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## Microwave-assisted Efficient H/D Exchange Method of 9H-Carbazole and 2-Phenylpyridine as Organic Light-emitting Materials

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Organic light-emitting materials have much interest in material science and many researchers have developed various materials with new conceptual synthetic strategy. Especially, research interest on phosphorescent and thermally activated delayed fluorescence (TADF) materials have been devoted to get high power efficiency of device, because of their unique photophysical properties (e.g., theoretically 100% internal quantum efficiency) and the potential for a new field of applications in organic light-emitting diodes (OLEDs).<sup>1</sup> Device life time and stability are important issues and interestingly studied in terms of intrinsic material stability as well as device architectures to improve life time and power efficiency. Recently, isotope effect has been reported to be advantageous for genuine material stability. The deuterium exchange has been applied to many functional layers such as host<sup>2</sup> and dopant<sup>3</sup> of emitting layer, electron-transport layer (ETL), and hole-transport layer (HTL),<sup>4</sup> reporting longer device life time and higher quantum efficiency.

Deuterated compounds were prepared via several deuterium exchange methods<sup>1a,5</sup> and, for aromatic compounds such as organic light-emitting materials, one of useful approaches is the use of transition metal catalyst (Pd/C or Pt/C) under hydrogen atmosphere and deuterated water. In our study, we prepared deuterated 9H-carbazole and 2-phenylpyridine using microwave reactor. Carbazole is useful precursor for hole-transport materials, electrontransport materials and emitting materials with high triplet energy  $(T_1)$ <sup>4</sup> Phenylpyridine is widely used as a ligand of phosphorescent dopant, such as cyclometallated iridium (III) complexes.<sup>1a</sup> Microwave reaction is known to be useful in metal catalytic reaction.<sup>6</sup> As shown in Scheme 1, we run H/D exchange reactions (Pd/C or Pt/C, D2O) under microwave irradiation and several conditions were investigated to obtain highly deuterated compound.

H/D exchange conditions were optimized, based on temperature, amount of catalyst and running time using microwave reactor (Tables 1 and 2). According to optimized results, 9H-carbazole was found to have a high deuterium substitution rate of 93% (Table 1. Entry 8) from the repeated run of entry 7 product. Yamamoto *et al.*<sup>7</sup> has reported that carbazole-D<sub>8</sub> was obtained for 48 h under



**Scheme 1.** H/D exchange route of 9H-carbazole(1) and 2-phenylpyridine(2) in microwave.

hydrothermal conditions (240 °C), which was gave 80% yield and 94% deuterium of the aromatic proton sites.<sup>4</sup> Microwave condition provides advantages of heterogeneous metal catalyst reaction, which enable shorter reaction period and lower reaction temperature than hydrothermal substitution methods.

In Table 2, H/D exchange condition showed 2-phenylpyridine was found to have efficient deuterium substitution rate of 90% with 160 °C, Pd/C catalyst 25 wt % and 1 h running time. It was previously reported deuterated 2-phenylpyridine was obtained from two different methods. One was synthetic reaction from deuterated bromobenzene and deuterated pyridine<sup>3</sup> and the other was hydrothermal reaction of 2-phenylpyridine using Pt/C catalyst, Al powder in D<sub>2</sub>O.<sup>1a</sup> Compared with those two methods, microwave-assisted H/D exchange scheme shows direct and efficient deuteration of aromatic protons. From the results of H/D exchange condition (Tables 1 and 2), both Pd/C and Pt/C catalysts do not show any significant difference of deuteration efficiency for aromatic protons under microwave irradiation condition.

In <sup>1</sup>H NMR spectrum (Figure 1), each proton of 9Hcarbazole (1) and 2-phenylpyridine (2) were individually assigned and D content of each proton position was quantitatively calculated from an internal standard (Table 3). 9H-carbazole (1) and 2-phenylpyridine (2) in Figure 1 correspond to entry 8 in Tables 1 and 2, respectively. It has

Table 1	H/D	exchange	conditions	of 9H-	carbazole <sup>a</sup>
Table 1.	$\Pi D$	exchange	continuons	01 211-	carbazore.

Entry	Temperature (°C)	10% Pt/C (wt %)	Time (h)	D content $(\%)^b$
1	80	10	1.5	25
2	120	10	1.5	57
3	160	5	1.5	36
4	160	10	0.5	55
5	160	10	1.5	79
6	160	10	3	84
7	160	25	1.5	81
8	160	25	1.5	93 <sup>c</sup>

<sup>a</sup> All data performed by microwave reactor.

<sup>b</sup> The deuterium contents (D content) were determined by <sup>1</sup>H NMR spectrum using internal standard.

 $^{c}$  Second run. The 81% deuterated substrate (the product of entry 7) was used as the starting material.

Table 2. H/D exchange conditions of 2-phenylpyridine.<sup>a</sup>

	Temperature	10% Pd/C	Time	
Entry	(°C)	(wt %)	(h)	D content $(\%)^b$
1	80	10	1	10
2	120	10	1	67
3	160	5	1	77
4	160	5	2	56
5	160	10	0.5	80
6	160	10	1	62
7	160	10	2	72
8	160	25	1	90

<sup>a</sup> All data performed by microwave reactor.

<sup>b</sup> The deuterium contents (D content) were determined by <sup>1</sup>H NMR spectrum using internal standard.

found that H/D exchange ratio at d-position (77%) of 9H-carbazole and e, i-position (82%) of 2-phenylpyridine was relatively low, which might be caused by steric hindrance.  $^{5a}$ 

And high deuterium substitution rate at the a, b, c-position of 9H-carbazole (approximately 96–97%) and pyridyl group protons (a, b, c,and d) of 2-phenylpyridine (approximately 95–98%) was observed.

These results indicate that deuterium exchange is more advantageous in the vicinity of nitrogen, because metal catalysts such as palladium and platinum have high affinity for a lone pair of nitrogen atom.

In conclusion, we propose microwave reaction to enable effective deuterium exchange of aromatic proton for the application of organic light-emitting material without any preference of Pt or Pd metal catalyst. And we provide optimized experimental conditions for deuterium exchange, based on temperature, amount of catalyst and reaction time using microwave reactor.

## Experimental

**General.** All the chemicals were obtained commercially and used without further purification. 10% Palladium on carbon and 10% platinum on carbon were purchased from Aldrich Chemical Co. (St. Louis, MO, USA) and deuterium oxide (D, 99.9%) was purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA).

The H/D exchange reactions were performed using a CEM Discover<sup>®</sup> SP microwave reactor (CEM Corporation, Matthews, NC, USA) (10 mL vessel capacity, 250 psi maximum pressure, 300 °C maximum temperature). The <sup>1</sup>H NMR spectra were recorded on 600 MHz spectrometer (Varian, Santa Clara, CA, USA). The high resolution FAB mass spectra were recorded on JMS-700 (JEOL, Tokyo, Japan) and 6890 series (Agilent, Santa Clara, CA, USA).

Estimation of Deuterated Ratio. D content(%) was calculated by the internal standard method and obtained from relative proton  $(^{1}H)$  integration ratio between deuterated compounds (1 and 2) and 1,4-dioxane as an internal



**Figure 1.** <sup>1</sup>H NMR spectra of (a) 9H-carbazole (1) and (b) 2-phenylpyridine (2) obtained by H/D exchange (600 MHz,  $CDCl_3$ , 1,4-dioxane as an internal standard).

Table 5. Each proton position D content (7).											
		D content(%) substituted in each proton									
Compounds <sup>b</sup>	Catalyst	a	b	c	d	e	f	g	h	i	D content(%)
9H-Carbazole	Pt/C	97	97	96	77	_	_	_	_	_	93
2-Phenylpyridine	Pd/C	98	95	96	96	82	91	91	91	82	90

**Table 3.** Each proton position D content(%).<sup>a</sup>

<sup>a</sup> D content(%) was determined by <sup>1</sup>H NMR spectrum using 1,4-dioxane internal standard.

<sup>b</sup> Compounds were obtained by H/D exchange under microwave irradiation condition.

standard.<sup>8</sup> D content(%) of deuterated compound can be calculated using the following formula:

Starting material yield(%)

 $= \frac{{}^{1}\text{H NMR Integral of starting material}}{{}^{1}\text{H NMR Integral of internal standard}} \times n$ 

*n*: The ratio of the internal standard to the initial amount of starting material.

 $D \operatorname{content}(\%) = 100\% - \operatorname{starting material yield}(\%)$ 

Deuterated 9H-Carbazole. A mixture of 9H-carbazole (30 mg, 0.18 mmol), 10% Pt/C (7.5 mg, 25 wt % substrate) in D<sub>2</sub>O (2 mL) in a microwave vessel was bubbled with H<sub>2</sub> for 10 min and charged with H<sub>2</sub> for 10 min, followed by microwave irradiation, using the following parameters (mode: dynamic, power: 160 W, temperature: 160 °C, time: 1.5 h, pressure: 200 psi, high stir, cooling off). After cooling, the reaction mixture was partitioned with dichloromethane and water. The organic extracts were filtered through a membrane filter (Whatman<sup>TM</sup>-PTFE, 0.20 µm) to remove Pt/C catalyst. The filtrate was concentrated in vacuo (28 mg, yield 94%, D content 81%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 1,4-dioxane as an internal standard)  $\delta$  8.08 (d), 7.43 (d), 7.25 (d); HR-MS (FAB, positive): mass calculated C12H1D8N1  $[M + H]^+$ , 175.1237; for observed 175.1236 m/z, int 90.0%, Err -0.5 ppm.

Deuterated 2-Phenylpyridine. mixture А of 2-phenylpyridine (50 mg, 0.32 mmol), 10% Pd/C (12.5 mg, 25 wt % substrate) in D<sub>2</sub>O (2 mL) in a microwave vessel was bubbled with H<sub>2</sub> for 10 min and charged with H<sub>2</sub> for 10 min, followed by microwave irradiation, using the following parameters (mode: dynamic, power: 160 W, temperature: 160 °C, time: 1 h, pressure: 200 psi, high stir, cooling off). After cooling, the reaction mixture was partitioned with dichloromethane and water. The organic extracts were filtered through membrane filter (Whatman<sup>TM</sup>-PTFE, 0.20 µm) to remove Pd/C catalyst. The filtrate was concentrated in vacuo (29.9 mg, yield 60%, D content 90%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 1,4-dioxane as an internal standard)  $\delta$  8.70 (s), 7.99 (s), 7.74 (d), 7.44 (d), 7.24 (m); HR-MS (FAB, positive): mass calculated for C11H1D9N1 [M + H]<sup>+</sup>, 165.1378; observed 165.1380 *m/z*, int 64.7%, Err +1.2 ppm.

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