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Citation	Erten, Ş, Özçelik, S, and Eren, E, "Synthesis and Photophysical Characterizations of Thermal -Stable Naphthalene Benzimidazoles" Journal of Fluorescence © 2011 Springer
As Published	http:// 10.1007/s10895-011-0845-z
Publisher	Springer Science+Business Media
Version	PUBLISHED ARTICLE
Accessed	FRI JULY 5 11:44:23 GMT 2013
Citable Link	http://hdl.handle.net/11147/
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Synthesis and Photophysical Characterizations of Thermal -Stable Naphthalene Benzimidazoles

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Received: 24 November 2010 / Accepted: 10 January 2011 / Published online: 29 January 2011
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Abstract Microwave-assisted synthesis, photophysical and electrochemical properties of thermal-stable naphthalene benzimidazoles and naphthalimides are studied in this paper. Microwave-assisted synthesis of naphthalene benzimidazoles provide higher yields than the conventional thermal synthesis. Comparative photophysical properties of naphthalene benzimidazoles and naphthalimides are revealed that conjugation of electron-donating group onto naphthalimide moiety increases fluorescence quantum yields. Fluorophore-solvent interactions are also investigated using Lippert-Mataga equation for naphthalimides and naphthalene benzimidazoles. Thermal stabilities of naphthalene benzimidazoles are better than naphthalimides due to increased aromaticity. The experimental E_{LUMO} levels of naphthalene benzimidazoles are found to be between 3.15 and 3.28 eV. Therefore, naphthalene benzimidazole derivatives consisting of anchoring groups are promising materials in organic dye sensitized solar cells.

Keywords Naphthalene benzimidazole · Naphthalimide · Absorption · Emission · Cyclic voltammetry · TGA curves

Introduction

Naphthalimides are well-known as promising anticancer agents showing broad-spectrum activity against a variety of human solid tumor cells [1, 2]. Several derivatives have reached the phases of clinical trials [3]. N-Substituted 1,8-naphthalimides find a wide range of applications as organic dyes and luminophores.

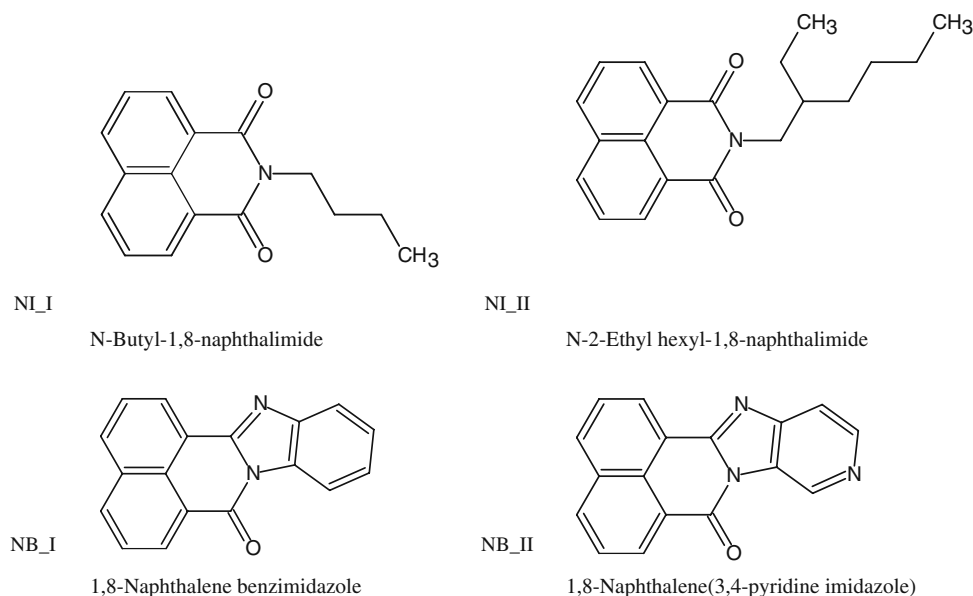
1,8-Naphthalimides are generally fluorescent compounds for which a series of biological (local anesthetics [4], DNA cleaving agents [5], tumoricidals [6] and non-biological optical brighteners [7], lucifer dyes [8]) applications have been found. 1,8-Naphthalimide and bisnaphthalimide derivatives are promising anticancer agents [9, 10], the sulfonated derivatives are good antiviral agents with selective in vitro activity against the human immunity deficiency virus, HIV-1 [11]. Due to their photo-physical and photo-chemical properties the 1,8-naphthalimide derivatives can be used as fluorescence dyes for solar energy collectors and photosynthesis under concentrated sunlight [12], fluorescent markers in biological cells [13] as well as laser active media [14–16]. Recently, naphthalimides have also found applications in organic thin film field-effect transistors (OFETs), integrated circuit, displays, memory cards, chemical and pressure sensors, smart price tags and labels [17].

The electronic absorption and emission spectra of naphthalimides are effected by substitutions. In general, naphthalimides present lower fluorescence quantum yields. Photophysical behaviors of naphthalene benzimidazoles are different from naphthalimides. Conjugation of electron-donating groups onto naphthalimide moiety increases fluorescence emission. This study presents the microwave assisted synthesis of thermal-stable naphthalene benzimidazoles. Fluorescence quantum yields of NB_I and NB_II are found to be 0.36 and 0.60, respectively. This is very

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Table 1 Synthesized naphthalimide and naphthalene benzimidazole derivatives

similar to what we calculated in the case of naphthalene benzimidazole (NB_I) derivative [18–20]. The photophysical and electrochemical properties of naphthalene benzimidazoles (NBs) were compared to naphthalimides (NIs). Conventional thermal synthesis of naphthalimides requires 8–10 h. Instead of this conventional process, we have used microwave method to synthesize naphthalimides and naphthalene benzimidazoles. We obtained 85–90% yields with microwave heating in 20 min. When compared with conventional thermal heating method, microwave heating

method has some advantages such as high reaction yield, faster reaction time, rapid heating of the medium, enhanced reaction selectivity and saving energy due to completed reactions in short time.

And also, general and specific solvent effects of naphthalene benzimidazoles (NBs) and naphthalimides (NIs) were investigated using Lippert-Mataga equation. Molecular structures of naphthalimide (NI) and naphthalene benzimidazole (NB) derivatives are presented in Table 1.

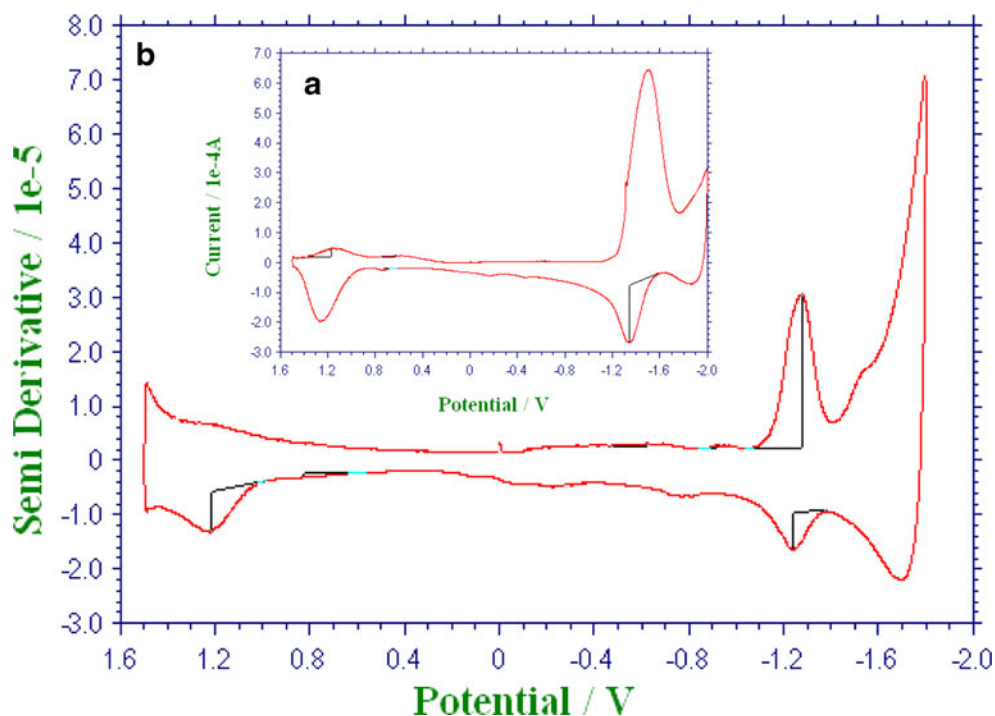
Fig. 1 Cyclic voltammogram of NI_II (a), and NB_I (b), in acetonitrile

Table 2 E_{LUMO} and E_{HOMO} energy levels of synthesized NI and NB derivatives

	E_0-E_{-1} , Volt	E_{LUMO} , eV	E_{HOMO} , eV	Band Gap, eV
NI_I	-1.34	3.07	5.51	2.44
NI_II	-1.39	3.02	5.59	2.57
NB_I	-1.26	3.15	5.62	2.47
NB_II	-1.14	3.28	5.57	2.29

$E_{\text{ferrocene}} = 0.39$ V (Ferrocene is internal reference electrode)

E_0-E_{-1} = Reduction potentials of synthesized derivatives

Experimental

Materials

1,8-Naphthalic anhydride, 2-ethyl hexyl amine, butyl amine, *o*-phenylene diamine, 3,4-diamino pyridine, anthracene were purchased from Aldrich. Quinine sulfate was supplied from Acros Organics. The fluorescence quantum yields of naphthalene benzimidazoles were measured using quinine sulfate as the reference compound ($\phi_f=0.546$ in 1N H_2SO_4).

All solvents were of spectroscopic grade and were used without any further purification.

Materials Characterization

The UV–vis absorption spectra were recorded in an Analytic JENA S 600. Fluorescence spectra were obtained in a PTI QM1 fluorescence spectrophotometer. Concentrations were arranged to 10^{-6} M in order to avoid aggregation or reabsorption effects for absorption, fluorescence and quantum yield measurements. Quinine sulfate was used as the fluorescence quantum yield standard for naphthalene benzimidazole and 1,8-naphthalene(3,4-pyridine imidazole). Anthracene was used as the fluorescence quantum yield standard for naphthalene imides. Cyclic voltammetry measurements of synthesized naphthalimide and naphthalene benzimidazole derivatives were taken using CH-Instrument 660 B Model Potentiostat equipment. Thermal stabilities were determined by means of thermal gravimetry measurements (TGA) with the equipment of Perkin Elmer- Thermogravimetric Analyzer Pyris 6 TGA.

Synthesis and Characterization of Naphthalimide (NI) and Naphthalene Benzimidazole (NB) Derivatives

A microwave oven, CEM MARS-5, frequency 2.45 GHz, maximum power 700 W, was used to synthesize naphthalimide and naphthalene benzimidazole derivatives. Naphthalimides and naphthalene benzimidazoles have been synthesized by condensation reaction of 1,8-naphthalic anhydride and primary amine or *o*-phenylene diamine in imidazole solutions, using microwave oven. 1,8-Naphthalic anhydride (1 g, 0.005 mol), a primary amine (0.36 g, 0.005 mol) or *o*-phenylene diamine (0.55 g, 0.005 mol) and imidazole (10 g) were placed in to XP-1500-plus vessel of

microwave oven. The reaction has been completed in 20 min which was found to be an optimum time. After 20 min, solution was cooled and treated with 2 N of HCl to remove excess imidazole. Then, the material was filtered and washed with water. The crude product was purified by silicagel column chromatography, using CH_2Cl_2 as eluent. The reaction yield is 90% for naphthalimide (white color); 85% for naphthalene benzimidazole (yellow color) for microwave heating method. Solubility of N-butyl-1,8-naphthalimide is 300 mg/ml in CH_2Cl_2 , N-2-ethyl hexyl-1,8-naphthalimide is 450 mg/ml in CH_2Cl_2 ; solubility of 1,8-naphthalene benzimidazole is 60 mg/ml in CH_2Cl_2 . solubility of 1,8-Naphthalene(3,4-pyridine imidazole) is 40 mg/ml in CH_2Cl_2 . Materials were characterized using $^1\text{H-NMR}$, IR and Elemental Analysis.

-N-Butyl-1,8-naphthalene imide; NI_I, IR (KBr): cm^{-1} , 3050, 2950, 1700, 1650, 1575, 1455, 1380, 1250, 1190, 1085, 990, 880, 750.

$^1\text{H NMR}$ (CDCl_3), (ppm), 8.6(2H, s), 8.2(2H, s), 7.7(2H, s), 4.3(2H, m), 1.7(2H, m), 1.45(2H, m), 1.0 (3H, m).

$\text{C}_{16}\text{H}_{15}\text{NO}_2$ (253): Calcd: C 75.87%, H 5.97%, N 5.53%, O 12.63%; found: C 75.88%, H 5.99%, N 5.52%, O 12.64%.

-N-2-Ethyl hexyl-1,8-naphthalene imide, NI_II, IR (KBr): cm^{-1} , 3063, 2957, 2924, 2872, 2856, 1700, 1654, 1625, 1590, 1534, 1498, 1512, 1459, 1438, 1416, 1388, 1346, 1318, 1278, 1236, 1205, 1185, 1168, 1133, 1083, 1073, 1026, 949, 916, 900, 857, 847, 799, 783, 738.

$^1\text{H NMR}$ (CDCl_3): (ppm), 8.6 (2H, s), 8.2 (2H, s), 7.6 (2H, s), 4.1 (2H, m), 1.9 (H, m), 1.3 (8H, m), 0.9 (6H, m).

$\text{C}_{20}\text{H}_{23}\text{NO}_2$ (309): Calcd: C 77.64%, H 7.49%, N 4.53%, O 10.34%; found: C 77.65%, H 7.51%, N 4.53%, O 10.34%.

-1,8-Naphthalene benzimidazole, NB_I, IR (KBr): cm^{-1} , 3060, 1696, 1671, 1640, 1618, 1583, 1551, 1501, 1449, 1362, 1322, 1289, 1230, 1177, 1150, 1122, 1072, 1029, 917, 880, 840, 750, 700, 670, 617.

$^1\text{H NMR}$ (CDCl_3): (ppm), 8.80 (2H, d), 8.56 (H, m), 8.26 (H, d), 8.12 (H, d), 7.88 (H, m), 7.78 (2H, m), 7.48 (2H, m).

$\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}$ (270): Calcd: C 79.99%, H 3.73%, N 10.36%, O 5.92%; found: C 79.96%, H 3.75%, N 10.36%, O 5.93%.

-1,8-Naphthalene(3,4-pyridine imidazole), NB_II, IR (KBr): cm^{-1} , 3057, 1700, 1640, 1619, 1540, 1500, 1440, 1362, 1327, 1261, 1236, 1181, 1140, 1031, 819, 770, 601.

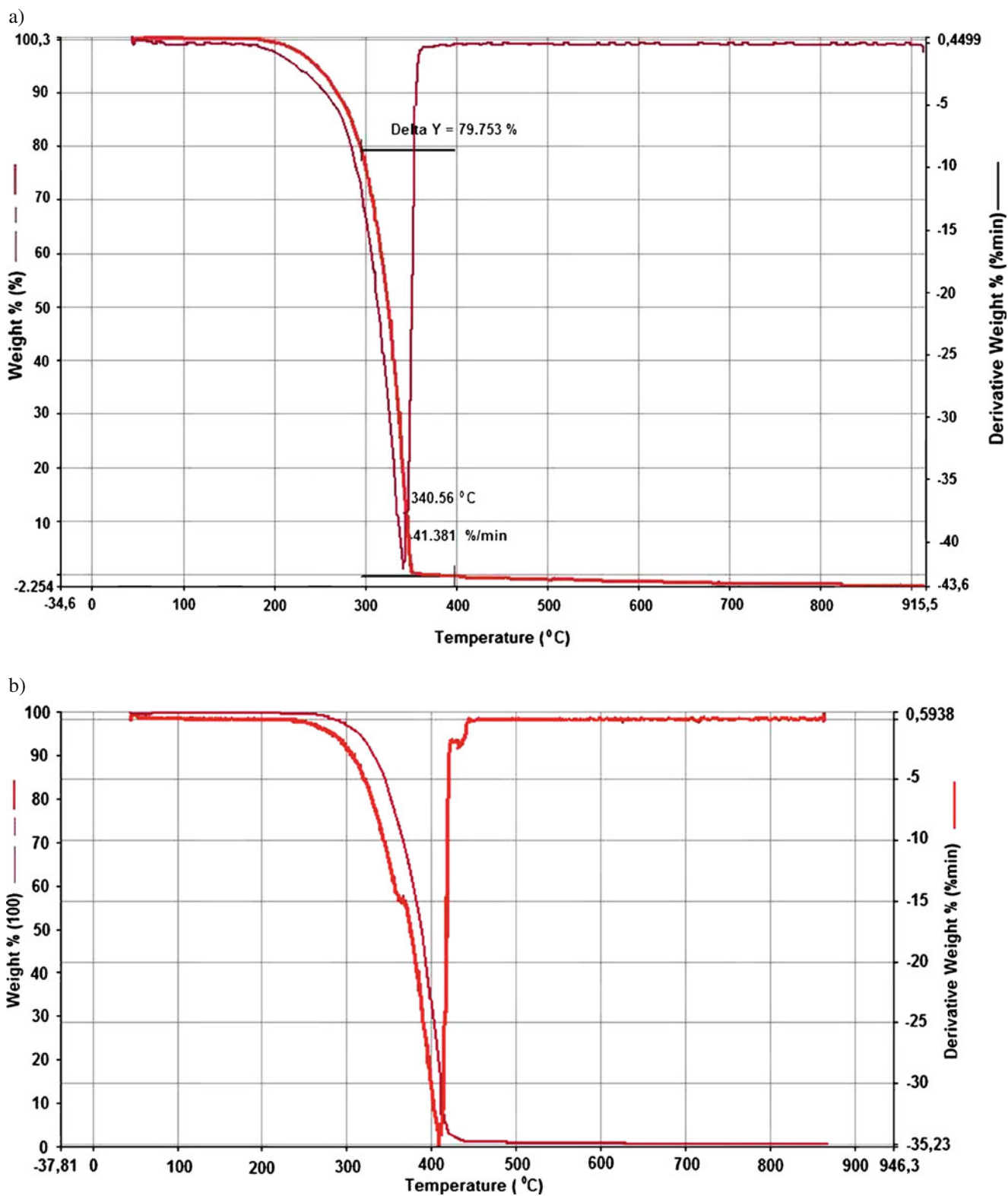


Fig. 2 TGA curve of NI_II (a), and NB_I (b)

Table 3 UV/Vis spectroscopy data and Fluorescence emission maxima of NI_I and NI_II in dichloromethane, DMF, Acetonitrile, THF, Hexane, Methanol

		ϵ	Refraction index	λ_1 (nm)	ϵ_1 ($M^{-1}cm^{-1}$)	λ_2 (nm)	ϵ_2 ($M^{-1}cm^{-1}$)	λ_3 (nm)	ϵ_3 ($M^{-1}cm^{-1}$)	λ_f^{max} (nm)	Stokes shift (cm^{-1})
NI_I	Acetonitrile	37.5	1.3441	318	11767	332	16098	348	14359	380	1190
	DMF	36.7	1.4303	318	13460	334	18755	349	16456	384	1410
	Dichloromethane	8.93	1.4242	319	17050	334	24000	344	21875	383	1600
	THF	7.6	1.4076	318	10632	332	14178	345	12552	377	1210
	Hexane	1.87	1.372	312	9202	326	12474	342	12308	364	590
	Methanol	33.1	1.326	316	7182	333	10651	343	10167	384	2417
NI_II	Acetonitrile	37.5	1.3441	317	9130	332	12640	347	11940	382	1570
	DMF	36.7	1.4303	320	10945	334	14810	349	13520	384	1630
	Dichloromethane	8.93	1.4242	320	11235	334	15450	349	13340	381	1330
	THF	7.6	1.4076	318	9440	332	13730	347	12015	378	1190
	Hexane	1.87	1.372	312	8101	328	10695	343	10378	368	910
	Methanol	33.1	1.326	316	6718	333	9656	343	9046	387	2200

λ_f^{max} , nm, fluorescence emission maxima

ϵ_1 , $M^{-1} cm^{-1}$, molar extinction coefficient

1H NMR ($CDCl_3$): (ppm), 9.24 (H, s), 8.90 (H, d), 8.82 (H, d), 8.68 (H, d), 8.50 (H, d), 8.35 (H, d), 8.24 (H, d), 7.86 (2H, m).

$C_{17}H_9N_3O$ (271): Calcd: C 75.27%, H 3.34%, N 15.49%, O 5.90%; found: C 75.26%, H 3.34%, N 15.50%, O 5.92%.

Electrochemistry of Naphthalimide (NI) and Naphthalene Benzimidazole (NB) Derivatives

E_{HOMO} and E_{LUMO} values of NIs and NBs were calculated using cyclic voltammograms with scan rates in the range of

100–500 mV/s under nitrogen at 25 °C. Solutions of NI and NB derivatives were prepared in chloroform (10^{-3} M). A three electrode cell was used consisting of glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl reference electrode, all placed in a glass vessel. Tetrabutylammonium hexafluorophosphate (TBAPF₆), 0.1 M, was used as supporting electrolyte. Ferrocene was used as internal reference electrode. NI and NB derivatives show both quasi-reversible reduction and oxidation potential in Fig. 1. In calculation, the zero vacuum level of ferrocene was taken as 4.8 eV [21, 22]. We used the following equation to calculate E_{HOMO} and E_{LUMO} energy level of

Table 4 UV/Vis spectroscopy data and fluorescence emission maxima of NB_I and NB_II in dichloromethane, DMF, Acetonitrile, THF, Hexane, Methanol

		ϵ	Refraction index	λ_1 (nm)	ϵ_1 ($M^{-1}cm^{-1}$)	λ_2 (nm)	ϵ_2 ($M^{-1}cm^{-1}$)	λ_f^{max} (nm)	Stokes shift (cm^{-1})
NB_I	Acetonitrile	37.5	1.3441	331	6840	379	12435	492	6060
	DMF	36.7	1.4303	331	6080	383	9965	490	5700
	Dichloromethane	8.93	1.4242	333	10135	385	15710	488	5560
	THF	7.6	1.4076	333	7980	382	13480	485	5480
	Hexane	1.87	1.3720	343	6523	380	10590	470	4010
	Methanol	33.1	1.3260	344	8693	382	13295	499	6140
NB_II	Acetonitrile	37.5	1.3441	347	8808	374	12466	469	5420
	DMF	36.7	1.4303	348	12602	378	17791	470	5180
	Dichloromethane	8.93	1.4242	350	12873	380	18713	464	4760
	THF	7.6	1.4076	347	10276	375	13800	464	5110
	Hexane	1.87	1.3720	347	7826	373	9990	455	3870
	Methanol	33.1	1.3260	350	10263	372	13151	450	4660

λ_f^{max} , nm, fluorescence emission maxima

ϵ_1 , $M^{-1} cm^{-1}$, molar extinction coefficient

Table 5 Fluorescence emission maxima and quantum yield of naphthalimides and naphthalene benzimidazoles, in acetonitrile

	λ_f^{\max} (nm)	Φ_f (Quantum yield)
NI_I	380	0.018
NI_II	380	0.011
NB_I	492	0.36
NB_II	469	0.60

λ_f^{\max} , nm, fluorescence emission maxima

ϕ_f , Quantum yield

NIs and NBs, $E_{LUMO} = -e(E_{1/2(redox)} - E_{fer.}) + 4.8$ [19]. E_{HOMO} and E_{LUMO} energy levels of NI and NB derivatives are found to be in between 5.51 and 5.62 eV and 3.02 and 3.28 eV, respectively. The CV values are presented in Table 2. E_{LUMO} energy levels of naphthalene benzimidazole derivatives are higher than the conduction band of TiO_2 , $E_{CB}(TiO_2)=4.2$ eV. Naphthalene benzimidazole derivatives absorb in the visible region. They are promising materials for organic photovoltaics [21, 22].

Results and Discussion

Thermal Stabilities of Naphthalimide (NI) and Naphthalene Benzimidazole (NB) Derivatives

Thermal stabilities of synthesized compounds are determined using thermal gravimetry measurements. TGA curves of NI_II and NB_I are presented in Fig. 2. Naphthalene benzimidazole derivatives are found to be more stable than naphthalimide derivatives. Decomposition temperature of naphthalimides starts from 200 °C and ends at 341 °C, Fig. 2

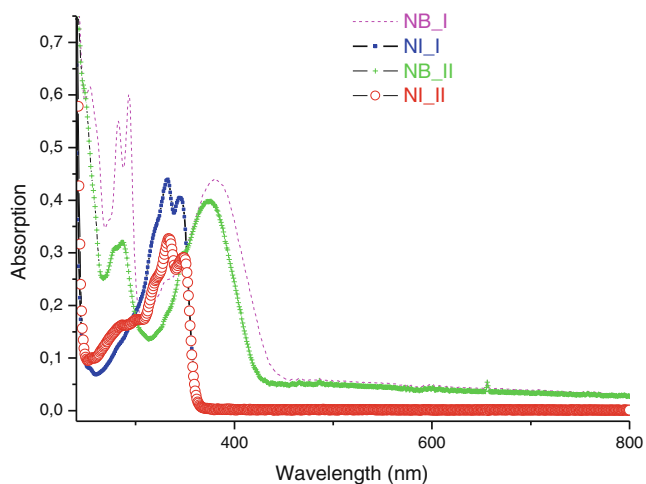


Fig. 3 Absorption spectra of N-butyl-1,8-naphthalimide, NI_I; N-2-ethylhexyl-1,8-naphthalimide, NI_II; 1,8-naphthalene benzimidazole, NB_I; 1,8-naphthalene benzimidazole, NB_II, in acetonitrile

(a); the temperature range for naphthalene benzimidazoles is between 300 °C and ends at 415 °C, Fig. 2(b). Naphthalene benzimidazole derivatives have high thermal stabilities, pointing their favorability in photovoltaic applications.

Absorption and Fluorescence Emission of Naphthalimide (NI) and Naphthalene Benzimidazole (NB) Derivatives

The UV–vis absorption spectra and fluorescence emission spectra of NI and NB derivatives have been studied in various solvents of different polarity and the spectral data have been collected in Table 1. UV–vis Absorption and fluorescence emission spectra of NI and NB derivatives were taken in acetonitrile, DMF, dichloromethane, THF, methanol and hexane in Figs. 5 and 6. Quantum yields were calculated using fluorescence quantum yield standards. Excitation wavelengths of NIs and NBs are determined as 333 nm and 350 nm, respectively. Fluorescence quantum yields of the NIs and NBs, measured in acetonitrile, are collected in Table 5. Among compounds, N-butyl and N-2-ethylhexyl substituted naphthalimides give three characteristic band at 320 nm, 334 nm, 349 nm in Table 3.

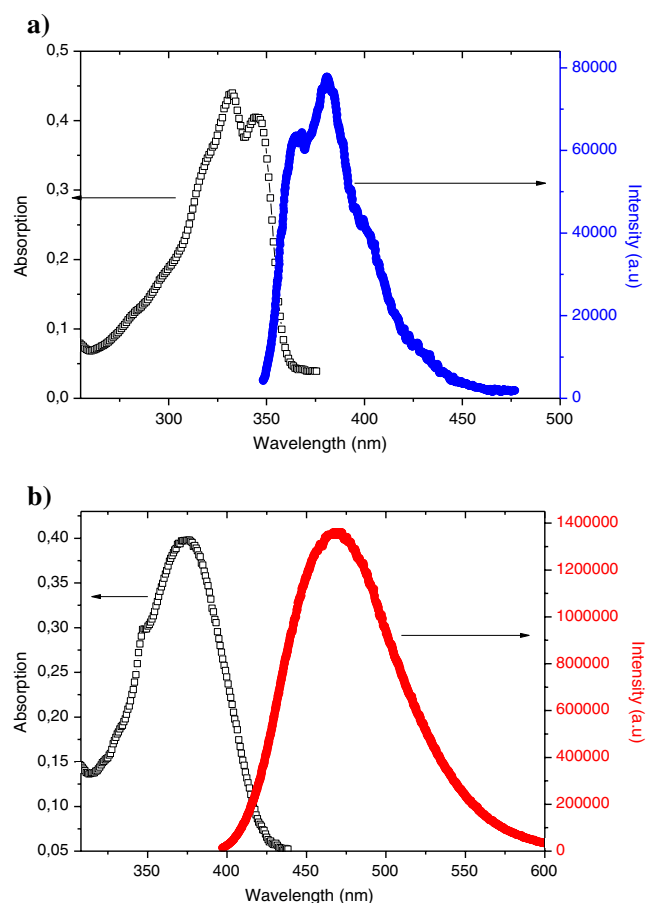


Fig. 4 Absorption and Fluorescence emission spectra of NI_II (a) and NB_II (b) in acetonitrile (Mirror Image)

N-substituted 1,8-naphthalimides have a wavelength of maximum fluorescence emission (λ_f^{\max}) of 380 nm in Table 5. Absorption bands of naphthalene benzimidazole and 1,8-naphthalene(3,4-pyridine imidazole) range from 300 nm to 430 nm in different solvents, Table 4. As shown in Table 5, NB_I and NB_II have wavelengths of maximum emissions of 469 nm and 492 nm. The results show that electron-donating substituents such as phenylene onto naphthalimide moieties had very strong influence on the absorption, fluorescence emission and lead to a red-shifted phenomena.

N-butyl and N-2-ethylhexyl-1,8-naphthalimides display a weak fluorescence quantum yields; $\Phi_f=0.018$ and 0.011, respectively. In agreement with literature data, E. Martin et al. and V. Wintgens et al. have reported that the low value of fluorescence quantum efficiency for naphthalimides is associated to an effective intersystem crossing (ISC) between the singlet excited state S_1 and the nearby triplet state; the ISC efficiency is reported around 0.95 and 1.0 in acetonitrile and hexane solution, respectively [21–23]. On the other hand, 1,8-naphthalene benzimidazole having an electron-donating substituent are highly fluorescent. The presence of a conjugated electron-

donor group condensed onto the naphthalimide moiety alters the emission spectra considerably (Figs. 5 and 6). These substituents cause high red-shifts in fluorescence spectra ($\Delta\lambda^f$: 89–112 nm) and substantially increase the fluorescence yields (Φ_f) from 0.011, 0.018 to 0.36, 0.60, (Figs. 3, 4 and Table 5). NB_I shows higher fluorescence quantum yield of 0.36, with respect to naphthalimides of NI_I and NI_II, a clear observation of enhanced conjugation effect by phenylene ring condensation. Highest quantum yield observed for NB_II ($\Phi_f=0.60$). The presence of electron donating substituents may also increase the separation between the singlet (S_1) and its closer triplet excited state, thus decreasing the intersystem crossing (ISC) and favoring the fluorescence deactivation channel [24–32] (Figs. 5 and 6).

The band position of Absorption and emission spectra for NIs and NBs depend on the change in solvent's polarity.

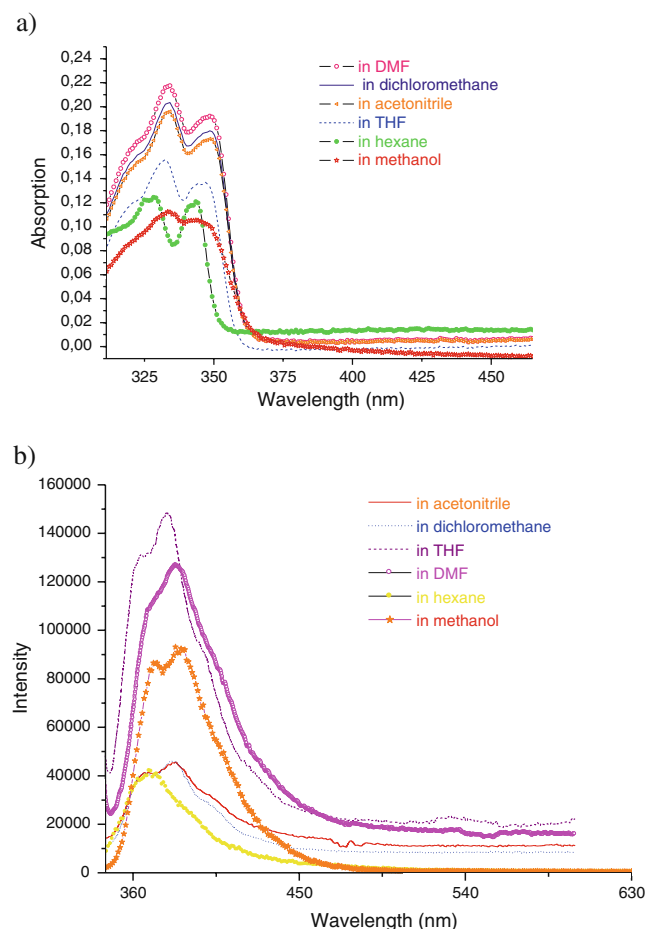


Fig. 5 Absorption (a) and Fluorescence Emission (b) spectra of N-2-ethylhexyl-1,8-Naphthalimide, NI_II in different solvents

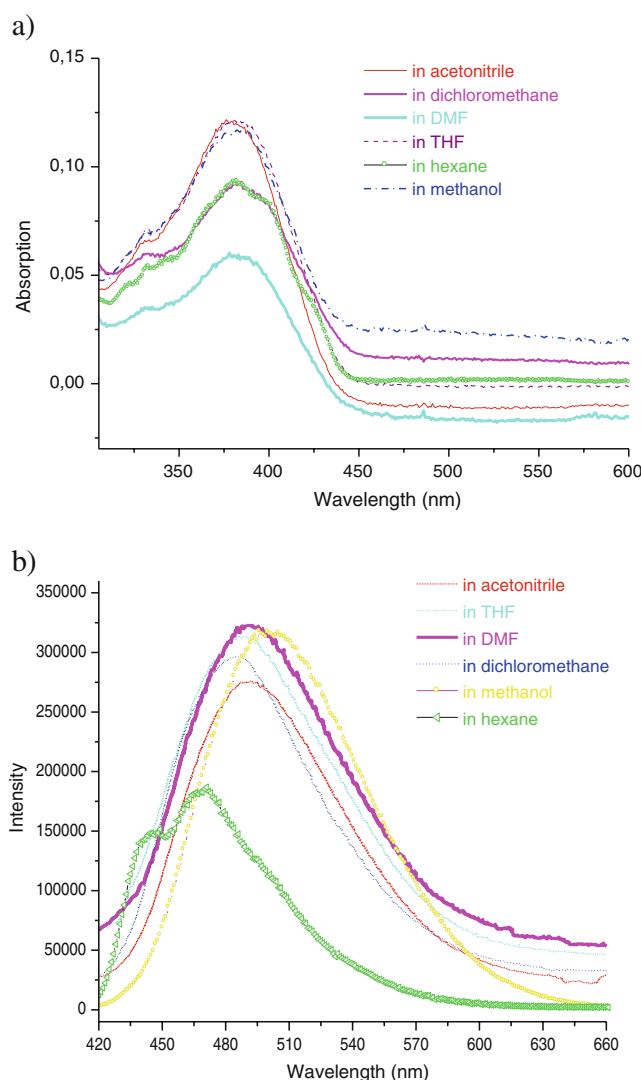
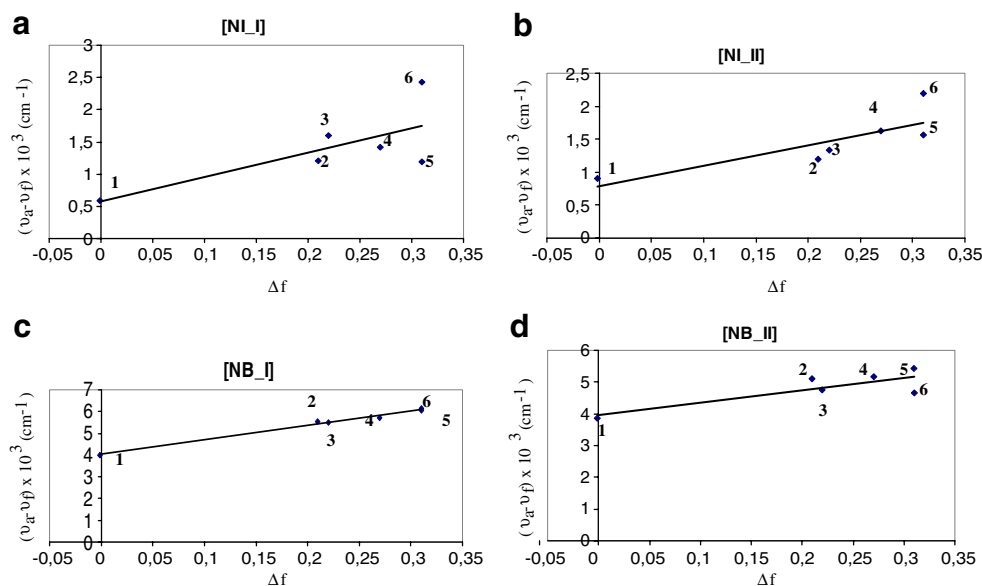


Fig. 6 Absorption (a) and Fluorescence emission (b) spectra of 1,8-naphthalene benzimidazole, NB_I in different solvents

Fig. 7 Effects of solvent polarity in the Stokes' shift of NIs and NBs in the solvents (**a**, **b**, **c**, **d**). The numbers refer to the following solvents: 1, hexane; 2, THF; 3, dichloromethane; 4, DMF; 5, acetonitrile; 6, methanol



We also tried to examine the effect of solvent's polarity on the molecular structures. The Absorption bands of naphthalimides are revealed an influence of the solvent's polarity. The solvent effects the characteristics of the spectra of solute molecules. The responses of NI and NB derivatives to solvent polarity can be analyzed in terms of the difference in the dipole moments in the ground and excited states. This can also be further estimated from a Lippert-Mataga plot (Fig. 7), which is essentially a plot of the Stokes shift of the fluorescence emission vs the solvent polarity. The difference in the maximum absorption and emission wavelengths, expressed in wavenumbers ($\Delta\bar{U}$), is fitted to the following equation. The difference between the maximum absorption and emission wavelengths, expressed in wavenumbers ($\nu_a - \nu_f$), is correlated with the solvent polarity parameter (Δf).

$$\bar{U}_a - \bar{U}_f = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + constant$$

Where, $\mu_e - \mu_g$ is the difference ($\Delta\mu$) between the dipole moments of the excited and the ground states, respectively, c is the velocity of light, and R is the radius of the Onsager cavity around the fluorophore. The parameters ϵ and n are the solvent dielectric constant and refraction index, respectively, which are grouped in the term Δf , known as orientation polarizability. A plot of $\Delta\bar{U}$ versus Δf gives $\Delta\mu$ [33–35].

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

The linearity of these plots is often regarded as evidence for the dominant importance of general solvent effects in

spectral shifts. Specific solvent effects lead to nonlinear Lippert Plots. General solvent effects are due to the interactions of the dipole of the fluorophore with its environment. Specific solvent effects is because of fluorophore-solvent interactions and specific effects can be due to hydrogen bonding or charge-transfer interactions. Stokes' shifts for NI and NB derivatives have been calculated in various solvents of different polarity and the data have been collected in Tables 3 and 4. As a result, it is found that Lippert curves for NI derivatives are non-linear, Lippert curves for naphthalene benzimidazoles are linear (Fig. 7).

Conclusion

In conclusion, thermal-stable naphthalene benzimidazoles were successfully synthesized. Absorption and emission spectra were studied in different solvents. Moreover, it was observed that phenylene groups onto naphthalimide moiety effect the Absorption and emission wavelengths, quantum yields, thermal stabilities and electrochemistry of naphthalene benzimidazoles. Naphthalene benzimidazole compounds may serve as good light-emitting materials, because they emit light in the range of 420 nm–630 nm. E_{LUMO} values of naphthalene benzimidazoles are found to be between 3.15 and 3.28 eV. Naphthalene benzimidazole derivatives can inject electrons to the conduction band of titanium dioxide in dye sensitized solar cell. Naphthalene benzimidazole derivatives are also promising materials in organic solar cells.

Acknowledgements We acknowledge financial support from Scientific and Technological Research Council of Turkey, TUBITAK,

TBAG_106T061 and the Alexander von Humboldt Foundation of Germany and European Science Foundation (ESF) for research supports. I thank Mechanical Engineer DI. Cagatay Ela for proof-reading.

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