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Synthesis and spectral characteristics of di-substituted 1,8-naphthalimides: Bi-radical formation

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Abstract

Novel probes representing connection of 1,8-naphthalimides as chromophore and two structural units of sterically hindered amine stabilizer (HAS) were synthesized. One HAS unit was situated on naphthalene ring in position 4 and second HAS created imide composition. HASes were in the form of parent amine – DINH, stable nitroxyl radical – DINO and substituted hydroxylamine DINOR. Absorption and fluorescence spectra of probes were taken in solution as well as in polymer films. In absorption spectrum the longest wavelength band was shifted from 410 nm in non-polar cyclohexane to 440 nm in polar methanol. In fluorescence spectrum the maximum of the broad band is red shifted from 460 nm in cyclohexane to 530 nm in methanol. All derivatives exhibit similar solvatochromism in absorption as well as in fluorescence spectrum. The fluorescence is observed for all probes but there is distinctly much higher fluorescence intensity for parent amine DINH and alkoxyamine DINOR than for adequate bi-radical DINO. The extent of fluorescence enhancement comparing amine and alkoxyamine derivatives with bi-radical is in the range 10–70 depending on the medium.

Using laser flash photolysis the probe DINH exhibited transient absorption after 266 nm excitation in the nanosecond time scale region which is ascribed to triplet state. This transient absorption is red shifted in going from non-polar cyclohexane (460 nm) to polar methanol (520 nm). No (or extremely weak transient) absorption spectra was observed for stable nitroxyl bi-radical DINO.

Keywords: 1,8-Naphthylimine-sterically hindered amines; Fluorescence; Quenching; Stable nitroxyl bi-radical

1. Introduction

Multifunctional fluorescence probes, used to monitor various processes in vivo and in vitro, are based on different type of fluorophores [1–5]. In principle these probes are basic part of fluorescent sensors and switches. The probes are based on a property or parameter which is sensitive and highly dependent on the environment (medium). Fluorescence of the system is the parameter of choice because it exhibits high sensitivity, simple detection and quantitative evaluation and pronounced medium effect. The most important unit of any system is the fluorophore therefore its selection has got high importance. The 1,8-naphthalimide (benzo[*de*]isoquinoline-1,3-dione), substituted in various position, was widely employed as basic unit in different probes during the 1990s and first part of this decade [6–14]. This structural unit substituted in different position mainly by electron donating substituents exhibits interesting spectral properties namely strong fluorescence. Recently we have spectrally characterized probe composed from 1,8-naphthalimide (NI) and 2,2,6,6-tetramethyl-4-aminopiperidine (HAS) in solution and in polymer matrices [7]. Later the adduct of NI–HAS was functionalized with double bond and these products were tested as polymer stabilizers and dye simultaneously [8]. This unit of 1,8-naphthalimide was involved in probe sensing anions [9] as well as dyad with dansylamide for proton induced fluorescence switching [10]. Just recently, poly(amidoamine) dendrimer of second generation functionalized with 1,8-naphthalimide units was probed as potential sensor for metal cations [11]. Strong solvatochromism of the 4-methoxy-*N*-methyl-1,8-naphthalimide was employed for testing of ethanol–water mixtures [12]. Similar effect was observed for 4-phenoxy derivative as well [13]. Novel luminescent dyes containing 1,8-naphthalimide units were prepared and used as well [14].

Less attention was paid to the spectral characterization at the triplet level. The triplet state of un-substituted 1,8-naphthalimide

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was characterized and compared with phthalimide [15]. The triplet route of deactivation was explored for several adducts of 1,8-naphthalimide and HAS as parent amines and stable nitroxyl radical [16,17].

The goal of this study is to explore the spectral properties of di-substituted 1,8-naphthalimide with HAS as parent amine, stable nitroxyl radical and alkoxyamine at singlet and triplet level and to estimate the extent of intramolecular quenching on both levels as well.

2. Experimental

2.1. Synthesis of probes

The structures of the synthesised fluorescence probes are shown in Scheme 1.

2.1.1. 4-(2′,2′,6′,6′-Tetramethyl-4′-piperidylamino)-N-(2″,2″,6″,6″-tetramethyl-4″-piperidyl)-1,8-naphthalimide (DINH)

4-Bromo-1,8-naphthalic anhydride (0.9 g, 3 mmol) and 4-amino-2,2,6,6-tetramethylpiperidine (1.25 g, 8 mmol) was dissolved in 60 mL of 1-methyl-2-pyrrolidone. The mixture was heated for 24 h at 70 °C. Excess of 4-amino-2,2,6,6-tetramethylpiperidine and 1-methyl-2-pyrrolidone were removed by vacuum distillation and residual was dissolved in chloroform and extracted with water. Organic layer was separated and dried over Na_2SO_4. After solvent evaporation the crude product was purified by column chromatography on silica gel using a mixture of chloroform and isohexane (4:1) yielding 1.05 g (71%) of yellow crystals with mp = 322–323 °C.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ (s, 12H, 4x CH_3ax), 1.25 (m, 2H, 2x C*H*H), 1.40 (s, 12H, 4x CH_3eq), 1.65 (m, 2H, 2x C*H*H), 2.20 (m, 2H, 2x CH*H*), 2.50 (m, 2H, 2x CH*H*), 4.05 (m, 1H, C*H*N), 5.05 (wide s, 1H, N*H*), 5.65 (m, 1H, C*H*–N–CO), 6.80 (d, $J = 5.6$ Hz, 1H, C*H* (napht. −3)), 7.60 (t, 1H, C*H* (napht. −6)), 8.05 (d, $J = 5.7$ Hz, 1H, C*H* (napht.)), 8.40 (d, $J = 8.1$ Hz, 1H, C*H* (napht.)), 8.55 (d, $J = 7.5$ Hz, 1H, C*H* (napht.)).

FTIR ($CHCl_3$), cm^{-1}: $\nu(CO_{sym})$ 1685, $\nu(CO_{asym})$ 1648, $\nu(C{=}C)$ 1590, $\nu(C{-}N)$ 1366. UV (methanol) 437 nm, ($\log \varepsilon = 4.316$).

2.1.2. 4-(1′-Oxy-2′,2′,6′,6′-tetramethyl-4′-piperidylamino)-N-(1″-oxy-2″,2″,6″,6″-tetramethyl-4″-piperidyl)-1,8-naphthalimide (DINO)

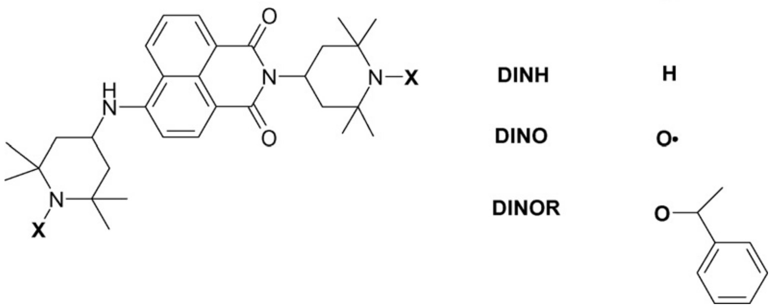
4-Bromo-1,8-naphthalic anhydride (0.9 g, 3 mmol) and 4-amino-1-oxy-2,2,6,6-tetramethylpiperidine (1.4 g, 8 mmol) was dissolved in 60 mL of 1-methyl-2-pyrrolidone. The mixture was heated for 24 h at 70 °C. Excess of 1-oxy-4-amino-2,2,6,6-tetramethylpiperidine and 1-methyl-2-pyrrolidone were removed by vacuum distillation and residual was dissolved in chloroform and extracted with water. Organic layer was separated, dried over Na_2SO_4. After solvent evaporation the crude product was purified by column chromatography on silica gel using a mixture of chloroform and isohexane (2:1), yielding 1 g (64%) of orange crystals with mp = 110–112 °C. Purity of the bi-radical was proved by EPR spectroscopy.

^{1}H NMR (300 MHz, $CDCl_3$, in the presence of pentafluorophenyl hydrazine): $\delta = 1.25$ (m, 2H, 2x C*H*H), 1.30 (2x s, 12H, 4x CH_3ax), 1.35 (2x s, 12H, 4x CH_3eq), 1.65 (m, 2H, 2x C*H*H), 2.15 (m, 2H, 2x CH*H*), 2.95 (m, 2H, 2x CH*H*), 4.00 (m, 1H, C*H*–N), 5.10 (wide s, 1H, N*H*), 5.20 (s, 2H, 2x N–O*H*), 5.65 (m, 1H, C*H*–N–CO), 6.75 (d, $J = 4.5$ Hz, 1H, C*H* (napht. −3)), 7.60 (t, 1H, C*H* (napht. −6)), 8.05 (d, $J = 4.2$ Hz, 1H, C*H* (napht.)), 8.45 (d, $J = 4.2$ Hz, 1H, C*H* (napht.)), 8.55 (d, $J = 4.1$ Hz, 1H, C*H* (napht.)).

FTIR ($CHCl_3$), cm^{-1}: $\nu(CO_{sym})$ 1688, $\nu(CO_{asym})$ 1650, $\nu(C{=}C)$ 1588, $\nu(C{-}N)$ 1365. UV (methanol) 433 nm, ($\log \varepsilon = 4.185$).

2.1.3. 4-(1′-Phenylethoxy-2′,2′,6′,6′-tetramethyl-4′-piperidylamino)-N-(1″-phenylethoxy-2″,2″,6″,6″-tetramethyl-4″-piperidyl)-1,8-naphthalimide (DINOR)

DINO (0.37 g, 0.7 mmol), $Mn(OAc)_3$ (1.5 g, 5.6 mmol) and styrene (0.58 g, 5.6 mmol) were suspended in 25 mL solvents mixture (ethanol/toluene/acetic acid 2:2:1) and stirred vigorously at room temperature. $NaBH_4$ (0.32 g, 8.4 mmol) was added slowly in very small portions and reaction was monitoring by TLC. After 5 h the mixture was filtered and washed two times with dichloromethane. The organic layers were combined, concentrated and the residue was dissolved in 50 mL of dichloromethane. The solution was washed with aqueous $NaHCO_3$ solution and with water. Organic layer was separated



Scheme 1.

and dried over Na_2SO_4. Purification by column chromatography using dichloromethane/isohexane (2:1) as eluent gave a yellow wax. Crystallization from isohexane yielded 0.29 g of yellow crystals (57%) with mp = 192–194 °C.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.70$ (s, 6H, CH_3ax), 1.20 (s, 3H, CH_3ax), 1.25 (s, 3H, CH_3ax), 1.30–1.40 (4x s, 12H, CH_3eq), 1.40–1.60 (m, 4H, 4x C*H*H), 1.50 (s, 6H, 2x CH_3–CH–Ph), 1.95 (d, 1H, CH*H*), 2.10 (d, 1H, CH*H*), 2.80 (m, 1H, CH*H*), 2.95 (m, 1H, CH*H*), 3.95 (m, 1H, C*H*N), 4.80 (m, 2H, 2x CH_3–C*H*–Ph), 4.95 (wide s, 1H, N*H*), 5.55 (m, 1H, C*H*–N–CO), 6.75 (d, $J = 4.2$ Hz, 1H, C*H* (napht. −3)), 7.25–7.40 (m, 10H, 2x Ph), 7.60 (t, 1H, C*H* (napht. −6)), 8.00 (d, $J = 3.9$ Hz, 1H, C*H* (napht.)), 8.40 (d, $J = 3.9$ Hz, 1H, C*H* (napht.)), 8.55 (d, $J = 3.6$ Hz, 1H, C*H* (napht.)).

FTIR ($CHCl_3$), cm^{-1}: $\nu(CO_{sym})$ 1688, $\nu(CO_{asym})$ 1642, ν(C=C) 1586, ν(C–N) 1365. UV (methanol) 441 nm, ($\log \varepsilon = 4.099$).

Reagents were obtained from Sigma–Aldrich and used without further purification. Analytical TLC was performed on commercial Merck plates coated with silica gel 60 F_{254} (0.20 mm). For flash chromatography Merck Silica gel 60 (0.0603–0.200 mm) was employed.

2.2. Spectral measurements

^{1}H NMR spectra were recorded in solution on a Bruker AC-300P (300.1 MHz) spectrometer, with the TMS proton signal as an internal standard. FTIR spectra were measured on Impact 400 (Nicolet, USA) and ESR spectra on X-band spectrometer E-4 Varian (USA) interfaced with PC using program Symphonia Bruker.

Anthracene was zonnally refined (Lachema n.e., Brno, CR). Methanol was for UV spectroscopy. Chloroform, tetrahydrofuran (Slavus, SR) was analytical reagents. Quencher: 1-oxo-2,2,6,6-tetramethylpiperidine (TEMPO) was received from Aldrich.

Polymer films doped with DINH, DINO and DINOR were prepared by casting from solution. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.), poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting of 1 mL chloroform solution of polymer (5 g/100 mL) containing the respective amount of probe on a glass plate (28 mm × 35 mm). The solvent was evaporated slowly. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared by similar way by casting from tetrahydrofuran solution.

UV–vis absorption spectra were taken on a spectrometer UV 1650PC (Shimadzu, Japan).

Emission spectra were recorded on spectrofluorophotometer RF-5301PC (Shimadzu, Japan) and on Perkin-Elmer MPF-4 (Perkin-Elmer, Norfolk, CT, USA), which was connected through interface and A/D convertor to ISA slot of PC using home made program for data collection. Program Origin 6.1 (Microsoft) was used for data plotting. Fluorescence of solution was measured in 1 cm cuvette in the right angle arrangement. The quantum yield was determined using anthracene as standard and assuming its insensitivity to the medium. The quantum yield was determined relative to anthracene in cyclohexane, chloroform or methanol. The quantum yields in solution and in film were determined according to the relation

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(\nu)\,d\nu}{\int_0^\infty I_F^S(\nu)\,d\nu} \left(\frac{1-10^{-A^S}}{1-10^{-A}}\right)$$

where Φ_F^S is the quantum yield of anthracene as a standard, which was assumed to be 0.2 for all solvents [18,19]. Integrals $\int_0^\infty I_F(\nu)\,d\nu$ and $\int_0^\infty I_F^S(\nu)\,d\nu$ are the areas under emission curves of the probe and standard, respectively, and A and A^S are the absorptions of the probe and the standard at the excitation wavelength. Anthracene was excited at $\lambda_{ex} = 355$–375 nm depending on the medium.

Fluorescence of polymer films was taken in front face arrangement on the solid sample holder. Since the determination of quantum yields of fluorescence of doped probes in polymer matrice is charged with large error, the extent of fluorescence enhancement expressed as ratio Φ_{NH}/Φ_{NO} or Φ_{NOR}/Φ_{NO} of doped polymer films was determined using integral fluorecence corrected for different absorption at wavelength of excitation. The fluorescence spectra were taken at excitation into the maximum of the longest wavelength absorption band.

The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.), which operates as a stroboscope. The excitation source is a nitrogen laser emitting at 337 nm and the emission is selected by cut-off filter. The output signal of Box Car Integrator was digitized and transferred to the PC using home made program. The fluorescence decay curves were evaluated by simple phase plane method [20] using program of J. Snyder based on [21]. The standard deviation $G^{1/2} = \sum((I_{exp} - I_{calc})^2/n)^{1/2}$, where I_{exp} and I_{calc} are the intensity of emission experimental and calculated, respectively, is used to judge if the decay is mono-exponential. It is assumed that the decay curve satisfies the monoexponential when $G^{1/2}$ is lower than 5%. The fitting of fluorescence decay curves for a model of biexponential decay was preformed using adapted FluoFit MatLab package [22].

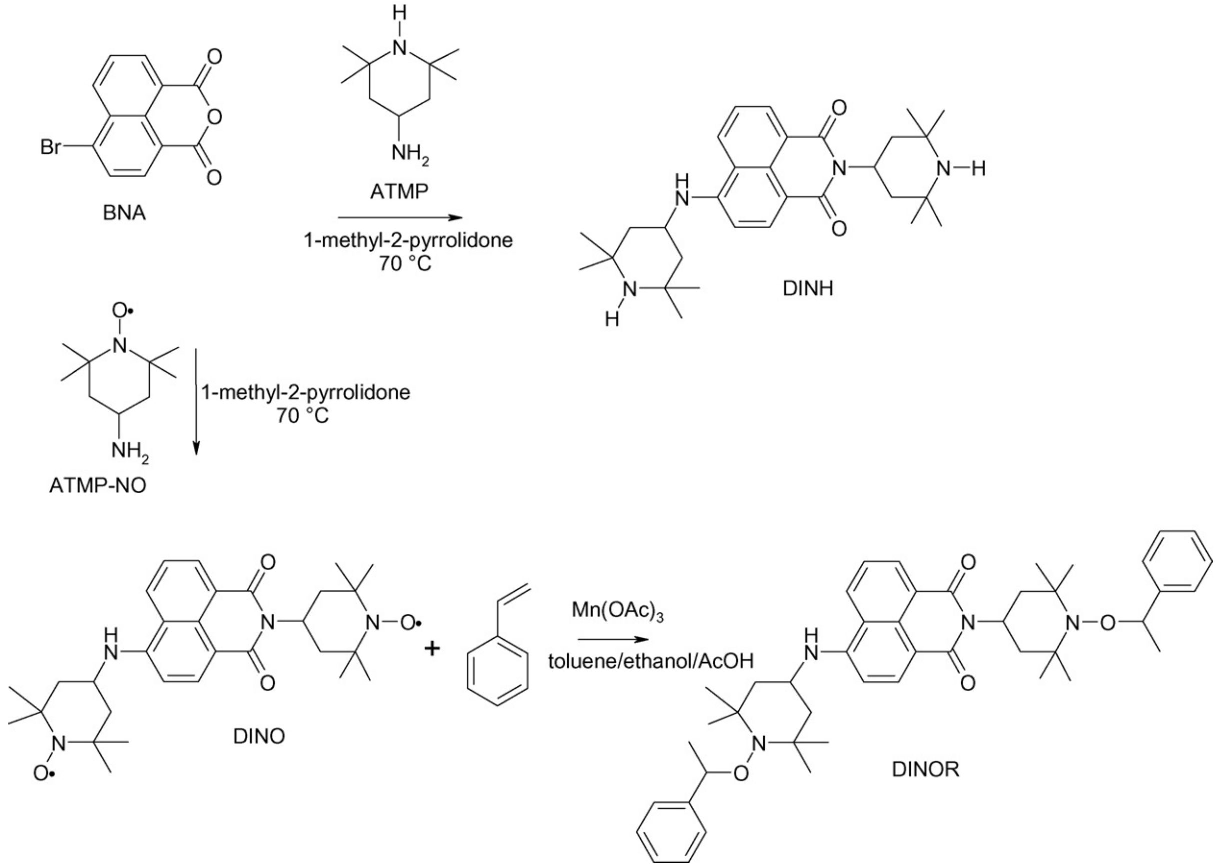
The laser flash photolysis measurements of the probes in solution and processing of the data was performed in the same way as previously [16,17].

The steady state and time resolved measurements were performed in aerated solutions. All measurements on polymer films were done in the presence of air.

3. Results and discussion

3.1. Synthesis

Synthetic strategy was developed for the preparation of series of 4-substituted 1,8-naphthalimides from the starting 4-bromo-1,8-naphthalic anhydride (Scheme 2). Interaction of 4-bromo-1,8-naphthalic anhydride with 4-amino-2,2,6,6-tetramethylpiperidine (ATMP) in hot ethanol gave substitution only in the anhydride ring. Substitution of bromine in position 4 of naphthalic ring did not proceed under these conditions. Using of 1-methyl-2-pyrrolidone and increasing the tempera-



Scheme 2.

ture to 70 °C afforded final double substituted product DINH in good yield. Stable nitroxyl bi-radical DINO was prepared by the same procedure just instead of parent amine ATMP stable nitroxyl radical ATMP-NO was used. Structure of DINO was proved by NMR spectroscopy. NMR spectrum was measured in the presence of reduction agent. This reagent converted N–O radical to hydroxylamine N–OH. The purity of DINO was checked by EPR spectroscopy. Quantitative measurements were performed in benzene solutions ($c = 1 \times 10^{-3}$ mol dm^{-3}). Integral of EPR spectra for DINO was compared with the integral of standard measured under the same conditions. As the standard 4-hydroxy-2,2,6,6-tetramethyl-piperidine-*N*-oxyl was used. Surprisingly EPR spectrum of the DINO bi-radical (Fig. 1) was same as the spectrum of standard mono-radical. Both were triplets with equal line intensities. It means that there is no intramolecular spin–spin interaction between two nitroxides in DINO most probably due to the very hard naphthalic anhydride structure. The distance between two nitroxyl radical centers is not sufficient for interactions. The values of integrals are proportional to the number of radicals so the relative concentration c_r provides information about amount of radical in the DINO. We assume that the concentration of radicals in the standard is 100%. The value c_r for DINO was 190%, which is the proof of the very high purity. Purity was checked by TLC too. Synthesis of the corresponding alkoxyamine DINOR from the nitroxide DINO was then accomplished by the novel method described by Krause et al. [23] using $Mn(OAc)_3$ as electron-transfer agent. The low cost of $Mn(OAc)_3$ compared to the commonly used Jacobsen's catalyst, high yields and easy product purification are the main advantages of this new synthetic method.

3.2. Singlet deactivation route

The spectral data of the probes under study are obtained in solution as well as in polymer matrices. Basically, it is assumed that the solvation power of solvent and polymer matrix is the same or similar if the same structural units are involved. The

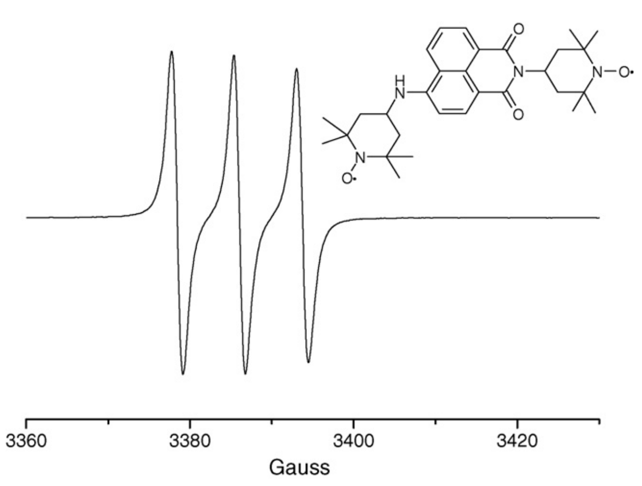


Fig. 1. ESR spectrum of stable nitroxyl bi-radical DINO in benzene.

main difference is due to difference in mobility of the salvation envelope of low molecular solvent and polymer matrix. It might be expected that the effect of mobility is not so important for absorption spectra but it plays important role in fluorescence spectra.

The absorption spectra of 1,8-naphthalic anhydride and 4-bromo-1,8-naphthalic anhydride in methanol exhibit the broad longest wavelength band with maximum at 300 and 310 nm, respectively [17]. The absorption spectra of monosunstituted *N*′-(2′,2′,6′,6′-tetramethyl-4′-piperidyl)-1,8-naphthaleneimide and *N*′-(2′,2′,6′,6′-tetramethyl-4′-piperidyl)-4-bromo-1,8-naphthaleneimide exhibits the longest wavelength band as a broad bands with maximum shifted to around 335 and 345 nm, respectively, in polar methanol as a consequence of donor substituent 2,2,6,6-tetramethyl-piperidylimino. These features are preserved in polymer matrices as well [7,16]. Substitution on naphthalene ring in position 4 by the same electron donor substituent 2,2,6,6-tetramethylpiperidylimino (DINH, DINO and DINOR) has much stronger effect and shifts the maximum of the longest wavelength band batochromically to the range 400–450 depending on the polarity of solvent (Fig. 2 and Tables 1–3). In non-polar cyclohexane there is seen some indication of the fine vibrational structure as shoulders around 405 and 430 nm and a maximum around 414 nm. In polar protic methanol the longest wavelength band is red shifted up to 440 nm and it is rather broad without vibrational structure. The absorption is strong with log $\varepsilon = 4.316$ for DINH in methanol. The bathochromic shift of the longest wavelength absorption bands in going from mono- to di-substituted derivative due to electron donating substituent in position 4 is 5300 cm^{-1} in non-polar and 6260 cm^{-1} in polar medium.

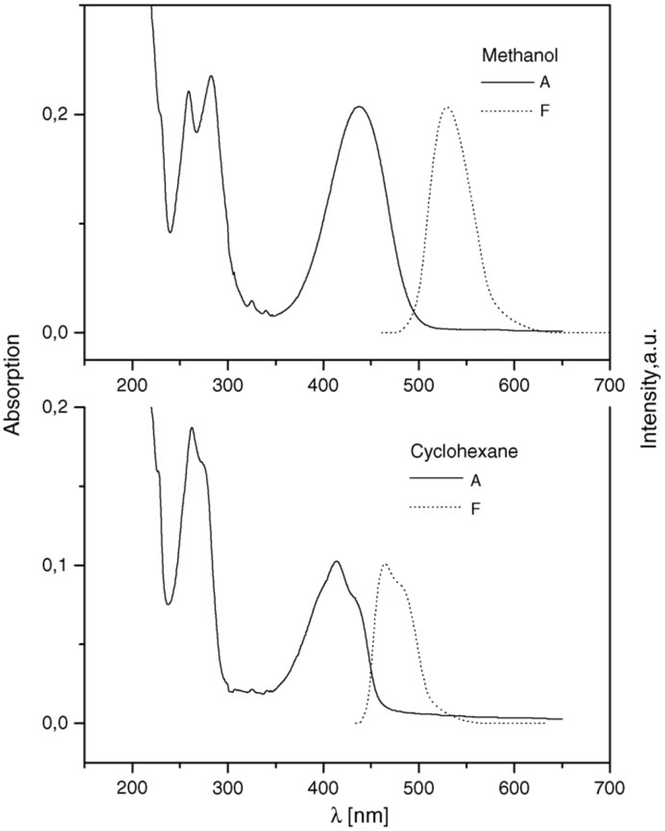


Fig. 2. Absorption and fluorescence spectra of DINH in methanol at 10^{-5} mol dm^{-3} and in cyclohexane (saturated solution, according to absorption spectrum 5×10^{-6} mol dm^{-3}).

Table 1
Spectral characteristics of DINH in different media

Medium[a]	λ_{max}[b] [nm]	λ_{max}[c] [nm]	$\Delta\nu$[d] [cm^{-1}]	Φ[e]	Φ_{NH}/Φ_{NO}[f]	τ[g] [ns]
MeOH	440	530	3860	0.46	19.2	6.7
Cy	413, 432sh	464	1596	0.88	13.6	
PS	426, 440sh	487sh, 506	2193		25.2[h]	5.1
PMMA	431	504	3282		10.6[h]	8.1
PVC	435	520	3757		17.6[h]	7.3

[a] Medium: MeOH, methanol; Cy, cyclohexane; PS, polystyrene; PMMA, poly(methyl methacrylate); PVC, poly(vinyl chloride).

[b] Wavelength of maximum absorption.

[c] Wavelength of maximum fluorescence excited at the maximum of absorption.

[d] Stoke's shift.

[e] Quantum yield of fluorescence using anthracene as standard. Error ±10%.

[f] The extent of intramolecular quenching using relative quantum yield of Φ_{NO} of DINO from Table 2.

[g] Lifetime.

[h] Determined by ratio of the integral intensity of fluorescence in of parent amine and nitroxide in respective matrix. Error ±50%.

The absorption spectrum of DINH, DINO and DINOR in polymer matrices has got similar features as those in solution of similar polarity. The absorption spectrum of probes in PS has got some indication of fine structure on the longest wavelength band as in cyclohexane. On the other hand, probes in PVC and PMMA exhibit broad red shifted absorption band similarly as in methanol (Fig. 3).

Fluorescence of *N*-substituted *N*′-(2′,2′,6′,6′-tetramethyl-4′-piperidyl)-1,8-naphthaleneimide in non-polar and polar solvents as well as in polymer matrices features one unresolved band

Table 2
Spectral characteristics of DINO in different media

Medium[a]	λ_{max}[b] [nm]	λ_{max}[c] [nm]	$\Delta\nu$[d] [cm^{-1}]	Φ[e]	τ[f] [ns]	τ[g] [ns]
MeOH	435	532	4192	0.022	2.2	0.5 (0.97), 11.8 (0.03)
Cy	394	460, 483sh	3640	0.064		
PS	417 434sh	494	2799	–	4.9	0.027 (0.96) 6.1 (0.04)
PMMA	429	497	3189		3.8	
PVC	432	503	3267		3.1	

[a] Medium: MeOH, methanol; Cy, cyclohexane; PS, polystyrene; PMMA, poly(methyl methacrylate); PVC, poly(vinyl chloride).

[b] Wavelength of maximum absorption.

[c] Wavelength of maximum fluorescence excited at the maximum of absorption.

[d] Stoke's shift.

[e] Quantum yield to based on anthracene. Error 10%.

[f] Lifetime fitted to monoexponential. Error above 5%.

[g] Lifetime fitted to biexponential.

Table 3
Spectral characteristics of DINOR in different media

Medium[a]	λ_{max}[b] [nm]	λ_{max}[c] [nm]	$\Delta\nu$[d] [cm^{-1}]	Φ[e]	Φ_{NOR}/Φ_{NO}[f]	τ[g] [ns]
MeOH	440	532	3960	0.4	18.2	6.2
Cy	414, 432sh	462, 480sh	1503	0.62	10.0	
PS	410, 432sh	492	2823		73.9[h]	7.5
PMMA	430	500	3256		17.8[h]	8.9
PVC	433	509	3448		34.8[h]	7.9

[a] Medium: MeOH, methanol; Cy, cyclohexane; PS, polystyrene; PMMA, poly(methyl methacrylate); PVC, poly(vinyl chloride).

[b] Wavelength of maximum absorption.

[c] Wavelength of maximum fluorescence excited at the maximum of absorption.

[d] Stoke's shift.

[e] Quantum yield based on anthracene. Error ±10%.

[f] The extent of intramolecular quenching using relative quantum yield of Φ_{NO} of DINO from Table 2.

[g] Lifetime fitted to monoexponential. Error ±5%.

[h] Determined by ratio of the integral intensity of fluorescence in of alkoxide and nitroxide in respective matrix. Error ±50%.

around 385 nm [7]. Fluorescence of di-substituted probes DINH, DINO and DINOR lies red shifted (4607 up to 6905 cm^{-1}) in the wide range 460 up to 530 nm being around 465 nm in cyclohexane and around 530 nm in methanol showing rather strong solvatochromism. In non-polar cyclohexane there is again some indication of vibrational resolution for probe DINH and DINOR. The Stoke's shift is about 1500 cm^{-1} for DINH and DINOR in cyclohexane and more than double (around 3500 cm^{-1}) for methanol. From it follows that the fluorescence of DINH and DINOR in methanol originates from the structure which is more relaxed or solvated as compared to cyclohexane.

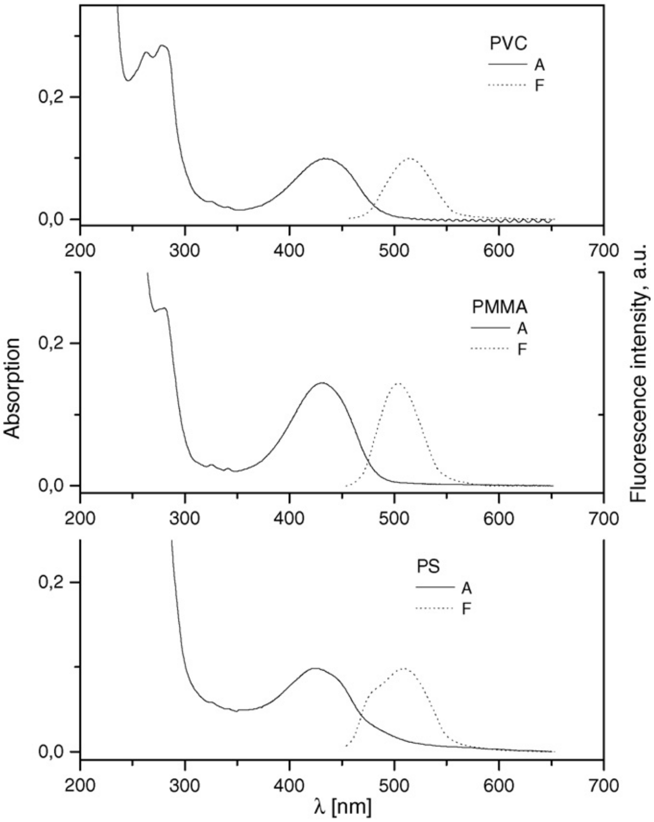


Fig. 3. Absorption and fluorescence spectra of DINH in films (50 μm) PS, PMMA and PVC at 0.002 mol kg^{-1}.

The fluorescence of probes doped in polymer matrices has got similar features as in solution and Stoke's shift lies between 2500 up to 3500 cm^{-1} indicating some extent of relaxation of the structure of the probe in the first excited state even in the more rigid polymer matrix at ambient temperature well under T_g.

The quantum yield based on anthracene indicates that the fluorescence of DINH and DINOR is rather strong (0.4–0.9) in solution. The quantum yields of probes in the solid film were large but their determination was charged with large error therefore they are not given (Tables 1 and 3). The reason why we used anthracene as standard is that anthracene is soluble in all media therefore it is suitable for comparison. The values of quantum yield of fluorescence of bi-radical DINO in solution are much lower (0.02–0.06) than for parent amine DINH and alkoxyamine DINOR. Presence of two quencher structures in DINO are responsible for this decreasing. The extent of intramolecular quenching based on the ratio of quantum yields of parent amine DINH and alkoxyamine DINOR to quantum yield of DINO lies in the range 10–20 in solution. In solid films the extent of intramolecular quenching was determined as ratio of integrals under fluorescence curve in respective matrices. These data are in range 10 up to 70. The intramolecular quenching is lower in solution and higher in polymer films where the scatter of these data is considerable. Although these data taken from polymer films are charged with large error they clearly show that new radiationless channel in DINO starts to operate.

The lifetime of DINH and DINOR is in the range 5–9 ns in different media and is clearly monoexponential. The decay of DINO is more complex and might be fitted to biexponential. Since there is only limited number of data on decay, the fitting is not very precise. In any case the short lifetime is under 0.5 ns and the long lifetime is about 5 ns. Taking into account only short life, the extent of intramolecular quenching about 10 seems to be realistic. If this new channel is efficient, then all deactivation should proceeds through it and consequently monoexponential decay is to be observed with short lifetime. In order to explain two different lifetimes, two different conformations of the probe DINO are invoked. One conformation should be planar where there is no quenching effect of *N*-oxyl and the second one with perpendicular arrangement piperidine moiety to the 1,8-naphthalimine plane where it is possible to expect stronger interaction of excited chromophore with radical centre. At present some quantum chemical calculations are performed to support this suggestion.

The Stern–Volmer constants for intermolecular quenching by *N*-oxyl (TEMPO) and oxygen are summarized in Table 4. The values of K_{SV} indicate an efficient intermolecular quenching by TEMPO and oxygen in both studied solvents. Rather high values of K_{SV} are for the quenching of probes by TEMPO in

Table 4
Quenching of naphthalene chromophore in different media by oxygen and TEMPO

Probe	Solvent	K_{sv} O_2[a] [L mol^{-1}]	K_{sv} TEMPO[b] [L mol^{-1}]
DINH	MeOH	96	77
	Cy	91	218
DINO	MeOH	50	54
	Cy	62	136
DINOR	MeOH	63	80
	Cy	86	143

[a] Stern–Volmer constant based on single point assuming oxygen concentration 0.002 mol dm^{-3}.

[b] Stern–Volmer constant for TEMPO based on plot.

cyclohexane. Moreover, the intensity of fluorescence quenched by TEMPO and it obeys the Stern–Volmer plot (Fig. 4). Taking lifetime of DINH 6.7 ns and DINOR 6.2 ns in methanol, the bimolecular rate of quenching is about 1.1×10^{10} and 1.3×10^{10} dm^3 mol^{-1} s^{-1}, respectively, using data for K_{SV} from Table 4.

3.3. Triplet deactivation route

The transient species of unsubstituted 1,8-naphthaleneimide upon laser excitation (337.1 nm) produces absorption spectrum with absorption maximum 360 and 470 nm which decays monoexponentially with lifetime 9 μs in dimethylformamide [15]. Upon excitation with 266 and 355 nm the *N*-substituted *N*′-(2′,2′,6′,6′-tetramethyl-4′-piperidyl)-1,8-naphthaleneimide and 4-bromo derivative exhibit transient absorption at 410 and 470 nm in de-airated methanol [16,17]. The transient of 4-dimethylamino-*N*′-(2′,2′,6′,6′-tetramethyl-4′-piperidyl)-1,8-naphthaleneimide upon 355 nm excitation in methanol was rather weak [17].

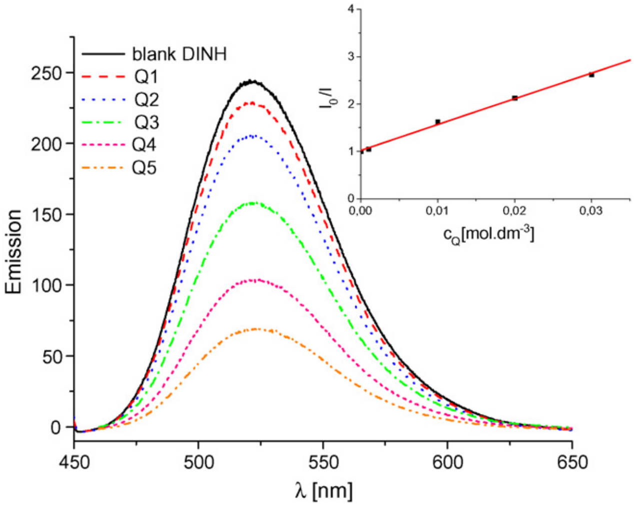


Fig. 4. Changes of fluorescence spectra of DINH in methanol quenched by TEMPO ($Q1 = 10^{-3}$, $Q2 = 3 \times 10^{-3}$, $Q3 = 10^{-2}$, $Q4 = 2 \times 10^{-2}$, $Q5 = 3 \times 10^{-2}$ mol dm^{-3}) and Stern–Volmer plot.

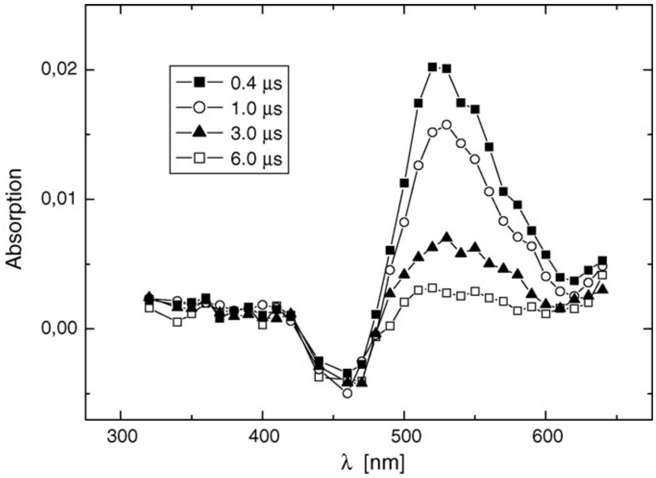


Fig. 5. Spectra of transient absorption of DINH (2.6×10^{-5} mol dm^{-3}) in methanol at 266 nm excitation.

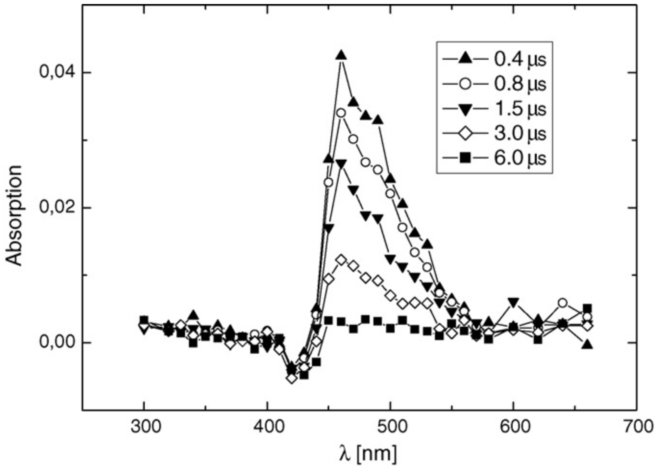


Fig. 6. Spectra of transient absorption of DINH (2.6×10^{-5} mol dm^{-3}) in cyclohexane at 266 nm excitation.

The laser flash photolysis study showed that the probe DINH exhibits transient absorption after 266 nm excitation in the nanosecond region which is ascribed to triplet state (Figs. 5 and 6). This transient absorption is red shifted in going from 460 nm for non-polar cyclohexane (Fig. 6) to 520 nm in polar methanol (Fig. 5). No (or extremely weak transient) absorption spectra was observed for stable nitroxyl bi-radical DINO. Excited triplets are quenched by nitroxyl radicals which are part of the molecule. This intramolecular quenching is faster than the shortest time we can use for measurement. This is the similar behaviour as in the case of (2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide and 4-bromo-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide described in refs. [16,17]. Moreover in this case we have shown that this free nitroxyl radical is able to quench first itself and after than act as an effective quencher for another chromophore.

4. Conclusions

Novel probes were prepared where 1,8-naphthalimine is combined with two sterically hindered amine structural units in form of the parent amine, stable nitroxyl bi-radical and alkoxyamine. The parent amine DINH and alkoxyamine DINOR exhibit quite intense fluorescence in the range 460–530 nm depending on the medium. The fluorescence is intensively quenched if the probe is in the form of free nitroxyl bi-radical DINO. The extent of quenching (ratio of quantum yields of DINH and DINOR over DINO) is above 15 in solvent and rather high in polymer matrix (ratio of fluorescence intensities of DINH and DINOR over DINO).

DINH exhibits transient absorption after 266 nm excitation in the nanosecond region which is ascribed to triplet state. Presence of two stable free nitroxyl radicals in one molecule results in formation of very efficient deactivation channels and triplet state of DINO is difficult to observe in sub-microsecond region.

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