) devices.

Highly electron-rich and redox-active compounds are potentially useful building blocks in material sciences. In the course of our studies to develop new electronic and magnetic materials, we have required electron-donating π-electronic systems possessing oxidation potentials in the range of $+0.1$ to $+0.3$ V vs SCE. 5,10-Disubstituted 5,10-dihydrophenazines seem to be attractive compounds satisfying such conditions. The 5,10-dialkyl-substituted dihydrophenazines can be easily synthesized from phenazine in high yields by the following sequence of procedures: reduction−alkylation,[1] reduction−lithiation−alkylation,[2] alkylation−reduction−lithiation−alkylation,[2] and reduction−di(methoxymethylation) followed by reaction with Grignard reagents.[3] However, the method for the synthesis of diaryl-substituted dihydrophenazines has hitherto mainly been achieved by the Cu-catalyzed coupling reaction of 5-aryldihydrophenazinyllithium with aryl halides reported by Gilman and Diedrich in 1957.[1] The coupling requires severe conditions (210 °C for 12 h for 5,10-diphenyl-5,10-dihydrophenazine), and the yield is not high (16%). Although the reported method is, in principle, applicable to unsymmetrically substituted diaryldihydrophenazines, such a procedure has not been reported. Other methods involving electrochemical[4] or aromatic nucleophilic[5] cyclizations have also been reported for the compounds with special functional groups. We report an efficient and general synthetic method applicable for both symmetrically and unsymmetrically substituted 5,10-diaryl-5,10-dihydrophenazines using recently developed Pd(0)-mediated cross-coupling reactions.[6,7] For the synthesis of

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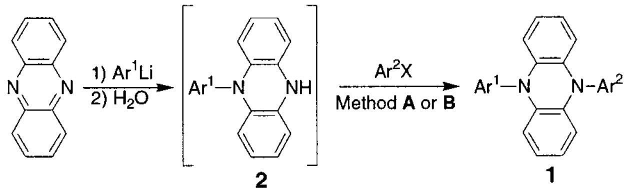
Scheme 1. Unsymmetric 5,10-Diaryldihydrophenazine Synthesis



unsymmetrical diaryldihydrophenazines, the in situ preparation of 5-aryl-5,10-dihydrophenazine is a key step. Application to EL devices is also reported for some of the derivatives.

Scheme 1 illustrates the synthesis of unsymmetrically substituted 5,10-diaryl-5,10-dihydrophenazines. The reaction of aryllithium (Ar^{1}Li; 1.3−1.4 equiv in ether or ether−cyclohexane) with phenazine (1.0 equiv) in toluene or *o*-xylene proceeds smoothly at room temperature. Quenching of the reaction with deaerated water gave air-sensitive 5-aryl-5,10-dihydrophenazine (**2**). The organic layer containing **2** was transferred with a syringe into another flask containing dried Na_2SO_4 under inert atmosphere and kept in a refrigerator as a stock solution of **2**. The cross-coupling reaction of **2** with aryl halide (Ar^{2}X; 0.75 equiv, mainly bromide) was achieved using a catalyst combination of NaO^{t}Bu (1.50 equiv)−Pd(OAc)$_2$ (0.020 equiv)−P(^{t}Bu)$_3$ (0.015 equiv) in toluene or *o*-xylene under heated conditions (method A),[6] or using NaO^{t}Bu (1.50 equiv)−Pd(dba)$_2$ (0.020 equiv)−P(^{t}Bu)$_3$ (0.015 equiv) at room temperature (method B),[7] giving the desired unsymmetrically substituted diaryldihydrophenazines **1** (Table 1).[8]

5-*p*-Formylphenyl-10-phenyl-5,10-dihydrophenazine **1d** was synthesized through the protection of the aldehyde group. 4-Cyanophenyl and heteroaromatic thienyl groups could also be introduced, although the yields were moderate.

Table 1. Synthesis of Unsymmetrically Substituted 5,10-Diaryl-5,10-dihydrophenazines

1	Ar^1	Ar^2, X (method, solvent, *T* (°C), time (h))	yield (%)
1a	Ph	*p*-tolyl, Br (A, *o*-xylene, reflux, 3)	79
1b	Ph	*p*-anisyl, Br (A, *o*-xylene, reflux, 3)	55
1c	Ph	*p*-(dimethoxymethyl)phenyl, Br (A, *o*-xylene, reflux, 3)	74
1d	Ph	*p*-formylphenyl (from **1c**)	95
1e	Ph	*p*-cyanophenyl, Br (A, *o*-xylene, reflux, 3)	44
1f	Ph	2-thienyl, Br (A, *o*-xylene, reflux, 3)	37
1g	*p*-*n*-butylphenyl	Ph, Br (A, toluene, reflux, 3)	42
1h	*p*-*n*-butylphenyl	*p*-tolyl, Br (A, toluene, reflux, 3)	52
1i	*p*-*n*-butylphenyl	*p*-anisyl, Br (A, toluene, reflux, 3)	53
1j	Ph	*p*-(*N*,*N*-diphenylamino)phenyl, Br (A, *o*-xylene, reflux, 3)	48
1j	Ph	*p*-(*N*,*N*-diphenylamino)phenyl, Br (B, *o*-xylene, rt, 3)	69
1k	Ph	*p*-[*N*-(1-naphthyl)-*N*-phenylamino]-phenyl, Br (B, *o*-xylene, rt, 3)	66
1l	Ph	*p*-(*N*,*N*-diphenylamino)biphenyl, I (B, toluene, reflux, 4)	70

The reaction similarly proceeded when Ar^1 was an *n*-butylphenyl group (**1g**−**i**). These experiments (for **1g**−**i**) are useful when one applies them to compounds with multiple coupling sites, where the products may have poor solubility in organic solvents. For instance, we could easily prepare 5,5′-(*m*-phenylene)bis(10-*p*-*n*-butylphenyl-5,10-dihydrophenazine) using *m*-diiodobenzene as a double-coupler in a good yield (∼65%). The *n*-butyl derivative was soluble in various organic solvents in contrast to the hardly soluble 5,5′-(*m*-phenylene)bis(10-phenyldihydrophenazine).[9]

Furthermore, this method can be extended to prepare electronically interesting diarylamine-incorporating dihydrophenazines **1j**−**l**, which are potentially useful compounds as electroluminescent materials.

Synthesis of symmetrically substituted diaryldihydrophenazine is much simpler than that of the unsymmetrically substituted ones, as illustrated in Scheme 2.

The double-coupling reaction of dihydrophenazine (1.0 equiv) with bromobenzene (2.0 equiv) in the presence of NaO^{t}Bu (3.0 equiv)−Pd(OAc)$_2$ (0.040 equiv)−P(^{t}Bu)$_3$ (0.030 equiv) in toluene at 80 °C (method A) produced 5,10-diphenyl-5,10-dihydrophenazine (**3a**) in 85% yield, in contrast to the poor 16% yield by the Ullmann-type procedure.[1] A similar procedure using NaO^{t}Bu (3.0 equiv)−Pd(dba)$_2$ (0.040 equiv)−P(^{t}Bu)$_3$ (0.030 equiv) (method B) effectively

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(8) **Selected Compound Data. 1f**: colorless needles; mp 251 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 5.80 (dd, 2H, J = 7.8, 1.3 Hz), 6.21 (dd, 2H, J = 7.8, 1.3 Hz), 6.31 (td, 2H, J = 7.7, 1.4 Hz), 6.36 (td, 2H, J = 7.6, 1.3 Hz), 6.64−6.68 (m, 2H), 6.82 (dd, 1H, J = 5.3, 1.6 Hz), 7.03 (t, 1H, J = 7.4 Hz), 7.07 (d, 2H, J = 7.3 Hz), 7.14 (d, 2H, J = 7.7 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 113.21, 114.03, 121.45, 122.24, 126.25, 126.79, 128.28, 128.46, 131.33, 131.53, 136.48, 137.03, 140.60, 142.90; MS (FAB) *m*/*z* 340 $[M]^+$. Anal. Calcd for $C_{22}H_{16}N_2S$: C, 77.62; H, 4.74; N, 8.23. Found: C, 77.50; H, 4.57; N, 8.12. **1j**: yellow powder; mp 270 °C dec; ^{1}H NMR (400 MHz, C_6D_6) δ 5.81 (dd, 2H, J = 7.8, 1.5 Hz), 6.03 (dd, 2H, J = 7.8, 1.4 Hz), 6.28 (td, 2H, J = 7.6, 1.2 Hz), 6.35 (td, 2H, J = 7.6, 1.2 Hz), 6.85 (tt, 2H, J = 7.1, 1.2 Hz), 7.00−7.10 (m, 17 H); ^{13}C NMR (100 MHz, C_6D_6) δ 113.05, 121.34, 121.43, 123.67, 125.29, 129.75, 131.37, 131.60, 132.21, 134.11, 137.26, 137.34, 140.82, 147.84, 147.95; HRMS (FAB) *m*/*z* calcd for $C_{36}H_{27}N_3$ 501.2205, found 501.2225. **1k**: yellow powder; mp 254 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 5.78−5.81 (m, 2H), 6.01−6.04 (m, 2H), 6.25−6.37 (m, 4H), 6.79 (t, 1H, J = 7.1 Hz), 6.95−7.24 (m, 17H), 7.53 (d, 1H, J = 7.7 Hz), 7.63 (d, 1H, J = 7.1 Hz), 8.11 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ 113.01, 121.29, 121.41, 122.73, 122.90, 123.65, 124.53, 126.57, 126.68, 126.84, 126.96, 128.80, 129.62, 131.36, 131.60, 131.71, 132.19, 135.88, 137.25, 137.38, 143.76, 148.27, 148.51; MS (FAB) *m*/*z* 551 $[M]^+$. Anal. Calcd for $C_{40}H_{29}N_3$: C, 87.08; H, 5.30; N, 7.62. Found: C, 86.91; H, 5.25; N, 7.55. **1l**: yellow powder; mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 5.82−5.85 (m, 2H), 5.92−5.95 (m, 2H), 6.26−6.34 (m, 4H), 6.87 (t, 2H, J = 7.0 Hz), 7.04−7.23 (m, 17 H), 7.34 (d, 2H, J = 8.6 Hz), 7.49 (d, 2H, J = 8.4 Hz); ^{13}C NHR (75 MHz, C_6H_6) δ 113.11, 113.19, 121.45, 123.38, 124.18, 124.93, 129.62, 129.67, 131.41, 131.60, 131.93, 134.42, 137.13, 137.18, 139.39, 140.67, 140.79, 147.99, 148.14; MS (FAB) *m*/*z* 577 $[M]^+$. Anal. Calcd for $C_{42}H_{31}N_3$: C, 87.32; H, 5.41; N, 7.27. Found: C, 87.03; H, 5.34; N, 6.97.

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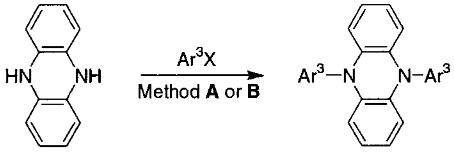
Scheme 2. Symmetric 5,10-Diaryldihydrophenazine Synthesis



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proceeded for bulkier aryl halides in milder conditions in high yields (Table 2).[10] The coupling products are interesting as materials applicable to EL devices.

Table 2. Synthesis of Symmetrically Substituted 5,10-Diaryl-5,10-dihydrophenazines

3	Ar^3, X (method, solvent, T (°C), time (h))	yield (%)
3a[1]	phenyl, Br (A, toluene, 80 °C, overnight)	85
3b	*p*-(*N*,*N*-diphenylamino)phenyl, Br (B, *o*-xylene, rt, 3)	83
3c	*p*-[*N*-(1-naphthyl)-*N*-phenylamino]phenyl, Br (B, *o*-xylene, rt, 3)	64

Table 3 summarizes the oxidation potentials of the prepared diaryldihydrophenazines. The first oxidation potentials are reversible in all cases and are in the range between +0.25 and +0.38 V vs SCE.

Table 3. Oxidation Potentials[a] of 5,10-Diaryl-5,10-dihydrophenazines

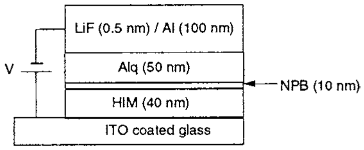
compd	$E^1_{1/2}$	$E^2_{1/2}$	compd	$E^1_{1/2}$	$E^2_{1/2}$	E^3
1a	+0.27	+0.96	**1i**	+0.26	+0.95	
1b	+0.26	+0.95	**1j**	+0.26	+1.02[b]	+1.29[b]
1c	+0.30	+1.00	**1k**	+0.27	+0.94	+1.35[b]
1d	+0.34	+1.02	**1l**	+0.30	+0.94[c]	+1.12[c]
1e	+0.35	+1.02	**3a**[1]	+0.30	+1.00	
1f	+0.38	+1.05	**3b**	+0.27	+0.97[b]	+1.29[b]
1g	+0.28	+0.98	**3c**	+0.25	+0.96[b]	+1.35[b]
1h	+0.27	+0.96				

[a] Measured in DMF at room temperature in the presence of n-Bu_4NClO_4 (0.1 mol/L) as an electrolyte with scan rate of 50 mV/s using glassy carbon as a working electrode and SCE as a reference electrode, where the values are corrected by the ferrocene (Fc) oxidation potential of $E_{1/2}$ (Fc/Fc$^+$) = 0.48 V vs SCE. [b] Peak potentials (irreversible step). [c] Peak potentials due to overlapping peaks.

Since aryl-substituted dihydrophenazines have a large dihedral angle between the C(sp^2)–N–C(sp^2) plane in the central ring of the dihydrophenazine moiety and the aryl ring,[11] the rather narrow change for the first oxidation potentials is reasonable. However, there is still a tendency for the electron-donating substituents to give lower oxidation potentials than electron-withdrawing groups. The plot of the first oxidation potentials of the four 5-X-phenyl-10-phenyl-dihydrophenazines (**1a**,**b**,**e** and **3a**) to the Brown–Okamoto σ^{+}[12] gave a straight line with a rather small slope of 0.065 ± 0.011 (correlation factor = 0.97).

Such highly electron-rich compounds are potentially useful as hole-injecting materials (HIMs) in organic EL devices.[13,14] When the HIM layer is inserted between an ITO electrode and a hole-transporting layer, it enables the devices to operate with longer lifetimes and higher luminous efficiency. One of the requirements for HIMs is high morphological stability due to roughness on the ITO surface. For application to EL devices, we chose two derivatives, **1k** and **3c**, both of which form amorphous films by thermal deposition under high vacuum on the ITO surface with high amorphous-stability above room temperature. The compounds **1k** and **3c** had high glass transition temperatures (T_g) of 105 and 133 °C, respectively. To evaluate the performance of dihydrophenazine-based devices, ITO/HIM (**1k** or **3c**, 40 nm)/**NPB** (10 nm)/**Alq** (50 nm)/LiF(0.5 nm)/Al (100 nm) were fabricated, where **NPB** (*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-4,4′-biphenyl, $E^1_{1/2}$ = +0.85, $E^2_{1/2}$ = +0.98 V vs SCE measured under the conditions in Table 3) and **Alq** [tris(8-hydroxyquinolino)-aluminum] are hole-transporting and emitting materials, respectively. The devices emit green light (550 nm) from **Alq**.[15] Table 4 summarizes the characteristics of the present devices as well as a control device with 50 nm of **NPB** without HIM.

Table 4. Properties of **1k** and **3c** as HIMs in the EL Devices ITO/**1k** or **3c**/**NPB**/**Alq**/LiF/Al



	characteristics at 100 cd/m^2				at 50 mA/cm^2
compd	V	mA/cm^2	cd/A	lm/W	half-life (h)
1k	4.8	2.8	3.6	2.3	83
3c	4.5	3.2	3.1	2.2	102
a	3.9	3.9	2.5	2.1	10–28

[a] In the absence of HIM-layer with 50 nm of **NPB**.

The half-life in the table is the decay time to half of the initial luminance without any sealing technique at a severely

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[10] **Selected Compound Data. 3b**: yellow needles; mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.01–6.07 (m, 4H), 6.35–6.40 (m, 4H), 6.85 (tt, 4H, J = 7.1, 1.5 Hz), 7.01–7.10 (m, 24H); ^{13}C NHR (100 MHz, C_6D_6) δ 121.39, 123.66, 125.29, 125.31, 129.75, 132.23, 134.06, 137.47, 147.80, 147.94; HRMS (FAB) *m/z* calcd for $C_{48}H_{36}N_4$ 668.2940, found 668.2939. **3c**: yellow powder; mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 5.99–6.03 (m, 4H), 6.34–6.37 (m, 4H), 6.78 (t, 2H, J = 7.3 Hz), 6.94–7.22 (m, 24H), 7.52 (d, 2H, J = 7.9 Hz), 7.62 (d, 2H, J = 7.3 Hz), 8.10 (d, 2H, J = 7.9 Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 122.68, 122.87, 124.54, 126.56, 126.68, 126.82, 126.93, 127.62, 128.78, 129.60, 131.70, 135.87, 143.76, 148.26, 148.47; HRMS (FAB) *m/z* calcd for $C_{56}H_{40}N_4$ 768.3253, found 768.3256.

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high current-density (50 mA/cm^2), which corresponds to 1750−2250 cd/m^2. It is clear that the device-longevity is considerably improved by the insertion of these HIMs with higher luminous efficiencies (lm/W). These data can also be compared with recently developed **Alq**-emitting devices modified by siloles as efficient electron-transporting materials, whose half-life and luminous efficiency are ∼50 h and ∼2.2 lm/W.[16,17] It is thus concluded that the 5,10-diaryldihydrophenazines are excellent HIMs in organic EL devices.

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Supporting Information Available: The DSC charts of the first and second heating for **1k** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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