

# Photooxidation quantum yield efficiencies of naphthalene diimides under concentrated sun light in comparisons with perylene diimides

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## Abstract

Thermal stabilities, solubilities redox potentials and photophysical parameters of 10 synthesized *N*-alkyl(aryl) derivatives of naphthalene diimides were studied for selecting the best derivatives at concentrated sun light experiments. *N*-aryl substitutions created better thermal stabilities than the *N*-alkyl substitution in naphthalene diimides. LUMO energy levels of NDIs, calculated from redox potentials, in the range of  $-3.55/-3.68$  eV, proved that the naphthalene diimides can inject electrons efficiently in titania based organic dye sensitized solar cells. Fluorescence lifetimes of naphthalene diimides,  $\tau_f = 11-34$  ps, are faster than that of perylene diimides,  $\tau_f = 4$  ns. Calculated photooxidation quantum yields with a naphthalene diimide photosensitizer for the direct sun light oxidation reaction of anthracene is  $\phi = 0.014$ , and for the concentrated sun light of 10.2 sun is  $\phi = 0.044$ . In general photooxidation quantum yield efficiencies of naphthalene diimides under concentrated sun light irradiations are found to be higher with respect to the perylene diimide photosensitizers, due to production of both singlet oxygen and superoxide anion radical and enhancement of low wavelength solar radiation with aluminium surfaced mirror under concentrated sun light.

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**Keywords:** Photooxidation; Quantum yields; Redox potentials; Naphthalene diimides; Fluorescence lifetimes; Fluorescence quenching

## 1. Introduction

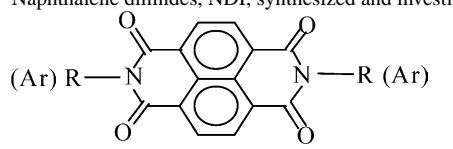
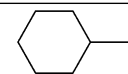
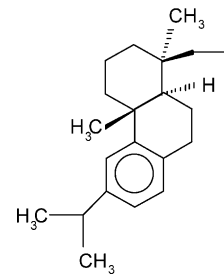
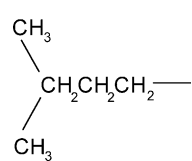
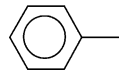
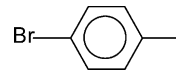
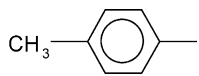
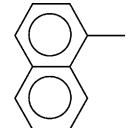
Naphthalene diimides, NDI, attract interests in biological and medical areas as well as in supramolecular chemistry and material science, based on their thermal and photo stabilities and as well efficient photo energy transfer abilities [1–4].

Photooxidation reactions are the major types for photo processes that are employed for the photosynthesis of fine chemicals. Quantum yields of these reactions can be calculated in laboratory conditions efficiently under constant irradiation conditions with lamps. Photooxidations under sun light are foreseen to have high potentials for technologi-

cal applications, specifically under concentrated sun light. In order to be able to achieve a true scientific correlation among the solar photooxidation processes, one has to be able to give the accurate number of photons absorbed by the chemical reactants at the reaction time and be able to calculate the quantum yields. A major problem for the outdoor solar photooxidations is the unpredictable solar irradiations; varies by day light period, date, geographical locations, atmospheric conditions, etc. The transfer of sun light into the spectrofluorometer laboratory room with a fiber optic cable during solar experiments, capabled us to measure quantum yields under direct/concentrated sun light fast and efficiently. An application of the measurement of quantum yields under concentrated sun light with the use of perylene diimides was done by Dincalp–Icli at photooxidation reactions [5].

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Table 1  
Naphthalene diimides, NDI, synthesized and investigated for photophysical parameters and for photoenergy transfer studies

 (Ar) R—N—C(=O)—C <sub>10</sub> H <sub>6</sub> —C(=O)—N—R (Ar)		[NDI]	
R-		R-	
<i>n</i> -Butyl [NDI]-I	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —	[NDI]-IV cyclohexyl	
<i>n</i> -Dodecyl [NDI]-II	CH <sub>3</sub> (CH) <sub>10</sub> CH <sub>2</sub> —	[NDI]-V dehydroabietyl	
Isoamyl [NDI]-III			
Ar-		Ar-	
Phenyl [NDI]-VI		[NDI]-VIII <i>p</i> -bromophenyl	
<i>p</i> -Toluidine [NDI]-VII		[NDI]-IX $\alpha$ -naphthyl	

This work is an application to the standard photooxidation reaction of anthracene in the presence of naphthalene diimide photosensitizer under direct and concentrated sun light.

NDIs are proven to form both the anion radical of oxygen and the singlet oxygen, ~10%, in presence of oxygen under irradiation > 350 nm [6]. *N*-alkyl derivative of NDIs reduce  $\alpha$ -terpinene to *p*-cymene, endoperoxide and oxygenated products during the photooxidation [7]. *N*-butyl NDI photooxidizes successfully citronellol to rose oxide under direct and concentrated sun light [8]. In general aromatic diimides have low solubilities in organic solvents. One of the possible approaches to overcome this solubility problem is the molecular modification of the naphthalene diimides – i.e. introduction of flanking bulky aliphatic and aromatic substituents in order to prevent aggregations [9]. We have synthesized seven derivatives of naphthalene diimides, studied photophysical parameters (Table 1), thermal stabilities, photo energy transfer on fluorescence emission quenching with aromatic donors, measured HOMO–LUMO energy levels for predictions on their capabilities in electrically conducting

systems. The aim to study the thermal stabilities, photophysical parameters and redox potentials at seven derivatives of naphthalene derivatives was to be able to select the most proper molecular model at photooxidation studies under concentrated sun light with an aromatic diimide photocatalyst. We have selected a reference compound anthracene for the solar photooxidation reaction, in presence of *N*-phenyl naphthalene diimide [NDI]-VI, under direct and concentrated sun light. Studied the quantum yield efficiencies of photooxidation reaction under varying intensity of sun light.

## 2. Experimental

### 2.1. Materials

Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), ferrocene, naphthalene, anthracene, pyrene, perylene were obtained from Fluka and Merck. The organic solvents which used in spectroscopic measurements (acetonitrile, chloroform) were of spectrophotometric grade.

## 2.2. Organic synthesis

The preparation method and molecular structures of naphthalene *N,N'*-disubstituted imides were explained in our previous articles [4,6,7].

## 2.3. Spectroscopic measurements

Fluorescence lifetimes of synthesized compounds were measured with a Time Correlated Single Photon Counting System. The fluorescence decay times and time-resolved spectra of naphthalene *N,N'*-disubstituted imides in chloroform solutions have been determined by the sub-nanosecond pulsed LEDs. The system consists of a pulsed laser driver and interchangeable LED heads. LED heads with center wavelengths of 460 nm are available and can be provided with optional spectral bandpass filters to excite samples with a narrow spectral range. In addition, the pulse width and power level can be tuned with the adjustable power level control of the PicoQuant driver, to tailor the pulse shape and power level to the application requirements. The fluorescence decay histograms were recorded in 2893 channels and the fluorescence decays were analyzed by using a Marquardt Algorithm (Knutson et al., 1983) with a multiexponential fluorescence decay fit (FluoFit) software. The quality of the fits has been judged by the fitting parameters such as  $\chi^2 < 1.2$  as well as by the visual inspection of the residuals and autocorrelation function (O'Connor and Phillips, 1984). The instrument response function (IRF) has been measured using a ludox scattering solution. All measurements have been performed in 1 cm optical path length cuvettes. The compounds have been dissolved in chloroform at an optical density of below 0.1.

TGA curves of NDI were taken by using Perkin-Elmer Thermogravimetric Analyzer Pyris 6 TGA. Cyclic voltammetry measurements were done with a Metrohm 746 VA Trace Analyser equipment. The intensity of the solar radiation between 300 and 800 nm was measured by a Kipp & Zonnen CM 11 piranometer as  $\text{W m}^{-2}$ .

Photooxidation processes were performed using an automatic focused solar concentrator as described previously [8].

## 3. Result and discussion

### 3.1. Thermal stabilities of naphthalene diimides

Naphthalene diimides are reported to be thermal and photostable molecules [7–9]. Thermal stabilities are best proven on their thermal gravimetry measurements. TGA curves of four NDI derivatives of *N,N'*-bis(*n*-butyl)-1,4,5,8-naphthalene diimide [NDI-I], *N,N'*-bis(*n*-dodecyl)-1,4,5,8-naphthalene diimide [NDI-II], *N,N'*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide [NDI-VI], and *N,N'*-bis(*p*-bromofenil)-1,4,5,8-naphthalene diimid [NDI-XI], were seen to give a thermal stability in a range of 300–470 °C.

*N,N'*-bis(*n*-butyl)-1,4,5,8-naphthalene diimide [NDI-I]; decomposition temperature starts from 300 °C and ends 398 °C.

*N,N'*-bis(*n*-dodecyl)-1,4,5,8-naphthalene diimide [NDI-II], loses 10% of its weight at 399 °C, 40% of its weight at 426 °C, 70% of its weight at 442 °C, and 86% of its weight at 451 °C. Decomposition temperature starts from 341 °C and ends 452 °C. The side chain on naphthalene diimide group is an aliphatic alkyl group with 12 carbons (Fig. 1).

*N,N'*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide [NDI-VI] has a bulky diterpene group with an aromatic ring. It appears to be more stable than other derivatives with aliphatic alkyl substituents. This molecule is the most soluble one because the presence of bulky flanking moiety [5]. Molecule loses 10% of its weight at 437 °C, 40% of its weight at 466 °C, 70% of its weight at 482 °C, 90% of its weight at 494 °C. Decomposition process is completed between 400 and 500 °C.

*N,N'*-bis(*p*-bromofenil)-1,4,5,8-naftalene diimid [NDI-XI], loses 10% of its weight at 469 °C, 40% of its weight at 510 °C, 70% of its weight at 528 °C, and 83% of its weight

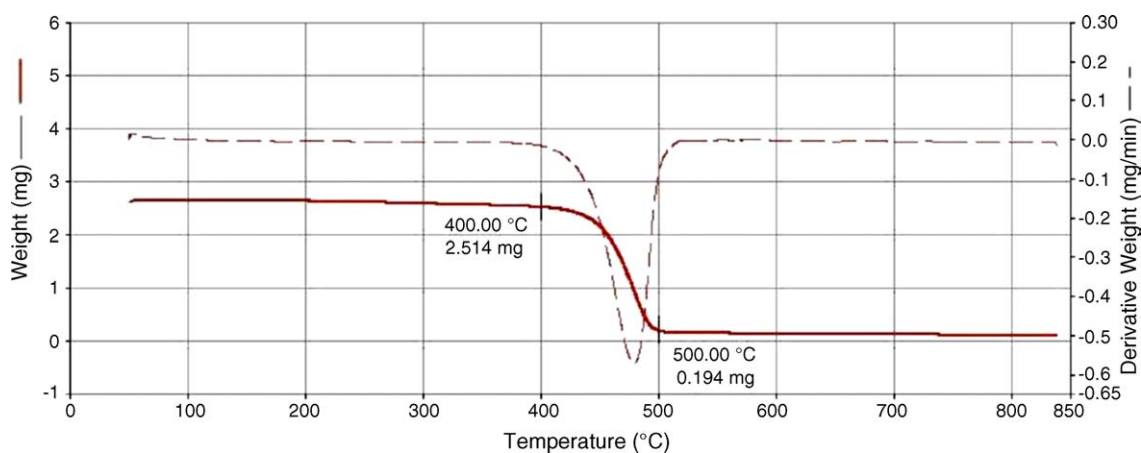


Fig. 1. TGA Curve of *N,N'*-bis(*n*-dodecyl)-1,4,5,8-naphthalene diimide [NDI-II].

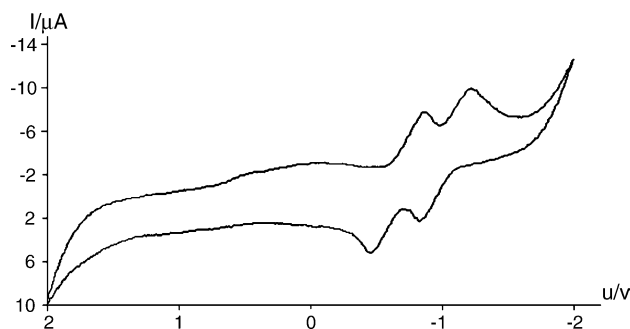


Fig. 2. Cyclic voltammogram of *N,N'*-bis(isoamyl)-1,4,5,8-naphthalene diimide [NDI-3].

at 537 °C. Decomposition process is completed between 400 and 537 °C. This result proves that presence of a pure aromatic *N*-substitution, thermal stability is the highest. Although temperature in the reaction vessels do not rise more than 5–10 °C, selection of *N*-aryl substituted naphthalene diimide derivatives for concentrated sun light experiments may be a better choice.

### 3.2. CV measurements for NDI derivatives

CV measurements for nine NDI derivatives were taken by using Metrohm 746 VA Trace Analyser equipment. For measurements, glassy carbon electrode as working electrode, Pt electrode as counter electrode, Ag/AgCl electrode as reference electrode were used. Solutions were prepared in chloroform as  $1 \times 10^{-3}$  M concentration. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), 0.1 M, was used as supporting electrolyte. In cyclic voltammetry measurement, ferrocene was used as internal reference electrode and scanning rate 100 mV/25 °C in inert atmosphere.

Cyclic Voltammogram of *N,N'*-bis(butyl)-1,4,5,8-naphthalene diimide [NDI-1], is seen in Fig. 2. In agreement with the CV data of reported earlier measurements for all of the NDI derivatives two reversible reductions were observed as first reduction potential,  $E_0 - E_{-1}$ , in the range of  $-0.48/-0.67$  V and second reduction potential,

Table 3

UV,  $\lambda_{\max}$  (nm) and fluorescence spectroscopy data, fluorescence quantum yields,  $\phi_f$ , fluorescence lifetime,  $\tau_f$  (ps) of NDI in acetonitrile

R (Ar)	$\lambda_{\max}$	$\tau_f$	$\phi_f$	$\lambda_{fl}^1$	$\lambda_{fl}^2$	$\lambda_{fl}^3$
Butyl [NDI-1]	376	14	0.006	394	409	435
<i>n</i> -Dodecyl [NDI-2]	378	15	0.006	392	403	436
Isoamyl [NDI-3]	377	15	0.005	395	409	435
Cyclohexyl [NDI-4]	377	11	0.004	392	409	442
Dehydroabietyl [NDI-5]	378	18	0.002	396	403	437
Phenyl [NDI-6]	376	30	0.002	395	403	437
<i>o</i> -Chloro phenyl [NDI-7]	375	12	0.002	395	405	437
<i>p</i> -Bromo phenyl [NDI-8]	376	11	0.002	395	404	441
<i>p</i> -Tolyl [NDI-9]	376	23	0.004	393	404	440
$\alpha$ -Naphthyl [NDI-10]	376	34	0.005	392	403	438

$E_{-1} - E_{-2}$ , in the range of  $-0.91/-1.10$  V [10,11]. The results are shown in Table 2. Cyclic voltogram measurements confirm the electron acceptor capabilities of naphthalene diimides in reduction process. LUMO energy values for NDI derivatives were calculated by using CV voltammogram. In calculations, for zero vacuum level belong to ferrocene was taken as 4.8 eV. The equation employed at calculations of redox potentials and HOMO–LUMO energies NDIs is;  $E_{LUMO} = -e(E_{1/2(\text{redox})} - E_{\text{fer}} + 4.8)$ ,  $E_{HOMO} = hc/\lambda_{\text{offset}} - E_{LUMO}$ , where  $hc = 1240$  eV,  $\lambda_{\text{offset}} = 400$  nm,  $E_{\text{average}}$  values are the average of first and second reduction potentials, and  $E_{\text{fer}}$  is 0.39 V (versus Ag/AgCl). LUMO energy levels of NDIs are in the range of  $-3.55/-3.68$  eV. This value is higher than for the TiO<sub>2</sub>;  $-4.2$  eV and similar to the perylene diimides;  $-3.5/-3.7$  eV [12]. A clear indication that the naphthalene diimides can present photo electron injection capabilities in organic dye sensitized solar cells [13]. A basic handicap is very low absorption of NDIs in the visible region.

### 3.3. Fluorescence lifetime and quenching studies measurements studies

UV absorbance and fluorescence spectroscopy data are seen in Table 3. Fluorescence lifetime measurements are done with

Table 2

Redox potentials and LUMO–HOMO energy levels of naphthalene diimides calculated from cyclic voltammetry measurements

R (Ar)	$E_0 - E_{-1}^a$ (Volt)	$E_{-1} - E_{-2}^b$ (Volt)	$E_{\text{average}}^c$ (Volt)	LUMO (eV)	HOMO (eV)
Butyl [NDI-1]	−0.58	−1.10	−0.84	−3.57	−6.67
<i>n</i> -Dodecyl [NDI-2]	−0.66	−0.99	−0.83	−3.58	−6.68
Isoamyl [NDI-3]	−0.65	−1.05	−0.85	−3.56	−6.66
Cyclohexyl [NDI-5]	−0.67	−1.05	−0.86	−3.55	−6.65
Dehydroabietyl [NDI-6]	−0.66	−1.05	−0.86	−3.55	−6.65
Phenyl [NDI-7]	−0.55	−0.95	−0.75	−3.66	−6.76
<i>p</i> -Bromophenyl [NDI-11]	−0.54	−0.91	−0.73	−3.68	−6.78
<i>p</i> -Tolyl [NDI-12]	−0.59	−1.04	−0.81	−3.59	−6.69
$\alpha$ -Naphthyl [NDI-13]	−0.48	−0.95	−0.71	−3.69	−6.79

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

<sup>a</sup>  $E_0 - E_{-1}$  = first reduction potential for NDI derivatives.

<sup>b</sup>  $E_{-1} - E_{-2}$  = second reduction potential for NDI derivatives.

<sup>c</sup>  $E_{\text{average}}$  = the average of first and second reduction potentials used for calculation of LUMO–HOMO energy levels.

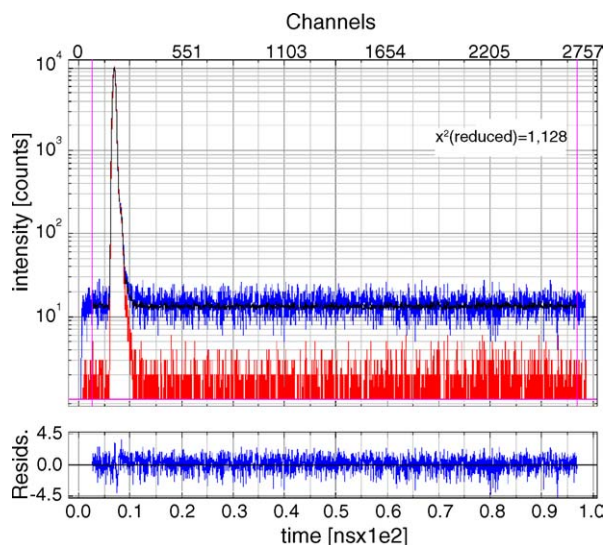


Fig. 3. The fluorescence lifetime scattering of *N,N'*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide [NDI-5].

time resolved fluorescence spectrophotometer at picosecond accuracies (Fig. 3). Absorbance, emission, fluorescence life times and fluorescence quantum yields of 10 naphthalene diimide derivatives are in agreement with the similar data that are given in earlier reports [4,6–11]. Fluorescence lifetimes of naphthalene diimides,  $\tau_f = 11\text{--}34$  ps, are faster than that of perylene diimides,  $\tau_f = 4$  ns [14], which may be attributed to the higher number of condensed aromatic rings in perylene moiety (Fig. 4).

Naphthalene diimides are well-known as electron acceptors [2–4,6–10]. Fluorescence quenching rate constants,  $k_q$ , were calculated using the Stern–Volmer plots [7] (Fig. 5). In order to avoid the aggregation effects, most soluble derivative among the 10 NDIs, *N,N'*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide is chosen for quenching experiments [6]. Concentration of quencher solution in chloroform [NDI-3], *N,N'*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide was  $10^{-3}$  M. All of the chloroform solutions of the

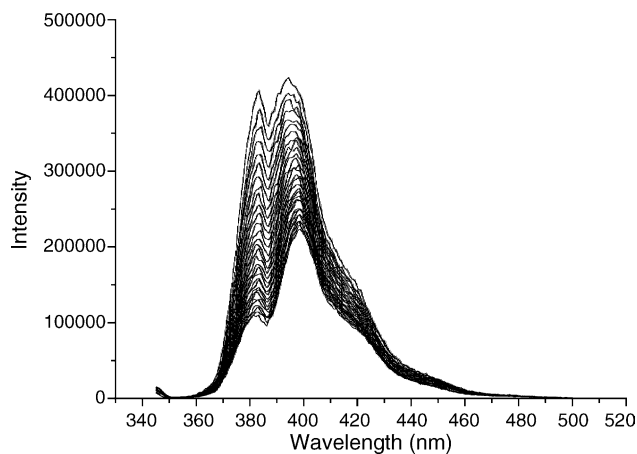


Fig. 4. Fluorescence emission quenching of pyrene in chloroform solution, with increasing [NDI-5] concentration.

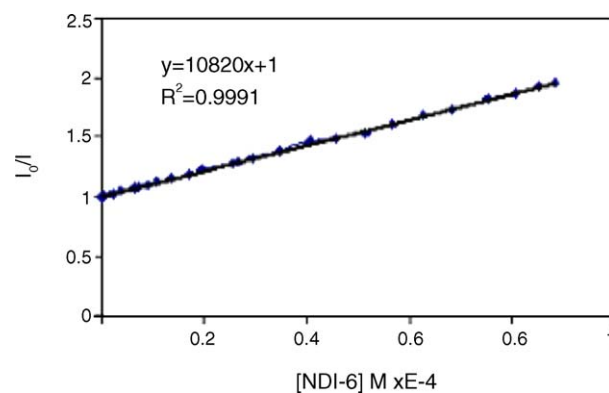


Fig. 5. Stern–Volmer plot.

Table 4

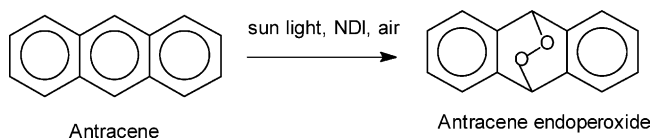
Fluorescence quenching rate constants of aromatic donor molecules by addition of *N,N'*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide in chloroform

Donor molecule	$k_q$ ( $\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ )
Naphthalene	1.1
Anthracene	1.5
Pyrene	2.3
Perylene	2.5

aromatic donor molecules, naphthalene, anthracene, pyrene, perylene, were prepared at  $10^{-5}$  M. Fluorescence quenching measurements were carried out each time by adding 20  $\mu\text{l}$  of quencher into donor molecule solution. This process was repeated 30 times. The quenching rates are found to increase from  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  to  $2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , with the increase of  $\pi$ -electron donor capacity of the quencher molecule. A similar trend is seen with perylene diimides but at higher quencher rates,  $10^{12} \text{ M}^{-1} \text{ s}^{-1}$  [15], which may be again attributed to the presence of higher number of condensed aromatic rings (Table 4).

### 3.4. Actinometry studies

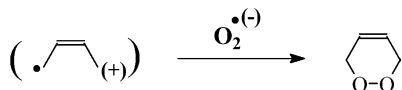
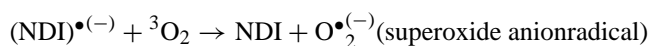
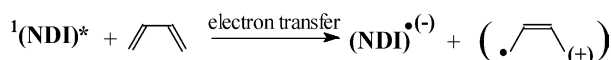
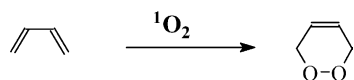
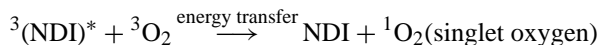
Naphthalene diimide—NDI photosensitizers are known to produce singlet oxygen as well as super oxide anion radical in presence of oxygen [4,6–10]. Anthracene is expected to give an endoperoxide product with singlet oxygen or oxygenated products at 9,10-positions with super oxide anion radical in presence of NDI, direct or concentrated sun light at aerated solutions. One can measure the rate of oxidation by recording the absorbance and/or fluorescence emission band of anthracene during course of solar irradiation.



Singlet oxygen is known to form from the triplet excited state and superoxide anion radical to form from the singlet excited state of naphthalene diimide, NDI. Naphthalene



diimides are reported to form both the singlet oxygen by energy transfer and superoxide anion radical through the formation of cation radical by electron transfer [8]. NDI photocatalyst generated photooxidation reaction mechanisms both with the singlet oxygen and the superoxide anion radical is shown in the scheme below:



Naphthalene diimide is expected to photooxidize unsaturated organic molecular structures more efficiently with respect to perylene diimides by the formation of two oxidative reagents of singlet oxygen and superoxide anion radical. Perylene diimides, singlet photosensitizers form only superoxide anion radical. Disadvantage of naphthalene diimides at solar photooxidation reactions is they absorb only a small part of solar spectrum, where perylene diimides absorb more in visible region.

The quantum yield  $\phi$  for photooxidation of anthracene was calculated using the following equation [16,17].

$$\phi = \frac{C_o - C_t}{I_{\text{abs}} / V_R t}$$

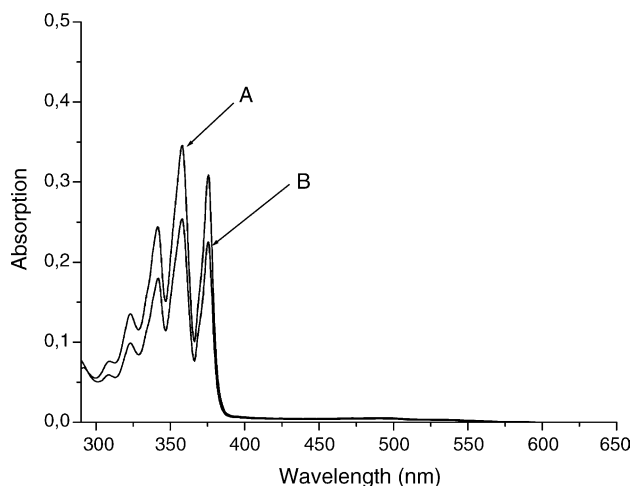


Fig. 6. The absorption spectra of anthracene (A) before irradiation under direct sun light, (B) after irradiation under direct sun light (1 sun), in presence of phenyl derivative [NDI-VI] in air bubbled acetonitrile solution. Anthracene (before irradiation):  $[c_0] = 1.76 \times 10^{-6}$  M,  $\lambda_1 = 323$  nm,  $\lambda_2 = 339$  nm,  $\lambda_3 = 356$  nm,  $\lambda_4 = 374$  nm.

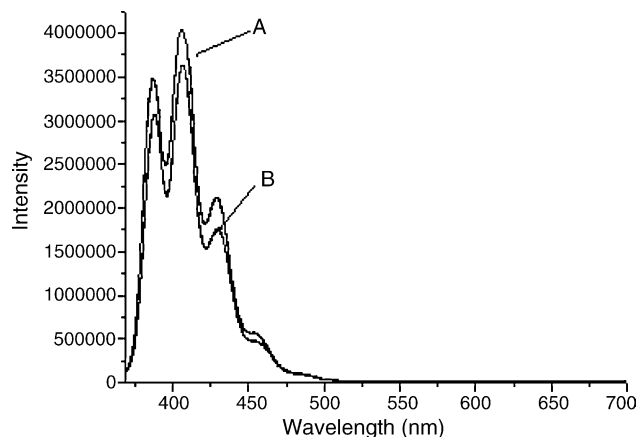


Fig. 7. Fluorescence emission spectra of anthracene (A) before irradiation under direct sun light ( $\lambda_{\text{exc}} = 366$  nm), (B) after irradiation under direct sun light (1 sun), in presence of phenyl derivative [NDI-VI] in air bubbled acetonitrile solution. Anthracene:  $[c_0] = 1.76 \times 10^{-6}$  M.

where  $C_o$  and  $C_t$  are the anthracene concentrations prior to and after the irradiation,  $V_R$  the reaction volume,  $t$  the irradiation time per cycle in seconds, and  $I_{\text{abs}}$  is

$$I_{\text{abs}} = \alpha \left[ \frac{I_o}{N_A} \right] \quad \text{with } \alpha = 1 - 10^{-A}$$

$$I_o = 0.975 E (4.716 \times 10^8)^{-1} S_A N_A$$

where  $A$  is the absorbance of naphthalene diimide sensitizer,  $I_o$  the intensity of the incident light in photons  $\text{s}^{-1}$ ,  $E$  the incident solar energy in  $\text{mW cm}^{-2}$ ,  $4.716 \times 10^8$  the number of milijoules per einstein,  $S_A$  the surface area of the reaction vessel,  $12 \text{ cm}^2$  at direct sun light and concentrated sun light experiments,  $N_A$  is the Avogadro's constant. Direct sun light,

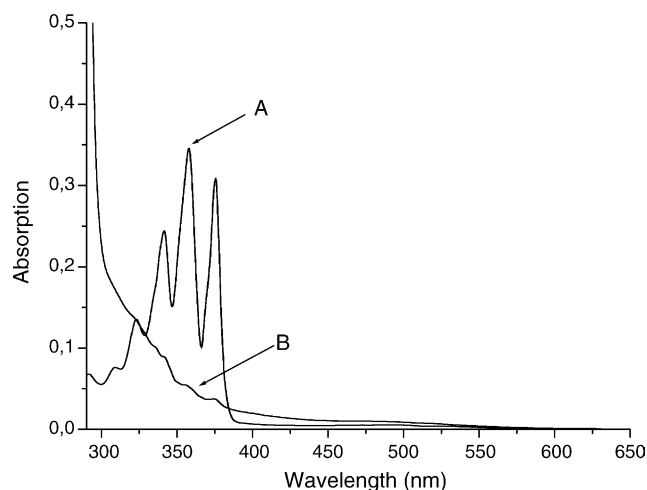


Fig. 8. The absorption spectra of anthracene (A) before irradiation under concentrated sun light, (B) after irradiation under concentrated sun light (10.2 sun), in presence of phenyl derivative [NDI-VI] in air bubbled acetonitrile solution. Anthracene:  $[c_0] = 1.76 \times 10^{-6}$  M,  $\lambda_1 = 323$  nm,  $\lambda_2 = 339$  nm,  $\lambda_3 = 356$  nm,  $\lambda_4 = 374$  nm.

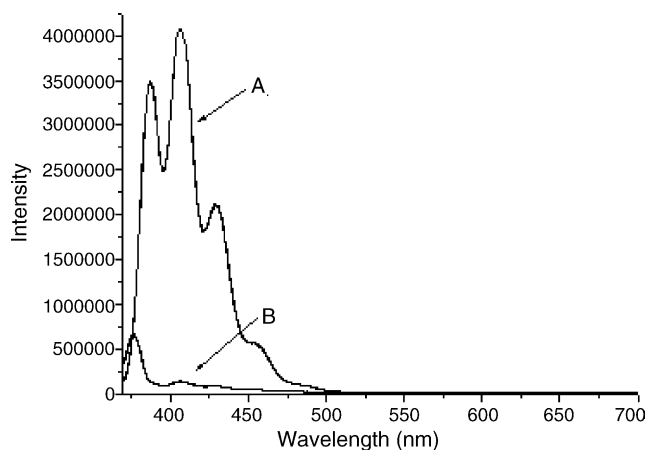


Fig. 9. Fluorescence emission spectra of anthracene (A) before irradiation under concentrated sun light ( $\lambda_{\text{exc}} = 366 \text{ nm}$ ), (B) after irradiation under concentrated sun light (10.2 sun), in presence of phenyl derivative [NDI-VI] in air bubbled acetonitrile solution. Anthracene:  $[c_0] = 1.76 \times 10^{-6} \text{ M}$ .

on 20 February at 12.30 h is taken as 1 sun, and the intensity of the concentrated sun light is 10.2 sun as found by the recorded emission spectrum of sun light, transferred into the laboratory by a fiber optic cable. Total irradiation values are found to be  $1.679 \times 10^{17} \text{ photons s}^{-1}$  for direct sun light and  $1.713 \times 10^{18} \text{ photons s}^{-1}$  for concentrated sun light on the reaction vessel, by the use of fiber optic actinometry method [5]. Calculated quantum yields for the direct sun light photooxidation reaction of anthracene is  $\phi = 0.014$ , and for the concentrated sun light of 10.2 sun is  $\phi = 0.044$ . It appears that 10-fold increase of sun light intensity results in three-fold enhancement of quantum yield efficiency, in presence of naphthalene diimide photo-sensitizer. A photooxidation quantum yield value of  $\phi = 0.015$  with a perylene diimide sensitizer under concentrated sun light (20 sun) was reported earlier by us at photooxidation reaction of cinnamic acid in protic solvent of methanol [5]. Although anthracene is an aromatic hydrocarbon and cinnamic acid is an olefin, this result may prove that naphthalene diimides give more vigorous photooxidation under concentrated sun light. Another evidence is seen at photooxidation reaction of citronellol olefin to rose oxide, under concentrated sun light, both with naphthalene diimide and perylene diimide sensitizers, NDI was superior to perylene diimide [8]. Perylene diimides capable of producing only superoxide anion radical in aerated solutions, whereas naphthalene diimides produce both super oxide anion radical and singlet oxygen [8]. Therefore, photooxidation quantum yield efficiencies of naphthalene diimides are thought to be higher with respect to the perylene diimides under concentrated sun light even though naphthalene diimides absorb a small portion solar spectrum, if the sun light is being concentrated by the use of an aluminium surfaced mirror. An aluminium mirror is known to reflect low wavelength part of

the solar spectrum, but a silver surfaced mirror do not reflect the radiation below 400 nm (Figs. 6–9).

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