

# Solvatoemissive dual fluorescence of N-(pyridylmethyl)-3-nitro-1,8-naphthalimides

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**Abstract** Solvatoemissive dual fluorescence emission observed in the three positional isomers of N-(n-pyridylmethyl)-3-nitro-1,8-naphthalimide [ $n=2$  (**1**), 3 (**2**), 4 (**3**)] are described. Dual fluorescence emission in this class of compounds occurs from the excited states with extended conjugation via  $\pi$ -stacking interactions. The crystal structure of the compound **1** and the chloride salt of **2** were determined. The compound **1** forms dimeric assemblies through  $\pi$ -stacking interactions. Whereas the structure of the chloride salt of **2** is composed of dimeric assemblies of the cationic part which hold cyclic hydrated anionic assemblies through weak C-H $\cdots$ Cl interactions. Anionic hydrated assemblies between water and chloride ions have cyclic tetrameric structure through O-H $\cdots$ Cl interactions.

**Keywords** Dual fluorescence · Naphthalimide · Pyridine · Optical properties · Solvatoemissive properties

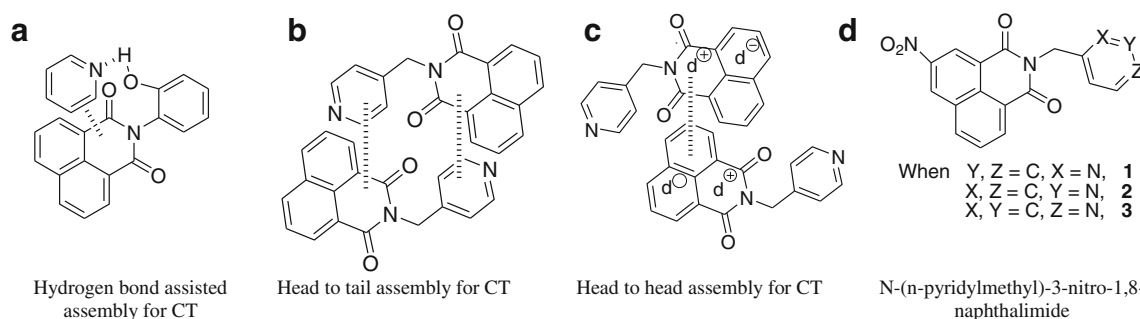
## Introduction

Optical properties of the naphthalimides derivatives are influenced by substituent and functional groups [1–7]. Functional group such as nitro group present on naphthalimide ring enhances scope for structural modifications and also brings about changes in fluorescence mechanism [8]. Switching of

fluorescence emission is commonly generated in N-functionalised naphthalimides through photo-electron transfer (PET) mechanism [9–11]. The naphthalimides find application in signals transduction [12]. On the other hand, higher fluorescence intensity was observed from the N-pyridyl-1,8-naphthalimide over the N-aryl-naphthalimide [13]. Besides these, some naphthalimide derivatives show dual fluorescence emission [14–16]. The N-(4-hydroxyphenyl)-1,8-naphthalimide shows dual fluorescence in pyridine due to excited state with extended conjugation (ESEC) [14]. It occurs due to the presence of O-H $\cdots$ N interaction between pyridine and hydroxy group, which provides suitable orientation to the pyridine to have  $\pi$ -interactions with the naphthalimide ring. To explain the role of pyridine in dual fluorescence Heagy and his co-workers suggested the formation of hydrogen-bond assisted assembly as illustrated in the Fig. 1a [14]. Dual fluorescent molecules are useful analytical reagents for various substrates [17]. Dual fluorescence bands can spread over the entire visible region, so there is scope to use the molecules showing such property as new lighting source [16]. It also further necessitates to take up studies on the fluorescence emission properties of the molecules having pyridine ring covalently linked to naphthalimides or related systems. To pursue research in this trend we have chosen to study pyridylmethyl tethered 1,8-naphthalimide which may form dimeric assemblies through head to tail or head to head arrangements as depicted in Fig. 1b and c. Such self-assemblies are expected to show dual fluorescence by ESEC due to the twist provided by the methylene spacer to observe a particular spatial orientation of a pyridine ring favouring or disfavoring charge transfer process. With such an anticipation, fluorescence emission of three positional isomers of N-(n-pyridylmethyl)-3-nitro-1,8-naphthalimide ( $n=2, 3$  or 4) **1-3** (Fig. 1d) were studied and the results are analysed here.

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**Fig. 1** **a** A hydrogen-bonded assembly of N-(2-hydroxyphenyl)-1,8-naphthalimide with pyridine that is suitable for excited state charge transfer. Description of possible **b** head to tail and **c** head to head arrangements

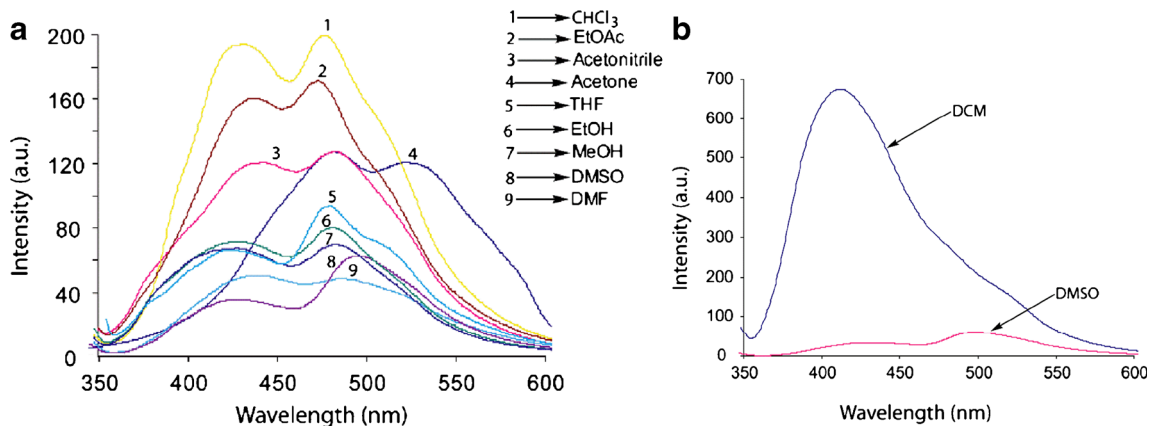
of molecules in dimeric self-assembly of N-(pyridylmethyl)-1,8-naphthalimide. **d** Structure of N-(n-pyridylmethyl)-3-nitro-1,8-naphthalimide [ $n=2$  (**1**), **3** (**2**), **4** (**3**)]

## Results and Discussion

The three positional isomers, N-(n-pyridylmethyl)-3-nitro-1,8-naphthalimide ( $n=2, 3, 4$ ) **1-3**, each showed dual fluorescence emission. It has been observed that the fluorescence emission wavelengths as well as emission intensities of the compounds **1-3** were governed by solvents. As a representative case the fluorescence emission of the compound **1** in different solvents are shown in Fig. 2a. The variations on position of emission as well as the intensities of emission with solvents for the compound **1-3** along with their Stokes shifts are listed in Table 1. The solvents in the first column of the Table 1 are arranged as per ascending order of solvent polarity. Conventionally, the relative polarity of a solvent [18] is directly related to polarity index. The compound **1** or **3** showed dual emission peaks in dichloromethane (DCM) but the emission peak at short-wavelength (SW) was prominent in each case. The long-wavelength (LW) emission was observed as shoulder in DCM. The intensities of the SW peak in DCM was highest in compound **1** or **3**; and least emission intensities were observed when dimethylsulphoxide (DMSO) (Fig. 2b) was used as the solvent. Relative difference in intensity of emission of the compound **1** in DCM, measured at the wavelength at which highest emission occurred was about 600

times higher than the intensity that was observed in DMSO. Hence, for the purpose of easy comparison the emission spectra of the compound **1** in DCM and DMSO are shown in Fig. 2b. The compound **1** dissolved in DMSO had the LW peak with higher intensity than SW peak. The chemical shifts of the protons in  $^1\text{H}$ NMR of the compound **3** in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  (supporting information) were identical. So no structural changes took place in these solvents before excitation. On the other hand, in comparison to change caused by solvent in fluorescence emission of the compounds **1** or **3**, there were no drastic shift in the wavelength of emission of the compound **2** by the solvents, though the relative intensities in fluorescence emission were significantly changed in solutions of compound **2** in different solvents. We did not observe linear correlations between polarity and the shift of position of emission peaks or intensities of fluorescence emission in any of the positional isomer.

The fluorescence lifetimes of the isomeric compounds in dichloromethane were recorded and the values are listed in Table 2. The emission life-time decay of the respective isomeric compounds **1-3** measured at 398 nm, 416 nm and 398 nm, respectively showed bi-exponential fluorescence decay in each case. Out of the two life-times of the SW peak observed for these three compounds, the second lifetime was



**Fig. 2** Fluorescence emission spectra of the **a** compound **1** in different solvents; **b** compound **1** in DMSO and DCM ( $10^{-4}$  M in each case)

**Table 1** Fluorescence emission data of the compounds **1-3**

Solvent (polarity index)	Compound 1			Compound 2			Compound 3		
	$\lambda_{\max}$ (nm)	Intensity (a.u.)	Stokes shift (nm)	$\lambda_{\max}$ (nm)	Intensity (a.u.)	Stokes shift (nm)	$\lambda_{\max}$ (nm)	Intensity (a.u.)	Stokes shift (nm)
Dichloromethane (3.1)	404	658	78	494	265	168	398	652	68
	–	–	–	420	247	94	–	–	–
THF (4.0)	424	64	98	430	79	104	420	56	90
	480	91	154	491	82	165	507	21	177
CHCl <sub>3</sub> (4.1)	432	192	106	489	206	94	420	152	90
	478	197	152	411	121	85	–	–	–
Ethylacetate (4.4)	440	158	114	418	248	92	426	144	96
	476	179	150	483	159	157	491	73	161
Acetone (5.1)	485	125	159	428	108	102	431	80	101
	–	–	–	494	74	168	–	–	–
MeOH (5.1)	429	65	103	441	174	115	434	26	104
	431	33	105	442	93	116	510	19	180
EtOH (5.2)	430	70	104	439	166	113	420	33	90
	483	78	157	496	95	170	–	–	–
Acetonitrile (5.8)	445	119	119	430	202	104	421	107	91
	485	125	159	494	114	168	–	–	–
DMF (6.4)	442	49	116	433	150	107	415	18	85
	487	47	161	498	178	172	–	–	–
DMSO (7.2)	430	34	104	445	38	119	436	18	106
	494	60	168	504	104	178	–	–	–

The concentration of each solution was  $10^{-4}$  M and the excitations were carried out at  $\lambda_{\text{ex}}=340$  nm

found to be longer than the first one. The LW emission of the compound **2** had a relatively long life-time, 8.917 ns, it showed higher stability of the excited state of the LW transition. Generally dual fluorescence occurs through twisted intramolecular charge transfer (TICT) [19–21], or through planarised intramolecular charge transfer (PICT) emission [22, 23]. Generally, in the case of the 1,8-naphthalimide derivatives dual fluorescence occur from two kinetically connected states for either short wavelength emission or for long wavelength emission. These two states are consequence of vibrational relaxation of Franck-Condon states [16]. It was earlier shown that a pyridine molecule placed on top of the naphthalimide ring by weak hydrogen-bond interactions with

functional groups such as hydroxy group of N-4-hydroxyphenyl group attached to 1,8-naphthalimide unit, showed  $\pi$ -interaction between pyridine and the naphthalimide ring [14]. It was also suggested that the LW emission of N-4-hydroxyphenyl naphthalimide in pyridine, was due to transition from excited state with extended conjugation (ESEC) [14]. However, in the present case the pyridine rings are connected to the N-atom of 1,8-naphthalimide ring by an intervening methylene group. Such tethering provides orientations to pyridine ring favouring or disfavouring  $\pi$ -interactions with dipolar 1,8-naphthalimide ring. In the present study, the pyridine units are tethered through intervening methylene group which is  $sp^3$  hybridised. So the TICT

**Table 2** Fluorescence life-time ( $\lambda_{\text{ex}}$ , 375 nm) of the compounds **1-3** in dichloromethane

Compound No.	Emission ( $\lambda_{\text{max}}$ , nm)	$\chi^2$ (regression value)	Life time, $\tau$ in ns (%)	$\tau_{\text{error}}$
1	398	1.084	1.834 (76.65)	0.005
			5.917 (27.35)	0.002
2	416	1.016	1.924 (46.71)	0.020
			4.972 (53.29)	0.009
3	495	1.041	8.917 (100)	0.0005
			398	1.032
			7.275 (33.07)	0.002

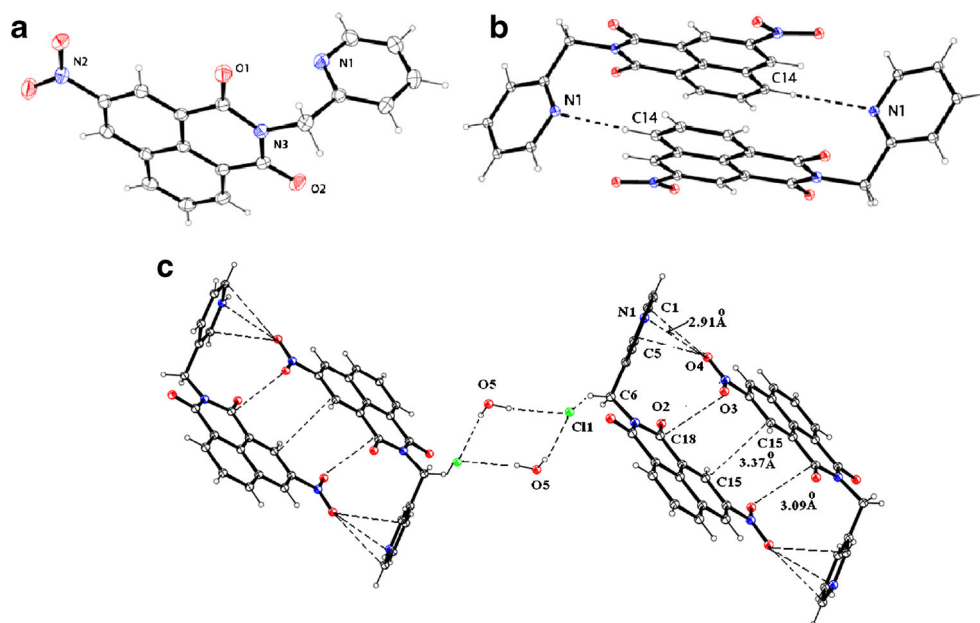
mechanism explained earlier [14] has to be slightly modified to explain fluorescence mechanism of our system. The compounds **1–3** have sickle shape geometry and these molecules easily form dimeric structures [24]. Thus, there is possibility of ESEC by intermolecular interactions between the pyridine and 1,8-naphthalimide or between dipolar 1,8-naphthalimide rings. Such assemblies shown in Fig. 1b would result in excited states having different orientations to favour charge transfer or not. Such orientations cause the LW and SW emissions respectively, in these isomeric compounds. The SW emission arises from excited state with the orientation which is devoid of charge transfer interaction; this emission resembles conventional fluorescence emission observed in naphthalimide. The LW emission occurs due to the excited state with an orientation favouring  $\pi$ -interaction. Based on the stability of such excited states in different solvents dual fluorescence from the isomeric compounds was observed. We have recently shown that holding an anion over a naphthalimide ring through weak interactions of imidazole ring can either cause quenching or enhancement of fluorescence [25].

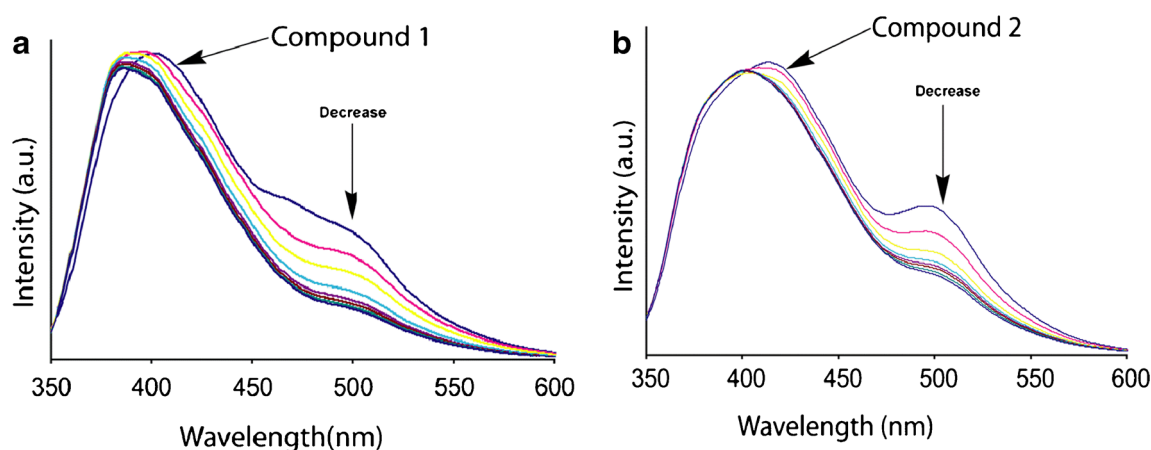
The single crystal structure determined by X-ray of the compound **1** (Fig. 3a) shows that the structure is comprised of dimeric assemblies of molecules held in head to tail arrangements. Such assemblies are formed through C-H $\cdots$ N interactions ( $d_{\text{C14-H}\cdots\text{N}}$ , 3.539 Å and  $\angle$  C14-H $\cdots$ N 155.5°) as shown in Fig. 3b. We also determined the structure of the chloride salt of the compound **2**. It also formed cations dimeric assemblies in head to tail fashion comprising of two protonated units of **2**, or namely by two N-(3-pyridiniummethyl)-3-nitro-1,8-naphthalimide cations. There is significant amount of  $\pi$ -interactions in these dimeric assemblies of the salt. These interactions are reflected in some of the distances of separation

of aromatic rings and functional groups. For example, the O3-C18 distance is 3.01 Å, and the O4-N1 distance is 2.91 Å, which suggests existence of O $\cdots$  $\pi$ -interactions. Moreover, there is possibility for significant amount of  $\pi$ -stacking interactions between the 3-nitro-1,8-naphthalimide rings as the distance between C15 atoms of two such parallel rings are 3.37 Å. In the crystal lattice there are cyclic tetramer formed between two chloride anions and two water molecules. The tetramers are formed by O-H $\cdots$ Cl interactions in which hydrogen bonds of water molecules forms bridges the chlorides. The dimers of protonated N-(3-pyridylmethyl)-3-nitro-1,8-naphthalimide cations are separated by such cyclic chloride-water tetramers.

The isolation of the chloride salt and further characterisation by structure determination supported the protonation of compound **2** by hydrochloric acid in solution. The structural study also provided support to the possibility involvement of excited state extended conjugation via  $\pi$ -stacking mechanism. For such a mechanism illustrated earlier for the unprotonated form to be operative in the case of the salt of compound **2**, the dual fluorescence should significantly change on protonation. This is expected as the protonation of the nitrogen atom on pyridine caused changes in the  $\pi$ -stacking pattern of the 3-nitro-1,8-naphthalimide rings of **2**. Since it is proposed that the LW wavelength is generated by ESEC mechanism, the LW peak should get quenched when hydrochloric acid is added to either of the compound **1–3**. As anticipated, addition of hydrochloric acid solution to solution of either of the compound **1–3** caused the loss of LW emission peak. The observed changes of the fluorescence emission of the compounds **1** and **2** by different aliquots of hydrochloric acid solution are shown in Fig. 4a and b. In both these cases the LW emission appearing as shoulder, got quenched on addition

**Fig. 3** The structure of **a** **1**, **b** dimeric assemblies of **1** and **c** A part of packing pattern showing assemblies of chloride salt of **2** through various weak interactions (50 % thermal ellipsoids)





**Fig. 4** The change in the fluorescence emission spectra ( $\lambda_{\text{ex}}=340$  nm) of the **a** compound **1** (2.5 ml,  $10^{-4}$  M in DCM) on addition of HCl (10  $\mu$ l aliquots of  $10^{-2}$  M solution of HCl); **b** compound **2** (2.5 ml,  $10^{-4}$  M in DCM) on addition of HCl (10  $\mu$ l aliquots of  $10^{-2}$  M solution of HCl)

of hydrochloric acid, whereas, protonation of pyridine of the compounds did not affect the SW emission peaks.

Thus, we have analysed the fluorescence emission properties of three positional isomeric compounds of N-(methylpyridyl)-3-nitro-1,8-naphthlimide which exhibits solvent dependent dual fluorescence emission.

## Experimental

All reagents and solvents were purchased commercially and were used without further purification.  $^1\text{H}$ NMR data were recorded by a Varian 400 MHz FTNMR spectrometer. The FT-IR spectra were recorded by using a PerkinElmer spectrum one spectrometer in the KBr pellets in the range 4,000–400  $\text{cm}^{-1}$ . The UV/Vis spectra and fluorescence spectra were recorded using PerkinElmer Lambda 750 spectrometer and PerkinElmer LS 55 spectrometer respectively. Fluorescence measurements were carried out with a Carry Eclipse spectrometer using 20 mm path length quartz cuvette with the slit width 10 nm. Fluorescence emission spectra of the compounds ( $10^{-4}$  M) in respective solvents were recorded by exciting at 340 nm. Quantum yields were calculated using quinine sulphate (in 1N  $\text{H}_2\text{SO}_4$ ) as standard solution. The fluorescence life-times were measured on a pico-second time-resolved cum steady state luminescence spectrometer of Eddinburg instruments, model: FSP920 and LifeSpec II.

## Structure Determination

The X-ray data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 3.0 KW sealed tube, with  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073$  Å) at 298 K, with increasing  $\omega$  (width of 0.5 per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were done with SAINT

and XPREP software. Structures were solved by direct methods using SHELXS-97 and refined with full matrix least-squares on  $F^2$  using SHELXL-97 software. All the non-H atoms were refined in the anisotropic approximation against  $F^2$  of all reflections. The H-atoms, except those attached to nitrogen atoms were placed at their calculated positions and refined in the isotropic approximation; those attached to nitrogen were located in the difference Fourier maps, and refined with isotropic displacement coefficients.

## N-(2-pyridylmethyl)-3-nitro-1,8-naphthalimide (**1**)

To solution of 3-nitro-1,8-naphthalic anhydride (0.49 g, 2 mmol, in DMF 20 ml), 2-aminomethyl pyridine (0.2 ml, 2 mmol) was added. The solution was refluxed at 110 °C for 12 h. Then the reaction mixture was cooled and added to a water (100 ml) containing ice. A yellow precipitate was obtained; it was dried in air and characterized. Yield, 81 %. IR (KBr,  $\text{cm}^{-1}$ ): 3,444 (b), 3,070 (w), 1,782 (m), 1,743 (w), 1,708 (s), 1,664 (s), 1,595 (s), 1,539 (s), 1,508 (m), 1,480 (m), 1,428 (s), 1,347(s), 1,334 (w), 1,293 (m), 1,242 (s), 1,180 (m), 1,157 (w), 1,116 (w), 1,079 (w), 1,046 (w), 1,018 (w), 995 (w), 978 (m), 913 (w), 786 (s), 756 (s), 699 (m), 501 (m). Elemental anal calcd. for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_4$  Calcd (%) C, 64.86; H, 3.33; N, 12.61; found C, 64.88; H, 3.32; N, 12.59.  $^1\text{H}$ NMR(400 MHz,  $\text{CDCl}_3$ ): 9.3 (d, 1H, 2.4Hz), 9.13 (d, 1H, 2.4Hz), 8.79 (d, 1H, 7.6Hz), 8.45 (d, 1H, 4.8Hz), 8.43(d, 1H, 7.6Hz), 7.95 (t, 1H, 7.2Hz), 7.56 (t, 1H, 7.6Hz), 7.36 (d, 1H, 8.0Hz), 5.52 (s, 2H). Fluorescence emission (Methanol  $\lambda_{\text{ex}}=340$  nm) 486 nm ( $\Phi=0.191$ ). Crystallographic details: CCDC no. 919178; crystal system, monoclinic; space group,  $\text{P}2_1/\text{c}$ ; Temp.=298(2) K; Wavelength=0.71073 Å;  $a=11.0481(4)$  Å;  $b=8.6239(4)$  Å;  $c=15.8686(7)$  Å;  $\alpha=90.00^\circ$ ;  $\beta=94.986(4)^\circ$ ;  $\gamma=90.00^\circ$ ;  $V=1506.19(11)$  Å $^3$ ;  $Z=4$ ; Density=1.470  $\text{g}\cdot\text{cm}^{-3}$ ; Abs. coeff.=0.107  $\text{mm}^{-1}$ ;  $F(000)=688$ ; Total no. of reflections=2,717; Reflection,  $I>2\sigma(I)$  1,680; Max.  $2\theta$ , 50.5; Ranges (h, k, l) –



$13 \leq h \leq 13$ ;  $-10 \leq k \leq 6$ ;  $-11 \leq l \leq 19$ ; Completeness to  $2\theta = 99.3\%$ ; Refinement method, full-matrix least-squares on  $F_2$ ; Data/restraints/parameters, 2717/0/226; Goof ( $F_2$ ), 1.091; R indices [ $I > 2\sigma(I)$ ]=0.0599; R indices (all data)=0.0976.

N-(n-pyridylmethyl)-3-nitro-1,8-naphthalimide (when  $n=3$ , (2), when  $n=4$ , (3))

The compound **2** or **3** was prepared in a similar procedure to that of the compound **1**; except **3** or 4-aminomethyl pyridine respectively, was used instead of 2-aminomethyl pyridine. In each case a brown precipitate of **2** or **3** was obtained. N-(3-pyridylmethyl)-3-nitro-1,8-naphthalimide: Yield 86 %. IR (KBr,  $\text{cm}^{-1}$ ): 3,433 (b), 1,703 (s), 1,661 (s), 1,594 (s), 1,535 (s), 1,509 (m), 1,478 (w), 1,433 (s), 1,372 (m), 1,334 (s), 1,245 (s), 1,176 (m), 1,112 (w), 1,079 (w), 1,048 (w), 1,030 (w), 973 (m), 928 (w), 829 (w), 792 (s), 759 (s), 734 (m), 709 (s). Elemental anal calcd for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_4$ , Calcd (%) C, 64.86; H, 3.33; N, 12.61; found C, 64.81; H, 3.30; N, 12.72.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 9.31 (d, 1H, 2.0 Hz), 9.12 (d, 1H, 2.4 Hz), 8.81 (s, 1H), 8.78 (d, 1H, 7.6 Hz), 8.50 (d, 1H, 3.6 Hz), 8.42 (d, 1H, 8.0 Hz), 7.95 (d, 1H, 8.0 Hz), 7.91 (t, 1H, 8.0 Hz), 7.23 (t, 1H, 3.2 Hz), 5.53 (s, 2H). Fluorescence emission (Methanol  $\lambda_{\text{ex}}=340$  nm) 430 nm ( $\Phi=0.0664$ ). N-(4-pyridylmethyl)-3-nitro-1,8-naphthalimide: Yield 94 %. IR (KBr,  $\text{cm}^{-1}$ ): 3,411 (b), 1,706 (s), 1,667 (s), 1,598 (s), 1,561 (w), 1,537 (s), 1,506 (m), 1,421 (s), 1,346 (m), 1,333 (m), 1,243 (s), 1,176 (m), 1,111 (w), 976 (w), 789 (s), 756 (m). Elemental anal calcd for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_4$ , Calcd (%) C, 64.86; H, 3.33; N, 12.61; found C, 64.89; H, 3.31; N, 12.80.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 9.31 (s, 1H), 9.14 (s, 1H), 8.79 (d, 1H, 7.2 Hz), 8.53 (d, 1H, 4.8 Hz), 8.45 (d, 1H, 8.4 Hz), 7.96 (t, 1H, 7.6 Hz), 7.37 (d, 1H, 5.2 Hz). Fluorescence emission (Methanol  $\lambda_{\text{ex}}=340$  nm) 512 nm ( $\Phi=0.0784$ ).

Chloride Salt of N-(3-pyridylmethyl)-3-nitro-1,8-naphthalimide

Few drops of 70 % HCl was added to a solution of compound **2** (1 mmol) in a binary mixture of ethanol-chloroform (10 ml 1 : 1 v/v). The clear solution obtained was filtered and kept undisturbed at room temperature. On standing, brown needle shaped crystals appeared after 7–8 days. Yield 62 %. IR ( $\text{cm}^{-1}$ ): 3,497 (w), 3,417 (w), 3,068 (m), 2,549 (br), 1,708 (s), 1,662 (s), 1,596 (w), 1,537 (m), 1,331 (s), 1,245 (m), 1,105 (w), 1,048 (w), 797 (s), 688 (m). Crystallographic details: CCDC No. 916143. Crystal system, Triclinic; Space group, P-1; Temp=298(2) K; Wavelength=0.71073 Å;  $a=6.6249(6)$  Å;  $b=10.1436(8)$  Å;  $c=13.6640(10)$  Å;  $\alpha=104.476(6)^\circ$ ;  $\beta=90.535(7)^\circ$ ;  $\gamma=103.812(7)^\circ$ ;  $V=861.03(12)$  Å<sup>3</sup>;  $Z=2$ ; Density=1.496  $\text{g cm}^{-3}$ ; Abs. coeff. = 0.259  $\text{mm}^{-1}$ ;  $F(000)=400$ ; Total no. of reflections=3,100; Reflection,  $I > 2\sigma(I)$  1,438; Max.  $2\theta$ , 50.5; Ranges (h, k, l)  $-7 \leq h \leq 7$ ;  $-12 \leq k \leq 9$ ;  $-$

$16 \leq h \leq 16$ ; Completeness to  $2\theta = 99.9\%$ ; Refinement method, Full-matrix least-squares on  $F_2$ ; Data/restraints/parameters, 3100/0/252; Goof ( $F_2$ ), 0.999; R indices [ $I > 2\sigma(I)$ ]=0.0595; R indices (all data)=0.1292.

## References

- Nandhikonda P, Begaye MP, Cao Z, Heagy MD (2009) Discovery of dual fluorescent 1,8-naphthalimide dyes based on balanced seesaw photophysical model. *Chem Commun* 4941–4953
- Kucheryvy P, Li G, Vyas S, Hadad C, Glusac KD (2009) Electronic properties of 4-substituted naphthalimides. *J Phys Chem A* 113: 6453–6451
- Veale EB, Gunnlaugsson T (2010) Synthesis, photophysical, and DNA binding studies of fluorescent Troger's base derived 4-amino-1,8-naphthalimide supramolecular clefts. *J Org Chem* 75:5513–5525
- Loving G, Imperiali B (2009) Thiol-reactive derivatives of the solvatochromic 4-N, N-Dimethylamino-1,8-naphthalimide Fluorophore: a highly sensitive toolset for the detection of biomolecular interactions. *Bioconjug Chem* 20:2133–2141
- Duke RM, Veale EB, Pfeffer FM, Kruger PE, Gunnlaugsson T (2010) Colorimetric and fluorescent anion sensors: an overview of recent developments in the use of 1,8-naphthalimide-based chemosensors. *Chem Soc Rev* 39:3936–3953
- Socher E, Imperiali B (2013) FRET-capture: a sensitive method for the detection of dynamic protein interactions. *ChemBioChem* 14:53–57
- Yang M, Song Y, Zhang M, Lin S, Hao Z, Liang Y, Zhang D, Chen PR (2012) Converting a solvatochromic fluorophore into a protein-based pH indicator for extreme acidity. *Angew Chem Int Ed Engl* 51: 7674–7679
- Middleton RW, Parrick J (1985) Preparation of 1,8-naphthalimides as candidate fluorescent probes of hypoxic cells. *J Heterocycl Chem* 22: 1567–1572
- Vazquez ME, Rothman DM, Imperiali B (2004) A new environment-sensitive fluorescent amino acid for Fmoc-based solid phase peptide synthesis. *Org Biomol Chem* 2:1965–1966
- DeSilva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher J, Rice TE (1997) Fluorescent photoinduced electron transfer (PET) sensors for anions; from design to potential application. *Chem Rev* 97:1515–1566
- Guha S, Goodson FS, Corson LJ, Saha S (2012) Boundaries of anion/naphthalene-diimide interactions: From anion- $\pi$  interactions to anion-induced charge-transfer and electron-transfer phenomena. *J Am Chem Soc* 134:13679–13691
- Gunnlaugsson T, Kruger PE, Jensen P, Pfeffer FM, Hussey GM (2003) Simple naphthalimide based anion sensors: deprotonation induced colour changes and  $\text{CO}_2$  fixation. *Tetrahedron Lett* 44:8909–8913
- Nandhikonda P, Begaye MP, Chao Z, Heagy MD (2010) Frontier molecular orbital analysis of dual fluorescent dyes: predicting two-color emission in N-aryl-1, 8-naphthalimides. *Org Biomol Chem* 8: 3195–3201
- Paudel S, Nandhikonda P, Heagy MD (2009) A comparative study into two dual fluorescent mechanisms via positional isomers of N-hydroxyarene-1,8-naphthalimides. *J Fluoresc* 19:681–691
- Biczok L, Valat P, Wintgens V (1999) Effect of molecular structure and hydrogen bonding on the fluorescence of hydroxy-substituted naphthalimides. *Phys Chem Chem Phys* 1:4759–4766
- Cao H, Chang V, Hernandez R, Heagy MD (2005) Matrix screening of substituted N-aryl-1,8-naphthalimides reveals new dual fluorescent dyes and unusually bright pyridine derivatives. *J Org Chem* 70: 4929–4934

17. Demeter A, Breces T, Biczok L, Wintgens V, Valta P, Kossanyi J (1996) Monoboronic acid sensor that displays anomalous fluorescence sensitivity to glucose. *J Phys Chem* 100:2001–2011
18. Reichardt C (1994) Polarity study of some 1-alkyl-3-methylimidazolium ambient -temperature ionic liquids with the solvatochromic dye, Nile Red. *Chem Rev* 94:2319–2358
19. Inoue Y, Jiang P, Rsukada E, Wada T, Shimizu H, Tai A, Ishikawa M (2002) Unique dual fluorescence of sterically congested hexaalkyl benzenehexa carboxylates: mechanism and application to viscosity probing. *J Am Chem Soc* 124:6942–6949
20. Grabowski Z, Rotkiewicz K, Rettig W (2003) Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures. *Chem Rev* 103: 3899–4031
21. Bettermann H, Bienosckek M, Ipendorf H, Martin HD (1992) Dual fluorescence of novel modified carotenoids. *Angew Chem Int Ed Engl* 31:1042–1043
22. Druzhinin SI, Kovalenko SA, Senyushkina TA, Demeter A, Machinck R, Noltemeyer M, Zachariasse KA (2008) Intramolecular charge transfer with the planarized 4-cyanofluorazene and its flexible counterpart 4-cyano-N-phenylpyrrole. Picosecond fluorescence decays and femtosecond excited-state absorption. *J Phys Chem A* 112:8238–8253
23. Yoshihara T, Druzhinin SI, Demeter A, Kocher N, Stalke D, Zachariasse KA (2005) Kinetics of intramolecular charge transfer with N-phenylpyrrole in alkyl cyanides. *J Phys Chem* 109:1497–1509
24. Sarma RJ, Tamuly C, Barooah N, Baruah JB (2007) Role of  $\pi$ -interactions in solid state structures of a few 1,8-naphthalimide derivatives. *J Mol Struct* 829:29–36
25. Nath JK, Baruah JB (2013) Water assisted anion chains and anion dependent fluorescence emission in salts of N, N'-bis(3-imidazol-1-ylpropyl)naphthalenediimide. *New J Chem* 37: 1509–1519