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Highly solvatochromic fluorescent naphthalimides: Design, synthesis, photophysical properties and fluorescence switch-on sensing of ct-DNA

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ABSTRACT

We report the design, synthesis and photophysical properties of highly solvatochromic donor/acceptor substituted naphthalimide based fluorophores. The synthesized naphthalimides containing propargyl ends showed highly solvatochromic intramolecular charge transfer (ICT) feature as was revealed from the UV–visible, fluorescence photophysical properties of these fluorophores and DFT/TDDFT calculation. Fluorescence life times for the imide fluorophores were also measured in different solvents. The solid state photophysical property of donor substituted naphthalimide **1** showed promising for future application in material sciences. Furthermore, both the donor/acceptor substituted naphthalimide fluorophores **1**–**2** were exploited in sensing calf-thymus DNA via switch-on fluorescence response. The propargyl linker containing naphthalimides can further be exploited for the synthesis of labeled biomolecular building blocks.

Solvatochromic fluorescent molecules are widely known to serve as extremely sensitive probes in biological systems for the detection and probing of structures, dynamics, micropolarity around a biomolecule and interbiomolecular interactions.[1] Therefore, the development of such fluorescent molecules is a very important research target for understanding biological events associated with interbiomolecular interactions. As for example, highly solvatochromic fluorescent probes and fluorescently labeled biomolecular building blocks such as solvofluorochromic nucleosides/amino acids have been successfully utilized for the sensing and detection of biomolecular microenvironment/biomolecules.[2] However, many of such explored fluorophores emitted at a short wavelength region, possessed low emission intensity and/or suffered from a quenching incidence rendering them unsuitable for practical use.[3] Therefore, bright and long-wavelength emissive fluorescent molecules with emission in the visible region have attracted great interest in recent time as new fluorescent probes for the detection and sensing of biomolecules without any interference by the background signal generated from the autoabsorption and autofluorescence of biomolecules.

As a part of our ongoing program for the design and synthesis of highly solvatochromic fluorophores with a linker unit for possible future use in labeling of biomolecular building blocks and taking into consideration of the importance of naphthalimide derivatives[4] in biological applications, we were thus very much interested in the possibility of synthesizing 1,8-naphthalimide derivatives with donor/acceptor substituents as new potential solvatochromic fluorophores. Naphthalimide derivatives aroused the interest of chemists, physicists and biologists for various reasons. The 4-amino and/or alkyl amino-1,8-naphthalimide chromophore or their anologues have been reported for their several interesting photophysical properties and utilized for chemosensory applications.[4i] Because of the 'push–pull' nature of its internal charge transfer (ICT) excited state, they have been utilized in several biological applications.[4] Naphthalenimides show a diversified reactivity towards biological substrates including DNA and proteins. Furthermore, because of their potential anti-tumor activity upon electronic excitation with UV light 1,8-naphthalimides have attracted much attention in the fields of biology and medicine. 4-Amino-1,8-naphthalimide also have been utilized in supramolecular fields as well as DNA targeting molecule. Troger's base compounds as well as metal complexes of napthalimides have been developed and found to interact strongly with DNA.[4i–l] However, there is no report of 1,8-naphthalimide in which 4-position is conjugated to donor/acceptor substituted phenylacetylenes to achieve much longer absorption wavelength.

Therefore, in this particular we report the syntheses and photophysical properties of donor/acceptor containing 1,8-naphthalimide derivatives **1**–**2** in which chromophores have free acetylene arms which can be exploited further for future applications such as for the synthesis of labeled biomolecular building blocks. We explored the sensitivity in fluorescence response upon changing the solvent polarity of these fluorophores. We also wanted to examine

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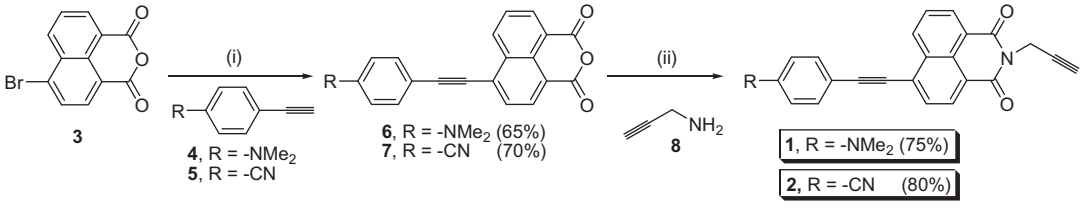
the ability of the fluorophores **1**–**2** in possible sensing of biomolecule like ct-DNA.

Therefore, we have chosen 4-bromo-1,8-naphthalic anhydride as our starting material. The reason behind our choice was to achieve charge transfer fluorescence response upon incorporating a donor unit by a substitution at 4-bromo functionality. Thus, there might be a possibility of getting emission at longer wavelength region because of the conjugation between the donor substituent and the acceptor naphthalimide core leading to a long range charge transfer (CT) process and hence we expectedly would observe an excellent solvofluorochromicity.[4,5] On the other hand we also wanted to know the effect of an acceptor substituent and compare the photophysical behavior with that of the donor substituted one. Therefore, the fluorophores might show high solvatofluorochromicity which could be utilized for probing of biomolecular microenvironment.

With this background and aim we have first synthesized the fluorophores **1**–**2**. The routes adopted for the synthesis of target compounds **1**–**2** is shown in Scheme 1. Thus, a Pd(0)-mediated 'click-reagent version' of Sonogashira coupling[4b,6] of anhydride **3** with 4-ethynyl-*N,N*-dimethylaniline and 4-ethynylbenzonitrile, respectively, in dry DMF at 80 °C for 4 h, yielded 4-substituted-1,8-naphthalic anhydrides, **6**–**7**. After recrystalization from hot toluene pure naphthalic anhydride derivatives **6**–**7** in 65% and 70% yields, respectively, were afforded. Next, conjugated anhydrides **6**–**7** were allowed to react with propargyl amine in dry ethanol under reflux for 50 h to afford 4-(4-*N,N*-dimethylaminophenylethynyl)-*N*-(2-propynyl)-1,8-naphthalimide (**1**, $^{4\text{-DMAPE}}$**NI**) and 4-(4-cyanophenylethynyl)-N-(2-propynyl)-1,8-naphthalimide (**2**, $^{4\text{-CPE}}$**NI**), respectively, with good yields (Scheme 1). Washing the products in water and ethanol and recrystalization gave pure compound **1** as red crystalline solid and **2** as yellow powdered solid in very good yields. The structures of the final products were characterized by NMR, mass spectrometry, and by X-ray single crystal analysis of compound **1**.

The crystal structure of fluorophore **1** showed a very interesting arrangement (Fig. 1). Thus, the donor substituted planar naphthalimide with the pendent propargyl arm crystallized in a layered sheet-like arrangement. The planar sheets are layered on top of each other, with slip-stacked ArCH–π-bonding (3.29 Å) between internal alkyne and aromatic C–H of naphthalimide core. The layers are held by C–C–π (3.37 Å) bonding between donor/acceptor aromatics and π-stacking between the donor unit in one layer and the acceptor naphthalimide core of the other layer (Fig. 1a). Head-to-tail arrangements of donor *N,N*-dimethylanilino unit of one molecule in one layer and acceptor naphthalimide core of a separate molecule in second layer makes the system stable by forming a strongly π-stacked and charge transfer stabilized stacked layer like structure.[7] The layers are so arranged that the donor-*N,N*-dimethylphenyl moiety interacts via π-stacking and charge transfer interactions with the acceptor naphthalimide ring in the molecule in the layer above and below with an average interlayer distance being 3.31 Å. The pendant terminal acetylenic-H involved in H-bonding with –C=O of naphthalimide group (2.37 Å) of a molecule in a different layer giving rise to a bent-stair-like arranged third stacked layer (Fig. 1a and b).

After getting all the compounds in hand in very pure form we turned our attention to study their photophysical properties. Thus, the UV–vis absorption spectra of the naphthalimide fluorophores **1**–**2** were studied in various solvents of different polarity. The longest wavelength absorption of compound **1** was characterized by a broad band with the maxima appearing between 450 and 467 nm



Reagents and conditions: (i) $Pd(PPh_3)_4/Et_3N/DMF/CuSO_4/Na$-ascorbate/80 °C, 4 h; (ii) EtOH/Reflux, 50 h.

Scheme 1. Synthesis of donor/acceptor labeled naphthalimide fluorophores **1**–**2**.

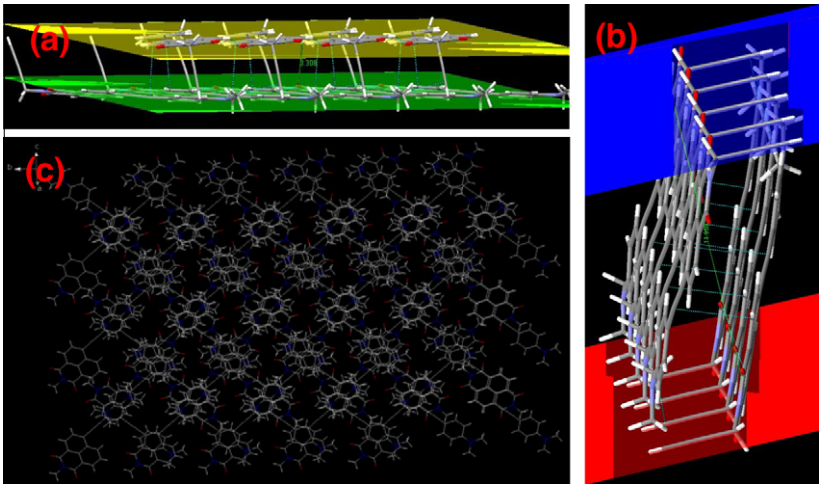


Figure 1. Crystal structure (a–b) showing inter planar distance and the two planes formed by two pendent acetylenic arms. (c) Crystal network of the molecule **1** (the CCDC number is CCDC 882241).

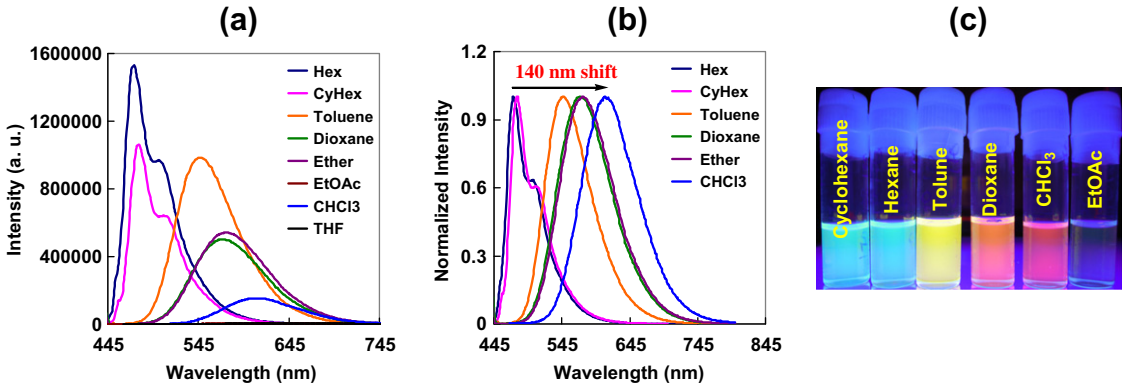


Figure 2. (a) Emission and (b) normalized emission spectra of **1** ($^{4\text{-DMAPE}}$**NI**) in different solvents (10 μM, rt; $\lambda_{ex} = \lambda_{max}$ = 445–465 nm). (c) Colors:colours in different solvents after irradiation of **1** in UV light (λ = 254 nm) under a UV-transilluminator.

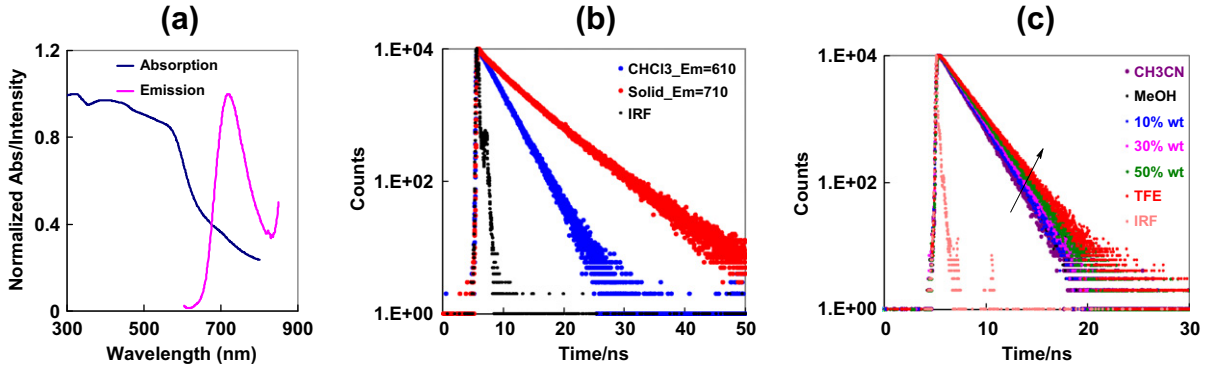


Figure 3. (a) Solid state UV–visible/fluorescence spectra and (b) time resolved fluorescence traces in solution and solid states of fluorophore **1**. (c) Time resolved fluorescence traces of fluorophore **2** in various solvents.

depending on the polarity of the solvents (see Supplementary data). This band was unambiguously assigned as intramolecular charge transfer (ICT) band that was generated out of charge transfer from the donor 4-*N,N*-dimethylaminophenyl group to the acceptor naphthalimide ring system via the internal alkyne. The origin of ICT was also evident from the fairly broad, intense and the large solvatochromicity of the band.[5b,8] Thus, an increase in polarity of the media led to a red shift of the absorption maxima of about 14–24 nm when changing the solvent from hexane to chloroform to DMSO suggesting that the ground state of the molecule was significantly polar. However, for the fluorophore **2**, a blue shift of about 17 nm of the absorption band on changing the solvent from dioxane to trifluoroethanol (between 389 and 372 nm) was observed which might be because of the presence of electron acceptor cynophenyl unit in conjugation with the naphthalimide ring system (see Supplementary data). This observation indicated that the ground state was not so polar and the fluorophore **2** was lipophilic in nature. Therefore, the donor *N,N*-dimethylaminophenyl unit was responsible for the enhancement of the charge separation in the molecule **1** which ultimately led to a large red shift of the absorption maxima.

Next, we evaluated the fluorescence photophysical properties of the fluorophores. Thus, for all the cases it was observed that the effect of the solvent polarity on the emission maxima was more pronounced than that on the absorption maxima (Figs. 2–4). The fluorescence spectra of all the compounds consisted of structureless broad band except in highly low polar solvent like hexane, cyclohexane where some structured bands appeared. However, an increase in the polarity of the solvent led to large Stokes shift of emission maxima for compound **1** and comparatively less for compound **2**. Thus, from the fluorescence spectra of imide fluorophore **1** (Fig. 2a and b), it was clear that as the solvent polarity increases a strong red shift of about 140 nm ($\lambda_{max,hexane}$ 474 nm, and $\lambda_{max,chloroform}$ 611 nm) was observed with decrease in both the fluorescence intensity and the quantam yield (Table 1). Therefore, the fluorophore **1** is highly solvatochromic. The red shift and signal broadening of the spectra indicated that the conjugation is extended well between the acceptor imide carbonyl group and the donor *N,N*-dimethylanilino unit through internal alkyne. Same observation was reflected in the fluorescence images of the compound in different solvents at a wavelength of 254 nm under a transilluminator (Fig. 2c). Thus, in hexane/cyclohexane it showed a strong greenish blue color while the color changed from greenish blue to yellow in toluene, pink in dioxane and ultimately to red in chloroform. Surprisingly, no emission was observed when polarity of the solvent increased to methanol through ethylacetate.

Red colored crystalline solid nature, highly ICT character and non-emissive nature of the fluorophore **1** in protic polar solvent drew our interest to evaluate its' solid state photophysical property for possible future material applications. Thus, the solid state UV–visible spectra showed two absorption bands at 444 and 560 nm (Fig. 3a). The solid state emission spectra revealed a strong emission at 721 nm with a Stokes shift of 161 nm when excited at its long wavelength absorption band (Fig. 3b). The time resolved fluorescence in solid state showed a longer life time (τ_1 = 5.59 nm) compared to its solution state (Fig. 3c). More interestingly, the gas phase/solution phase energy gap between HOMO and LUMO (2.6–2.7 eV) remained very closer to that of a band gap of an organic semiconductor.[9] Thus, our observations on solid state photophysical property clearly showed that the fluorophore **1** might

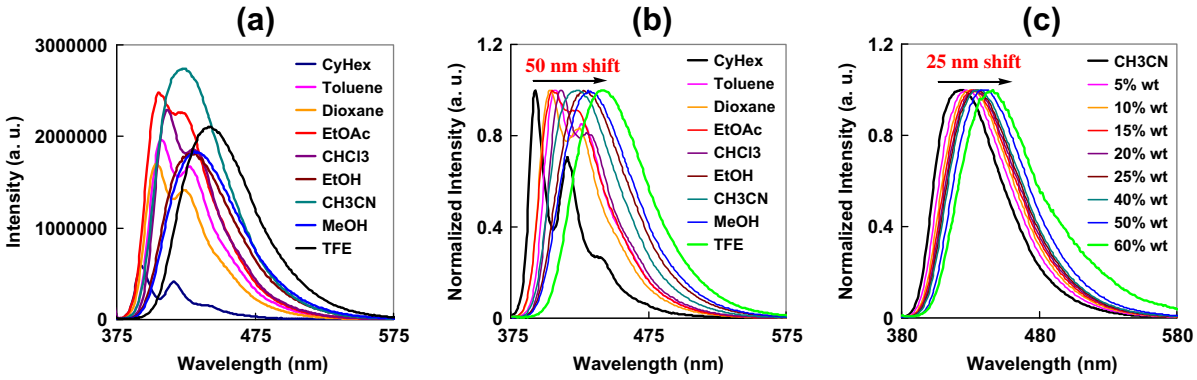


Figure 4. (a) Emission and (b) normalized emission spectra of **2** (**$^{4\text{-CPE}}$NI**) in different solvents. (c) Normalized emission spectra in CH_3CN titrated with water (10 μM, rt; λ_{ex} = 370 nm).

Table 1
Photophysical data of substituted naphthalimide **1** and **2**

Solvents	λ_{abs}^{max}	λ_{em}^{max}	Φ_f[a]	τ_1 (ns)	χ^2	k_r (10^9 s^{-1})	k_{nr} (10^9 s^{-1})
			Fluorophore **1** (**$^{4\text{-DMAPE}}$NI**)				
Hexane	453	474	0.79	2.80	1.05	0.28	0.07
Cyclohexane	459	480	0.66	2.84	1.02	0.23	0.12
Toluene	454	548	0.53	3.74	1.03	0.14	0.13
Dioxane	448	572	0.24	3.75	1.17	0.06	0.20
Ether	446	577	0.23	—	—	—	—
$CHCl_3$	467	611	0.14	2.58	1.04	0.05	0.33
EtOAc	449	—	—	—	—	—	—
THF	456	—	—	—	—	—	—
DMSO	470	—	—	—	—	—	—
CH_3CN	453	—	—	—	—	—	—
MeOH	459	—	—	—	—	—	—
	λ_{abs}^{max}	λ_{em}^{max}	Φ_f[a]	τ_1 (ns)	χ^2	k_r (10^9 s^{-1})	k_{nr} (10^9 s^{-1})
			Fluorophore **2** (**$^{4\text{-CPE}}$NI**)				
Dioxane	389	403	0.57	1.45	1.11	0.39	0.30
Toluene	392	408	0.48	1.62	1.03	0.29	0.32
EtOAc	387	406	0.56	1.52	1.17	0.36	0.29
$CHCl_3$	393	411	0.49	1.38	1.16	0.35	0.37
CH_3CN	387	423	0.54	1.66	1.13	0.32	0.28
10% H_2O in CH_3CN	387	431	0.53	1.74	1.08	0.30	0.27
30% H_2O in CH_3CN	387	436	0.41	1.83	1.07	0.22	0.32
50% H_2O in CH_3CN	387	441	0.32	1.91	0.99	0.16	0.36
MeOH	387	434	0.54	1.79	1.04	0.30	0.25
TFE	372	442	0.55	2.05	1.10	0.27	0.22

[a] The fluorescence quantum yields (Φ_f) were determined using perylene[10a,10b] as a reference with the known Φ_f = 0.94 in cyclohexane for fluorophore **1** and in quinine sulphate[10c] as a reference with the known Φ_f = 0.54 in 0.1 molar solution in sulfuric acid for **2**.

find applications in material sciences such as in organic semiconductors/electronic devices.

After investigating the photophysical properties of fluorophore **1** both in solution and in solid state we next evaluated the fluorescence photophysical property of fluorophore **2**. Thus, for the case of acceptor containing naphthalimide fluorophore **2**, upon changing the solvent polarity, both the intensity and the quantam yield of emission were found to be increased with a moderate Stokes shift of about 50 nm when compared between the solvents cyclohexane and TFE (Fig. 4a–c).

Overall, it was observed that the fluorescence quantum yields markedly decreased with increase in solvent polarity for the case of fluorophore **1**. Protic solvents, like methanol, are known to induce fluorescence quenching through non-radiative pathways via hydrogen bonding. Thus, the fluorescence in methanol was died away due to protic solvent–solute interactions. These properties indicated that compound **1** has strong charge transfer (CT) character. The conjugation between the *N,N*-dimethyl aminophenyl moiety as an electron donor and the naphthalimide core as an electron acceptor played an important role in the large dipole change during excitation and made fluorophore **1** highly solvatochromic.

To get an insight into the strong solvent polarity sensitive emission behaviors of compounds **1**–**2**, the fluorescence spectral dependency on solvent polarity parametres (Δf) was studied on the basis of Lipert-Mataga model.[11] Thus, a good linear correlation of the absorption and fluorescence maxima ($\tilde{\nu}_{max}^{abs}$, and $\tilde{\nu}_{max}^{fl}$ respectively, in cm^{-1}) of fluorophores **1**–**2** with the solvent polarity functions Δf indicated that for the fluorophore **1**, the $\tilde{\nu}_{abs}$ values apparently correlated linearly with Δf. This result suggested that the ground state of **1** was moderately polar in nature. However, a less correlation was observed in case of the fluorophore **2**, suggesting a nonpolar ground state (see Supplementary data). The reasonably high slopes of $\tilde{\nu}_{fl}$ versus Δf plots for all the fluorophores **1**–**2** further suggested that the fluorescent states of these fluorophores were highly polar in nature, most possibly of intramolecular charge transfer (ICT) character.[12,13] Thus, the change of emission wavelength of the fluorophores with solvent polarity indicated their potential ICT features. A good linear correlation with large slopes of the $\Delta\tilde{\nu}$

versus Δf plots suggested that the fluorescence states were highly polar in nature for all the fluorophores (See Supplementary data). Substantially high values of $(\mu_e - \mu_g)$ obtained from the plot (22.6 D for **1** and 13.9 for **2**) indicated that the fluorescence state of **1** is of higher ICT character than **2** (see Supplementary data). The excited state dipole moment determined from Stokes shift was found to be more than the ground state for fluorophore **1**. This might be associated with partial transfer of electron from the donor *N,N*-dimethylamino group to the acceptor naphthalimide core.

To understand the fluorescence behavior more precisely, we measured fluorescence life time in different solvents and found that the decay followed a single exponential fitting for all the fluorophores. The effect of polarity was very similar to what was observed for the fluorescence quantum yield (Table 1). While in case of compound **1** increase in the polarity of the solvent led to a shortening of the lifetime, in case of compound **2**, life time increased as the polarity of the solvent was increased. The dependence of the quantum yield of fluorescence of **1** on the nature of the solvent was mainly dictated by changes in the rate of radiationless deactivation as was revealed from the change in the rate constants of radiationless deactivation on going from hexane to chlorofom (Table 1). However, the opposite was obviously the result in case of fluorophore **2** correlating its dependency of quantum yield with the change in solvent polarity. Time dependent DFT calculation[14] also revealed that the emissive state of **1** was characterized with more significant electron redistribution, that is, ICT feature and rationalized the explanation of ICT origin and the solvent polarity dependency of the fluorophores' emission (see Supplementary data).

Being inspired by the interesting solvatochromic emission property, we next turned our attention to explore the possible sensing of microenvironment of ct-DNA using fluorophore **1** and **2**. Naphthalimides are well known as probes of nucleic acids and many naphthalimide chromophores have been utilized in fluorescence based elucidation of structure, dynamics and conformation of proteins.[4c,3d,4d–h] Therefore, we envisaged that the naphthalimide moiety of our probes might significantly interact with the aromatic bases in DNA via intercalative stacking/H-bonding and/or electrostatic interaction. This idea along with the intense emission of the probes in low polar media compared to high polar media and/or buffer drew our attention to exploit fluorophores **1**–**2** in the possible sensing of microenvironment of calf-thymus DNA (ct-DNA) which is easily available biomolecules with widespread applications.[15]

Therefore, we studied the interaction behavior of our probes with ct-DNA by spectroscopic means in aqueous phosphate buffer (pH 7.0). Thus, the absorption maxima of fluorophore **1** and **2** located at 445 and 395 nm, respectively, showed a negligible effect on the change in wavelength position and intensity as ct-DNA was added gradually (see Supplementary data).[16] Next, fluorescence titration experiment was carried out. Thus, upon gradual addition of ct-DNA, the emission intensity (λ_{em} = 525 nm) of the fluorophore **2** was found to be significantly enhanced with slightly red shifted pattern. The emission became saturated at 75 μM concentration of ct-DNA compared to 30 μM probe concentration (Fig. 5a). This observation clearly indicated a well-defined binding of the probe **2** with ct-DNA. On the contrary, fluorophore **1** which is of greater ICT character compared to fluorophore **2**, showed a sudden enhancement of fluorescence intensity with very little blue shifted pattern at probe: ct-DNA concentration ratio of 1:1. Beyond this ratio no regular trend in decreased emission upon addition of increasing amount of ct-DNA was observed when excited at 460 nm (Fig. 5c). The emission response of fluorophore **2** upon binding with ct-DNA represented the possible binding of the probes along the groove side thereby facing more polar microenvironment leading to an enhancement of fluorescence intensity of probe **2** and an anomalous behavior in emission for the case of fluorophore **1**. The quenching incidence of probe **1** could easily be explained if we consider the non-radiative deactivation via solvent solute H-bonding interaction when exposed to the more polar microenvironment along the groove side. These observations are in accord with the intrinsic emission behaviors of the probes as was revealed from the solvent polarity dependent emissions of each fluorophores.[15] The association constant of probe **2** with ct-DNA was also determined by a Benesi-Hildebrand plot (inset, Fig. 5a) which was found to be $3.98 \times 10^4\ M^{-1}$ with an experimental free energy of binding, $G = -6.3$ kcal/mol.

Thermal denaturation experiment indicated no destabilization of ct-DNA upon binding with the probe **2** suggesting that the probe possibly bind to a groove of ct-DNA (see Supplementary data).[16] To investigate the binding mode of the probes with ct-DNA an intercalation or a groove binding, a competitive binding experiment was performed. Thus, upon addition of increasing amount of probe **1** and/or **2**, no significant change in fluorescence of ethidium bromide of EB–ct-DNA complex was observed indicating that both the probes were not interacting with ct-DNA as intercalators but may be groove binders (see Supplementary data).[17] Though, naphthalimides are known as intercalators,[4c,3d,4d–h] because of appended propergyl units the probes were unable to intercalate sterically between the DNA bases rather they preferred to bind along side the groove position of ct-DNA via possible π-stacking/H-bonding interactions which was also supported from the fluorescence experiment.

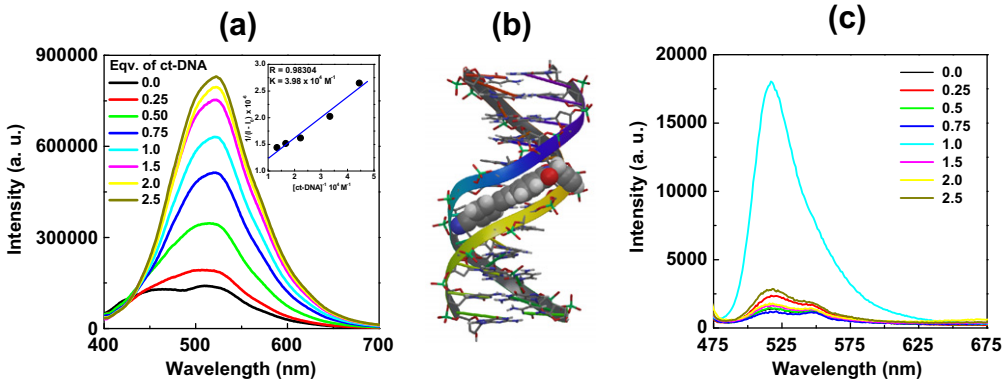


Figure 5. (a) Fluorescence titration of probe **2** (λ_{ex} = 362 nm). Inset: Benesi-Hildebrand plot for determination of association constant in respective media. (b) Amber* energy minimized geometry of probe **2** with DNA, showing the minor groove binding mode of the probe. The DNA sequence was 5′-d(*CP*GP*CP*GP*AP*AP*TP*TP*CP*GP*CP*G)-3′, (PDB Id: 1DNH). (c) Fluorescence titration of probe **1** (λ_{ex} = 460 nm) with various concentration of ct-DNA ([probe] = 30 μM, phosphate buffer, pH 7.0, rt).

To support minor groove binding event, we have carried out MacroModel calculation by Maestro, version 9.0 with AMBER* force field in water.[18] For the optimization we chose the DNA sequence [5′-d(*CP*GP*CP*GP*AP*AP*TP*TP*CP*GP*CP*G)-3′, (PDB Id: 1DNH)] where Hoechst 33258 dye enter into the minor groove. Thus, Amber* optimized geometry of our probe **2** with the model DNA sequence (Fig. 5b) showed and support our experimental observation of groove binding event especially in the minor groove.

Therefore, it was clear from the above findings that the probe **2** was more efficient compared to probe **1** in sensing microenvironment of ct-DNA via the generation of enhanced fluorescence signal. The low fluorescence intensity of the probes in phosphate buffer in absence of biomolecules is not due to the insolubility of the probe but may be attributed to the radiationless channel assisted by intermolecular hydrogen bonding present in aqueous solution.[5a,b] However, as the probes bound to the groove side they experienced restricted radiationless channel inside the groove of ct-DNA ultimately leading to a fluorescence switch-on signal with high intensity and quantum yield.

In conclusion, we developed new donor/acceptor conjugated fluorescent naphthalimide based fluorophores. The fluorescence of naphthalimide containing terminal alkynes were of highly ICT character and very sensitive to solvent polarity. We showed that the died down fluorescence of probe **1** in buffer could be recovered in presence of ct-DNA. We also investigated that both the probes are capable of sensing of microenvironment of ct-DNA via a generation of enhanced fluorescence signal. The solid state fluorescence property of the probe **1** might find application in materials sciences. The exploitation of the terminal acetylenes to the synthesis of fluorescently labeled biomolecular building blocks such as labeled nucleosides and amino acids and their applications thereof is our current research target.

Acknowledgments

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Supplementary data

Supplementary data (experimental procedure, characterization, photophysical spectra, DFT calculation, macromodel structures and crystal structure) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bmcl.2012.11.003.

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