Photophysics, pH Sensing, and Hydrolysis Study of a Novel 1,8-Naphthalimide Derivative

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Abstract: In this study, a novel highly emissive compound was synthesized via a two-step synthetic procedure and characterized by ^{1}H-NMR, ^{13}C-NMR and FTIR. Then its photophysical properties, pH sensing behaviors and pH-dependent hydrolysis were systematically investigated by ultraviolet and fluorescence spectroscopy. Photophysics studies were carried out in fourteen common organic solvents and absorption/emission spectra were recorded in Britton Robinson buffers (pH=3-12) to determine pH sensing behaviors. From the photophysical results, it has been shown that the novel compound exhibits strongly solvent polarity dependent emission and has high quantum yield (up to 0.72). Furthermore, at pH=12, absorbance started to decrease while emission was increasing and blue-shifting due to basic hydrolysis after a several minutes. Therefore, time dependent hydrolysis was also investigated at mentioned pH.

Keywords: Naphthalimide, Thiazoline, Photophysical, Fluorescence, pH Sensing, Hydrolysis.

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INTRODUCTION

Fluorescent molecules are quite important and have been extensively studied due to their usability in optoelectronic area. In the same manner, there are a lot of publications about optical and organic electronics applications of naphthalimide derivatives, and this structure can appear as a different subclass of fluorescent dyes. Especially, donor group containing derivatives at 4-position are generally photo-stable materials and have relatively high fluorescence quantum yield thanks to compact donor-acceptor architecture. Therefore, it is possible to use them as high effective fluorescent materials, fluorescent brightening agents, pH/metal/anion sensors, light harvesting materials, light emitting diodes, and more (1-5).

Light-induced absorption of naphthalimide derivatives occurs by decomposition into charge carriers in the conjugate system. For this reason, the application of naphthalimide derivatives in organic electronic area depends on the relationship between the chemicals. For example, photovoltaic cells require materials with an effective charge separation capability, and therefore high electron mobility is required to increase the probability of electron migration to a charge separation region. Naphthalimide derivatives can be shifted to longer wavelengths by extending the π-conjugation system via structure modification. In addition, the photophysical properties can be changed by modifications on the naphthalimide molecule. With suitable structural arrangements, naphthalimide derivatives can act as energy donor or acceptor in various energy transfer systems (6-10).

pH sensors widely take place in various fields such as chemical process control, environmental analysis, medical diagnostics, and industrial applications (11). Fluorescence-based pH probes have become promising tools due to their high sensitivity, selectivity, and low cost. In order to understand many physiological processes better, the development of effective chemosensors to monitor pH changes has a great deal of precaution (12-15). For example, a proportional pH sensor based on fluorescence resonance energy transfer (FRET) has been recently reported to visualize the stimulus-sensitive changes in intracellular pH values by integrating an amino-naphthalimide pH probe as a FRET acceptor with a pH-insensitive coumarin fluorophore as a FRET donor (16).

In brief, 1,8-naphthalimides are quite suitable candidates for optoelectronic and organic electronics applications and it is essential to synthesize their new derivatives and comprehensively investigate of some properties on photo-physics, pH/metal/anion sensing, and chemical/photo-stability *etc*. to provide development in these areas. In our study, the aim was to combine naphthalimide and thiazoline fragment which might contribute to photophysics and pH sensing behavior of the target compound. For this reason, we synthesized a novel naphthalimide-thiazoline compound as a fluorophore. Then, comprehensive photophysics, pH sensing and hydrolysis behaviors were also investigated via absorption and emission studies.

EXPERIMENTAL SECTION

DMA-NI (dimethylamino-naphthalimide compound) was synthesized by two steps synthetic method depicted in Scheme 1. The reactions were monitored by Silica Gel TLC plates in CH_2Cl_2/Ethyl acetate mixture (1:1). All the chemicals used in this study were purchased from Merck, Alfa, Sigma, and Fluka. Purification of crude DMA-NI was realized by a silica column chromatography by using dichloromethane and ethyl acetate mixture. Melting point was determined on a Electrothermal IA-9200. FTIR spectra were recorded on a Shimadzu Prestige-21 (200 VCE) spectrometer combined with ATR apparatus. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker Avance-II spectrometer at 400 and 100 MHz, respectively and TMS (tetramethylsilane) was used as internal standard. The solutions of acetic acid (0.10 M), sodium acetate (0.10 M), KH_2PO_4 (0.10 M), $Na_2B_4O_7.10H_2O$ (0.025 M), hydrochloric acid (0.10 M), sodium hydroxide (0.10 M) and Na_2HPO_4 (0.05 M) were used to prepare Britton Robinson buffer solutions in pH range 3.0 to 12.0. All the photophysical measurements (absorption and emission) were realized by a PG Instruments T80 double beam spectrophotometer and Shimadzu RF 5301PC fluorescence spectrophotometer, respectively, in common organic solvents by a 1 cm path length quartz cells at ~22 ºC.

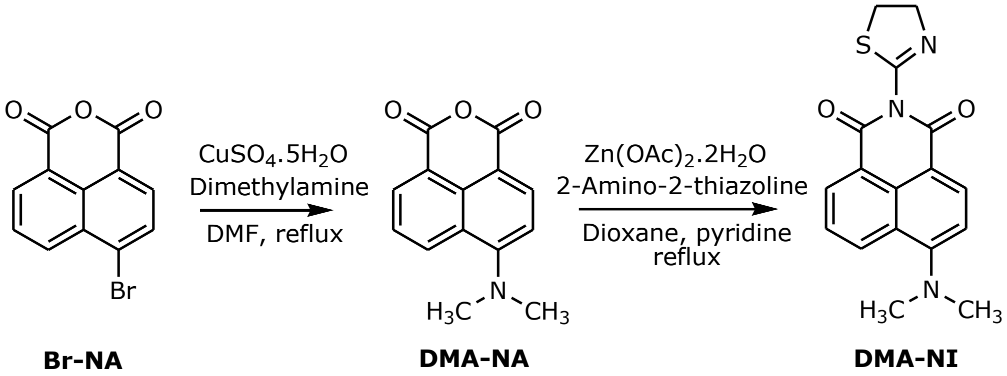
Synthesis

Synthesis of DMA-NA

DMA-NA (dimethylamino-naphthalic anhydride compound) was synthesized and purified according to the known procedure (17). This reaction includes bonding of dimethylamine to 4-bromonaphthalene-1,8-dicarboxylic anhydride in the presence of $CuSO_4{\cdot}5H_2O$ as catalyst. Spectral data (^1H, ^{13}C NMR and FTIR) are fully in accordance with the literature mentioned above.

Synthesis of DMA-NI

0.120 g (0.5 mmol) of DMA-NA, 0.051 (0.5 mmol) 2-amino-2-thiazoline, and 10% mol of zinc acetate dihydrate refluxed in dioxane (5 mL) and pyridine (5 mL) for 2 days. After evaporation of volatiles in the reaction flask, the residue was extracted by adding chloroform and water. Combined organic phases dried over Na_2SO_4, evaporated under vacuum, and the crude product was purified by silica column chromatography by using CH_2Cl_2 and ethyl acetate as eluent. Yield: 75%; melting point: 198-201 °C; FTIR: 2918, 2873, 1699, 1654, 1581, 1354, 1012, 769, 758; ^1H NMR (400 MHz, $CDCl_3$): 8.52 (dd, *j*= 6.0 Hz, 1.2 Hz, 1H), 8.43-8.40 (m, 2H), 7.60 (dd, *j*= 6.8 Hz, 5.6 Hz, 1H), 7.05 (d, *j*= 6.4 Hz, 1H), 4.44 (t, *j*= 6.8 Hz, 2H), 3.71 (t, *j*= 6.8 Hz, 2H) 3.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.0, 162.3, 157.6, 157.6, 133.3, 132.1, 131.7, 130.9, 125.3, 124.9, 122.5, 114.0, 113.3, 61.5, 44.8 (2C), 36.40.



Scheme 1: Synthesis of the target compound.

Photophysics

All the absorption and emission measurements were performed at 10^{-5} M concentration. Quantum yields *(Φ)* of DMA-NI in common organic solvents were determined by comparing with a perylene reference solution. For this, the following equation has been used to calculate relative quantum yields (18).

$$\Phi_{samp} = \Phi_{ref} \frac{\eta^2}{\eta^2{}_{ref}} \frac{I}{I_{ref}} \frac{A_{ref}}{A} \qquad (1)$$

Where η and η_{ref} are the refractive indices of sample and reference solvents, I and I_{ref} are the integrated areas of the emission signal for the sample and reference, respectively. A and A_{ref} are the absorbance values for the sample and reference at the excitation wavelength, respectively. Perylene solution in toluene used as reference and this compound has a known fluorescence quantum yield of 0.75 under these conditions (19).

pH Sensing

pH sensing studies were performed based on absorption and emission of DMA-NI solution (10^{-4} M) in the pH range of 3.0–12.0 at room temperature with slight modification of previous study (20). For this, firstly, 16.2 mg of DMA-NI dissolved in 100 mL acetonitrile to prepare the $5.0\text{x}10^{-4}$ M solution. Britton Robinson buffers in the pH range of 3.0–12.0 have been prepared by following a published method (21). Then 0.5 mL of DMA-NI and 2.0 mL buffer solution were mixed and absorption/emission spectra were recorded. This recording was repeated for each integer of pH between 3 and 12.

Hydrolysis

Hydrolysis of DMA-NI was monitored via adaptation to the literature (20). For this, firstly, 0.5 mL of 5.0×10^{-4} M DMA-NI solution in acetonitrile and 2.0 mL of Britton Robinson buffer (pH=12) were mixed in a 1 cm path length quartz UV cuvette to get 1.0×10^{-4} M concentration and absorption spectrum has been recorded immediately for t=0. Then, emission spectrum of same mixture was displayed without losing time. Absorption and emission recordings were repeated for t=3, 10, 30, 90 and 180 minutes.

RESULTS AND DISCUSSION

Synthesis

Anhydride compound (DMA-NA) was synthesized and purified according to the known procedure (17) and NMR results verified its structure and purity. Synthesis of its imide derivative (DMA-NI) containing aminothiazoline fragment was accomplished by adaptation of literature method (22). This method contains 10% mol $Zn(OAc)_2$ catalyst under dioxane and pyridine refluxing during 2 days. At the end of this reaction time, it has been shown that a tiny amount of starting compound could be separated from the target compound with column chromatography. ^{1}H NMR spectrum is fully in accordance with proposed structure. Five different signal groups at aromatic region, roughly four doublets (two doublets overlap) and a triplet, verifies the structure. Also two different aliphatic triplets and a singlet having 2, 2 and 6 integration values clearly shows the presence of two $-CH_2-$ and $N(CH_3)_2$ groups, respectively. In the ^{13}C NMR spectrum of DMA-NI, four downfield carbon signals are shown corresponding to two carbonyl carbon, dimethylamino group attached carbon and imine carbon of thiazoline fragment. In aromatic region, nine carbon signals can be seen which concerns naphthalene skeleton except of dimethylamino attached carbon. Also, three aliphatic signals are ascribed to methylene carbons and dimethylamino carbons. Lastly, FTIR spectrum verifies the structure with these specific signals at 2918 (aliphatic C-H), 1699 (C=O), 1654 (C=O), 1581 (C=N) and 1354 (C-N amine) cm^{-1}.

Photophysics

Normalized emission spectra of DMA-NI are shown in Figure 1 and all photophysical results were summarized in Table 1. Absorption values of DMA-NI are affected from solvent polarity as expected and they change between 396-438 nm (Table 1). These changes are directly affected from solvent polarity and increasing of solvent polarity causes bathochromic shift. Fluorescence λ_{max} values are shown between 460-537 nm. These results are also affected form solvent polarity like absorption values. Stokes' shift values are not polarity-related and change between 62-105 nm. The fluorescence quantum yield (Φ_F) varies over a wide range and roughly decreases with increasing solvent polarity.

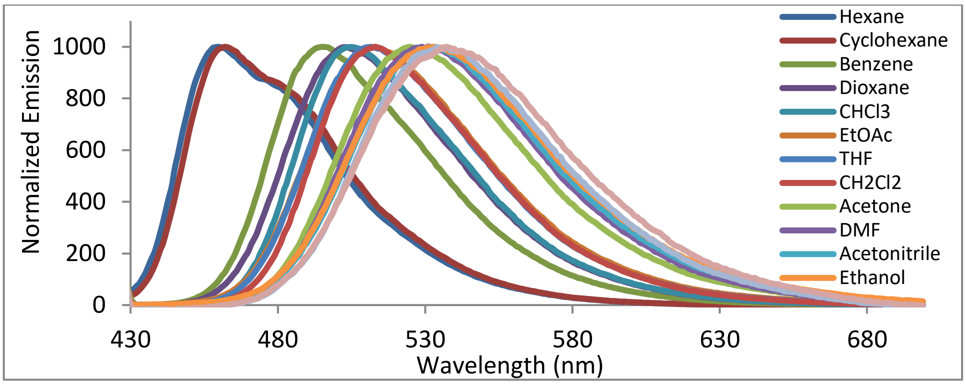


Figure 1: Normalized emission spectra of DMA-NI in common organic solvents.

Table 1: Photophysical results for DMA-NI.

Solvent	**λ_{max}(abs)**	**λ_{max}(ems)**	**Stokes' shift**	**Φ_F**
Hexane	396	460	64	0.451
Cyclohexane	400	462	62	0.464
Benzene	410	495	85	0.551
Dioxane	410	503	93	0.282
$CHCl_3$	412	505	93	0.722
EtOAc	412	513	101	0.347
THF	412	512	100	0.372
CH_2Cl_2	412	513	101	0.510
Acetone	432	525	93	0.015
DMF	434	530	96	0.007
Acetonitrile	428	533	105	0.031
Ethanol	432	533	101	0.014
DMSO	438	534	96	0.008
Methanol	434	537	103	0.006

λ_{max}(abs): maximum absorption wavelength, λ_{max}(ems): maximum emission wavelength, Φ_F: fluorescence quantum yield.

pH Sensing

At first, the aim was to investigate pH sensing behaviors at different pH values based on changing the absorption and emission spectra. For this, 10^{-4} M DMA-NI solutions at known pH was prepared by mixing 5.0×10^{-4} M DMA-NI solution and Robinson Britton buffers in 1:4 volume ratio. After immediately recording absorption and emission spectra, any different spectrum has not been observed at first. However, in a second recording a several minutes later, absorption band started to diminish and λ_{max}(ems) started to blue shifting and enhancing peak area for pH=12. In an hour, the change was clearly observed in absorption and emission spectra (Figure 2). In the literature, it can be shown that a lot of examples about hydrolyzing imide derivatives are present at strong acidic and basic media. For this reason, we think that this change comes from hydrolysis reaction and new spectrum is ascribed to the hydrolysis product of DMA-NI.

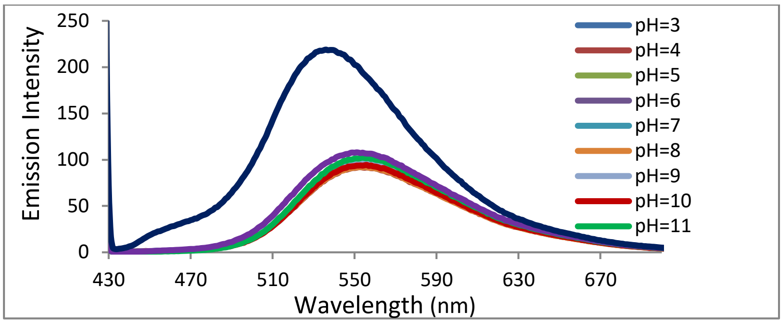


Figure 2: Emission spectra of DMA-NI at different pH values.

Hydrolysis

In order to clarify the special changing in photophysical results, we started to investigate time-dependent hydrolysis of DMA-NI and pH=12 was selected as hydrolysis pH because it has optimal reaction rate value. Investigations have been carried out at 10^{-4} M concentrations and first measurement was made as soon as possible after preparation for t=0. At the third minute, it has been shown that the absorbance value started to decrease and following recordings exhibited similar behaviors in absorption value (Figure 3). From the graphical representation in Figure 4, it can be seen that the decreasing is not linear for selected two different wavelength points and this situation can indicate that the degradation is dependent on DMA-NI and/or OH^- concentrations.

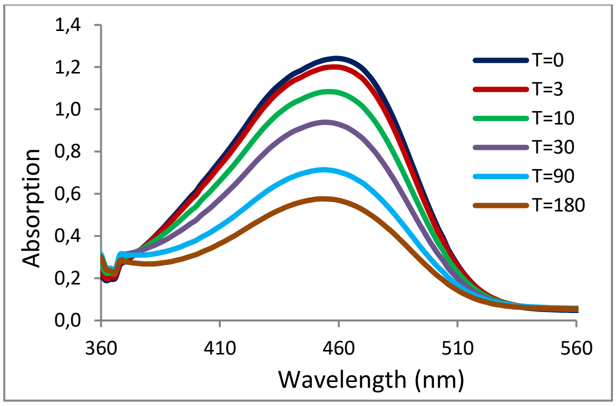


Figure 3: Absorption graphics for DMA-NI hydrolysis at pH=12 (t=min).

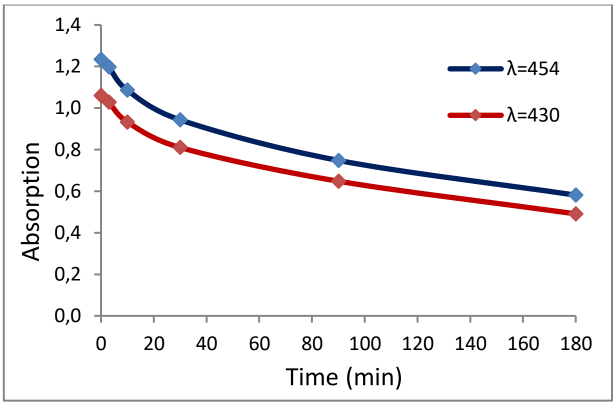


Figure 4: Absorption vs. time graphics of DMA-NI hydrolysis at pH=12.

After a long time, this absorption band completely disappeared because of the completion of hydrolysis reaction. The results have showed a drastic decrease of absorbance with time. Long time experiments under ambient light have been applied to large scale pH values (pH=3-12) and Figure 5 shows the situation of 10^{-4} M solutions of DMA-NI a week later. As seen in Figure 5, at strong basic conditions, the colors of solutions changed from yellow to colourless for pH=10, 11 and 12 and this situation gives an evidence for the significant reactivity of this molecule in alkaline solution. These results show that this compound is quite photo-stable at acidic and neutral pH values.

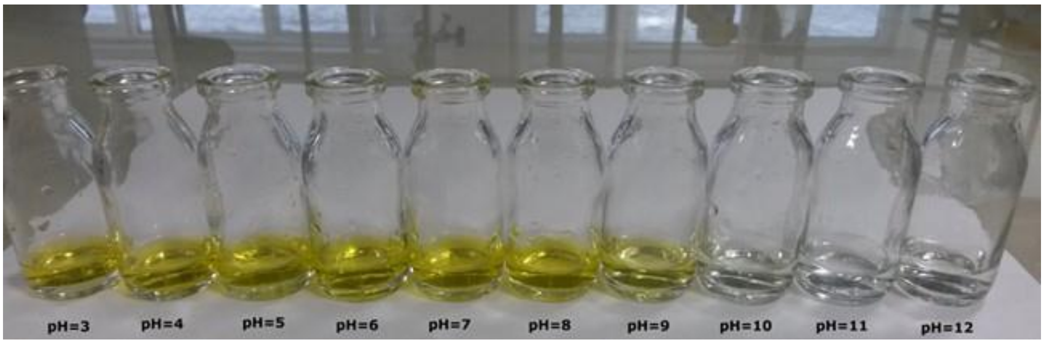


Figure 5: Bleaching of DMA-NI in different pH values a week later.

CONCLUSIONS

In conclusion, we have described the synthesis, photophysics, pH sensing behaviors, and hydrolysis investigation of a new naphthalimide compound (DMA-NI). Herein, the fluorophore was selected as naphthalimide because of its high photo-stability, high fluorescence quantum yield, large Stokes' shift, and simplicity of modification. Samples of DMA-NI were successfully prepared in two steps (amination and imide formation) starting from 4-bromonaphthalic anhydride. The yields were quite high and the procedure was extremely easy and clear. The originality of this structure was the presence of thiazoline fragment which could change the whole characteristics of target compound and we investigated here its effect on the nature of this compound. Then photophysical profile of this compound has been illuminated by absorption and emission studies. DMA-NI compound displayed broadband visible region absorption and emission band, and its emission band is quite broad and featureless due to intramolecular charge transfer of compact donor-acceptor structure. An exception to this generality arises in non-polar solvents, such as n-hexane and cyclohexane, where the emission spectrum is slightly structured. This situation may arise from the relative stability of bipolar resonance structure of excited state in polar solvents. Photophysical calculations based on perylene standard showed that this molecule has the highest quantum yield in chloroform (Φ_F=0.72). In addition, this molecule has high quantum yields in benzene (Φ_F=0.55) and dichloromethane (Φ_F=0.51) as well. For other solvents, quantum yields were less than 0.5. In pH sensing studies and long time pH effect investigations, it has been shown that the compound has similar absorption and emission spectra for all pH values, but differentiated with time. This situation shows no specific pH sensing and stems from hydrolysis of DMA-NI. As a result, the DMA-NI compound is quite photo-stable and resistant to hydrolysis under the neutral and acidic conditions. Therefore, it can be used in optoelectronic and organic electronic devices that need photostability and high fluorescence quantum yield under acidic and neutral pH values. In addition, more effective novel derivatives of 1,8-naphthalimide can be synthesized and investigated for similar electronic applications in the illumination of this study.

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