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Spectral properties of new *N*,*N*′-bis-alkyl-1,4,6,8-naphthalenediimide complexes

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Abstract

The photophysical properties of two *N*,*N*′-bis-alkyl-1,4,6,8-naphthalenediimide (DCN1 and DCN2) have been studied in chloroform and *N*,*N*-dimethylformamide solvents. The ability of DCN2 in *N*,*N*-dimethylformamide to detect metal cations have been monitored by the fluorescence emission spectroscopy. It has been shown that the fluorescent intensity is very sensitive to the concentration of Fe^{3+} cations. The reaction of iodine with *N*,*N*′-bis-alkyl-1,4,6,8-naphthalenediimide in chloroform solution have been investigated by spectrophotometric method. The results indicate the formation of two CT-complexes $[(DCN1)I]^+{\cdot}I_3^-$ and $[(DCN2)I]^+{\cdot}I_3^-$ at donor:acceptor molar ratio of 1:2. The $[(DCN1)I]^+{\cdot}I_3^-$ shows the characteristic absorptions of I_3^- ion at 290 and 360 nm while the charge-transfer transition of $[(DCN2)I]^+{\cdot}I_3^-$ occurs at 310 nm. Three characteristic bands at the far infrared region in each iodine complex are observed around 135, 105 and 85 cm^{-1} due to ν_{as} (I–I), ν_s (I–I) and δ (I_3^-), respectively with C_{2v} symmetry. The values of the complex formation constant, *K*, and the absorptivity, ε have been calculated.

Keywords: 1,4,6,8-Naphthalenediimide; Spectroscopy; Fluorosensors; Metal cations; Charge transfer complex; Iodine; Photophysics

1. Introduction

The cyclic imides as maleimides, glutarimides, succinimides, 1,8-naphthalimides and 1,4,6,8-naphthalendiimides are a group of organic compounds having significant therapeutic and biological potentials [1].

In the recent few years *N*,*N*′-bis-substituted-1,4,6,8-naphthalendiimides have been investigated intensively because of their promising applications. They can be used in solar energy collectors [2], electronic and molecular devises [3], DNA sensors [4a] or antibacterial agents [4b,c] and photoactive materials [5]. The quenching effect on the fluorescence intensity of *N*,*N*′-bis-substituted-1,4,6,8-naphthalendiimides have been investigated [5a,c]. A systematic quantitative study of the solubility of various naphthalendiimides in organic solvents with different polarity has been investigated by means of UV–vis spectroscopy [6].

Charge-transfer complexes (CT-complexes) are being regarded as important materials due to their applications [7–9]. Such complexes have been reported as important reaction intermediates in many chemical reactions [10,11]. These complexes have been studied in organic conductors and photoconductors [12,13]. Major impetus to the rapid development in the field of electron donor–acceptor interactions arose from the UV–vis spectrophotometric study on iodine complexes by Benesi and Hildebrand [14], and the theoretical interpretation of spectra by Mulliken [15]. Our preliminary investigations into the synthesis and investigation of CT complexes was published previously [16–19].

In this article the results from investigations on the synthesis and photophysical properties of two *N*,*N*′-bis-alkyl

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derivatives of 1,4,6,8-naphthalenediimide (DCN1 and DCN2) in chloroform and *N*,*N*′-dimethylformamide solutions are presented. The influence of different metal cations on the fluorescence intensity is discussed with regard for their potential application as fluorescent sensors. Another main task of the present work has been to study the interaction of iodine with these compounds and to characterize the reaction products. The emphasis has been put upon the elucidation of the nature of iodine complexes formed in course of reactions reported.

2. Experimental

2.1. Synthesis of N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide

The synthetic route for obtaining 1,4,6,8-dicarboxy-naphthalenes is presented in Scheme 1.

DCN1 and DCN2 were synthesized by condensation of 1,4,6,8-tetracarboxilic dianhydride (2.68 g, 0.01 mol) and 2-aminoethanol (1.9 ml, 0.04 mol) for DCN1 or 2-*N*,*N*-dimethylethylamine (3.5 ml, 0.04 mol) for DCN2 in aqueous solution. The suspension was heated at 80 °C for 8 h. The precipitate was filtered and washed with acetone.

2.2. N,N′-bis[(2-hydroxyethyl)]-1,4,6,8-naphthalene diimide (DCN1)

Yield (81%) m.p. = 321–323 °C; FT-IR (KBr) $\mathrm{cm^{-1}}$: 1704, 1660, 1337, 768; ^{1}H NMR-(DMSO-d6): δ (ppm): 8.46 (s, 4H) 4.85 (t, 2H, OH); 4.10 (t, 2× $\mathrm{HOCH_2}$); 3.63 (q, 4H, 2× $\mathrm{CH_2N}\!<$) ^{13}C NMR-(DMSO-d6): 162.4 (2× C=O), 130.3 (4C, CH), 125.9 (C-quat., 4C), 125.7 (C-quat., 2C), 57.6 (2× $\mathrm{NCH_2}$), 42.2 (2× $\mathrm{CH_2OH}$). Elemental analysis—$\mathrm{C_{18}H_{14}N_2O_6}$ (354.1): calculated (%) C 61.86, H 3.95, N 7.91; found (%) C 61.79, H 3.86, N 7.83.

2.3. N,N′-bis[(2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalene diimide (DCN2)

Yield (86%) m.p. = 279–281 °C; FT-IR (KBr) $\mathrm{cm^{-1}}$: 1704, 1663, 1339, 766; ^{1}H NMR-(DMSO-d6): δ (ppm) 8.72 (s, 4H); 4.34 (t, 4H, 2× $\mathrm{NCH_2}$); 2.68 (t, 4H, 2× $\mathrm{CH_2N}\!<$); 2.35 s, (12H, $\mathrm{NCH_3}$). ^{13}C NMR-(DMSO-d6): 162.1 (2× C=O), 130.9 (4C, CH), 126.6 (C-quat., 2C), 126.5 (C-quat., 4C), 56.8 (2× $\mathrm{NCH_2}$), 45.7 ($\mathrm{NCH_3}$), 38.5 (2× $\mathrm{CH_2N}\!<$). Elemental analysis—$\mathrm{C_{22}H_{24}N_4O_4}$ (408.1): calculated (%) C 67.70, H 5.88, N 13.72; found (%) C 67.49, H 5.78, N 13.64.

2.4. Synthesis of iodine complexes

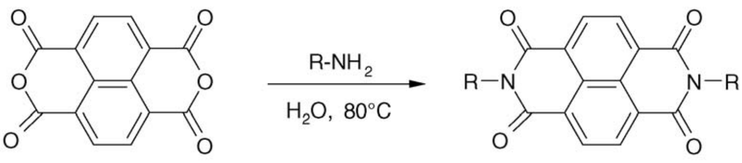
The iodine complex $[(\mathrm{DCN1})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ was isolated as a dark brown solid by the addition of 1×10^{-3} mol DCN1 dissolved in 25 ml of chloroform to the 2×10^{-3} mol of iodine dissolved in 25 ml of chloroform. After 30 min stirring the reaction mixture has been reduced to 20 ml volume. The dark brown precipitate was filtered and dried under vacuum. The second light brown solid iodine complex $[(\mathrm{DCN2})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ was prepared using a similar method, but increased the time of stirring to about 5 h. The solid iodine complexes were characterized by their elemental analysis, electronic and infrared absorption spectral measurements.

Elemental analysis—$[(\mathrm{DCN1})\mathrm{I}]^{+}\mathrm{I_3}^{-}$: calculated (%) C 23.35, H 1.07, N 3.51, I, 62.76; found (%) C 23.51, H 1.10, N 3.43, I 62.16. $[(\mathrm{DCN2})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$: calculated (%) C 25.35, H 1.62, N 4.94, I, 60.06; found (%) C 25.60, H 1.66, N 4.98, I 60.17.

2.5. Materials and methods

All chemicals used throughout this investigation were of analytical grade.

UV–vis spectrophotometric investigations were performed on a UVIKON 930 spectrophotometer (KONTRON instruments). The fluorescence spectra were taken on a SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yield were determined on the basis of the absorption and fluorescence spectra. Anthracene was used as reference ($\Phi_0 = 0.26$). All organic solvents used in this study were of spectroscopic grade. The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^{1}H and ^{13}C, respectively using a dual 5 mm probe head. The measurements were carried out in DMSO-$\mathrm{d_6}$ solution at ambient temperature. The chemical shift were referenced to tetramethylsilane (TMS), standard experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the same conditions as the ^{13}C-NMR spectra and $\tau = (2\,{}^{1}J_{\mathrm{CH}})^{-1} = 3.45\ \mu$s was used. The 2D ^{1}H/^{1}H correlated spectra



where R = $\mathrm{CH_2CH_2OH}$ (DCN1); $\mathrm{CH_2CH_2N(CH_3)_2}$ (DCN2)

Scheme 1. Synthesis of *N*,*N'*-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide.

(COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, and size 1 K × 1 K. The 2D $^{1}H/^{13}C$ heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for ^{1}H and 9000 Hz for ^{13}C, relaxation delay1.5 s, FT size 1 K × 256 W.

The mid infrared spectra of the donors (DCN1 and DCN2) and iodine complexes were recorded from KBr discs using a Genesis II. FT-IR, while the far infrared spectra for the same compounds were recorded from Nujol mulls dispersed on polyethylene windows in the 50–300 cm^{-1} region using a Mattson infinity series FT-IR spectrometer. Photometric titrations of iodine and each of the donor (DCN1) and (DCN2) in chloroform were performed at 25 °C under the conditions of fixed donor concentration at 1.0×10^{-4} M for (DCN1) and (DCN2) while the concentration of the iodine was varied over the range from 0.25×10^{-4} to 4.0×10^{-4} M. These concentrations produce donor:I_2 ratios in each reaction from 1:0.25 to 1:4. The absorbance of the iodine complexes formed were measured in each case and were used to determined the reaction stoichiometries according to the known methods [20] and were also used to obtain the modified Benesi–Hildebrand plots [14,21,22] in order to calculate the formation constant, *K*, and the absorptivity, ε, values for the two triiodide complexes, $[(DCN1)I]^{+}\cdot I_3^{-}$ and $[(DCN2)I]^{+}\cdot I_3^{-}$.

3. Results and discussion

3.1. Photophysical characteristics of DCN1 and DCN2 in organic solvents

N,*N*′-Bis-alkyl derivatives of 1,4,6,8-naphthalenediimide under study can be treated as a combination of two subsystems: viz the naphthalene moiety and two fragments including four C=O groups linked through the CH_2CH_2OH and $CH_2CH_2N(CH_3)_2$ groups.

The photophysical properties of DCN1 and DCN2 were investigated in two organic solvents with different polarity: chloroform ($E_T30 = 39.1$ kcal mol^{-1}) and *N*,*N*-dimethylformamide ($E_T30 = 43.8$ kcal mol^{-1}) solutions at concentration of 10^{-4} mol l^{-1}. When the UV spectrum was recorded in chloroform solution a broad absorption was observed between 300 and 400 nm due to the ICT state (Fig. 1) with three characteristic bands at 342, 359 and 379 nm. Absorbing light, the investigated DCN1 and DCN2 passes from the basic singlet S_0 to the first excited state S_1. The energy of the first excited state and the corresponding λ_{S_1} has been determined. The energies of the lowest exited singlet state (E_{S_1}), $E_{S_1} = 305–311$ kJ mol^{-1} is obtained from the locations of intersections of the normalized absorption and fluorescence spectra of the diimides DCN1 and DCN2. Emitting fluorescence light, the chromophore molecules is deactivated on fluorescence light emission, and passes from the S_1 to the basic S_0 state. A week emission was observed between 370 and 500 nm with well-pronounced fluorescent maxima (λ_F) at 389, 408 and 433 nm (Fig. 1).

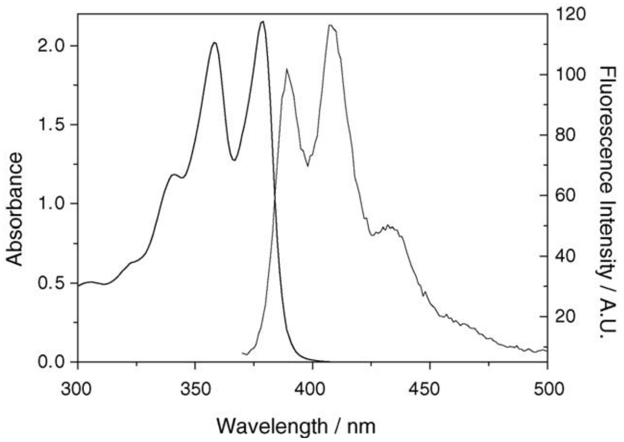


Fig. 1. Absorption and fluorescence spectra of DCN1 in chloroform solution ($\lambda_{ext} = 379$ nm).

As seen from Table 1 the position of the absorption maxima of both DCN1 and DCN2 compounds remain constant and do not depend on the polarity of the organic solvents. This reveals the negligible effect that the type of the substituent bonded to 1,4,6,8-naphthalenediimide has upon polarization of the chromophoric system.

The Stokes shift is an important parameter for the fluorescence compounds. This parameter indicates the difference in the properties and structure of the compounds between the ground state S_0 and the first exited state S_1. The Stokes shift has been estimated according to the following equation:

$$\nu_A–\nu_f = (1/\lambda_A - 1/\lambda_f) \times 10^{-7}\ cm^{-1} \quad (1)$$

Table 1
Photophysical characteristics of DCN1 and DCN2 in chloroform and *N*,*N*-dimethylformamide solutions (see text)

	Chloroform		*N*,*N*-Dimethylformamide	
	DCN1	DCN2	DCN1	DCN2
λ_A [nm] (log ε)	341 (4.07), 359 (4.30), 379 (4.33)	342 (4.09), 359 (4.35), 379 (4.39)	341 (3.97), 359 (4.17), 378 (4.19)	342 (4.05), 358 (4.22), 379 (4.24)
λ_F [nm]	389, 408, 433	390, 409, 435	403, 427, 452,	404, 428, 454
$\nu_A–\nu_F$ [cm^{-1}]	678	744	1641	1632
Φ_F	0.005	0.004	0.002	0.002
f	0.23	0.25	0.26	0.25
E_{S_1} [kJ mol^{-1}]	311.3	309.7	360.5	305.0

The calculated Stokes shift is very small: (ν_A–ν_F) = 678 and 744 cm^{-1} in the case of chloroform solution and (ν_A–ν_F) = 1632 and 1641 cm^{-1} in *N*,*N*-dimetylformamide for DCN1 and DCN2, respectively (Table 1). The values observed in both solvents are very similar to the values observed for other *N*,*N*′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide [3b,5a] and does not imply any change in the chromophores systems in the excited state. The overlap between the absorption and the fluorescence spectra is low and the re-absorption and aggregation effect are negligible at the concentration used (10^{-4} mol).

Oscillator strength (*f*) is an important parameter of the chromophores. It reveals the effective number of electrons taking part in the transition from the ground S_0 to the excited S_1 state. Values of oscillator strength can be calculated using the following formula:

$$f = 4.32 \times 10^{-9}\Delta\nu_{1/2}\varepsilon_{\max} \quad (2)$$

where $\Delta\nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at 1/2 $\varepsilon_{\max}$. The calculated value of the oscillator strength in chloroform solution is 0.23–0.25, and in *N*,*N*-dimethylformamide *f* = 0.25–0.26. The almost similar values show that the polarity of the solvents does not affect this parameter.

The ability of the DCN1 and DCN2 to emit absorbed light energy has been characterized quantitatively by the quantum yield of fluorescence Φ_F. The quantum fluorescence yield were determined using anthracene as the standard [23] (Φ_0 = 0.26). The quantum fluorescence yield of the diimides DCN1 and DCN2 has been calculated on the basis of the absorption and fluorescence spectra in chloroform using the following equation:

$$\Phi_F = \Phi_{st}\frac{S_u}{S_{st}}\frac{A_{st}}{A_u}\frac{n^2_{D_u}}{n^2_{D_{st}}} \quad (3)$$

where the Φ_F is the emission quantum yield of the sample, Φ_0 is the emission quantum yield of standard, A_{st} and A_u represent the absorbance of the standard and sample, respectively, while S_{st} and S_u are the integrated emission band area of the standard and sample, respectively, and n_{st} and n_u is the solvent refractive index of the standard and sample, u and st refers the unknown and standard, respectively.

The DCN1 and DCN2 display a quantum fluorescence yield Φ_F = 4.1–5.3 × 10^{-3} in chloroform and Φ_F = 1.7–2.1 × 10^{-3} in *N*,*N*-dimethylformamide solvents, when excited with light at 379 nm. The low fluorescence quantum yield of the DCN1 and DCN2 are in good correlation with literature data [5c] and shows a fast deactivation of the S_1 state, via intersystem crossing to a close-lying triplet state [5d].

3.2. Fluorescence quenching measurements

Currently there is a greet interest in the development of the effective and sensitive fluorescence chemical sensors, because the determination of transition and heavy metal cations in the environment is of tremendous importance. In this connection it was of interest to investigate the coordination of some metal cations with DCN1 or DCN2.

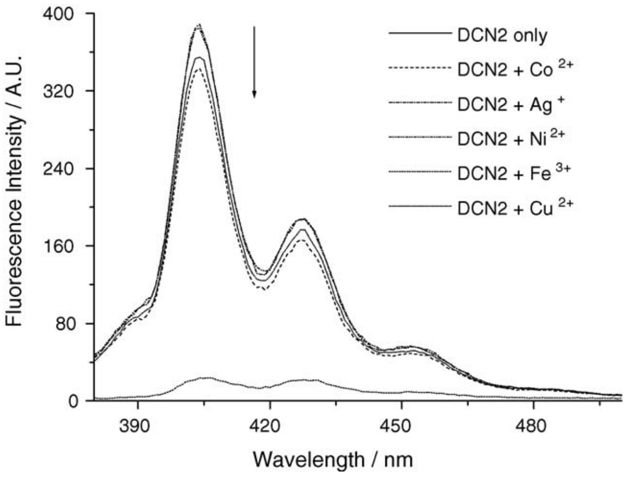


Fig. 2. Fluorecence spectra of DCN2 in *N*,*N*-dimethylformamide solution in the presence of different metal cations. The concentration of metal cations is 8 × 10^{-3} mol. The concentration of DCN2 is 1 × 10^{-4} mol.

The change of the fluorescence intensity induced by the metal cations was investigated and the respective fluorescence response of DCN2 chromophore is presented in Fig. 2. As seen the addition of metal cations leads to decrease of the fluorescence intensity of the DCN2 dissolved in *N*,*N*-dimethylformamide solution, different for each metal cations. In the case of Ag^{+} and Ni^{2+}, the metal cations have no effect upon the fluorescence intensity. In the case of Co^{2+} and Cu^{2+} the effect is insignificant about 8–10%. The highest effect has been observed in the presence of Fe^{3+} when 94% quenching of the fluorescence intensity has been achieved.

The typical change in the fluorescence intensity of DCN2 induced by Fe^{3+} cations has been presented in Fig. 3. The

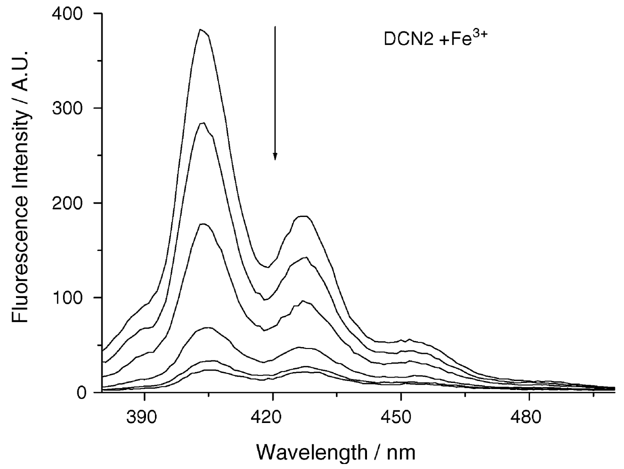


Fig. 3. Fluorecence spectra of DCN2 in *N*,*N*-dimethylformamide at various concentrations of Fe^{3+} cations. The concentrations of Fe^{3+} are in the order of decreasing intensity: 0, 1 × 10^{-5}, 1 × 10^{-4}, 8 × 10^{-4}, 5 × 10^{-3}, 8 × 10^{-3} mol. The concentration of DCN2 is 1 × 10^{-4} mol.

decreasing of fluorescence intensity occurs after the addition of Fe^{3+} cations in the range from 0 to 8×10^{-3} mol. It is seen that the initial addition of the Fe^{3+} cations (1×10^{-5} mol) to a DCN2 solution lead to a decrease of the fluorescent intensity and the respective quenching effect is 26% which indicates very good sensor sensitivity. Further addition of the Fe^{3+} cations into the DCN2 solution, decreases also the intensity of fluorescence. At high metal concentrations (8×10^{-3} mol) the non-fully quenching of the fluorescence is probably due to the competitive reactions occurring between the metal cations and the respective counter ions from the solution.

3.3. Complex formation between DCN1 or DCN2 and iodine

Reaction mixtures containing iodine with either DCN1 or DCN2 in chloroform absorb located at 290 and 360 nm for $[(DCN1)I]^{+}\cdot I_3^{-}$ and one absorption band at 310 nm for the second triiodide complex, $[(DCN2)I]^{+}\cdot I_3^{-}$, (Fig. 4). These absorptions in the two complexes do not belong to any of the reactants and are well known to be characteristic of the formation of triiodide ion, I_3^{-} in the process of complex formation between iodine and different electron donor ligands [16–18,24]. The stoichiometry of the DCN1–iodine and DCN2–iodine is at 1:2 ratio. These values are proposed on the basis of elemental analysis of the isolated solid complexes, mid infrared spectra (Fig. 5). They are in good agreement with the results from photometric titration measurements. These measurements based on the CT-absorption bands exhibited by the spectra of the two systems (mentioned above) and give in Fig. 6(A and B). The equivalence points of the DCN1 and DCN2–iodine systems indicate that the donor:acceptor ratios is 1:2 in good agreement with the elemental analysis data and infrared spectra of the solid CT-complexes. This study was also supported by measuring the far infrared spectra for both of the two complexes, Table 2. The spectra show a group of three bands do not exist in the spectra of the donors around 135, 105 and 85 cm^{-1}. These bands are known to be characteristic for the triiodide ion and can be assigned to ν_{as} (I–I), ν_s (I–I) and δ (I_3^{-}), respectively. The assignment of these band to these vibrations are in good agreement with the presence of a non-linear triiodide ion with C_{2v} symmetry and also with the previously [17,18,25] observed three infrared bands for other related complexes, as shown in Table 2. According to the foregoing discussion, the formed CT-complexes upon the reaction of the investigated 1,4,6,8-dicarboxynaphthalene substituted

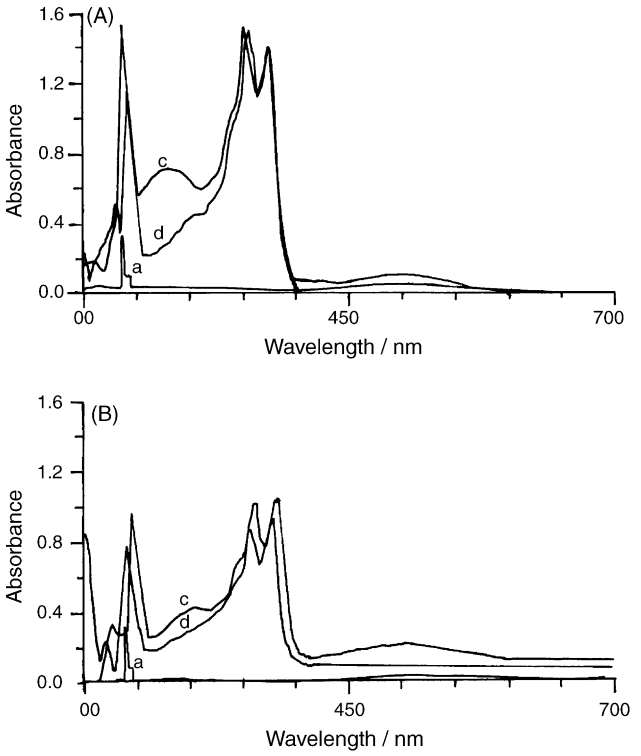


Fig. 4. Electronic absorption spectra of (A) $[(DCN1)]–I_2$ reaction in $CHCl_3$ and (B) $[(DCN2)]–I_2$ reaction in $CHCl_3$. (a) acceptor (1×10^{-4} M), (d) donor (1×10^{-4} M) and (c) donor–acceptor CT-complex.

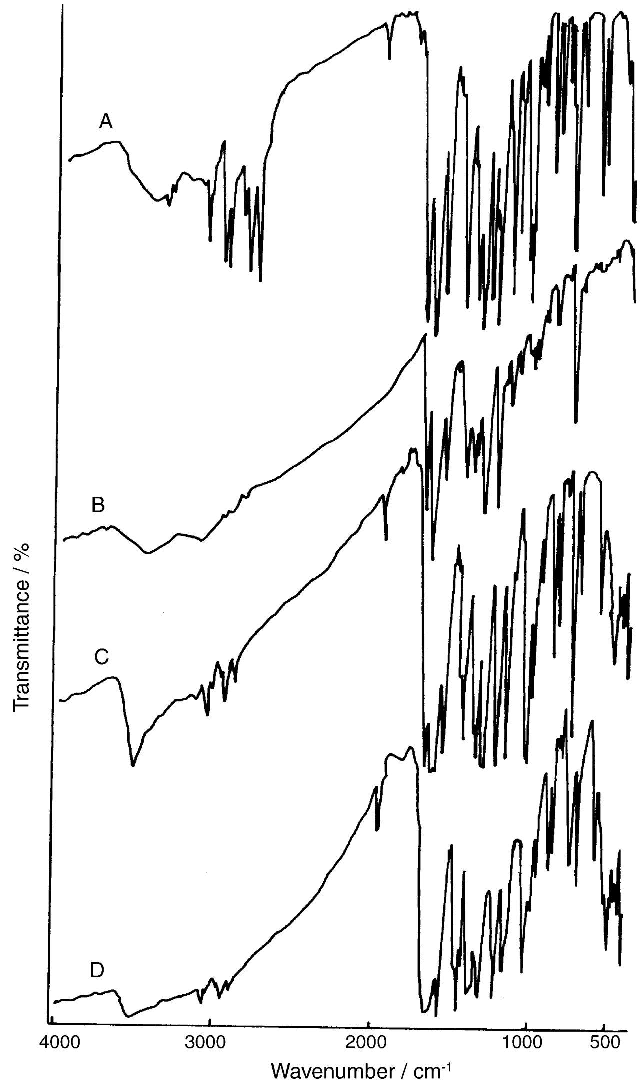


Fig. 5. Infrared spectra of (A) DCN1; (B) $[(DCN1)I]^{+}\cdot I_3^{-}$ complex; (C) DCN2 and (D) $[(DCN2)I]^{+}\cdot I_3^{-}$ complex.

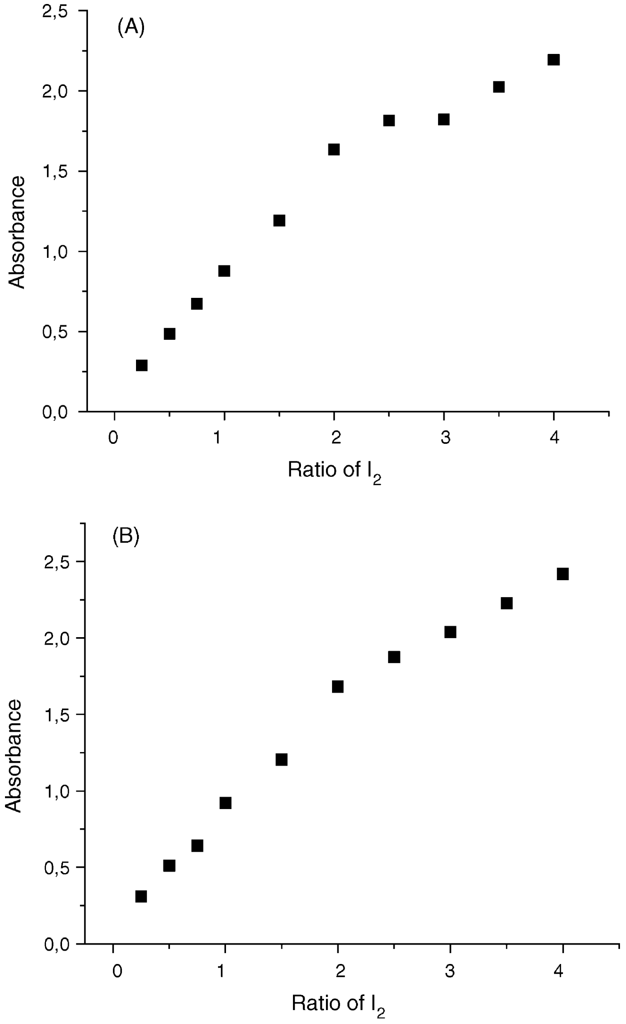


Fig. 6. Photometric titration curves for: (A) (DCN1)–iodine reaction in $CHCl_3$ at 290 nm and (B) (DCN2)–iodine react ion in $CHCl_3$ at 310 nm.

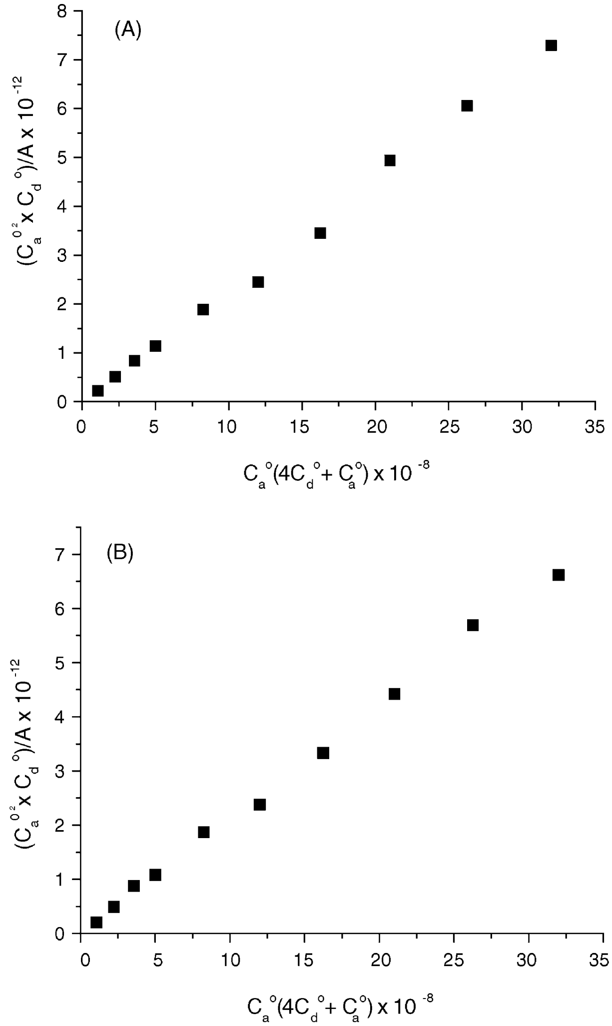


Fig. 7. The plot of $(C_{\mathrm{a}}^{0^2}C_{\mathrm{d}}^{0})/A$ values against $C_{\mathrm{a}}^{0}(4C_{\mathrm{d}}^{0}+C_{\mathrm{a}}^{0})$ values for the (DCN1)–iodine and (DCN2)–iodine reactions in $CHCl_3$ at 290 and 310 nm, respectively.

(DCN1 and DCN2) as donors with iodine in chloroform were formulated as $[(\mathrm{DCN1})\mathrm{I}]^+\cdot\mathrm{I}_3^-$ and $[(\mathrm{DCN2})\mathrm{I}]^+\cdot\mathrm{I}_3^-$, respectively.

The corresponding spectral parameters for the two triiodide complexes were calculated using the known [22] Eq. (4) of 1:2 complexes:

$$\frac{C_{\mathrm{a}}^{0^2}C_{\mathrm{d}}^{0}}{A}=\frac{1}{K\varepsilon}+\frac{1}{\varepsilon}C_{\mathrm{a}}^{0}\left(4C_{\mathrm{d}}^{0}+C_{\mathrm{a}}^{0}\right) \qquad (4)$$

where C_{a}^{0} and C_{d}^{0} the initial concentrations of the iodine and the donor, respectively, while A is the absorbance at the mentioned CT-bands. Plotting the values $C_{\mathrm{a}}^{0^2}C_{\mathrm{d}}^{0}/A$ versus $C_{\mathrm{a}}^{0}(4C_{\mathrm{d}}^{0}+C_{\mathrm{a}}^{0})$ values of Eq. (4), straight lines are obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Fig. 7. The values of both K and ε associated with these two complexes are given in Table 3. These complexes show high values of both the formation constants (K) and the extinction coefficients (ε). The high values of (K) in general indicate high stability of the formed CT-complexes as a result of the expected high donation of such 1,4,6,8-dicarboxynaphthalene, which contain a number of oxygen and nitrogen atoms. The high values of ε agree quite well with the existence of triiodide species, which is known to have a high absorbability values [24–26].

Table 2
Fundamental vibrations for some triiodide compounds

Compounds	Assignments[a]			Reference
	ν_1	ν_2	ν_3	
CsI_3	103	69	149	[25]
$[\mathrm{Ni(acac)_2}]_2\mathrm{I}^+\cdot\mathrm{I}_3^-$	101	84	132	[18]
$[\mathrm{Fe(acac)_3}]_2\mathrm{I}^+\cdot\mathrm{I}_3^-$.	102	76	150	[17]
$[(\mathrm{PAM1})\mathrm{I}]^+\cdot\mathrm{I}_3^-$	110	73	126	[16]
$[(\mathrm{PAM2})_2\mathrm{I}]^+\cdot\mathrm{I}_3^-$	112	75	124	[16]
$[(\mathrm{DCN1})\mathrm{I}]^+\cdot\mathrm{I}_3^-$	102	86	133	Present work
$[(\mathrm{DCN2})\mathrm{I}]^+\cdot\mathrm{I}_3^-$	107	82	137	Present work

[a] ν_1, ν_s (I–I); ν_2, δ (I_3^-); ν_3, ν_{as} (I–I).

Table 3
Spectrophotometric results of CT-complexes of $[(\mathrm{DCN1})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ and $[(\mathrm{DCN2})\ \mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ in $CHCl_3$

Complexes	K	$\lambda_{\max}$ [nm]	$\varepsilon_{\max}$
$[(\mathrm{DCN1})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$	$0.318 \times 10^{8}\,\mathrm{l\,mol^{-1}}$	290	$22.00 \times 10^{4}\,\mathrm{l\,mol^{-1}\,cm^{-1}}$
$[(\mathrm{DCN2})\ \mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$	$0.324 \times 10^{8}\,\mathrm{l\,mol^{-1}}$	310	$21.56 \times 10^{4}\,\mathrm{l\,mol^{-1}\,cm^{-1}}$

The infrared spectra of the $[(\mathrm{DCN1})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ and $[(\mathrm{DCN2})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ complexes and the free bases DCN1 and DCN2 are recorded and shown in Fig. 6. However, the spectra of $[(\mathrm{DCN1})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ and $[(\mathrm{DCN2})\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$ complexes are quite similar to those of the free donors, but with some changes in their band intensities and shifts of some band frequency values like ν(C=O), ν(C=C) and ν(C–H). The infrared band intensities of the free bases (DCN1) and (DCN2) are in general relatively higher than those associated with the infrared bands of their iodine complexes. This may indicate that, the symmetry of the DCN1 and DCN2 are increased upon complexation with iodine implying a smaller change in the dipole moment during the bases vibration in the two complexes form and hence, it show relatively weaker band intensities.

Finally, the formation of these two complexes upon the reaction of iodine with DCN1 and DCN2 may be understood on the basis of the following reactions:

$$\mathrm{DCN}n + \mathrm{I_2} \rightarrow [(\mathrm{DCN}n)\mathrm{I}]^{+}\cdot\mathrm{I}^{-},$$

$$[(\mathrm{DCN}n)\mathrm{I}]^{+}\cdot\mathrm{I}^{-} + \mathrm{I_2} \rightarrow [(\mathrm{DCN}n)\mathrm{I}]^{+}\cdot\mathrm{I_3}^{-}$$

4. Conclusion

Two *N*,*N*′-bis-alkyl-1,4,6,8-naphthalenediimide have been prepared and theirs photophysical properties in two organic solvents of different polarity have been studied. The investigations performed have shown that the contrary to the expectations the polarity of the solvent has a negligible effect upon the spectral and fluorescent characteristics. Moreover their quantum yield is very small in both solvents used. The formation of a complex between *N*,*N*′-bis-alkyl-1,4,6,8-naphthalenediimide derivatives and metal ions has been studied for the first time. The achieved very high sensitivity of the complex towards the presence of Fe^{3+} ions opens many prospects for its application as a highly effective fluorescent sensors of metal ions pollutants in the environment. The synthesis of stable complexes between *N*,*N*′-bis-alkyl-1,4,6,8-naphthalenediimide and iodine has been also reported for the first time. This is a serious step forward in the preparation of novel polyfunction materials.

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