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Synthesis and Characterization of Polyaromatic Compounds Using Tri(naphthyl)indium

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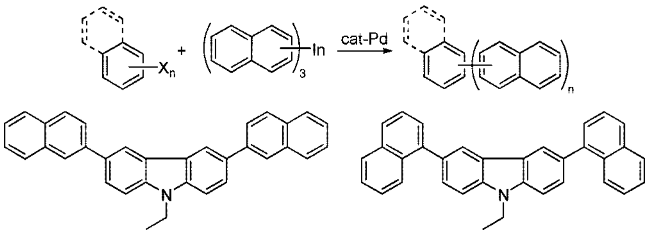

A variety of polyaromatic compounds bearing 1- and 2-naphthyl groups were prepared from the reactions of corresponding halides with tri(1- and 2-naphthyl)indium in good to excellent yields. Thermal, photophysical and electrochemical behaviors of carbazoles having naphthyl groups were studied. They have shown to be promising host and hole transporting materials in organic electroluminescence due to their high thermal stability, electrochemical reversibility and wide band gap.

In connection with synthesis of organic π-conjugated materials, introduction of naphthyl groups to polyaromatic compounds has attracted immense interest because of their potential applications as active elements in LED and OLED.[1] Polyaromatic compounds having naphthyl groups have formed an important class of highly efficient and stable blue-light emitting materials.[2] It has been suggested that nonplanar derivatives of naphthalene due to steric factors may hinder close packing and improve the device performance. In this regard, the EL polyaromatic compounds possessing naphthyl groups have been designed on the basis of this principle.[3] Therefore, there is still a strong need for a preparative method of polyaromatic compounds bearing naphthyl groups.

In general, the metal-catalyzed cross-coupling reactions of organic electrophiles with organometallics are one of the most straightforward synthetic methods for introduction of naphthyl groups to sp^2-hybridized carbon. Recently, we reported Pd-catalyzed cross-coupling reactions using organoindium reagents such as allylindiums[4] and allenylindiums[5] and carbonylative cross-coupling reactions of tri(organo)indiums[6] and tetra(organo)indates[7] with a variety of electrophiles. In addition, it was found that a variety of organoindiums could be used in Pd-catalyzed cross-coupling reactions as nucleophiles.[8] During the course of this study, we considered the possibility of extending Pd-catalyzed cross-coupling reactions using tri(naphthyl)indium and tetra(naphthyl)indate to synthesis of polyaromatic compounds having naphthyl groups. In continuation of our studies directed toward the development of indium-mediated organic reactions, we described herein efficient synthesis of polyaromatic compounds possessing naphthyl groups with tri(naphthyl)indium and their thermal, photophysical, and electrochemical behaviors were examined.

In initial studies, we examined the stoichiometry of tri(1-naphthyl)indium and the catalytic activity of several palladium catalysts in the reaction of 4,4′-dihalo-1,1′-biphenyl with tri(1-naphthyl)indium obtained from the reaction of InCl$_3$ (1 equiv) with 1-naphthyllithium (3 equiv).[9] The results are summarized in Table 1. The desired product **1** was obtained in 24%, 41%, and 55% yields from the reaction of 4,4′-diiodo-1,1′-biphenyl with tri(1-naphthyl)indium (0.69 equiv) in the presence of Pd(DPEphos)Cl$_2$, Pd(PPh$_3$)$_4$, and Pd(PPh$_3$)$_2$Cl$_2$, respectively (entries 2−4). Of the conditions screened, the best results were obtained with tri(1-naphthyl)indium (1.0 equiv) in the presence of 8 mol % of Pd(dppf)Cl$_2$ in THF (70 °C, 7 h), producing 4,4′-di(1-naphthyl)-1,1′-biphenyl (**1**) in 78% yield (entry 7). The use of tri(1-naphthyl)indium in less than 1.0 equiv resulted in sluggish reaction and gave lower yields. In the case of 4,4′-dibromo-1,1′-biphenyl, coupling product **1** was produced in 74% yield with tri(1-naphthyl)indium (1.0 equiv) in THF for 10 h (entry 11). The use of tetra(1-naphthyl)indate gave the desired product **1** in 60% yield (entry 12).

Under the optimized conditions, a range of polyaromatic compounds possessing iodide and bromide reacted with tri(1- and 2-naphthyl)indium (1−2 equiv) to produce polyaromatic compounds having naphthyl groups in good to excellent yield

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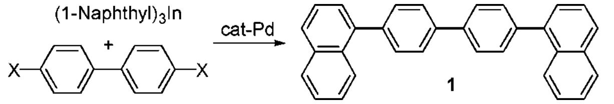
10.1021/jo800438n CCC: $40.75

TABLE 1. Reaction Optimization[a]



entry	X	R$_3$In (equiv)	Pd cat.	time (h)	yield[b] (%)
1	I	0.69	Pd$_2$dba$_3$CHCl$_3$/PPh$_3$	14	16[c]
2	I	0.69	Pd(DPEphos)Cl$_2$	18	24
3	I	0.69	Pd(PPh$_3$)$_4$	24	41
4	I	0.69	Pd(PPh$_3$)$_2$Cl$_2$	20	55
5	I	0.8	Pd(PPh$_3$)$_2$Cl$_2$	21	53
6	I	1.0	Pd(PPh$_3$)$_2$Cl$_2$	22	56
7	I	1.0	Pd(dppf)Cl$_2$	7	78[d]
8	Br	0.69	Pd(PPh$_3$)$_2$Cl$_2$	22	24(33)[e]
9	Br	0.69	Pd(dppf)Cl$_2$	22	43(35)[e]
10	Br	1.0	Pd(dppf)Cl$_2$	18	62
11	Br	1.0	Pd(dppf)Cl$_2$	10	74[d]
12[f]	Br	1.0	Pd(dppf)Cl$_2$	10	60[d](25)[e]

[a] Reactions were carried out with 4,4′-dihalo-1,1′-biphenyl (0.3 mmol) and 4 mol % of Pd catalyst in THF at 70 °C unless otherwise noted. [b] Isolated yield. [c] 2 mol % of Pd$_2$dba$_3$CHCl$_3$ and 16 mol % of PPh$_3$ were used. [d] 8 mol % of Pd catalyst was used. [e] 1-[4-(4′-Bromo-1,1′-biphenyl)]naphthalene. [f] Tetra(1-naphthyl)indate (0.3 mmol) was used.

(Table 2). Reaction of 9,10-dibromoanthracene with tri(naphthyl)indium gave the coupling products **2** (85%) and **10** (68%) (entries 3 and 11). The present method worked equally well with 2,7-dibromo-9,9′-dimethylfluorene to afford **3** and **11** in 73% and 79% yields (entries 4 and 12). However, reaction of 2-naphthylindium dichloride (2 equiv) with 2,7-dibromo-9,9′-dimethylfluorene did not proceed. Treatment of 3,6-dibromo-9-ethylcarbazole with tri(naphthyl)indium provided **4** and **12** in 73% and 83% yields, respectively (entries 5 and 13). Tri(1-naphthyl)indium reacted with 5,5′-dibromo-2,2′-bithiophene to furnish **5** and mono-cross-coupling product in 59% and 29% yields (entry 6). In the case of 2-bromo-9,9′-spirobifluorene and 1-bromopyrene, the desired products **6**, **7**, **13**, and **14** were obtained in good to excellent yields. Exposure of 4,4′-dihalo-1,1′-biphenyl to tri(2-naphthyl)indium gave rise to mono-cross-coupling product **8** and **9** despite the use of excess indium reagent (entries 9 and 10).

Organic compounds based on carbazole, such as 4,4′-dicarbazolyl-1,1′-biphenyl (CBP), 4,4′-bis(9-carbazolyl)-2,2′-dimethylbiphenyl (CDBP), etc., have attracted much attention as host or emitting materials in OLEDs because they have high triplet energy and thermal stability as well as good film-forming ability and quantum efficiency.[10] Therefore, we have investigated thermal, photophysical, and electrochemical characteristics of **4** and **12**. The UV/vis absorption and photoluminescence (PL) emission spectra of **4** and **12** in dilute CH$_2$Cl$_2$ solutions are depicted in Figure 1. The thermal, photophysical, and electrochemical data of **4** and **12** are summarized in Table 3.

The UV/vis spectra of **4** and **12** exhibit an intense absorption band between 250 and 400 nm ($\epsilon > 90000$ mol^{-1} dm^3 cm^{-1}), indicating that the electronic transitions are mostly carbazole to naphthalene $\pi-\pi^*$. Interestingly, the maximum peak observed for compound **4** exhibits a significant blue shift ($\lambda_{\max} =$ 230 nm) relative to that of **12**. In addition, the UV edge in **4** appears at a higher energy than in **12**, indicating that more effective π-conjugation between carbazole and naphthalene in **12** occurs than in **4**. This result can be attributed to the extent of steric repulsion between H3 (carbazole, C3′) and H8 (naphthalene). Compounds **4** and **12** emitted violet-blue light when irradiated by UV light. The photoluminescence (PL) emission spectra of both compounds exhibit a similar and structureless pattern with the emission maximum at 389 nm for **4** and at 406 nm for **12**. As compared to the PL quantum yield ($\Phi_{\mathrm{PL}} = 95\%$) of 9,10-diphenylanthracene (DPA), compounds **4** and **12** show values of 33% and 36%, respectively.

It is important to note that both compounds have narrow emission bands and small fwhm (full width at half-maximum, ca. 40 nm) values. The fwhm is one of the major issues associated with the improvement of color purity in electroluminescence (EL), since the two properties are generally related.[11] Molecules having small fwhm offer high color purity in EL. Both compounds **4** and **12** have fairly small fwhms compared with those of carbazole derivatives.[12] Based on this observation, application of these two compounds to EL technology would show high color purity. The small fwhm observed for **4** and **12** is likely attributable to the rigid naphthalene moiety.

The thermal properties of **4** and **12** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Both compounds showed only a 5% weight loss approximately 300 °C and were stable up to their melting points, showing no decomposition. The glass transitions of **4** and **12** occurred at 125 and 115 °C, respectively. These results suggest that the introduction of the naphthyl group into the carbazole unit increases thermal stability.

The two compounds showed similar electrochemical behaviors. Two oxidation potentials, which consist of reversible and irreversible processes, were observed at 1.31 and 1.82 V for **4** as shown in Figure 2. However, the oxidation potentials of compound **12** had slightly lower values than those of **4** (reversible at 1.22 V, irreversible at 1.68 V). This result can be attributed to the extent of effective π-conjugation as supported by their photophysical properties. The HOMO energy levels of **4** and **12** were calculated from the onset of oxidation potential according to the equation IP (ionization potential) = $[(E_{\mathrm{ONSET}})^{\mathrm{OX}} + 4.4]$ V[13] and the LUMO energy level was obtained by substracting of the optical band gap from the IP (Table 3). The difference of energy levels as well as oxidation potentials between the two compounds suggests that the position of the naphthalene substituents attached at carbazole affects the energy levels of the entire conjugated system. The high-lying HOMO energy levels, wide band gaps and reversible electrochemical oxidations of **4** and **12** suggest that both compounds have potential for host and hole transport in OLEDs.

In conclusion, a variety of polyaromatic compounds having naphthyl groups were effectively prepared by Pd-catalyzed cross-coupling reactions of polyaromatic halides with tri(naphthyl)indium in good to excellent yields. The present method complements the existing synthetic methods due to some advantageous properties of tri(naphthyl)indium such as availability, ease of preparation and handling, high reactivity and selectivity, operational simplicity, and low toxicity. These merits make tri(naphthyl)indium useful alternatives to other organometallics having naphthyl group used in cross-coupling reactions and also mark them out as promising reagents for organic synthesis. Some of new compounds, such as **4** and **12**, have

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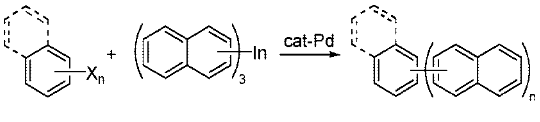
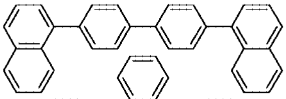
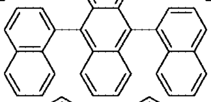
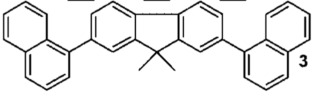
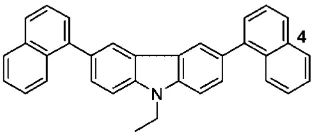
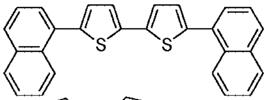
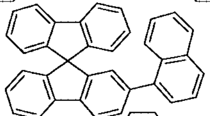
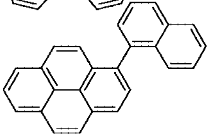
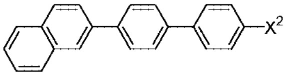
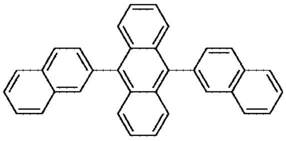
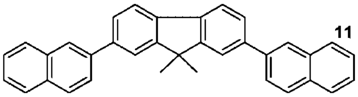
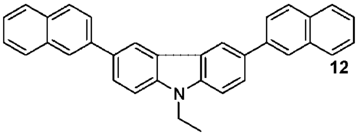
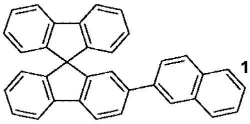
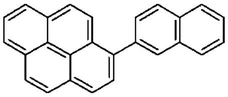
TABLE 2. Pd-Catalyzed Cross-Coupling Reactions of Tri(naphthyl)indium with Polyaromatic Halides[a]



entry	X	equiv. R_3In	time (h)	product		yield (%)[b]
1	I	1.0	7		**1**	78
2	Br	1.0	10			74
3	Br	1.5	8		**2**	85
4	Br	2.0	3		**3**	73
5	Br	2.0	4		**4**	73
6	Br	2.0	4		**5**	59(29)[c]
7	Br	0.5	2		**6**	90
8	Br	0.75	6		**7**	76
9	I	1.0	18		**8**	67[d]
10	Br	1.0	18		**9**	68[e]
11	Br	2.0	12		**10**	68
12	Br	2.0	3		**11**	79
13	Br	2.0	4		**12**	83
14	Br	0.5	3		**13**	82
15	Br	0.75	2		**14**	89

[a] 8 mol % of $Pd(dppf)Cl_2$ was used in THF at 70 °C. [b] Isolated yield. [c] 5-Bromo-5′-(1-naphthyl)-2,2′-bithiophene. [d] X^2 = I. [e] X^2 = Br.

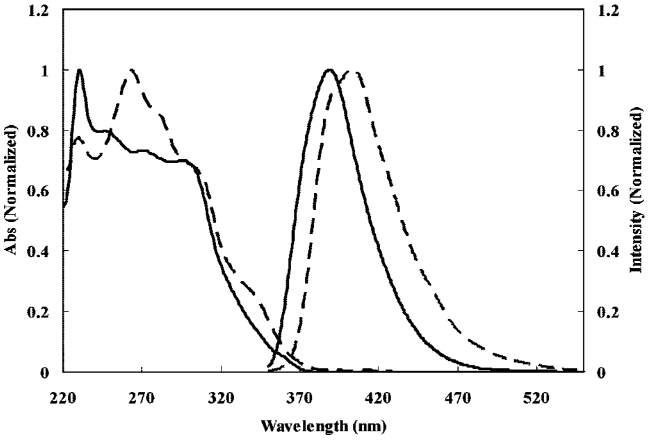


FIGURE 1. Absorption and emission spectra of **4** (solid line) and **12** (dashed line) in CH_2Cl_2 at 25 °C.

TABLE 3. Thermal, Photophysical, and Electrochemical Data for 4 and 12

	λ_{abs} (ε),[a] nm	λ_{em},[b] nm	ϕ_{PL}[c]	E_{onset}^{ox} [d] (V)	E_g^{opt} (eV)	HOMO/LUMO (eV)	T_g, T_d[e] (°C)
4	230 (99140) 246 (76630) 271 (70400) 297 (67140)	389	0.33	1.23	3.3	−5.63/−2.33	125 243
12	229 (59340) 262 (75580) 280 (65080) 305 (50750) 339 (20650)	406	0.36	1.14	3.2	−5.54/−2.34	115 308

[a] Measured in dilute CH_2Cl_2 solution. [b] Excited at 290−305 nm. [c] PL quantum yields were obtained by comparison to 9,10-diphenylanthracene (0.95) as a reference. [d] E^{ox} (onset): onset oxidation potential. Potentials versus Ag/AgCl, working electrode Pt, 0.1 M *n*-Bu_4NPF_6−CH_2Cl_2, scan rate 100 mV s^{-1}. [e] Obtained from DSC measurements on the first heating cycle with a heating rate of 10 °C/min under N_2. T_d was defined as 5% weight loss.

been demonstrated to be potential promising host and hole transporting materials in organic electroluminescence due to their high thermal stability, electrochemical reversibility and wide band gap. Further investigation on electroluminescent characteristics of these molecules is in progress.

Experimental Section

Preparation of 4,4′-Bis(1-naphthyl)-1,1′-biphenyl (1) Using Tri(1-naphthyl)indium. 1-Naphthyllithium was prepared from 1-bromonaphthalene (0.126 mL, 0.9 mmol) by treatment with *t*-BuLi (1.8 mmol, 1.7 M in pentane) at −78 °C for 15 min followed by warming to room temperature. This compound was used immediately for the preparation of the corresponding tri(1-naphthyl)indium. To a solution of $InCl_3$ (66.4 mg, 0.3 mmol) in THF (2 mL) at −78 °C was added 1-naphthyllithium (0.9 mmol, 0.45 M in Et_2O) under a nitrogen atmosphere, and the mixture was stirred for 30 min. After the cooling bath was removed, the reaction

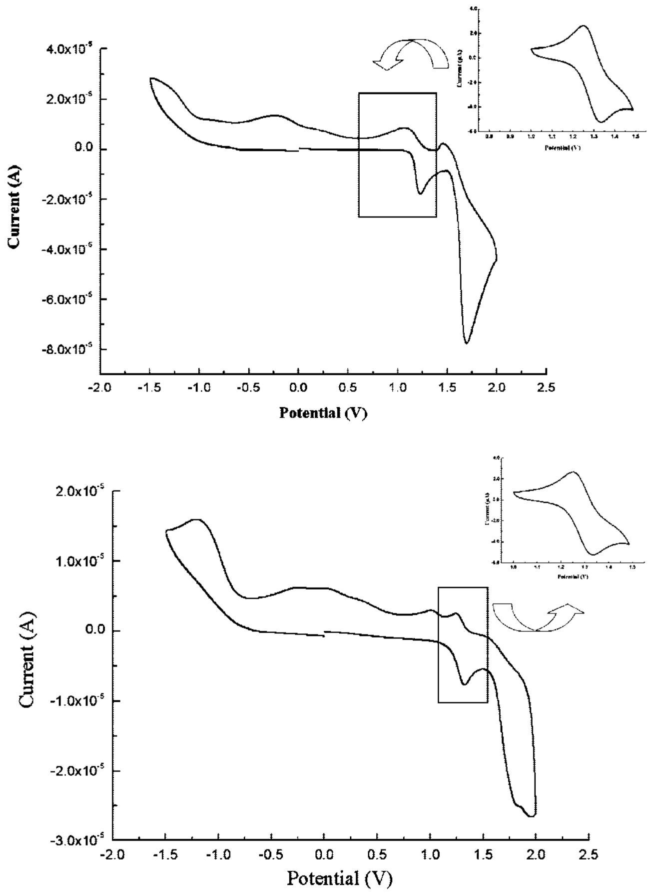


FIGURE 2. Cyclic voltammetry of **4** (top) and **12** (bottom).

mixture was warmed to room temperature for 30 min. The solution of tri(1-naphthtyl)indium (0.3 mmol, 0.15 M in THF) was subsequently added to a mixture of Pd(dppf)Cl_2 (0.024 mmol, 17.56 mg) and 4,4′-diiodo-1,1′-biphenyl (0.3 mmol, 121.8 mg) in THF (2 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 70 °C for 7 h until the starting material was consumed on TLC. After being cooled to room temperature, the reaction mixture was quenched by MeOH. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic layers were sequentially washed with aqueous 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), and saturated aqueous NaCl (20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane to give **1** (95.1 mg, 78%) as a white solid: mp 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.93 (d, $J = 7.7$ Hz, 2H), 7.89 (d, $J = 8.1$ Hz, 2H), 7.82 (d, $J = 8.1$ Hz, 4H), 7.63 (d, $J = 8.1$ Hz, 4H), 7.58−7.46 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.28, 140.26, 140.1, 134.3, 132.03, 131.0, 128.8, 128.2, 127.4, 126.6, 126.5, 126.3, 125.9; IR (film) 3044, 1590, 1493, 744 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{22}$ M$^+$ 406.1721, found 406.1723.

Preparation of 2-[4′-Iodo(1,1′-biphenyl)-4-yl]naphthalene (8) Using Tri(2-naphthyl)indium. 2-Naphthyllithium was prepared from 2-bromonaphthalene (189.5 mg, 0.9 mmol) by treatment with *t*-BuLi (1.8 mmol, 1.7 M in pentane) at −78 °C for 15 min followed by warming to room temperature. This compound was used immediately for the preparation of the corresponding tri(2-naphthyl)indium. To a solution of $InCl_3$ (66.4 mg, 0.3 mmol) in THF (2 mL) at −78 °C was added 2-naphthyllithium (0.9 mmol, 0.45 M in Et_2O) under a nitrogen atmosphere, and the mixture was stirred for 30 min. After the cooling bath was removed, the reaction mixture was warmed to room temperature for 30 min. The solution of tri(2-naphthyl)indium (0.3 mmol, 0.15 M in THF) was added to a mixture of Pd(dppf)Cl_2 (0.024 mmol, 17.56 mg) and 4,4′-diiodo-1,1′-biphenyl (0.3 mmol, 121.8 mg) in THF (2 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 70 °C for 18 h until the starting material was consumed on TLC. After being cooled to room temperature, the reaction mixture was quenched by MeOH. The aqueous layers were extracted with EtOAc (3 × 20 mL), and the combined organic layers were washed with aqueous 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), and saturated aqueous NaCl (20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane to give **8** (81.6 mg, 67%) as a white solid: mp 252−254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.93 (t, $J = 9.0$ Hz, 2H), 7.88 (d, $J = 6.8$ Hz, 1H), 7.83−7.78 (m, 5H), 7.70−7.67 (m, 2H), 7.55−7.48 (m, 2H), 7.41 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.6, 139.4, 138.3, 138.2, 134.0, 133.1, 129.3, 128.9, 128.6, 128.3, 128.1, 127.7, 126.8, 126.5, 126.2, 125.8, 93.6; IR (film) 2958, 1644, 1464, 734 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{15}I$ M$^+$ 406.0218, found 406.0221.

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Supporting Information Available: Spectral data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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