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Photoinduced energy–electron transfer studies with naphthalene diimides

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Abstract

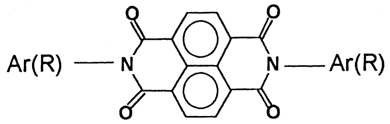
Seven derivatives of naphthalene diimides, synthesized, have shown similar photophysical properties. Low fluorescence quantum yields (0.002–0.006) and short fluorescence lifetimes (5–18 ps) have suggested rapid intersystem crossing processes from excited singlet state. Quenching of fluorescence emissions of aromatic donor molecules, i.e. naphthalene, phenanthrene and pyrene, at rates reaching to diffusion limits in acetonitrile ($2–8\times10^{10}$ M^{-1} s^{-1}), have proven the electron acceptor capacities of naphthalene diimides. Photooxydation of styrene to benzaldehyde, in presence of naphthalene diimide (NDI) molecule, is found to occur at similar rates with respect to perylene diimides. Addition of ferric and cupric ions to NDI, have enhanced the formation rate of benzaldehyde by about two-fold. Photooxidation of α-terpinene with naphthalene diimide, produced only *p*-cymene, no endoperoxide adduct was identified. Naphthalene diimides appear to produce no singlet oxygen, and photooxidation probably occurs on radical chain reactions of super oxide anion radical. But the electron transfer electron via excited triplet or singlet state, remains to be unclear. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: *N*,*N*′-bis-aryl(alkyl) 1,4,5,8-naphthalenediimides; Fluorescence quenching; Photoinduced electron transfer; Photooxidation

1. Introduction

Photophysical characterization of naphthalene diimides are limited to a few derivatives in literature. Politi and coworkers [1] reports the absorption and fluorescence parameters of *N*,*N*′-dibutyl derivative of naphthyl diimides. Fluorescence quantum yield is found to be very weak, Q_f=0.002, due to the n–π* character of lowest excited states, such as in phthalimides. Whereas in 1,8-*N*-butylnaphthylimides lowest excited state has π–π* character, fluorescence quantum yield is in the range of Q_f= 0.01–0.20 in organic solvents and Q_f=0.36 in water [2]. On the other hand naphthalene diimides are found to form stable anion radical on reduction [4], as observed with other condensed aromatic diimides, i.e. perylene diimides [3]. Naphthalene diimides are expected to form anion radical intermediate on photo electron transfer processes, as detected in perylene diimides [5].

We now report the photophysical characteristics of naphthyl diimides in solution, photoinduced energy transfer from aromatic π-electron donor molecules, and electron transfer from olefins on photooxidations.



	Ar		R
I	Phenyl	**V**	*n*-Butyl
II	*o*-Chlorophenyl	**VI**	*n*-Dodecyl
III	*p*-Tolyl	**VII**	Cyclohexyl
IV	α-Naphthyl		

2. Experimental details

2.1. Materials

1,4,5,8-Naphthalenedianhydride, aniline, *o*-chloroaniline, *p*-fluoroaniline, *p*-bromoaniline, *p*-toluidine, cyclohexylamine, *n*-butylamine, *n*-dodecylamine, phenanthrene, pyrene and perylene were obtained from Fluka and Merck, and were used as supplied. All the organic solvents that were used (acetonitrile, chloroform, methanol), were of spectrophotometric grade. α-Cyclodextrin was obtained from Avocado firm, and was used as supplied.

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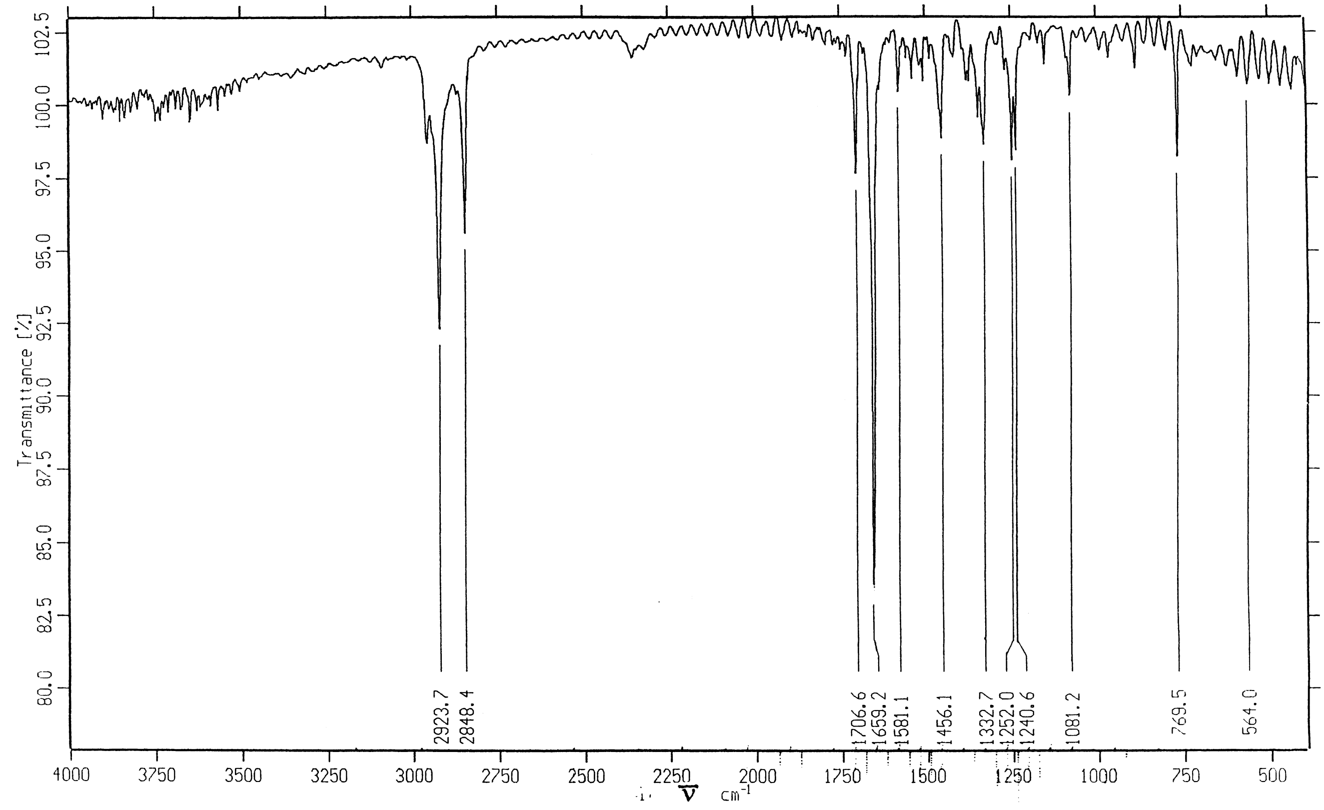


Fig. 1. IR spectrum of *N,N′*-bis-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI) in KBr.

2.2. Organic synthesis

N,N′-bis-aryl(alkyl) 1,4,5,8-naphthalenediimides were prepared by the method that were employed for the synthesis of *N*-substituted perylene diimides [6]. 1,4,5,8-Naphthalenedianhydride was reacted with appropriate amine derivative in *m*-cresol/isoquinoline at elevated temperatures (>200°C) for 4–6 h in order to yield the naphthalenediimide. Molecular structures were analyzed in IR (Fig. 1) and proton NMR spectra (Table 1 and Fig. 2).

2.2.1. *N,N′-bis-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI)*

The mixture of 1,4,5,8-naphthalenedianhydride (1 g, 3.75 mmol) and aniline (0.7 g, 7.5 mmol) was dissolved in 20 ml *m*-cresol and a few drops of isoquinoline was added. The temperature was gradually increased to 200°C. The mixture was kept at this temperature for 24 h. The viscous solution was diluted with 20 ml *m*-cresol and poured slowly into 30 ml of stirred acetone. The precipitate was filtered and washed thoroughly with warm acetone. Crude product was re-dissolved in chloroform and poured into acetone and filtered for purification. *N,N′*-bis-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI), $C_{24}H_{14}N_2O_4$, MW: 396.4 g/mol, was obtained in 0.92 g, 62% yield. Molecular structure was analyzed in IR and proton NMR spectra as seen in Table 1.

2.2.2. *N,N′-bis-n-butyl-1,4,5,8-naphthalenediimide (**V**)*

The mixture of 1,4,5,8-naphthalenedianhydride (1 g, 3.75 mmol) and *n*-butylamine (0.7 g, 10 mmol) was dissolved in 20 ml *m*-cresol and few drops of isoquinoline was added. The temperature was gradually increased to 160°C. The mixture was kept at this temperature for 6 h under nitrogen. The viscous solution was diluted with 20 ml *m*-cresol and poured slowly into 50 ml of methanol while stirring. The precipitate was filtered and washed thoroughly with warm acetone. Crude product was purified by column chromatography, using dichloromethane as eluent. *N,N′*-bis-*n*-butyl-1,4,5,8-naphthalenediimide (**V**), $C_{22}H_{22}N_2O_4$, MW: 378.4 g/mol, was obtained in 0.46 g, 32% yield. Molecular structure was analyzed in IR and proton NMR spectra (Table 1).

2.3. Spectroscopic measurements

Synthesized compounds were analyzed at Schimadzu IR4570 spectrophotometer for IR spectroscopy, at JASCO V-530 UV–VIS spectrophotometer for UV–VIS spectroscopy, at JEOL JNM-GX 400FT 400 MHz NMR for NMR spectroscopy analysis. Fluorescence emission spectra were recorded at a PTI QM1 fluorescence spectrophotometer.

Fluorescence quantum yields of naphthalene diimides were measured with reference to absorption and fluorescence

Table 1

Characteristic absorptions of synthesized *N*,*N′*-bis-aryl(alkyl) 1,4,5,8-naphthalene-diimides at IR (ν (cm^{-1}) in KBr) and proton NMR spectra (δ (ppm) in $CDCl_3/CF_3COOD$)

	Ar (R)	$\nu_{C=O}$	ν_{imide}	$\nu_{C–O}$	δ_{Naph}	$\delta_{N–Ar}$	$\delta_{N–CH}$	$\delta_{N–CH_2}$	$\delta_{Ar–CH_3}$	$\delta_{C–CH_2}$	$\delta_{C–CH_3}$
I	Phenyl	1711	1672	1124	7.26 (4H, s)	7.34–7.62 (10H, m)					
II	*o*-Chlorphenyl	1718	1677	1057	8.94 (4H, s)	7.38–7.42 (2H, dd) 7.47–7.57 (4H, m) 7.63–7.67 (2H, dd)					
III	*p*-Tolyl	1710	1670	1120	8.93 (4H, s)				2.46 (6H, s)		
IV	α-Naphthyl	1714	1675	1120	8.91 (4H, s)	7.45–7.47 (10H, m) 8.00–8.08 (4H, m)					
V	*n*-Butyl	1700	1650	1080	8.76 (4H, s)			4.20 (4H, t)		1.74 (4H, m); 1.46 (4H, m)	0.99 (6H, t)
VI	*n*-Dodecyl	1707	1648	1080	8.72 (4H, s)			4.16 (4H, t)		1.71 (4H, m); 1.40 (4H, m) 1.33 (4H, m); 1.22 (4H, m)	0.85 (6H, t)
VII	Cyclohexyl	1710	1650	1100	8.68 (4H, s)		4.99 (2H, m)			2.46 (4H, dq); 1.87–1.91 (4H, d^{broad}) 1.72–1.74 (6H, d^{broad}); 1.23–1.48 (6H, m)	

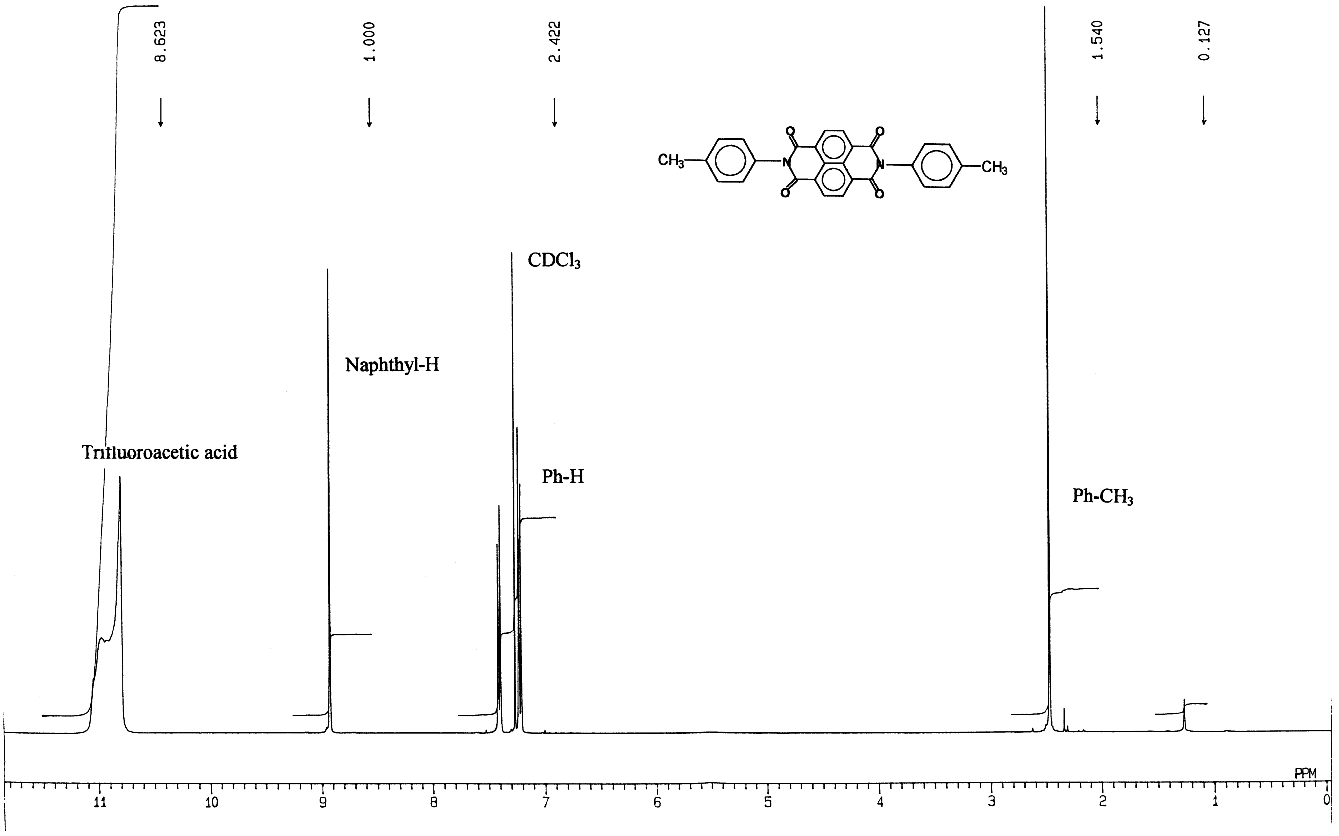


Fig. 2. Proton NMR spectrum of *N*,*N*′-bis-*p*-tolyl-1,4,5,8-naphthalenediimide (**III**) in $CDCl_3$/trifluoroacetic acid.

emission of anthracene, λ_{exc}=357 nm. GC-MS studies were performed with a Hewlett Packard HP 6890 instrument, using HP-5MS column at column temperature range of 40–200°C in 21 min.

3. Results and discussion

3.1. UV–VIS spectroscopy studies

UV absorption spectra of naphthalene diimides have shown three characteristic bands at 377, 357 and 340 nm in acetonitrile solutions. In accordance with the reported data of Politi et al. [2] (Fig. 3 and Table 2). *N*-aryl(alkyl) substitution did not alter absorption wavelengths λ, and molar extinction coefficients ε. Solubility differences in acetonitrile were observed among the seven derivatives. Most soluble naphthalene diimides were found to be the alkyl derivatives of **V**, **VI** and **VII**. The *n*-butyl derivative **V** was observed to be the most soluble in acetonitrile, chloroform and dichloromethane solvents. The least soluble naphthalene derivative was *o*-chlorophenyl derivative **II**. In general low solubilities of naphthalene diimides have caused the

Table 2
UV–VIS spectroscopic data (λ (nm) and ε ($l\,mol^{-1}\,cm^{-1}$)) of synthesized *N*,*N*′-bis-aryl(alkyl) 1,4,5,8-naphthalenediimides in acetonitrile

	Ar (R)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
I	Phenyl	377	32500	357	27800	340	17160
II	*o*-Chlorophenyl	376	42900	356	35100	339	20300
III	*p*-Tolyl	376	32800	356	9500	339	18800
IV	α-Naphthyl	377	33000	357	29000	340	17500
V	*n*-Butyl	377	43500	356	35100	339	21100
VI	*n*-Dodecyl	377	33900	357	28700	340	19100
VII	Cyclohexyl	378	30600	358	25800	342	15500

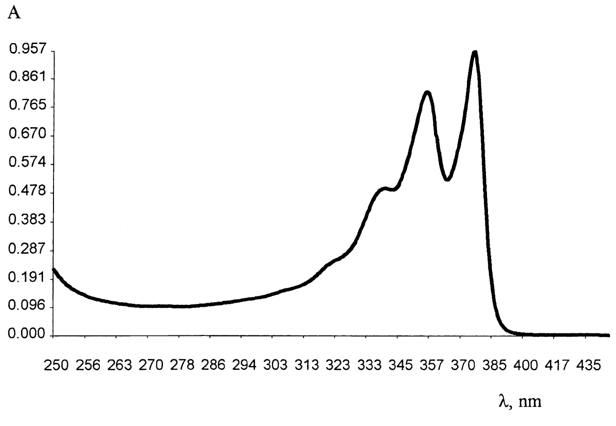


Fig. 3. UV absorption spectrum of *N*,*N*′-bis-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI) in acetonitrile.

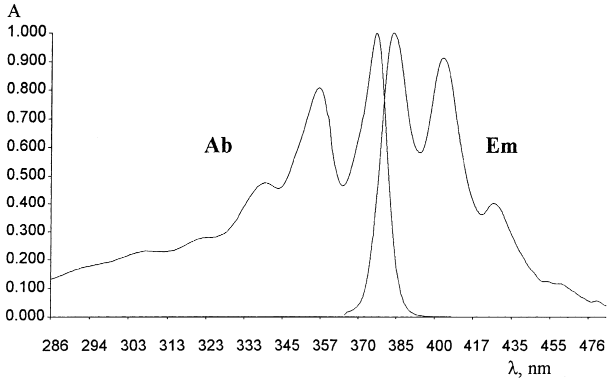


Fig. 4. Absorption (Ab) and emission (Em, λ_{exc}=356 nm) spectra of *N*,*N*′-bis-*n*-butyl-1,4,5,8-naphthalenediimide (**V**) in acetonitrile.

Table 3
Fluorescence quantum yields Q_f, radiative lifetimes τ_0 (ns), fluorescence lifetimes τ_f (ps), fluorescence rate constants, k_f ($10^8\,s^{-1}$), and singlet energies, E_s (kcal mol^{-1}) data of naphthalene diimides in acetonitrile

	Ar (R)	λ_{max}	ε_{max}	Q_f	τ_0	τ_f	k_f	E_s
I	Phenyl	377	32500	0.002	3.1	6.2	3.2	75.9
II	*o*-Chlorophenyl	376	42900	0.002	2.3	4.6	4.3	76.1
III	*p*-Tolyl	376	32800	0.004	3.1	12.4	3.2	76.1
IV	α-Naphthyl	377	33000	0.005	3.1	15.5	3.2	75.9
V	*n*-Butyl	377	43500	0.006	2.3	13.8	4.3	75.9
VI	*n*-Dodecyl	377	33900	0.006	3.0	18.0	3.3	75.9
VII	Cyclohexyl	378	30600	0.004	3.1	12.4	3.2	75.7

difficulties on measurements of absorption spectra. All the acetonitrile solutions were colorless.

3.2. Emission spectra and fluorescence quantum yields

Fig. 4 shows the absorption and emission spectra of *N*,*N*′-bis-*n*-butyl-1,4,5,8-naphthalenediimide (**V**) and *N*,*N*′-bis-*n*-dodecyl-1,4,5,8-naphthalenediimide (**VI**) compounds.

Mirror image appearance of the absorption and emission spectra is evident. In general, the solvent variation does not alter the absorbtion and emission spectra, arising from limited vibrational motions of the atoms of the carbon skeleton and evidence to the very rigid structure of the naphthalene diimide molecule.

The radiative lifetimes τ_0 were calculated by the formula: $\tau_0=3.5\times10^8/\nu_{max}^2\varepsilon_{max}\,\Delta\nu_{1/2}$, where ν_{max} is the wavenumber in cm^{-1}, ε_{max} the molar extinction coefficient at the selected absorption wavelength, and $\Delta\nu_{1/2}$ denotes the half-width of the selected absorption in wavenumber units of cm^{-1} [7]. Fluorescence lifetimes are estimated as $\tau_f=\tau_0 Q_f$ and the rates of fluorescence as $k_f=1/\tau_0$ (Table 3).

Fluorescence quantum yields are observed to be in the range of 0.002–0.006 in acetonitrile. A rapid intersystem crossing probably quenches the singlet excited state of naphthalene diimides [8]. Calculated fluorescence lifetimes are seen to be in the range of 5–18 ps, another evidence of ultra fast intersystem crossing from singlet excited state. This value is in good correlation with the literature data. Fox and Green [9] report fluorescence lifetimes for naphthalene diimides at lower values than 20 ps.

Politi and Brochsztain report that 1,4,5,8-naphthalene diimides are soluble in α-cyclodextrin (α-CD) via complex formation [8]. Absorption and emission spectra of *n*-butyl derivative of naphthalene diimide is being demonstrated in water solutions. *N*,*N*′-bis-*n*-butyl-1,4,5,8-naphthalenediimide (**V**) was stirred in 0.05 M aqueous solution of α-cyclodextrin for 6 h, warmed for 0.5 h and cooled solution was filtered from 0.2 μm pore size Acrodisc filters. Absorption spectrum of **V** had shown the bands at 387, 365 and 348 nm in α-CD aqueous solution, same as reported values. The emission spectrum, obtained at excitation of 345 nm, has yielded a quantum value Q_f of 0.031, that is five-fold higher with respect to Q_f of **V** in acetonitrile solution (Table 3). Literature reports the increase of Q_f of *n*-butyl derivative from 0.001 in acetonitrile to 0.014 in α-CD aqueous solution [8]. But all the attempts to dissolve all other six naphthalene derivatives in α-cyclodextrin have failed, in spite of warming and stirring for several days. No absorption spectra were detected from filtrates. It may be that only the *n*-butyl aliphatic chain fits into the cyclodextrin cone, as proposed by Politi and Brochsztain [8].

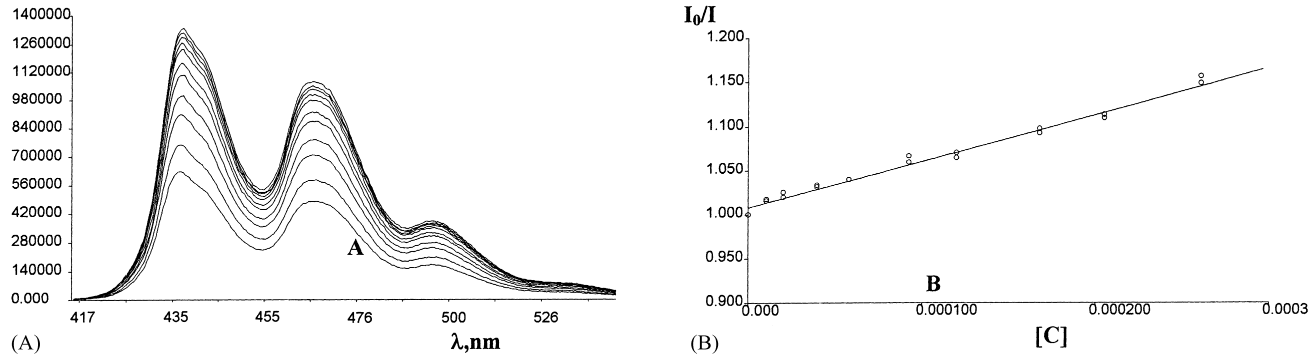


Fig. 5. Fluorescence quenching of perylene (λ_{exc}=nm) by *N*,*N*′-bis-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI) in acetonitrile at quencher concentrations of 1×10^{-5}–3×10^{-4} M (A) and the Stern–Volmer plot (B).

Table 4
Fluorescence quenching rate constants of condensed aromatic π-electron donor molecules by the addition of *N*,*N*′-bis-*N*-phenyl-1,4,5,8-naphthalendiimide (**I**; PNDI) in acetonitrile

Compound	k_q (M^{-1} s^{-1})
Naphthalene	$(2.63\pm0.55)\times10^{10}$
Phenanthrene	$(7.18\pm1.36)\times10^{10}$
Pyrene	$(1.91\pm0.24)\times10^{10}$
Perylene	$(7.62\pm0.65)\times10^{10}$

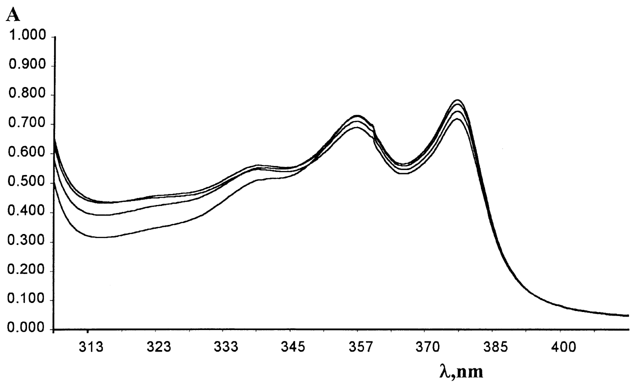
3.3. Fluorescence quenching studies

Naphthalene diimides are known to be electron acceptors [9]. *N*,*N*′-bis-aryl(alkyl)-1,4,5,8-naphthalenediimides are found to quench effectively the fluorescence emissions of aromatic donor molecules of naphthalene, phenanthrene, pyrene and perylene, in spite of their very low fluorescence quantum yields. Fig. 5 shows the quenching of fluorescence emissions of perylene by addition of *N*,*N*′-bis-*N*-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI) and the Stern–Volmer plot. All the spectra were corrected for inner and absorption effects before calculations. Calculated quenching rates are shown in Table 4. It is seen that quenching rates are on the diffusion limits for all the aromatic hydrocarbons. The differences of k_q values are seen to be about three-fold from naphthalene to phenanthrene (from 2.6×10^{10} to 7.2×10^{10} M^{-1} s^{-1}) and four-fold from pyrene to perylene (from 1.9×10^{10} to 7.6×10^{10} M^{-1} s^{-1}). These enhancements may be attributed to an increase on aromaticity of the condensed ring systems. A similar study with perylene diimides has resulted in enhancement of quenching rates in parallel to an increase in aromaticity of condensed rings [10]. But the rates of quenching were reported to have increased five-fold from naphthalene to phenanthrene (from 4.4×10^{11} to 2.8×10^{12} M^{-1} s^{-1}) and hundred-fold from phenanthrene to dihydrocarbazolo-carbazole (from 2.8×10^{12} to 2.5×10^{14} M^{-1} s^{-1}) in presence of perylene diimides. Energy transfer is seen to be more effective between aromatic donors and perylene diimides, compared to that between aromatic donors and naphthalene diimides. In general, fluorescence quenching of aromatic donors by naphthalene diimides and perylene diimides may be assumed to be at a comparative scale.

3.4. Photooxidations with naphthalenediimides

Similarities on molecular structures and on some photophysical properties between naphthalene diimides and perylene diimides, may suggest a similarity on photooxidations also [5,11]. Fluorescence quenching rates of aromatic hydrocarbons of naphthalene diimides, exceeding the diffusion limits ($k_q > 10^{10}$ M^{-1} s^{-1}), may point that an electron transfer may occur on irradiation leading to photochemical reactions. Photooxidation of styrene to benzaldehyde in acetonitrile solution was studied in presence of *N*,*N*′-bis-*N*-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI). The formation of benzaldehyde was monitored in UV spectra. PNDI is photostable under irradiation of 377 nm for 80 min. The UV spectra of PNDI with styrene in absence and in presence of ferric ions (ferric myristate) or cupric ions (cupric pivalate) during irradiation times of 0–75 min are given in Figs. 6 and 7, respectively. Perylene diimides are known to photooxidize olefins through singlet electron transfer yielding super oxide [5]. In order to compare, styrene was oxidized in acetonitrile solution with *N*,*N*′-bis-*N*-dehydroabietyl-3,4,9,10-perylenediimide, (PERIM) under the same conditions. The results are given in Table 5. It is seen that PNDI oxidizes styrene in 0.36% to benzaldehyde, where the same ratio is as 0.52% with PERIM, in absence of metal ions. In presence of ferric and cupric ions, photooxidation is enhanced both with PNDI and PERIM by about two-fold.

i) Irradiation of styrene solution at presence of PNDI



ii) Irradiation of styrene solution at presence of PNDI and Fe^{+3}

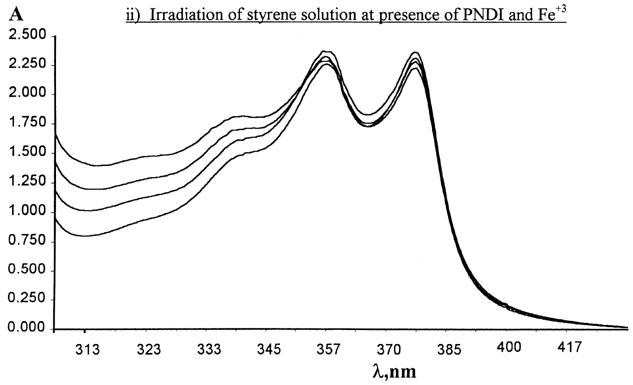


Fig. 6. UV absorption spectra of *N*,*N*′-bis-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI) in acetonitrile, during irradiation under 400 W sodium lamp for 0–75 min (i) in presence of styrene, and (ii) in presence of styrene and ferric myristate.

These results may suggest that the formation of super oxide from naphthalene diimide anion radical on photooxidation may be a logical route, as found in perylene diimides [5,11]. Formation of stable naphthalene diimide anion radical is proven at electrochemical reduction studies [12,13]. Fox and Politi report an effective intramolecular

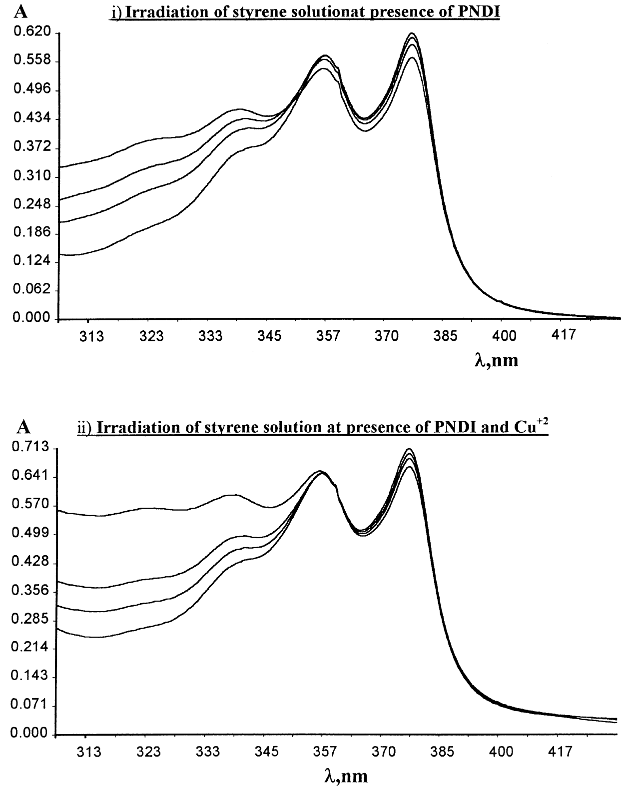
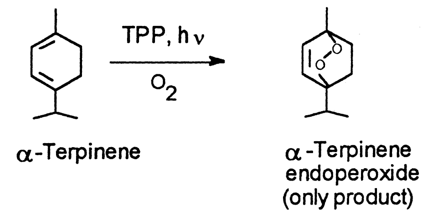


Fig. 7. UV absorption spectra of *N,N*′-bis-phenyl-1,4,5,8-naphthalene-diimide (**I**; PNDI), in acetonitrile, during irradiation under 400 W sodium lamp for 0–75 min (i) in presence of styrene, and (ii) in presence of styrene and cupric pivalate.

photoinduced electron transfer from nitroxyl radicals to 1,4,5,8-naphthalene diimide moiety [9]. In agreement with, Wasielewski has detected ultrafast photoinduced electron transfer in the triad molecule of zinc methyl 13^1-desoxo-pyropheophor-bide *a*-pyromellitide-1, 4, 5, 8-naphthalene-diimide [14]. It is expected that excited PNDI, molecule would abstract an electron from olefinic bonds to form a naphthalene diimide anion radical, that would transfer the electron to oxygen in an exciplex to cause oxidation reactions. The presence of metal ions of ferric and cupric, most likely promotes the rates of oxidation, via electron transfer from the naphthalene diimide anion radical to the metal ion in the exciplex, that may result in enhanced concentrations of olefin cation radical to react with superoxide anion or hydroperoxy radical (Scheme 1).The photoinduced rapid energy transfer from singlet to triplet $S_1 \rightarrow T_n$, suggests that an electron transfer would occur from triplet state in naphthalene diimides, in contrast to singlet excited state energy–electron transfer for perylene diimides. On the other hand Fox reports an energy gap of 27 kcal/mol for S_1-T_1 for *n*-dodecyl derivative of naphthalene diimide. Perylene diimides have the same S_1-T_1 energy gap. It seems that photo oxidative ability of naphthalene diimides are similar to perylene diimides.

α-Terpinene is known to produce endoperoxide adduct (ascardiol) on photooxidation with triplet sensitizers (rose bengal, tetraphenylporphrine-TPP).



It is also proven that α-terpinene is being converted to *p*-cymene in presence of perylene diimide [5] under solar irradiation, through a singlet state electron transfer in an exciplex, that forms hydroperoxy radicals reaching to *p*-cymene in radical chain reactions. α-Terpinene (0.1 M) and few mg of *N,N*′-bis-*N*-(*n*-butyl)-1,4,5,8-naphthalenediimide (**V**) (BNDI) in 100 ml acetonitrile, was irradiated with a 400 W sodium lamp for 15 h. Analysis in GC-MS has revealed the formation of a single product, identified as *p*-cymene (most abundant peaks in MS, *m/e*: 134; mp, 119 (bp); $MePhCHCH_2$, 91; Ph–CH_2, 77; Ph).

Table 5

Photooxidation of styrene in presence *N,N*′-bis-*N*-phenyl-1,4,5,8-naphthalenediimide (**I**; PNDI) or *N,N*′-bis-*N*-dehydroabietyl-3,4,9,10-perylenediimide (PERIM) with and without ferric(Fe^{3+}) and cupric(Cu^{2+}) ions after 75 min irradiation

Sensitizer	PNDI	PNDI	PERIM	PERIM
Sensitizer concentrations (M)	2.3×10^{-5}	7.3×10^{-5} M	1.9×10^{-5} M	0.6×10^{-5} M
Fe^{3+} (M)	–	3.6×10^{-4} M	–	3.6×10^{-4} M
Initial styrene concentration (M)	1.730	1.657	1.717	1.733
Benzaldehyde concentration (M)	0.0062	0.0174	0.0089	0.0106
Benzaldehyde yield (%)	0.36	1.05	0.52	0.61

Sensitizer	PNDI	PNDI
Sensitizer concentrations (M)	2.3×10^{-5}	7.3×10^{-5}
Cu^{2+} (M)	–	2.7×10^{-4}
Initial styrene concentration (M)	1.727	1.727
Benzaldehyde concentration	0.069 M	0.0110 M
Benzaldehyde yield (%)	0.40	0.64

$$\mathrm{PNDI} \xrightarrow{h\nu} \mathrm{PNDI^{*}}$$

$$\mathrm{PNDI^{*}} + \mathrm{olefin} \xrightarrow{e^{-}\text{transfer}} \underbrace{[\mathrm{PNDI^{(-\bullet)}} + \mathrm{olefin^{(+\bullet)}}]}_{\text{exciplex}}$$

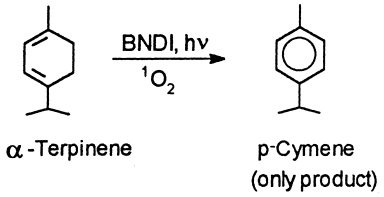
$$\underbrace{[\mathrm{PNDI^{(-\bullet)}} + \mathrm{olefin^{(+\bullet)}}]}_{\text{exciplex}} + \mathrm{O_2} \xrightarrow{e^{-}\text{transfer}} \mathrm{PNDI} + [\mathrm{olefin^{(+\bullet)}} + \underbrace{\mathrm{O_2^{(-\bullet)}}]}_{\text{superoxide}}$$

$$\mathrm{O_2^{(-\bullet)}} \xrightarrow[\text{olefin or solvent}]{\text{proton transfer from}} \underbrace{\mathrm{HOO^{\bullet}}}_{\text{hydroperoxy radical}}$$

$$\underbrace{[\mathrm{PNDI^{(-\bullet)}} + \mathrm{olefin^{(+\bullet)}}]}_{\text{exciplex}} + \mathrm{Fe^{+3}(Cu^{+2})} \xrightarrow{e^{-}\text{transfer}} \mathrm{PNDI} + \mathrm{olefin^{(+\bullet)}} + \mathrm{Fe^{+2}(Cu^{+})}$$

$$\mathrm{olefin^{(+\bullet)}} + \mathrm{O_2^{(-\bullet)}}\ (\text{or } \mathrm{HOO^{\bullet}}) \longrightarrow \text{olefin-hydroperoxide} \longrightarrow \text{Oxidation product}$$

Scheme 1.



These results prove that naphthalene diimides do not form singlet oxygen as the other triplet sensitizers. Electron transfer, from singlet or triplet level would produce the super oxide anion radical, which may cause the formation of hydroperoxyl radicals. Radical chain reactions of hydroperoxyl radicals would result in formation of benzaldehyde from styrene and *p*-cymene from α-terpinene. However, the mechanism of photoinduced energy–electron transfer with naphthalene diimides appear to be still unclear under the light of present data.

4. Conclusions

We have demonstrated that N-substituted naphthalene diimides have very short fluorescence lifetimes (5–18 ps) and quench the fluorescence emissions of electron donors above diffusion limits ($2\text{–}8\times10^{10}\ \mathrm{M^{-1}\,s^{-1}}$). It is detected that the solubility in α-cyclodextrin aqueous solution is only limited to *n*-butyl derivative, in contrast to generalization in literature. Photooxidation studies have proven that naphthalene diimides exert electron transfer via singlet or triplet excited state, no evidence to singlet oxygen reaction was observed. An ultrafast energy transfer from singlet excited state is evident, but the electron transfer from singlet or from triplet state is unclear.

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