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Excited state properties of bis-1,8-naphthalimides

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Abstract

A series of novel bis-1,8-naphthalimides (bis-1,8-NI), each of which consists of a 4-alkylamino-1,8-NI electron donor and an unsubstituted 1,8-NI electron acceptor, has been investigated. Time-resolved fluorescence and fluorescence quantum yields have been measured and the results indicate that fluorescence arising from the 4-alkylamino-1,8-NI residue can be quenched by intramolecular charge transfer from the 4-alkylamino-1,8-NI donor to the un-substituted 1,8-NI acceptor. The transient triplet absorption for the un-substituted 1,8-NI component in bis-1,8-NI has been studied by selective excitation using a 337 nm N_2 laser. We found that triplet quenching is an intramolecular process, and that the triplet quenching rate is faster than that of monomeric 1,8-NI quenched by external aliphatic amine in a solvent. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 1,8-Naphthalimide (1,8-NI); Fluorescence quantum yield; Singlet state; Triplet state

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1. Introduction

Due to its special photophysical properties and high charge generation, naphthalimide and its derivatives have been the subject of many studies [1–10]. Related work has involved the development of NI-contained supramolecular systems that exhibit ultrafast molecular photoswitchable properties [11,12]. Studies designed to develop photoinduced electron transfer models that mimic the essential feature of the bacterial photosynthetic reaction center in natural systems have been undertaken [13–17].

To further elucidate the connection between molecular structure and the emission properties of NI derivatives, chemists have undertaken new studies pertaining to naphthalimide derivatives [1–3,7–10]. Recently, de Silva [18] and our group [19] developed different kinds of 4-aminonaphthalimide model systems, and found that the excited state dipole of the fluorophore directs the electron flow. Due to rapid photoinduced electron transfer from the amino group to the naphthalimide moiety (fluorophore), many aminoalkyl-substituted fluorophores show weak fluorescence in basic solution. However, when the amino group is protonated, electron transfer is quenched and fluorescence recovers. These results revealed that electron transfer occurs along the aminoalkyl-to-fluorophore pathway.

Although considerable effort has been devoted to characterizing the photophysical behavior of 1,8-NI and its substituted derivatives, investigations involving bis-1,8-NI have been carried out less extensively, probably due to that fact that bis-1,8-NI

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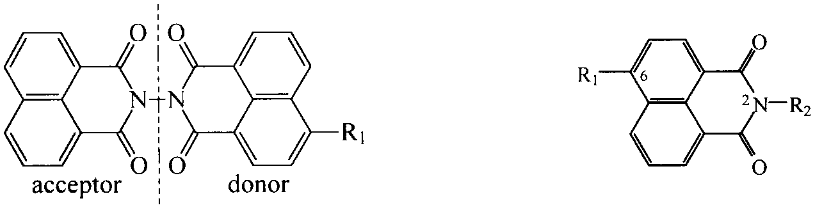
compounds are not readily available. In the field of medicine, bis-1,8-NI has been shown to possess significant anticancer activity [20] and has already entered clinical trials [21]. This compound also exhibits promising antiviral agents, with selective in vitro activity against the human immune deficiency virus, HIV-1 [22]. Furthermore, pronounced electroluminescence (EL) [23] and photorefractivity have also been observed in bis-1,8-NI compound [24,25]. Therefore, it seemed logical to study the photophysical properties of bis-1,8-NI. Further impetus for such a study arises from the occurrence of intramolecular charge transfer (ICT) in bis-1,8-NI. Determination of the relation between structure and the excited states of bis-1,8-NI compounds is essential to understanding EL and photorefractivity phenomena associated with these compounds.

The compounds studied in this paper are a series of novel bis-1,8-NI compounds, each of which consists of a 4-alkylamino-1,8-NI and an unsubstituted 1,8-NI with an N-N linkage joining the NI moieties. In these compounds, the 4-alkylamino-1,8-NI is an electron donor and the unsubstituted 1,8-NI is an electron acceptor [9,25]. Fig. 1 shows the chemical structures of the bis-1,8-NI compounds and their monomeric counterparts. It is worth noting that the N−N bond is important to establishing ultrafast molecular photoswitching. because the response rate is related to the distance between donor and acceptor [12].

2. Results and discussion

It is well known that the fluorescence of monomeric 4-alkylamino-1,8-NI compounds is derived from the radioactive decay of its excited singlet state, which is formed by a singlet $^1(n \rightarrow \pi^*)$ transition. Charge transfer (CT) from the nitrogen atom of the 4-alkylamino to the imide side of the NI compound is also a contributor [1,3,15]. The CT process is influenced by two factors, viz. the electron-donating ability of the 4-alkylamino group, which enhances the CT process and increases the fluorescence quantum yield (ϕ_f) [1], and the peri-effect, which causes lack of planarity between the 4-alkylamino group and the NI ring. The electron donating ability of the 4-alkylamino groups is in the order [1]: $\text{-N(CH}_3)_2 > \text{-NH(CH}_2)_3\text{CH}_3 \simeq \text{-NH(CH}_2)_7\text{CH}_3 > \text{-NH}_2$. With regard to the second factor, it is known that steric interaction occurs between one of the alkyl groups and the H-5 ring proton. CT is inhibited by the peri-effect [1].

The influence of the 4-alkylamino group on ϕ_f of monomeric 4-alkylamino-1,8-NI is determined



bis-1,8-NI compounds **monomeric 1,8-NI compounds**

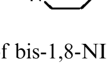
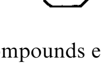
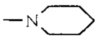
bis-1,8-NI compounds	R_1	*monomeric 1,8-NI compounds*	R_1	R_2
ANI-NI	-NH_2	ANI	-NH_2	$\text{-(CH}_2)_3\text{CH}_3$
DMANI-NI	$\text{-N(CH}_3)_2$	DMANI	$\text{-N(CH}_3)_2$	$\text{-(CH}_2)_3\text{CH}_3$
BANI-NI	$\text{-NH(CH}_2)_3\text{CH}_3$	BANI	$\text{-NH(CH}_2)_3\text{CH}_3$	$\text{-(CH}_2)_3\text{CH}_3$
OANI-NI	$\text{-NH(CH}_2)_7\text{CH}_3$	OANI	$\text{-NH(CH}_2)_7\text{CH}_3$	$\text{-(CH}_2)_7\text{CH}_3$
HPNI-NI		HPNI		C_6H_5

Fig. 1. Structures of bis-1,8-NI compounds and monomeric 4-alkylamino-1,8-NI compounds employed in the study.

by a combination of the above two factors. For DMANI, due to a significant peri-effect, CT is greatly inhibited despite the relatively high electron-donating ability of the dimethylamino group and this led to a very low ϕ_f (0.034) [1]. For BANI and OANI, the peri-effect is minimised by the alignment of the substituent so that the peri-hydrogen and that of the alkylamino groups are close and the alkyl group points away from the peri proton. Compound HPNI, which has a piperidino group instead of a dimethylamino, afforded ϕ_f of 0.72 [15]. Wasielewski et al. [15] believed that the enhanced fluorescence is due to a considerably decreased peri-effect arising from the cyclic structure of the alkylamino group. In this case, a planar molecule leads to reduced interaction between the 4-alkylamino and H-5 and stronger $^1(n \rightarrow \pi^*)$ change transfer. Table 1 shows ϕ_f values for different monomeric 4-alkylamino-1,8-NI compounds, and it is clear that the sequence $\phi_f(\text{BANI}) \approx \phi_f(\text{OANI}) > \phi_f(\text{ANI}) \gg \phi_f$ (DMANI) [1] does not correspond to the electron-donating ability of alkylamino groups.

Table 1
Fluorescence quantum yeild $(\phi_f)^b$ for bis 1,8-NI compounds and monomeric counterparts (excited at 440 nm)

4-Alkylamino Group	ϕ_f of monomeric 4-alkylamino-1,8-NI (in EtOH 1×10^{-5}M)	ϕ_f of bis-1,8-NI (in THF 1×10^{-5}M)
-NH_2	ANI 0.640[a]	ANI-NI 0.22
-$N(CH_3)_2$	DMANI 0.034[a]	DMANI-NI 0.51
-$N(CH_2)_7CH_3$	BANI 0.810[a]	BANI-NI 0.38
-$N(CH_3)_2CH_3$	OANI 0.72[a]	OANI-NI 0.36
	HPNI 0.72[c] (in THF)	

[a] Data from [1]:.

[b] Fluorescein in 0.1 mol dm^{-3} NaOH (ϕ_f=0.90) is used as a quantum yield standards. The fluorescence quantum yield is calculated for the relationship [1]. $\phi_x = \frac{F_x}{F_{\text{std}}}\cdot\left(\frac{n_x}{n_{\text{std}}}\right)^2\cdot\frac{\varepsilon_{\text{std}}C_{\text{std}}}{\varepsilon_x C_x}\cdot\phi_{\text{std}}$, where x refers to the sample, and std to the standard. F represents the integrated area under the emission band, n is is the refractive index of solvent, ϵ is molar extinction coefficient (10^4 dm^3 mol^{-1} cm^{-1}) and C is concentration (mol dm^{-3}) [26].

[c] Data from [15].

Although the ϕ_f of bis-1,8-NI was measured in a solvent (THF) of low polarity, ϕ_f of bis-1,8-NI is generally lower than that of the corresponding monomeric 4-alkylamino-1,8-NI in the highly polar solvent EtOH. An exception is compound DMANI-NI, whose ϕ_f is much higher than its monomeric counterpart DMANI. It is proposed that the large dipole moment of the lowest excited singlet state will give rise to a strong photo-generated electric field. A molecular electric field of this type can, depending on its sign and magnitude, inhibit or accelerate an electron transition in the model compounds. If an additional electron acceptor attached to the acceptor side of the bis-naphthalimides, making the acceptor in alignment with the molecular electric field of 4-alkylamino-1,8-NI [2], such molecular electric field will be enhanced [27]. Furthermore, the conjugated π-system is extended [15], and the time required to reach the maximum fluorescence intensity should increase because of the prolonged CT distance of the bis-1,8-NI systems (see Fig. 2). Conversion of the singlet 4-alkylamino-1,8-NI residue to a higher CT step by joining two NI components via. N—N bond competes with the radioactive decay of singlet

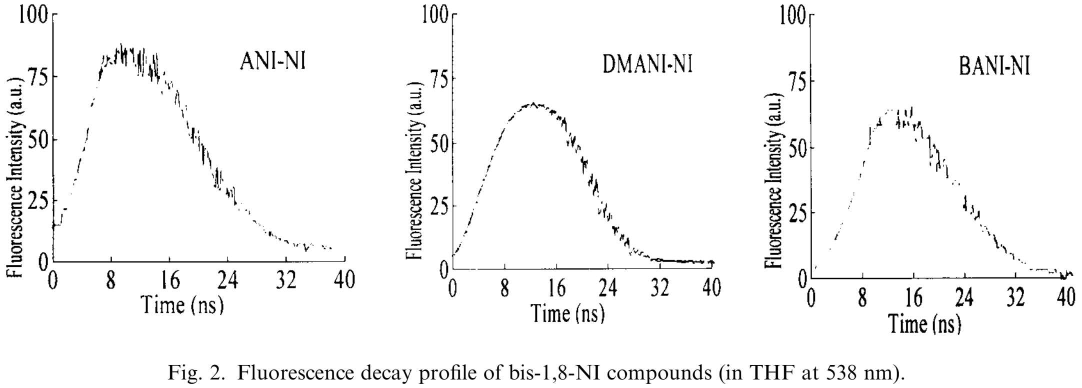


Fig. 2. Fluorescence decay profile of bis-1,8-NI compounds (in THF at 538 nm).

4-alkylamino-1,8-NI [15] and quenches its fluorescence. Similar fluorescence quenching, via CT from the 4-alkylamino-1,8-NI donor to the unsubstituted 1,8-NI acceptor, was observed in bis-1,8-NI compounds ANI-NI, BANI-NI and OANI-NI (see Table 1). In the case of DMANI-NI, however, fluorescence is enhanced.

In the case of DMANI-NI, the enhanced molecular electric field discussed above has two side effects. On the one hand, it causes CT from the DMANI component to the NI component and quenches the fluorescence of the former. On the other hand, the reduction in CT from the 4-nitrogen atom to the imide side of the DMANI residue due to a peri-effect, can be overcome by an enhanced molecular electric field. Thus, the fluorescence of the DMANI component is intensified with $\phi_f = 0.51$ for DMANI-NI versus 0.034 for DMANI. It should be pointed out that a similar fluorescence enhancement from the increased molecular electric field is not exhibited in the compounds without a peri-effect, e.g. ANI-NI, BANI-NI and OANI-NI.

In addition, the ground state absorption spectra of a bis-1,8-NI compounds such as ANI-NI correspond to the sum of the spectra of the corresponding individual components (see Fig. 3 and Table 2). This indicates that the interaction between donor and acceptor molecules is weak in the ground state which favors the formation of a charge separated state by CT from donor to acceptor [15].

The characteristic absorption bands of the triplet state and the radical anion of unsubstituted 1,8-NI are in the range of 470–500 nm and 400–425 nm, respectively [4,7]. The wavelength gap between principal absorption bands of the above species was distinct enough to allow us to detect the triplet state of the unsubstituted 1,8-NI component in bis-1,8-NI unambiguously. The triplet state appeared as a transient absorption at 488 nm (see Fig. 4 and Table 3), following excitation by 337 nm laser light. Each spectrum in Fig. 4 was recorded after laser flash photolysis (6–7 ns duration) in deaerated THF. The laser intensity was 30 mJ pulse^{-1}. We found that laser excitation at 337 nm and 298 K can efficiently excite the un-substituted 1,8-NI component of bis-1,8-NI because the characteristic absorption band of 1,8-NI at ground state ranges from 322 to 340 nm in THF (see Fig. 3 and Table 2).

The triplet lifetime of bis-1,8-NI compounds was less than 10 μs, much shorter than the reported

Table 2
Absorption and fluorescence lifetimes (τ_f) for bis-1,8-NI compounds (in THF 1×10^{-5}M)

bis-1,8-NI	λ^{abs}_{max}/ nm	$\epsilon/10^4$cm^{-1} mol^{-1}l	λ^{Ex}/ nm	λ^{Em}_{max}/ nm	τ_f/ns
ANI-NI	330.4	1.552	330.6	365.2, 506.1	10
	442.4	1.346	422.4	503.9	
DMANI-NI	332.0	0.99	332.0	364.6, 505.8	10.5
	412.0	1.23	422.0	503.8	
BANI-NI	329.8	0.72	329.8	364.7, 509.1	10.5
	422.2	0.735	422.2	505.1	
OANI-NI	330.5	0.743	330.5	365.1, 508.1	
	434.0	0.755	434.0	505.6	

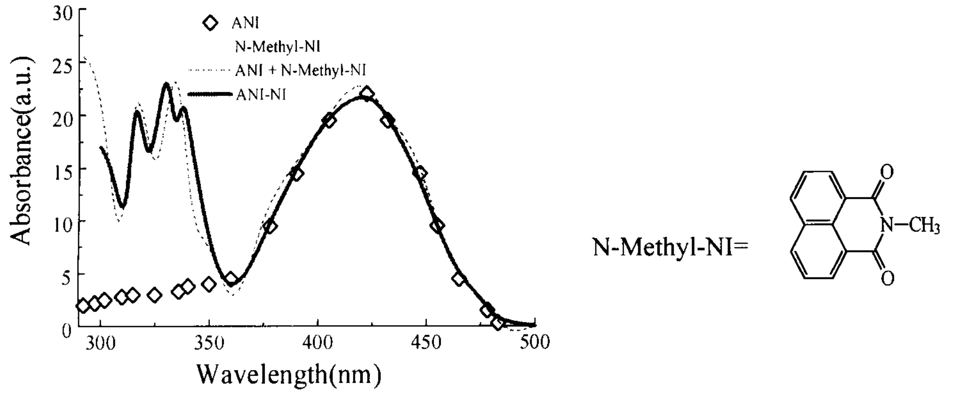
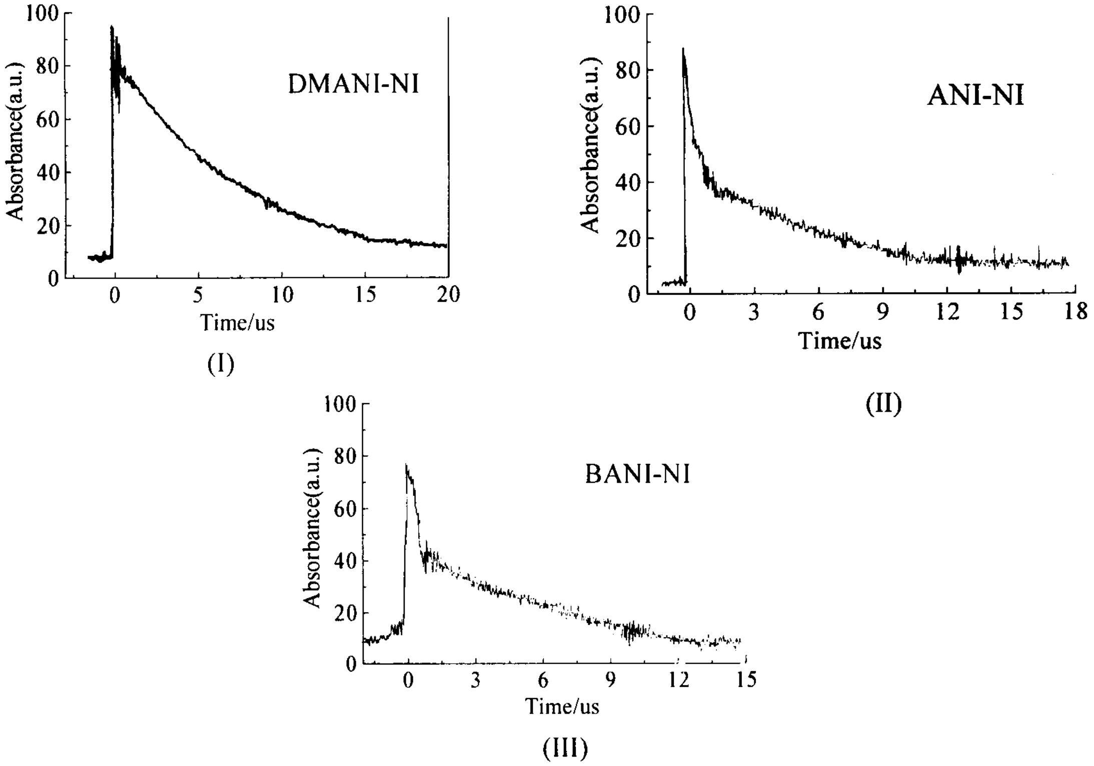


Fig. 3. Ground state absorption spectra of ANI-NI, N-Methyl-NI and ANI (in THF).



(I)

(II)

(III)

Fig. 4. Transient absorption at 488 nm for the unsubstituted 1,8-NI component in DMANI-NI(**I**), ANI-NI(**II**) and BANI-NI(**III**).

value of monomeric 1,8-NI, which is in the range of a few tenths of microseconds [7].

Table 3
Triplet decay lifetime (τ_T) and quenching rate constant ($k^T{}_q$) for bis -1,8-NI (in THF 1×10^{-5} M)

Compounds	τ_T (μs)	$k^T{}_q$ ($\times10^{10}$dm^3 mol^{-1}s^{-1})
ANI-NI	6.5	1.54
DANI-NI	9.0	1.1
BANI-NI	5.0	2.0

It is also known that the triplet state of 1,8-NI is quenched by aliphatic amines in organic solvents, through the formation of an intermolecular radical ion pair [7,8]. The k_q^T afforded by external aliphatic amine triplet quenchers triethylamine or triphenylamine) is 1-3$\times10^9$ dm^3 mol^{-1} s^{-1} [7,8]. Thus, it is reasonable to suggest that for bis-1,8-NI compounds, the triplet quencher is the 4-alkylamino groups on the ANI, DMANI and BANI of component bis-1,8-NI compounds. Because the ratio of the unsubstituted 1,8-NI component to 4-alkylamino group is invariably equal to 1, it is not possible to obtain k_q^T from the slope of a plot of τ_T^{-1} vs concentration of quencher. Therefore, the k_q^T of bis-1,8-NI (see Table 3) was derived directly from the ratio of τ_T^{-1} to the concentration of quencher (quencher), where [quencher] = 1×10^{-5} M. Table 3 shows that k_q^T of the unsubstituted 1,8-NI component in bis-1,8-NI is an order of magnitude higher than that quenched by external aliphatic amine. The triplet quenching of monomeric 1,8-NI by an external aliphatic amine quencher involves a transformation from the triplet state to a solvent separated ion pair (SSIP) via an intermolecular CT process [7,8]. It is believed that the triplet state of the unsubstituted 1,8-NI component in bis-1,8-NI is converted to a charge separation state (i.e. ANI$^{\delta+}$-NI$^{\delta-}$, DMANI$^{\delta+}$-NI$^{\delta-}$ and BANI$^{\delta+}$-NI$^{\delta-}$ by an intramolecular CT process from the 4-alkylamino moiety to the un-substituted 1,8-NI group. The intramolecular triplet quenching mechanism is faster than the intermolecular triplet quenching process. The existence of such ICT processes has been confirmed by time-resolved electron paramagnetic resonance spectroscopy (TREPR) in similar structures [17].

3. Experimental details

The bis-1,8-NI compounds used in this study were synthesized in our laboratory, the details of which have been reported previously [28]. UV-visible and fluorescence spectra were measured on Shimadzu UV-260 and HITACHI-850 instruments, respectively. Nanosecond time-resolved fluorescence decay kinetics was measured by a fast-response diode (DET2-Si, Thorlabs Inc.) equipped with a digital storage oscilloscope (Tektronix TDS 420). Laser light excitations were conducted using a nitrogen gas laser (Radiant Dyes Laser, 337 nm with a 6–7 ns pulse width). In front of the photodiode, there was a color optical filter (Type FAL, transitivity 0.7, half-width 66 nm, CZG, Germany), with wavelength centered at 538 nm. Transient absorption decay kinetics were measured by laser flash kinetic spectrophotometry. The solutions (in a 2×2 cm quartz cell) were excited at 337 nm, and transient optical density (ΔOD) at 488 nm (Ar ion laser, 5500 AWC, Ion Laser Technology) were detected by a diode. All measurements were performed in the presence of air at room temperature.

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