Synthesis, thermal, electrochemical, and photophysical characterization of 1,5bis(diarylamino)naphthalene derivatives as potential hole transport OLED materials¹

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Abstract: Novel 1,5-bis(diarylamino)naphthalene derivatives (1–9), which have potential as hole-transporting materials for electroluminescent devices, were obtained through palladium-catalyzed coupling of diarylamines and 1,5dibromonaphthalene. The thermal, electrochemical, and photophysical properties of these compounds were examined and the effects of the *N*-aryl substituents on these properties were investigated. These materials possess glass transition temperatures (T_g) that range from 70–131 °C and these values are related to the identity of the aryl substituents. Cyclic voltammetric measurements demonstrated that these compounds possess two reversible oxidation processes and were further used to estimate the HOMO energy levels of these materials by comparison with the ferrocene/ferrocenium couple. The intramolecular charge mobility, as gauged by the difference between the two oxidation potentials, indicates that compounds 1–8 have a similar degree of delocalization as *meta*-diaminobenzene derivatives while that of **9** is similar to **TPD**. Compounds 1–9 emit in the blue-green region and optical absorption and emission data for these materials can be rationalized in terms of the electronic donating properties of the aryl substituents. This data when combined with the electrochemically determined HOMO energies allowed estimation of the LUMO energy levels.

Key words: hole transport materials, diaminonaphthalene, thermal analysis, palladium-catalyzed arylation.

Résumé : Faisant appel à un couplage catalysé par le palladium de diarylamines et de 1,5-dibromonaphtalène, on a préparé des 1,5-bis(diarylamino)naphtalènes (1–9), qui ont le potentiel de transporter des trous pour les appareils électroluminescents. On en a examiné les propriétés thermiques, électrochimiques et photophysiques et on a étudié les effets des substituants *N*-aryles sur ces propriétés. Ces matériaux possèdent des températures de transition de verre (T_g) qui s'étalent de 70 à 131 °C et on a pu établir une corrélation entre cette propriété et l'identité des substituants aryles. Des mesures de voltampérométrie cyclique démontrent que ces composés possèdent deux processus d'oxydations réversibles qui ont, de plus, été utilisées pour évaluer les niveaux d'énergie de l'orbitale moléculaire haute occupée de ces composés par comparaison avec le couple ferrocène/ferrocénium. La mobilité de la charge intramoléculaire, telle qu'évaluée par la différence entre les deux potentiels d'oxydation, indique que les composés **1–8** possèdent un degré de délocalisation semblable à celui des dérivés du *méta*-diaminobenzène alors que celle du composé **9** est semblable à celle du **TDP**. Les composés **1–9** émettent dans la région du bleu-vert et les données d'absorption et émission optique de ces composés sont combinées avec les énergies de l'orbitale moléculaire haute occupée de ces données sont combinées avec les énergies de l'orbitale moléculaire haute occupée déterminée électrochimiquement, il est possible d'évaluer les niveaux d'énergie de l'orbitale moléculaire basse vacante.

Mots clés : matériaux pouvant transporter des trous, diaminonaphtalène, analyse thermique, arylation catalysée par le palladium.

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Introduction

Polyaromatic amines have been essential components in molecular electroluminescent (EL) devices beginning with the first report of a two-layer organic light-emitting diode (OLED) (1, 2). Generally the amine assumes the role of the hole transport (HT) material in such devices (3, 4). Aromatic diamine derivatives and in particular N,N,N',N'-tetraaryl-(1,1'-biphenyl)-4,4'-diamines remain synthetic targets for HT materials because of the ease with which they form

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Dedicated to Professor Howard Alper.

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¹This article is part of a Special Issue dedicated to Professor Howard Alper. ²Corresponding author (e-mail: darrin@science.uottawa.ca). amorphous thin films, their high hole mobility, and suitable HOMO energy level (5–8).

Benchmark compounds in this field are represented by N,N'-diphenyl-N,N'-di(*m*-tolyl)benzidine (**TPD**) and N,N'-bis(1-naphthyl)-N,N'-diphenyl-benzidine (**NPD**). Establishing relationships between the molecular structure of these and related compounds and their physical characteristics such as oxidation potential (9, 10), solid-state structures (11, 12), reorganization energy upon charge transfer (13–15), and environmental stability is of considerable interest, as each of these properties will influence the hole transport performance of the compound in a device.



The hole transport in these materials has associated with it a reorganization energy (λ) that is related to the geometric rearrangments between the neutral and radical cation states (e.g., **TPD** and **TPD**⁺). In the case of diamines with a biphenyl core such as **TPD** and **NPD**, the torsion angle between the two rings of the biphenyl bridges changes between the neutral and the cation radical and this has been ascribed to be the major barrier to electron exchange between these two species (13). Minimizing this reorganization term is one factor that may lead to improved hole mobility.

One of the chief failure modes for OLEDs is thermal instability in the molecular thin films, and in most devices, the HT component has the lowest thermal stability. Thermal stresses are inherent in device operation or can arise in the operating environment and can lead to significant expansion of the material or crystallization of the HT material. Furthermore, poor lifetimes for devices operated near room temperature have been attributed in part to thermal instabilities of the amorphous organic layers, which has been correlated with low glass transition temperatures (T_g) (2, 4, 16). For example, the T_g of tris(8-hydroxyquinolinato)aluminum (Alq), a common electron transport (ET) material, is 175 °C while those for **TPD** and **NPD** are reported to be 65 and 95 °C, respectively (17).

A major objective in developing new HT materials is the improvement of their thermal properties without sacrificing Chart 1.



the advantageous properties exhibited by compounds such as **TPD** and **NPD**. A variety of approaches have been undertaken to improve the performance features of the HT component in EL devices, many of which center around core modifications to the generic diamine represented in Chart 1 (3, 6, 18–25). In addition to variation of the core structure, the aryl groups have been modified to produce symmetric (17–20) and asymmetric compounds (21, 24). Among the improved properties that have been observed in these examples are increased thermal stability and novel emission properties (20, 21, 26–29). Certainly, further development of related species could have significant device implications.

Herein we report our results for potential HT materials designed around the 1,5-diaminonaphthalene structure and an examination of the effects of variations of the aromatic substituents in these species. Only one example of an HT material designed around the naphthyl core has been reported and this compound displayed improved thermal properties as well as potential as a blue light-emitting material (30). In this case, the implementation of a fused aromatic core will remove the torsional freedom of the biphenyl core. In addition to characterizing the thermal behavior of these new diamines, we present their electronic spectra and electrochemical properties for comparison with **TPD**. Our synthetic methodology exploited the versatile and efficient palladium catalyzed amine arylation reactions pioneered by Buchwald and co-workers (31, 32) and Hartwig (33, 34).

Experimental section

General information

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Aryl amines, aryl bromides, diphenylamine, tris(dibenzylidineacetone)dipalladium (Pd₂(dba)₃), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), and sodium *tert*-butoxide were purchased from the Aldrich Chemical Company and used without further purification. Tri-*tert*-butylphosphine was purchased from Strem Chemicals. 1,5-Dibromonaphthalene was synthesized from 1,5-diaminonaphthalene according to literature procedures (35). Toluene was purified by passage through a column of activated alumina using an apparatus from Anhydrous Engineering. Dichloromethane was freshly distilled under nitrogen using CaH₂ as the dessicant.

Reactions were monitored using Silica gel 60 F_{254} TLC aluminum sheets by UV lamp and (or) GC–MS using a mass selective detector from Agilent GC systems 6890 series with an HP-5 capillary column (cross-linked 5% PH ME siloxane).

¹H NMR spectra were collected on a Varian Gemini-200 or a Bruker 300 MHz spectrometer using the residual protons of the deuterated solvent for reference. The overlapping ¹³C peaks were identified through ¹³C DEPT and ¹H¹³C HMQC analysis on a Bruker 300 MHz spectrometer. Electron impact mass spectra (EI-MS) were recorded on a Kratos Concept IIH instrument using electron ionization at 70 eV. High resolution mass spectra (HR-MS) were obtained at the University of Ottawa on a Kratos Concept IIH instrument using electron ionization at 70 eV, acceleration 8 KV, and resolution $7\ 000 - 10\ 000$. The glass transition temperatures and melting points were measured using a TA 2010 differential scanning calorimeter (DSC) instrument. Heating rates of 5-20 °C/min were employed for these measurements. UV spectra were recorded in CH₂Cl₂ on a Varian Cary spectrophotometer. Steady-state fluorescence spectroscopy was carried out using a Photon Technology International version 1.2 X luminescence spectrometer with the same cuvette used for UV-vis spectra. Fluorescence quantum efficiency (Φ_f) of the compounds was determined by comparing with that of Coumarin-102 ($\Phi_f = 0.93$ in ethanol) (36) in CH₂Cl₂ solution. Cyclic voltammograms (CV) were obtained using a Hokuto Denko HA501 potentiostat connected to a Hokuto Denko HB105 programmable function generator. A Nicolet 310 oscilloscope was used to follow the in situ CV scans. A freshly polished Pt wire and Pt plate were used as working and counter electrode, respectively. A silver wire was employed as pseudo-reference electrode. All solutions were prepared in millimolar concentrations in dry CH₂Cl₂, which was freshly distilled from CaH2. Tetrabutyl ammonium hexafluorophosphate (TBAHFP) was used as the supporting electrolyte with a concentration of 0.1 mol/L. The electrochemical cell was degassed with nitrogen prior to analysis and was maintained under a nitrogen atmosphere during the potential scans. At the end of each set of CV scans, ferrocene (Cp₂Fe) was added to the solution and another potential scan was performed to provide the redox potential for the Cp_2Fe/Cp_2Fe^+ couple.

Compounds **a**–**h** were prepared via Pd catalyzed coupling of arylbromides and arylamines according to eq. [1] in Scheme 1. The general procedure for the synthesis of diarylamines followed that reported in the literature with details provided in the Electronic supplementary information (37, 38).³

General procedure for the synthesis of diaminonaphthalene derivatives

The general procedure for the synthesis of 1,5diaminonaphthalene derivatives (1–9) according to eq. [2] in Scheme 1 was modified from the literature (39). In a drybox, a Schlenk flask was charged with toluene, 1,5-dibromonaphthalene, and 2.2 equiv. of the appropriate diarylamines (**a**–i). To this solution was added 1% to 2% Pd(OAc)₂/P(*t*-Bu)₃ (ligand/Pd = 1) and 2.8 equiv. of NaO-*t*-Bu. The reaction mixture changed from orange to dark black over the first few seconds. The flask was sealed, removed from the drybox, and was heated at 120 °C overnight. The reaction was then cooled to room temperature, filtered, and the residue was washed with ethylacetate and combined with the toluene. The solvents were then removed by vacuum evaporation and the residue was dissolved in CHCl₃. Column chromatography was used to purify the product using CHCl₃ Scheme 1.



as the eluent. Collection of the product was monitored by TLC and all fractions were combined at the end of the separation procedure. The solvents were removed under vacuum to yield pure compounds.

1,5-Bis(di-*p*-methoxyphenylamino)naphthalene (1)

Yield: 50%. ¹H NMR (CDCl₃) δ : 3.79 (s, 12H), 6.64–6.80 (m, 8H), 6.91 (d, 8H), 7.08–7.30 (m, 4H), 7.84 (d, 2H). ¹³C NMR (CDCl₃) δ : 55.48, 114.41, 121.98, 123.44, 126.12, 126.25, 132.82, 142.98, 144.92, 154.54. *m/z*: 582 (M⁺). HR-MS (*m/z*) calcd. for C₃₈H₃₄N₂O₄: 582.2519; found: 582.2530.

1,5-Bis(*p*-methoxyphenylphenylamino)naphthalene (2)

Yield: 75%. ¹H NMR (CDCl₃) δ : 3.76 (s, 6H), 6.7–6.9 (m, 9H), 7.0–7.4 (m, 13H), 7.87 (d, 2H). ¹³C NMR (CDCl₃) δ : 55.46, 114.55, 119.84, 120.26, 122.43, 125.38, 126.56, 126.95, 128.93, 133.06, 141.55, 144.30, 149.5, 155.49. *m/z*: 522 (M⁺). HR-MS (*m/z*) calcd. for C₃₆H₃₀N₂O₂: 522.2307; found: 522.2328.

1,5-Bis(p-methoxyphenyltolylamino)naphthalene (3)

Yield: 80%. ¹H NMR (CDCl₃) δ : 2.28 (s, 6H), 3.77 (s, 6H), 6.81 (t, 8H), 7.02 (t, 8H), 7.16–7.34 (m, 4H), 7.88 (d, 2H). ¹³C NMR (CDCl₃) δ : 20.62, 55.46, 114.45, 120.77, 122.20, 124.59, 126.39, 126.58, 129.55, 130.11, 133.00, 142.18, 144.61, 147.05, 155.03. *m/z*: 550 (M⁺). HR-MS (*m/z*) calcd. for C₃₈H₃₄N₂O₂: 550.2620; found: 550.2642.

1,5-Bis(*p*-methoxyphenyl-*p*-fluorophenylamino)naphthalene (4)

Yield: 78%. ¹H NMR (CDCl₃) δ : 3.76 (s, 6H), 6.72–7.32 (m, 20H), 7.82 (d, 2H). ¹³C NMR (CDCl₃) δ : 55.48, 114.64, 115.63 ($J_{C-F} = 22.6$ Hz), 122.15 ($J_{C-F} = 5.0$ Hz), 122.22, 124.60, 126.49, 126.54, 132.84, 142.11, 144.59, 145.70, 155.33, 157.58 ($J_{C-F} = 240.2$ Hz). m/z: 558 (M⁺). HR-MS (m/z) calcd. for C₃₆H₂₈F₂N₂O₂: 558.2119; found: 558.2101.

1,5-Bis(*p*-methoxyphenyl-*p*-propylphenylamino)naphthalene (5)

Yield: 66%. ¹H NMR (CDCl₃) δ : 0.92 (t, 6H), 1.57 (m, 4H), 2.47 (t, 4H), 3.76 (s, 6H), 6.75–6.83 (m, 8H), 6.95–7.04 (M, 8H), 7.19–7.30 (m, 4H), 7.86 (d, 2H). ¹³C NMR

³Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3696. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 242552 and 242553 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Compound	3	5		
Empirical formula	$C_{38}H_{34}N_2O_2$	$C_{42}H_{42}N_2O_2$		
Formula weight	550.67	606.78		
Temperature (K)	203(2)	203(2)		
Wavelength (Å)	0.710 73	0.710 73		
Crystal system	Monoclinic	Monoclinic		
Space group	P2(1)/c	P2(1)/c		
Unit cell dimensions				
a (Å)	8.114(2)	14.394 6(19)		
<i>b</i> (Å)	16.800(5)	11.688 2(16)		
<i>c</i> (Å)	11.090(3)	21.188(3)		
β (°)	95.361(5)	109.706(3)		
V (Å ³)	1505.1(7)	3356.1(8)		
Ζ	2	4		
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.085 \ 8, \ wR_2 = 0.197 \ 0$	$R_1 = 0.079 2, wR_2 = 0.148 4$		

Table 1. Crystal data and structure refinement for compounds 3 and 5.

(CDCl₃) δ : 13.91, 24.62, 37.30, 55.45, 114.45, 120.50, 122.27, 124.65, 126.40, 126.68, 128.89, 133.07, 134.99, 142.12, 144.59, 147.21, 155.03. *m/z*: 606 (M⁺). HR-MS (*m/z*) calcd. for C₄₂H₄₂N₂O₂: 606.3246; found: 606.3229.

1,5-Bis(p-methoxyphenyl-p-biphenylamino)naphthalene (6)

Yield: 50%. ¹H NMR (CDCl₃) δ : 3.78 (s, 6H), 6.78–7.58 (m, 30H), 7.92 (d, 2H). ¹³C NMR (CDCl₃) δ : 55.47, 114.64, 119.74, 122.58, 125.64, 126.45, 126.70 (two overlapping singlets), 127.08, 127.55, 128.66, 132.82, 133.07, 140.79, 141.25, 144.14, 148.81, 155.51. *m/z*: 674 (M⁺). HR-MS (*m/z*) calcd. for C₄₈H₃₈N₂O₂: 674.2933; found: 674.2908.

1,5-Bis(*p*-methoxyphenyl-1-naphthylamino)naphthalene (7)

Yield: 80%. ¹H NMR (C_6D_6) δ : 3.20 (s, 6H), 6.54 (d, 4H), 6.72–7.22 (m, 16H), 7.44 (d, 2H), 7.63 (d, 2H), 8.25 (d, 2H), 8.41 (d, 2H). ¹³C NMR (C_6D_6) δ : 54.82, 114.88, 121.75, 123.85, 124.51, 124.92, 125.04, 125.16, 126.24, 126.43, 126.59, 127.12, 128.80, 130.35, 132.50, 135.83, 144.88, 146.34, 147.13, 155.29. *m/z*: 622 (M⁺). HR-MS (*m/z*) calcd. for $C_{44}H_{34}N_2O_2$: 622.2620; found: 622.2647.

1,5-Bis(di-m-methoxyphenylamino)naphthalene (8)

Yield: 50%. ¹H NMR (CDCl₃) δ : 3.61 (s, 3H), 3.68 (s, 3H), 6.15 (t, 1H), 6.18 (d, 1H), 6.33 (d, 1H), 6.82–7.33 (m, 14H), 7.96 (d, 2H). ¹³C NMR (CDCl₃) δ : 54.99, 55.61, 103.82, 104.02, 110.55, 112.79, 121.26, 122.81, 125.99, 126.13, 126.26, 128.76, 129.10, 132.86, 135.95, 143.78, 150.78, 155.31, 160.12. *m/z*: 582 (M⁺). HR-MS (*m/z*) calcd. for C₃₈H₃₄N₂O₄: 582.2519; found: 582.2509.

1,5-Bis(diphenylamino)naphthalene (9)

Yield: 52%. ¹H NMR (CDCl₃) δ : 6.90–7.31 (m, 24H), 7.88 (d, 2H). ¹³C NMR (CDCl₃) δ : 121.71, 121.95, 122.69, 126.73, 127.52, 129.09, 133.24, 144.00, 148.50. *m/z*: 462 (M⁺). HR-MS (*m/z*): calcd. for C₃₄H₂₆N₂: 462.2096; found: 462.2109.

Structural determination for compounds 3 and 5

Single crystals were mounted on thin glass fibers using viscous oil and then cooled to the data collection temperature. Crystal data and details of the measurements are summarized in Table 1. Data were collected on a Bruker AX SMART 1 k CCD diffractometer using 0.3° ω scans at 0° , 90°, and 180° in ϕ . Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library (40).

Results and discussion

Synthesis of naphthalene diamines

Our strategy for preparing new aromatic amines possessing a naphthyl core (1-9) is outlined with eqs. [1] and [2] in Scheme 1. Diarylamines (a-i) were either first prepared via Pd catalyzed coupling of arylbromide and arylamine (a-h) (37, 38) or purchased (i). A $Pd(OAc)_2/P(t-Bu)_3$ catalyst system was then employed for the coupling reactions between 1,5-dibromonaphthalene and diarylamines (39). We also explored an alternative route based on the coupling of 1,5diaminonaphthalene with aryl halides. This proved to be unsatisfactory and only led to products with a single arylation of each nitrogen center as the major products. The synthesis of a related diamine, 1,5-bis[N-(1-naphthyl)-N-phenyl]naphthalene diamine (NND) was recently reported via a modified Ullman condensation of 1,5-diiodonaphthalene and naphthylphenylamine, however, no details for this transformation were reported (30).

The naphthyl core diamines presented in Table 2 were isolated in good yields and were fully characterized by ¹H and ¹³C NMR and HR-MS. The versatility of this method provides an avenue to invoke a wide range of amine substituent variation including electron-donating and electron-withdrawing groups. The molecular structures of two of these diamines, compounds **3** and **5**, were definitively established using single crystal X-ray diffraction analysis (Table 1). The structures of **3** and **5** are presented in Figs. 1 and 2, respectively, and selected bond distances and angles are provided in Ta-

Ar Ar'			
(% Yield)			
	(0/ Viold) Ar		
	(% field) $T_{g}/T_{m}/T_{c}$		
$HN(p-C_{\epsilon}H_{\epsilon}OMe)$, a	<u> </u>		
(78)	$(Ar = Ar' = p - C_6 H_4 OMe)$		
	76/216/143 °C		
$N(C_6H_4OMe)(C_6H_5)$ b	2 (75)		
(80)	$(\text{Ar} = p - \text{C}_6\text{H}_4\text{OMe}, \text{Ar'} = \text{C}_6\text{H}_5)$		
	70/230/145 °C		
$HN(C_6H_4OMe)(C_6H_4Me)$ c	3 (80)		
(70)	$(\mathrm{Ar} = p - \mathrm{C}_{6}\mathrm{H}_{4}\mathrm{OMe}, \mathrm{Ar'} = \mathrm{C}_{6}\mathrm{H}_{4}\mathrm{Me})$		
	82/249/103 °C		
$HN(C_6H_4OMe)(C_6H_4F)$ d	4 (78)		
(84)	$(\operatorname{Ar} = p - \operatorname{C}_6 \operatorname{H}_4 \operatorname{OMe}, \operatorname{Ar}' = \operatorname{C}_6 \operatorname{H}_4 \operatorname{F})$		
	73/192/138 °C		
$HN(C_6H_4OMe)(C_6H_4Pr)$ e	5 (66)		
(86)	$(\operatorname{Ar} = p - \operatorname{C}_6 \operatorname{H}_4 \operatorname{OMe}, \operatorname{Ar}' = \operatorname{C}_6 \operatorname{H}_4 \operatorname{Pr})$		
	51/18//126°C		
$HN(C_6H_4OMe)(4,4$ -biphenyl) I	$0 (30) \\ (\mathbf{A}\mathbf{n} - \mathbf{n} \mathbf{C}\mathbf{H} \mathbf{O}\mathbf{M} \mathbf{n} \mathbf{A}\mathbf{n} \mathbf{h} - \mathbf{A}\mathbf{h} \mathbf{h} \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} n$		
(30)	$(\text{Ar} = p - \text{C}_6 \text{H}_4 \text{OMe}, \text{Ar} = 4,4^\circ - \text{higherry})$		
	116/283/200 °C		
HN(C H OMe)(1-nanhthyl) σ	7 (80)		
(50)	(Ar = p - C H OMe Ar' = 1 - naphthyl)		
	$131/220/NO ^{\circ}C^{a}$		
$HN(m-MeOC_{\ell}H_{\ell})$, h	8 (50)		
(40)	$(Ar = Ar' = m - C_e H_a OMe)$		
	72/220/NO °C ^a		
$HN(C_6H_5)_2$ i	9 (52)		
-	$(\mathrm{Ar} = \mathrm{Ar'} = \mathrm{C}_6\mathrm{H}_5)$		
	83/244/NO °C ^{<i>a</i>}		
TPD	65/175/167 °C		

Table 2. Summary of the synthesis and thermal properties of HN(Ar)Ar' and 1,5-bis(diarylamino)naphthalenes shown in Scheme 1.

 $^{a}NO = not observed.$

ble 3. Both species display planar nitrogen centers with propeller-like arrangement of the three aromatic groups on each nitrogen. In **3**, the N— $C_{naphthyl}$ distance (N(1)—C(1) = 1.462(3) Å) is longer than the corresponding distances for the outer aryl groups (N(1)—C(18) = 1.416(6) Å and N(1)—C(11) = 1.449(6) Å). In contrast, although the longest N—C distance in compound **5** is to the naphthyl core, the C—N distances in this compound span a narrower range from 1.423(4) to 1.435(4) Å. These trends in C—N distance are opposite to those observed for **TPD** and for *N*,*N'*-diphenyl-*N*,*N'*-bis(2,4-dimethylphenyl)-(1,1'-biphenyl)-4,4'-diamine, where the N— $C_{biphenyl}$ distances are the shortest distances with values of 1.411(5) and 1.415(5) Å, respectively (7, 8). There are no unusual C—C bond lengths within the peripheral or core aryl groups.

Thermal properties

To be of practical consideration for OLED fabrication, the diamines 1–9 should form stable glasses. This general feature of materials for OLED construction avoids problems as-

sociated with grain boundaries in polycrystalline materials and provides for a high degree of uniformity within thin films. Associated with this amorphous state is a characteristic temperature (or temperature range) where the glassy and amorphous state of the material begins to soften and flow, which is referred to as the glass transition temperature (T_g) . Above T_g , materials tend to crystallize generating grain boundaries and causing nonuniform thin films (17). The kinetics of the crystallization process will dictate whether or not a T_{g} is observed. Generally, large, globular, and rigid molecules or asymmetric molecules with high molecular masses and without strong intermolecular forces have high T_{g} values (17, 41). Such general features favor a high energy for the reorganization - molecular reorientation of the amorphous phase into a crystalline material. Strong intermolecular forces may favor organization of the molecules as they cool below their melting points, which, in turn, encourage crystallization at the expense of glass formation.

A typical DSC for the naphthalene diamines is shown in Fig. 3. The initial temperature scan of compound 3 shows a



Fig. 2. Molecular structure and atom numbering scheme for 5. Hydrogen atoms have been omitted for clarity.



crystalline phase transition ($T_{\rm tr} = 200$ °C) and a melting point ($T_{\rm m}$) at 249 °C. This sample was then allowed to cool to room temperature and heated a second time. This temper-

ature scan displayed the glass transition (T_g) at 82 °C. Continuing to heat this sample revealed an exotherm at 103 °C, which was associated with crystallization. Finally, the sam-

Compound 3		Compound 5	
Bond distances (Å)			
N(1)—C(18)	1.416(6)	N(1)—C(13)	1.423(4)
N(1)—C(11)	1.449(6)	N(1)—C(6)	1.427(4)
N(1) - C(1)	1.462(3)	N(1)—C(33)	1.429(4)
		N(2)—C(29)	1.423(4)
		N(2)—C(22)	1.429(4)
		N(2)—C(42)	1.435(4)
Bond angles (°)			
C(18)-N(1)-C(11)	123.3(4)	C(13)-N(1)-C(6)	120.7(3)
C(18)-N(1)-C(1)	118.5(4)	C(13)-N(1)-C(33)	119.1(3)
C(11)-N(1)-C(1)	116.5(4)	C(6)-N(1)-C(33)	117.5(3)
		C(29)-N(2)-C(22)	119.0(3)
		C(29)-N(2)-C(42)	118.4(3)
		C(22)-N(2)-C(42)	116.7(3)
Torsion angles (°)			
C(11)-N(1)-C(1)-C(2)	108.57	C(6)-N(1)-C(33)-C(34)	50.12

Table 3. Selected bond lengths (Å) and angles (°) for compounds 3 and 5.

Fig. 3. DSC of compound **3**. Heating rate of 20 °C/min. Curve (*a*) corresponds to first heating and curve (*b*) corresponds to second heating.



ple was observed to melt at $T_{\rm m}$. Similar DSC measurements allowed the determination of the $T_{\rm g}$ and $T_{\rm m}$ values of diamines **1–9** and these results are presented in Table 2. For comparison, the corresponding values for **TPD** are included in this table.

Figure 4 displays the DSC data for compound **6**. In the first run, compound **6** exhibits a coupled endothermic and exothermic phase transition prior to melting at 283 °C. This type of transition has been attributed to polymorphism of the crystalline materials (42). After the compound was flash cooled in liquid nitrogen to form the glassy state, the sample was subjected to a second heating cycle that allowed observation of the T_g (116 °C) and T_c (185 °C). Following this

second run, the compound was allowed to cool under ambient conditions to room temperature, and a third heating cycle was initiated. This run was stopped prior to melting. The purpose of this heating cycle was to anneal the sample into a crystalline phase. The fourth heating cycle confirmed that **6** was again a crystalline sample in that no T_g was observed but T_m was clearly seen. The data presented in Fig. 4 demonstrates that the rate of sample cooling of **6** has no effect on the T_g values, but it will effect T_c . For example, T_c is observed at 185 °C for the compound cooled in the liquid nitrogen, while T_c is 200 °C for the compound cooled under ambient conditions.

As summarized in Table 4, compounds 1-9 possess melting points from 187-283 °C, which all exceed that of TPD at 175 °C. With the exception of 5, diamines 1-9 have higher T_g values than **TPD** and in two cases surpass this value by more than 50 °C. We attribute the low T_g that was observed for 5 to the fact that it possesses a *n*-propyl group, a feature that makes it unique among these compounds and likely reduces the overall rigidity of this compound. The highest T_g values were observed for compounds 6 and 7, which have extended aromatic substituents. The 4,4'biphenyl and 1-naphthyl groups increase both the molecular weight and the rigidity of 6 and 7. The remaining compounds have $T_{\rm g}$ values that fall within the narrow range of 70-83 °C. Compound 9 possesses N-substituents that are simple phenyl rings and it exhibited a slightly higher T_{g} of 83 °C compared with the substituted aromatic analogues. This suggests that there is little gain in thermal properties by using simple methoxy, methyl, or fluoro substituents on the aromatic groups in these systems.

Electrochemistry

In a simple OLED, emission arises from the recombination of electrons originating in the ET layer with holes that are transported in the HT material. This combination can occur in either of the two layers and for charge transfer across the ET/HT interface some degree of HOMO and (or) LUMO matching is required. Matching of the HOMO level of the



Table 4. Summary of electrochemical and spectroscopic data for naphthyl core diamines.

Compound	$\Delta E_{\text{oxid}}^{a}$ (mV)	$\Delta E_{\rm p}^{\ b}$ (V)	Absorption (λ_{max}, nm)	Emission (λ_{emi}, nm)	Energy gap ^c (nm)	$(\Phi_{\rm f})^d$	HOMO ^e (eV)	LUMO ^f (eV)
1	145	0.081	375	500	433	0.18	5.10	2.24
2	130	0.160	372	475	421	0.19	5.11	2.16
3	144	0.091	376	480	425	0.22	5.14	2.22
4	140	0.135	370	476	420	0.20	5.15	2.20
5	140	0.123	379	480	429	0.20	5.09	2.20
6	121	0.106	375	475	425	0.19	5.16	2.24
7	160	0.125	375	465	410	0.08	5.14	2.11
8	169	0.202	361	441	395	0.46	5.24	2.10
9	255	0.210	362	441	401	0.48	5.31	2.22
TPD	220	0.127	350	404	385	$\mathbf{N}\mathbf{A}^{g}$	5.08	1.86

^aPotential difference between first and second oxidations.

^bPotential difference between the $Cp_2Fe^{+/0}$ and diamine^{+/0} couples.

Estimated from the intersection of the normalized absorption and emission graph.

^dRelative to Coumarin 102.

 e HOMO = (4.8 + ΔE_{p}) eV.

fLUMO = HOMO - energy gap (eV).

 ${}^{g}NA = not available.$

HT layer and that of the cathode is also important in EL device engineering. An electrochemical method based on cyclic voltammetry was used to estimate the HOMO energies of the naphthalene diamines 1-9 and to examine their electrochemical stability (43, 44).

Cyclic voltammetric scans were recorded under a N_2 atmosphere in CH_2Cl_2 solvent with a Ag wire pseudoreference electrode and with TBAHFP as the supporting electrolyte. At the end of each set of scans, Cp_2Fe was added to the solution and another potential scan was performed that provided a reference potential for the Cp_2Fe/Cp_2Fe^+ couple as a calibration standard.

Over the positive potential scan range (0 to ~1.5 V), compounds 1–9 exhibited two reversible oxidation waves (examples are shown in Fig. 5). If the potential scan is extended to more positive potentials (~2 V), irreversible oxidation processes were also observed for all the compounds with the exception of 8. The two reversible oxidation peaks in the CV

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Fig. 5. CV scans of compounds 6, 8, and 9 at 100 mV/s in CH₂Cl₂ with 0.05 mol/L TBAHP under N₂. Five scans are shown.

curves can be ascribed to one-electron oxidation processes of the two amine centers. The first oxidation process corresponds to the HOMO energy level of the diamine and correlates directly to the energy required for hole generation and transport in the HT layer. The $E_{1/2}$ value of the diamine/diamine⁺ couple relative to the $E_{1/2}$ value for the Cp₂Fe/Cp₂Fe⁺ couple was used to estimate the HOMO energy levels for compounds **1–9**. The established value of the ferrocene HOMO energy level of 4.8 eV was added to the difference in the two oxidation potentials to obtain the diamine HOMO energy values and the results of these calculations are summarized in Table 4 (43, 44).

The extent of intramolecular charge mobility can be estimated by the difference between the first and second oxidation events for each of the diamines (ΔE_{oxid}). In the case of a large degree of charge delocalization, the first positive charge should have a pronounced effect on the second nitrogen center making it more difficult to oxidize and leading to a large difference in the two oxidation potentials. On the other hand, if the two charges are isolated from each other, only one oxidation couple would be observed. For example, TPD shows a potential gap of 220 mV indicating electronic communication between the two nitrogens after the first oxidation. Aromatic di- and triamines in which the N centers are bridged by a single phenyl group with a para or ortho disposition often exhibit even larger potential gaps in the range 330-530 mV (45-48). In contrast, the corresponding values for meta-diaminobenzene derivatives are smaller at 161-191 mV, presumably reflecting a low degree of conjugation between the two N centers (49). A similar lack of charge delocalization is observed for compounds 1-8. Except for compound 9 ($\Delta E_{\text{oxid}} = 255 \text{ mV}$), the diaminonapthalene compounds 1–8 exhibit small ΔE_{oxid} values (121-169 mV).

The reproducibility of the voltammetric behavior over multiple potential scan cycles demonstrates the stability of these materials to the repeated redox steps they would experience in a device. When only the first two oxidation waves were scanned, compounds 1–9 showed reproducible CV behavior for at least five scan cycles as shown in the Fig. 5. With a wider potential range, compounds 1–7 continued to exhibit superimposible CV curves for at least five scan cycles. However, scanning of 8 and 9 over this wider potential range that included the third, irreversible oxidation process led to changes in the voltammograms. We attribute this instability to the deposition of the oxidized species onto the electrodes. In fact, during the CV scans for 9 a brown film was observed on the working Pt electrode, while for compound 8 a green precipitate was observed in the solution near the working electrode. These precipitates were not observed if the potential range did not extend beyond the second oxidation peak. The identity of these new species that are produced upon extensive oxidation of 8 and 9 has not been established, but the fact that this observation is associated with N-substitutents that do not have para substitution suggests that there may be a reaction of the oxidized species on the *N*-phenyl ring.

Electronic spectra

The naphthalene diamines **1–9** are white, yellow, or pale orange solids and they possess well-separated absorption and emission maxima with the later appearing in the blue to green region of the spectrum. The UV-vis absorption and emission spectra for these compounds is summarized in Table 4, and typical spectra for compounds **1**, **6**, **8**, and **9** are shown in Fig. 6. Except for compound **6**, these compounds exhibit a single λ_{max} in their absorption spectra. In the case of **6**, the value of λ_{max} was taken from the shoulder at 375 nm (Fig. 6). The HOMO–LUMO gap energy was also estimated from these spectra and is included in Table 4 (21, 22).

The absorption maximum for **TPD** at 350 nm has been assigned to an $n \to \pi^*$ electronic transition that is due to electron transfer from a nitrogen lone pair to the π^* orbital of the biphenyl group (41). We assign the λ_{max} absorption values for **1–9** as arising from a similar $n \to \pi^*$ electron transition with the π^* orbital residing on the naphthalene moiety. In the case of **6**, we propose that the rising absorption below 375 nm is a result of another $n \to \pi^*$ electron transition involving the nitrogen lone pair and the π^* orbital of the biphenyl group.

In comparison with compound 9, all of the parasubstituted phenyl compounds (1-7) exhibit a bathochromic shift in both absorption and emission, which can be ascribed to the electron-donating properties of the aromatic substituents. The electron-donating properties of the methoxy substituents appear to overwhelm the electron-withdrawing effects of the fluoro (4), phenyl (6), and naphthyl groups (7).





As a result, compound **1** displays the largest red shift for emission and Stokes shift.

Generally, the HT materials in an OLED are not used as the source of emission. This is due to the fact the hole mobility is much faster than electron mobility, and as a result, the charge recombination usually occurs in the ET layer and this is where the emission arises. However, if the difference of HOMO energy levels between HT and ET is large enough and the difference in LUMO energy levels is small, holes will be blocked within the HT layer. As a result, emission could arise in the HT layer and there are recent reports of diamine-based HT materials functioning in the role of emitter hosts and as emission sources (20, 26, 29, 50). The emission properties of HT materials, both the emission wavelength (λ_{emi}) and quantum efficiency (Φ_f) provide important performance criteria for OLED fabrication. The values of Φ_f for diamines 1-9 were measured in CH₂Cl₂ relative to Coumarin 102 as a standard (36) and the results are presented Table 4.

Compounds 1–9 fall into two groups based on their $\Phi_{\rm f}$ values. In particular, the $\Phi_{\rm f}$ values for 8 and 9 are identical and more than twice those of the other diamines. Furthermore, 8 and 9 have identical values for their absorption and emission maxima. This phenomenon can be ascribed to the electron-donating properties of the substituents on the *N*-aryl groups. Since the transition is $n \to \pi^*$ in the diamines, the electron-rich amines that possess electron-donating groups at the para position of the aryl substituents (i.e., 1–7) will display higher energies for the nonbonding HOMO electrons relative to those amines that do not have such groups (i.e., 8 and 9). The result will be a reduced HOMO–LUMO gap and a smaller energy difference between the singlet and triplet states, which in turn allows for increased rate of intersystem crossing and a reduction in the $\Phi_{\rm f}$ (51).

Estimates for the diamine LUMO energy levels were obtained by subtracting the HOMO energy values determined electrochemically from the HOMO-LUMO energy gap that was obtained from the absorption and emission spectra. With this method we can then compare the relative energy levels of the naphthyl core diamine compounds. From the data, we can see that meta-substituted 8 and unsubstituted 9 have the largest HOMO values, while all of the parasubstituted compounds have similar HOMO values. These two groupings of HOMO energies are consistent with a HOMO that is predominantly the nonbonding electrons localized on the nitrogen centers. Furthermore, the very similar values of the LUMO energies for all of the compounds are also in harmony with a naphthalene core localized π^* orbital. The overall effects of the aryl substituents provides direction for orbital level tuning of these and related materials for the matching of the energy levels between the charge transport layers that is required for successful OLED fabrication.

Conclusions

Pd catalyzed coupling reactions have been used to synthesize a series of naphthyl core diamines with the general formula 1,5- $[Ar(Ar')N]_2C_{10}H_6$ (Ar = MeOC₆H₄; Ar' = C₆H₅, MeOC₆H₄, p-MeC₆H₄, p-FC₆H₄, p-PhC₆H₄, 1-naphthyl) and the characterization of these species points to their potential as optoelectronic materials. We have examined the thermal, electrochemical, and photophysical properties of these materials. By varying the aryl groups, we have demonstrated the features that lead to the best thermal stability. All of these materials show enhanced glass forming ability and thermal stability compared to TPD. The relative HOMO and LUMO levels for these materials, important parameters for the design of efficient OLEDs, were assessed through electrochemical and spectroscopic measurements. Compounds 1-9 have the potential to function as hole transport materials and they emit in the blue to green color range. We are currently

investigating the transport properties of these materials and their use as HT materials in OLEDs.

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