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ScienceDirect
Dyes and Pigments 77 (2008) 125–128
DYES and PIGMENTS
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Synthesis and photochemical properties of novel 4-diarylamine-1,8-naphthalimide derivatives

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Received 8 December 2006; received in revised form 18 March 2007; accepted 22 March 2007
Available online 27 April 2007

Abstract

Several novel, diarylamine-substituted 1,8-naphthalimide derivatives were synthesized and characterized by FT-IR, ^{1}H, ^{13}C NMR, mass spectra and elemental analyses. The asymmetry inherent in the compounds prevented them from crystallizing and high thermal stability compounds were formed, with glass transition temperatures up to 105 °C. The UV–vis absorption and photoluminescent (PL) spectra of the compounds in *n*-hexane, tetrahydrofuran (THF) and CH_2Cl_2 were investigated. The lowest absorption band of the naphthalimide derivatives centered at ≈450 nm was assigned to charge-transfer transition with an emission at 494–506 nm in nonpolar solvents such as *n*-hexane and at 578–624 nm in polar solvents such as THF and CH_2Cl_2.

Keywords: Naphthalimide; Photochemical; Charge-transfer transition; Diarylamine-substituted

1. Introduction

Naphthalimide derivatives are of interest because of their use as colorants in the polymer industry [1,2], fluorescence probes for medical and biological purposes [3], and as n-type materials in organic light-emitting diodes due to their high electron affinity and low reduction potential [4–8]; they are potential HIV drugs [9], fluorescence cell makers [10,11], DNA-cleaving agents [12,13], liquid-crystal additives [14] and laser dyes [15–17].

It is well known that 1,8-naphthalimide substituted at the 4-position with electron-donating groups displays high fluorescent quantum yield and moves the emission to longer wavelengths [18–21]. Based on this, the diarylamine-substituted naphthalimides of the present study were made available by copper- and palladium-catalyzed reactions and the absorption and photoluminescent spectra of these derivatives in *n*-hexane, THF, CH_2Cl_2 were recorded so as to ascertain their spectral properties in various solvent polarities.

2. Experimental

2.1. General

IR spectra were recorded on a 5DX-FT-2 spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (ARX-500) spectrometer (500 MHz) in $CDCl_3$ using TMS as internal standard (chemical shifts are given as δ in parts per million). TOF-MS spectra were recorded on a ZAB-HS spectrometer while elemental analyses were obtained using an Elementar Vario Micro. UV–vis absorption spectra were recorded using a Hitachi U-300 spectrophotometer, while photoluminescent spectra were obtained using a Hitachi F-4050. Glass transition temperatures (T_g) were measured using a TA Instruments 910 differential scanning calorimeter.

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doi:10.1016/j.dyepig.2007.03.017

2.2. Synthesis

2.2.1. Method 1. Palladium-catalyzed synthesis

In a two-necked flask under nitrogen were added 4-bromo-*N*-phenyl-1,8-naphthalimide (1 mmol), a secondary amine (1.2 mmol), $Pd(OAC)_2$ (0.020 mmol), tri-*tert*-butyl phosphine (0.04 mmol) and sodium *tert*-butoxide (1.5 mmol). Toluene (3 mL) was then added via a syringe. The resulting mixture was stirred for 4–6 h at 120 °C; after cooling, water (3 mL) and then ethyl acetate (20 mL) were added. The organic layer was separated from the aqueous layer, washed with water and aq. brine solution, and then was dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded the crude solid. Purification on a silica gel column using a petroleum ether/ethyl acetate (10:1) mixture as the eluent gave the desired pure product.

2.2.2. Method 2. Copper-catalyzed synthesis

A mixture of 4-bromo-*N*-phenyl-1,8-naphthalimide (1 mmol), a secondary amine (1.2 mmol), potassium carbonate (2.0 mmol), copper(I) iodide (0.05 mmol), 18-crown-6 (0.05 mmol) and 3 mL *o*-dichlorobenzene was heated at 190 °C for 24–30 h under nitrogen. After cooling, the mixture was dissolved in chloroform and water, the organic layer was washed successively with water and aq. brine solution, and then dried over anhydrous magnesium sulfate. The crude solid was further purified by silica gel column using a petroleum ether/ethyl acetate (10:1) mixture as eluent.

*2.2.2.1. 4-(Diphenylamine)-N-phenyl-1,8-naphthalimide (**1a**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.60 (d, $J = 7.1$ Hz, 1H), 8.57 (d, $J = 8.0$ Hz, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 7.59–7.54 (m, 3H), 7.51 (dd, $J = 7.2$, 7.5 Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.35–7.23 (m, 6H), 7.12–7.07 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 164.84, 164.26, 151.63, 148.79, 135.92, 132.90, 132.06, 131.96, 131.14, 130.03, 129.74, 129.05, 128.51, 126.76, 125.89, 124.30, 124.19, 123.79; TOF-MS: *m/z* 440.1. Anal. Calcd for $C_{30}H_{20}N_2O_2$: C, 81.80; H, 4.57; N, 6.36. Found: C, 81.91; H, 4.57; N, 6.12; IR (KBr, cm^{-1}) 1687 (ν^{as} C═O), 1646 (ν^{s} C═O).

*2.2.2.2. 4-(1-Naphthylphenylamine)-N-phenyl-1,8-naphthalimide (**1b**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.61 (d, $J = 7.2$ Hz, 1H), 8.48 (d, $J = 8.2$ Hz, 1H), 8.34 (d, $J = 8.5$ Hz, 1H), 8.00 (d, $J = 8.5$ Hz, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.53–7.49 (m, 3H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.5$ Hz, 2H), 7.30–7.21 (m, 6H), 7.09 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 164.91, 164.35, 152.40, 150.18, 144.86, 136.07, 135.72, 132.96, 132.04, 131.72, 131.10, 130.35, 130.02, 129.76, 129.10, 129.02, 127.68, 127.34, 127.28, 126.95, 126.78, 126.54, 126.39, 123.92, 123.85, 123.70, 123.35, 118.65; TOF-MS: *m/z* 490.1. Anal. Calcd for $C_{34}H_{22}N_2O_2$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.30; H, 4.53; N, 5.60; IR (KBr, cm^{-1}) 1690 (ν^{as} C═O), 1662 (ν^{s} C═O).

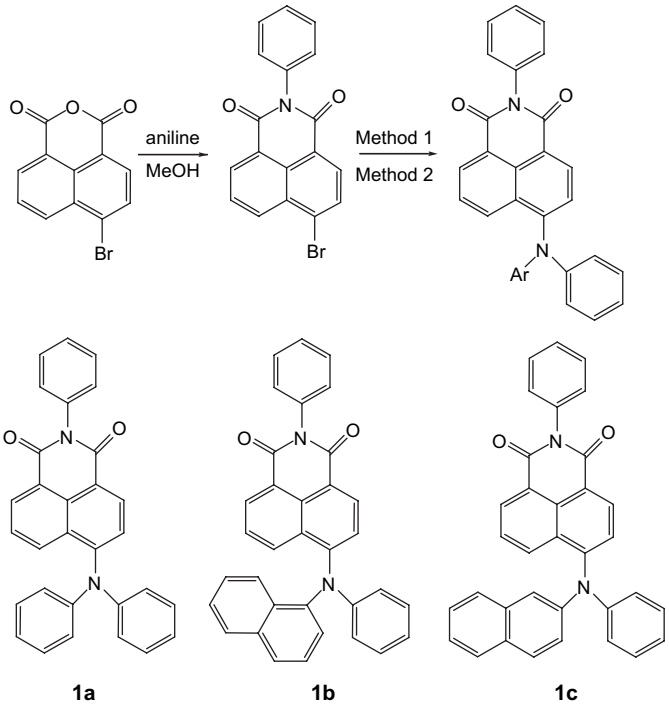
*2.2.2.3. 4-(2-Naphthylphenylamine)-N-phenyl-1,8-naphthalimide (**1c**).* ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.60 (d, $J = 4.3$ Hz, 1H), 8.59 (d, $J = 5.3$ Hz, 1H) 8.30 (d, $J = 8.5$ Hz, 1H), 7.82 (dd, $J = 7.0$ Hz, 8.8 Hz, 2H), 7.60–7.56 (m, 3H), 7.53 (t, $J = 7.5$ Hz, 6.4 Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 1H), 7.44–7.42 (m, 2H), 7.37–7.30 (m, 6H), 7.16–7.12 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 164.80, 164.27, 151.51, 148.72, 146.33, 135.93, 134.66, 132.11, 131.91, 131.17, 130.81, 130.12, 129.99, 129.75, 129.07, 128.54, 128.09, 127.51, 127.12, 126.92, 126.10, 125.60, 124.52, 124.44, 124.02, 123.84, 120.91, 119.37; TOF-MS: *m/z* 490.1. Anal. Calcd for $C_{34}H_{22}N_2O_2$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.42; H, 4.57; N, 5.52; IR (KBr, cm^{-1}) 1697 (ν^{as} C═O), 1657 (ν^{s} C═O).

3. Results and discussion

3.1. Synthesis of 1,8-naphthalimide derivatives and thermal properties

The route to the synthesis of 1,8-naphthalimide derivatives (**1a–1c**) is presented in Scheme 1. The starting 4-Br-*N*-phenyl-1,8-naphthalimide was synthesized according to methods previously described [20]. The reaction of 4-Br-1,8-naphthalic anhydride in 1:1 molar ratio with aniline in boiling ethanol for 12 h, gave 4-Br-*N*-phenyl-1,8-naphthalimide in good yield (80–85%).

The target 1,8-naphthalimide derivatives, **1a–1c** were obtained by nucleophilic substitution of the bromide atom at the 4-position in 4-Br-*N*-phenyl-1,8-naphthalimide with



Scheme 1. The synthesis routes of compounds (method 1: CuI/18-crown-6/K_2CO_3/*o*-dichlorobenzene; method 2: $Pd(OAC)_2$/($P(t\text{-}Bu)_3$/NaO*t*-Bu/toluene).

Table 1
Copper- and palladium-catalyzed synthesis of **1a–1c**

Compd	Yield, %		T_g (T_m), °C
	Copper-catalyzed	Palladium-catalyzed	
1a	35	80	72 (255)
1b	25	72	105
1c	27	75	97

a diarylamine group, by reaction with diphenylamine, naphthylphenylamine under copper- and palladium-catalyzed conditions. One of the most widely used methods for aryl C–N bond construction is the Ullmann condensation, in which a diarylamine is condensed with an aryl halide in the presence of base and a copper catalyst [22]. It has been found that the use of crown ethers as phase-transfer catalyst induces rate acceleration and improves yields in certain Ullmann condensation reactions [23]. Using a standard set of reaction conditions (CuI/18-crown-6/K_2CO_3/*o*-dichlorobenzene, 190 °C), we coupled an array of diarylamines with aryl bromides and obtained the desired, pure products in poor yield (25–35%) (Table 1). Various parameters such as catalyst precursors, base, ligands, and solvents were examined but no better results were obtained.

The use of a Pd/P(*t*-Bu)$_3$ catalyst system was first reported by Koie and a modified system was used by Yamamoto to efficiently couple diarylamines with aryl halides to prepare triarylamines [24]. In this work, we used ($Pd(OAC)_2$/P(*t*-Bu)$_3$/NaO*t*-Bu/toluene, 120 °C) to prepare the target 1,8-naphthalimide derivatives **1a–1c** in good yield (72–80%) (Table 1).

Starburst molecules having a triarylamine core have improved thermal stability [25,26]. The addition of diarylamine groups to naphthalimide rings has increased T_g from 72 °C to 105 °C (Table 1); the T_g of the compounds are higher than the commonly used hole-transporting material TPD [27]. Such an outcome may be due to the asymmetry inherent in these compounds which prevents these low molecular mass compounds from crystallizing, yielding high thermal stability.

3.2. Photophysical properties

The UV–vis absorption and photoluminescent (PL) spectra of the systems in *n*-hexane, THF, CH_2Cl_2 were recorded so as to study their spectral properties in various solvent polarities and to compare their emission. The wavelengths corresponding to the spectral peaks are shown in Table 2; some representative spectra are shown in Figs. 1 and 2. As indicated in the absorption spectra, these derivatives reveal a common low-energy

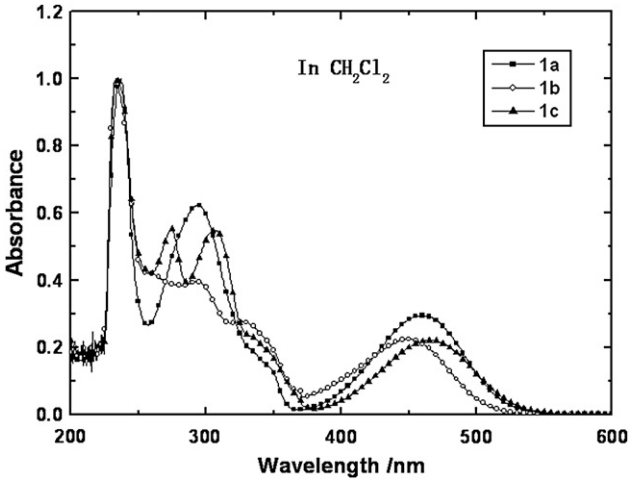


Fig. 1. Absorption spectra of **1a–1c** in CH_2Cl_2.

broad band at 430–460 nm which can be assigned to an intramolecular charge-transfer band from the arylamine group to the naphthalimide ring system in *n*-hexane, THF, and CH_2Cl_2 [28,29]. As is typical of charge-transfer transition, an increase in the polarity of the medium leads to a Stokes shift of the absorption maximum. A change of solvent from *n*-hexane to CH_2Cl_2 resulted in a 20 nm bathochromic shift of the absorption maximum. The magnitude of this shift suggests that the ground state of the molecules is significantly polar.

Photoluminescent spectra of the systems were recorded in various solvents of different polarity. The photoluminescent spectra of the systems consisted of one broad band except in the case of *n*-hexane, for which some structure could be observed. An increase in the polarity of the medium led to a Stokes shift of the photoluminescent maximum. The effect of the polarity of the medium on the photoluminescent maximum was more pronounced than that in the case of the absorption maximum; this is evident from the data presented in Table 2. While a change of the solvent from *n*-hexane to CH_2Cl_2 shifted the absorption maximum by around 20 nm, the magnitude of the spectral shift was one fifth as large as that of the photoluminescent shift. This observation suggests that the emitting state of the systems is more polar than the ground state.

4. Conclusions

Some novel fluorescence compounds containing 1,8-naphthalimide derivatives were synthesized in good yields using palladium-catalyzed conditions; the absorption and photoluminescent spectra of these derivatives in *n*-hexane, THF, CH_2Cl_2

Table 2
Absorption and photoluminescent data of **1a–1c** in different solvents

Compd	λ_{max}^{abs} nm ($\varepsilon_{max} \times 10^{-3}$ M^{-1} cm^{-1})			λ_{max}^{PL} nm (ϕ_f, %)			
	n-Hexane	THF	CH_2Cl_2	*n*-Hexane	THF	CH_2Cl_2	Film
1a	441 (16.92)	448 (16.38)	460 (17.02)	494 (70.4)	583 (2.34)	603 (4.85)	582
1b	430 (13.82)	438 (13.58)	450 (14.57)	495 (51.6)	578 (1.18)	601 (2.26)	590
1c	448 (14.26)	454 (14.88)	465 (15.06)	506 (52.3)	599 (1.60)	624 (2.24)	610

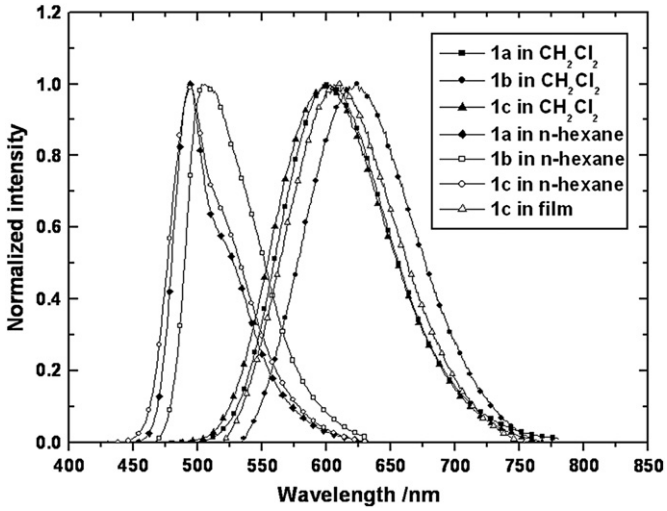


Fig. 2. Normalized PL spectra of **1a**–**1c** in *n*-hexane, CH_2Cl_2 and the thin film of **1c**.

were investigated. These compounds displayed a large Stokes shift in polar solvents; a change in solvent from *n*-hexane to CH_2Cl_2 resulted in a 20 nm bathochromic shift of the absorption maximum which was one fifth as large as that of the photoluminescent shift.

Acknowledgements

The support of this research by the Doctoral Program Foundation of Higher Education (20030286012) and the High-Technique Project Foundation of Jiangsu Province (BG 2005034) is gratefully acknowledged.

References

[1] McGehee MD, Heeger AJ. Adv Mater 2000;12:1655.
[2] Bojinov V, Grabchev I. Dyes Pigments 2001;51:57.
[3] Gao YQ, Marous RA. J Phys Chem A 2002;106:1956.
[4] Gan J, Song QL, Hou XY, Chen KC, Tian H. J Photochem Photobiol A 2004;162:399.
[5] Kolosov D, Adamovich V, Djurovich P, Thompson ME, Adachi C. J Am Chem Soc 2002;124:9945.
[6] Jiang XZ, Liu YQ, Tian H, Song XQ, Zhua DB. J Mater Chem 1997; 7:1395.
[7] Su JH, Xu T, Chen KC, Tian H. Synth Met 1997;91:249.
[8] Zhu WH, Hu M, Yao R, Tian H. J Photochem Photobiol A 2003;154:169.
[9] Rideout D, Schinazi R, Pauza CD, Lovelace K, Chiang LC, McCarthy M, et al. J Cell Biochem 1993;51:446.
[10] Stewart WW. Nature 1981;292:17.
[11] Saito I. Pure Appl Chem 1992;64:1305.
[12] Bailly C, Brana M, Waring M. Eur J Biochem 1996;240:195.
[13] Dorlars A, Schellhammer CW, Schroeder J. Angew Chem Int Ed Engl 1975;14:665.
[14] Martynski T, Mykowska K, Bauman D. J Mol Struct 1994;325:161.
[15] Marling JB, Hawley JG, Liston EM, Grant B. Appl Opt 1974;13:2317.
[16] Costela A, Moreno GI, Tian H, Su J, Chen K. Chem Phys Lett 1997; 277:392.
[17] Tian H, He YJ, Chang CP. J Mater Chem 2000;10:2049.
[18] Tian H, Xu T, Zhao YB, Chen KC. J Chem Soc Perkin Trans 2 1999;545.
[19] De Silva AP, Rice TE. Chem Commun 1999;2:163.
[20] Alexiou MS, Tychopoulos V, Ghorbanian S, Tyman JHP, Brown RG, Brittain PI. J Chem Soc Perkin Trans 2 1990;837.
[21] Gan JA, Tian H, Wang QC, Chen KC. Proc SPIE 2002;4464:359.
[22] Paine AJ. J Am Chem Soc 1987;109:1496.
[23] Gauthier S, Frechet JMJ. Synthesis 1987;383.
[24] Yamamoto T, Nishiyama M. Tetrahedron Lett 1998;39:2367.
[25] Tokito S, Tanaka H, Okada A, Taga Y. Appl Phys Lett 1996;69:878.
[26] Rommens J, Van der Auweraer M, De Schryver FC. J Phys Chem B 1997;101:3081.
[27] Shirota Y. J Mater Chem 2000;1.
[28] Saha S, Samanta A. J Phys Chem A 2002;106:4763.
[29] Islam A, Cheng CC, Cheng CH. J Phys Chem B 2005;109:5509.