Tetrahedron 65 (2009) 2173–2177

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Minimal modification approach to red-shifted absorption and fluorescence in 1,8-naphthalimides

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ARTICLE INFO

Article history:
Received 29 October 2008
Received in revised form 12 January 2009
Accepted 13 January 2009
Available online 20 January 2009

Keywords:
Naphthalimides
Sultonation
Red-shifted absorption
Pyridinium salts

ABSTRACT

As a minimum modification approach toward longer wavelength chromophores, a series of (4-diethylamino-1,8-naphthaloyl)-aminopyridines were prepared with the pyridine nitrogen located at the *ortho*, *meta*, and *para* positions. Comparison between these isomeric neutral dyes and their corresponding pyridinium-1,3-propanesulfonate salts reveals a red-shift in both absorption (up to an emission of 1682 cm^{-1} in ethyl acetate) and emission. These observed shifts along with increased fluorescence quantum yield are attributed to polarization induced by the quaternary nitrogen of the pyridinium cation.
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1. Introduction

A key design aim in the development of functional dyes involves the synthesis of structural elements that extend the absorption to longer visible wavelengths. Such properties are sought in both dye sensitized solar cells (DSSC) for panchromatic absorption[1] and in biological settings by extending the emission beyond the blue autofluorescence of cellular media.[2] Extending the conjugation and thereby increasing the size of the fluorophore remains a conventional approach toward increasing absorption and emission wavelengths. The Alexa fluor class of fluorescent dyes provides a typical example with a 46 nm bathochromic shift difference in absorption (Fig. 1).

An alternative approach requiring far fewer synthetic steps involves placement of positive charge along with functional groups that strongly polarize the molecule in both the ground and excited states. This synthetic design is an application of internal charge transfer (ICT) whereby introduction of donor/acceptor groups has been shown to extend the absorption and emission wavelengths without incorporating additional aromatic rings into the chromophore structure.[3] Recently Klymchenko et al. demonstrated the effect of proximal charge on the spectroscopic behavior of 3-hydroxyflavone (3HF) derivatives.[3a] Placement of a positively charged ammonium group within close proximity to 4-carbonyl stabilizes the Frank–Condon state, and the emissive excited states due to electrostatic interaction and results in greater fluorescence quantum yield and relatively large red-shifts of absorption and emission (typically 980–1100 cm^{-1}) in low polarity solvents.[3a]

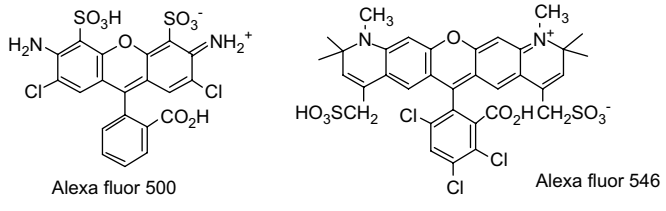

Figure 1. Comparison of structural features required for 1685 cm^{-1} shift in absorption.

In the case of *N*-arylnaphthalimides (NI), the dicarboximide functionality features a molecular orbital arrangement that allows us to explore the effects of donor/acceptor groups as substituents on both the NI ring and *N*-aryl component. Recently, there has been an upsurge in the number of reports on photophysics and applications of NI based dyes.[4] Beginning with Bérces et al., 1,8- and 2,3-naphthalimides were shown to display long wavelength emission due to large ICT character from donor group substitution on the naphthalimide ring.[5] This research group also found that protonation of the pyridyl arene component to form *N*-pyridinium-1,8-naphthalimides resulted in a 17,500 cm^{-1} Stokes shift.[6] Takahashi et al. utilized the electron deficient properties of the NI scaffold and created molecular dyads by appending electron rich dianisidyl group as the imide arene.[7] This design resulted in a 12,500 cm^{-1} Stokes shift. In both reports, however, the absorption wavelength maxima are well below 400 nm. Molecular orbital calculations for both systems show that the LUMO is localized on the acceptor NI

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0040-4020/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.tet.2009.01.048

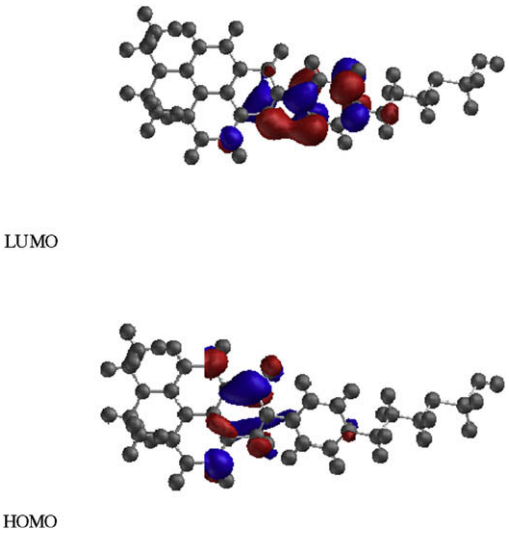


Figure 2. Calculated distribution of excited state charges predicted for NI–pyridinium salts shows how electrostatic stabilization of the excited state is responsible for shifting the absorption and emission bands to the red.[8] Graphically depicted using Chem3D.

component. This observation prompted us to alter the π-densities and their locations as an approach to longer wavelength absorption. Herein, we report on the implementation of appropriately placed substituent groups and the successful outcome of this minimum modification strategy.

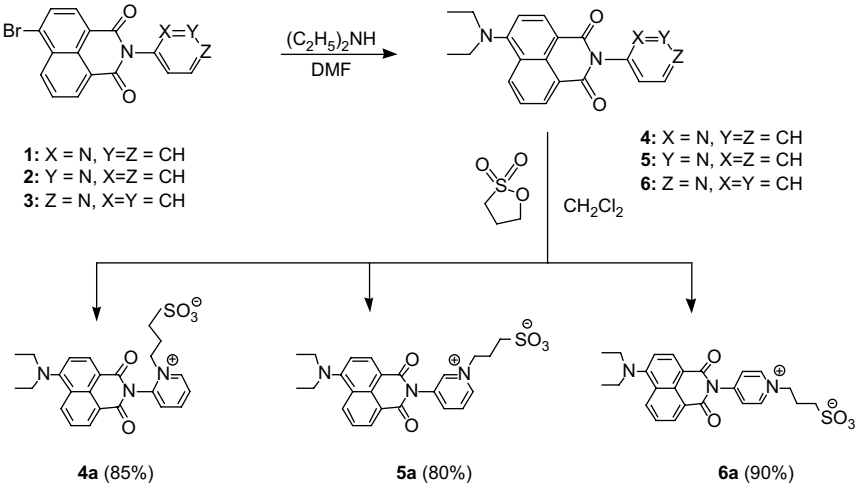
2. Results

Our strategy for manipulation of the NI π-system involves reversing the electron densities between HOMO and LUMO in comparison to these earlier reports. By attaching a donor diethylamino group on the NI ring and coupling electron deficient pyridine in a manner similar to Bérces et al.,[5] increased polarization through placement of positive charge and generating the *N*-pyridinium salt is expected to further enhance this polarization. Figure 2 shows the HOMO and to a greater extent LUMO localized away from the NI ring and centered at the pyridinium component. Using the three possible isomers of aminopyridine for the imide formation allowed us to study their photophysical differences with respect to position of the proximal pyridinium cation. The *ortho*, *meta*, and *para* isomers also provided a systematic study on charge separation, and compared to the 3-hydroxyflavone system, place the coulombic interactions at closer distances.

Scheme 1 outlines the synthetic route used to prepare compounds **4**–**6a**. Nucleophilic aromatic substitution proceeded smoothly using diethyl amine with the bromo-derivatives (**1**–**3**) in dry DMF.[9] Next, N-alkylation using 1,3-propane sultone has been shown to be selective for the pyridine nitrogen relative to similar heterocyclic systems bearing a diethylamino moiety.[10] Yields obtained from this reaction were excellent despite the need of chromatography for separation from starting materials.

Absorption spectroscopy of these dyes was carried out in solvents that allowed both the neutral dyes (**4**–**6**) to be compared with the sultone salts (**4a**–**6a**). As shown in Table 1, all of the dyes displayed red-shifted absorption spectra when comparing sultonated species with their respective neutral precursor. The largest bathochromic shifts occurred in the low polarity solvent, ethyl acetate. In particular, the *para*-isomer **6a**, displayed bathochromic behavior on par with the Alexa Fluor series mentioned above. Quaternization of the nitrogen heteroatom should increase the electron acceptor properties of the *N*-aryl group. This proximal charge appears to be responsible for the red-shift in absorption as it strongly withdrawals electron density from the imide nitrogen of the fluorophore compared to the neutral system.[11] A general trend for solvents more polar than chloroform is observed within each isomeric group such that *para*-sultone **6a** displayed the largest degree of red-shifted absorption relative to *ortho* and *para* isomers **4a** and **5a**. For the least polar solvent chloroform, the largest change in red-shifted absorption was observed with *ortho*-isomer **4**. Given the low dielectric constant for this solvent, it is likely that the proximal charges are less stabilized by solvent but have a greater electrostatic stabilization via their proximity in an *ortho*-ammonium arrangement. For the entire series however, dyes **5**, **5a** and **6**, **6a** generally gave larger bathochromic shifts in absorption. In the case of *ortho*-isomer **4a**, where steric hindrance is the strongest, the *N*-aryl group should be twisted from the plane of the fluorophore to the greatest extent. This larger twist angle is expected to decrease the electron-withdrawing effects of the proximal charge and result in less red-shifted absorption. Solvents less polar than chloroform such as hexane could not be included in the study due to insolubility of the sultone salts **4a**–**6a**. Conversely, neutral species **4**–**6** were insoluble in water whereas, salts **4a**–**6a** readily dissolved and their spectral data included in Table 1.

To examine the excited state features of these dyes, steady-state fluorescence spectroscopy also revealed bathochromic



Scheme 1.

Table 1
Spectral properties of the studied naphthalimides

Solvent	Entry	Abs λ_{max}, nm	Shift cm^{-1}	Em λ_{max}, nm	Shift, cm^{-1}	φ_F
$CHCl_3$, ε=4.8	**4**	424		505		0.04
	4a	430	329	508	117	0.07
	5	426		511		0.08
	5a	432	326	512	65	0.01
	6	428		508		0.05
	6a	433	269	514	230	0.02
EtOAc, ε=6.1	**4**	411		561		0.09
	4a	439	1552	572	342	0.26
	5	412		560		0.06
	5a	433	1177	565	158	0.01
	6	414		565		0.13
	6a	445	1682	517	−1643	0.02
Acetone, ε=20.4	**4**	428		564		0.07
	4a	439	585	573	278	0.38
	5	417		560		0.04
	5a	434	940	570	292	0.08
	6	421		568		0.03
	6a	438	922	565	−94	0.05
MeOH, ε=32.6	**4**	430		580		0.02
	4a	442	632	590	292	0.11
	5	425		582		0.02
	5a	438	698	587	158	0.02
	6	425		580		0.02
	6a	438	698	585	121	0.03
ACN, ε=36.0	**4**	425		570		0.03
	4a	442	688	584	420	0.17
	5	421		566		0.08
	5a	437	870	577	342	0.02
	6	421		572		0.02
	6a	439	974	576	121	0.001
DMSO, ε=46.5	**4**	426		527		0.01
	4a	436	538	538	388	0.01
	5	428		525		0.03
	5a	440	637	531	215	0.01
	6	427		529		0.04
	6a	439	640	531	70	0.01
Water, ε=78.4	**4**	—	—	—	—	—
	4a	440	—	604	—	0.01
	5	—	—	—	—	—
	5a	440	—	604	—	0.01
	6	—	—	—		—
	6a	440	—	600	—	0.01

behavior for each set of sultonated dyes relative to their neutral precursors. For both *ortho* sultone systems (**4** and **4a**) as well as *meta* versions (**5** and **5a**), bathochromic shifts were observed although not to the extent found in the optical absorption. Earlier reports on *N*-aryl-1,8-NI have pointed out that these dyes undergo adiabatic ring rotation in the excited state toward a co-planar configuration; the so-called *excited state with extended conjugation* mechanism.[12] This photophysical effect may provide the necessary energy to overcome some of the barrier to rotation imposed by *ortho*-substitution and lead to longer wavelength emission for isomer **4a** because of the decreased charge separation. Compared to the optical data, a wide range of emission was observed in the case of dye **6**, where a large hypsochromic shift was found in ethyl acetate and to a lesser extent in acetone. In solvents such as acetonitrile and methanol, bathochromic shifts of magnitudes similar to *ortho* and *meta* systems were evident. Comparisons between isomers show that *ortho*-isomer with the quaternized nitrogen has the largest fluorescence quantum yield. This observation is attributed to the reduced rotational freedom of the *ortho*-pyridinium salt relative to *meta* and *para*-isomers. Because of the insolubility of dyes **4**–**6** in water, no comparison between shifts in absorption can be made, nonetheless, for dyes **4a**–**6a**, the longest emission wavelengths were recorded in this solvent ranging between 600 and 604 nm. Such long wavelength emission properties in combination with solubility in aqueous solution could be useful for biological applications.

To summarize, a minimal modification approach on *N*-pyridyl-1,8-naphthalimides was shown to be effective in shifting the wavelengths of both absorption and emission toward the red for all three isomers of the pyridyl moiety. In some cases such as **6a** in ethyl acetate, a 1682 cm^{-1} shift in absorbance was observed. Such large increases in wavelength compared favorably to the 1685 cm^{-1} red-shift of Alexafluor series, but with fewer synthetic steps. Moreover, an increase in fluorescence quantum yield was observed for each of the charged dyes relative to their neutral precursors. This bathochromic behavior is attributed to the polarization induced on the NI scaffold via positive charge of the cationic nitrogen in compounds **4a**–**6a**. Our initial studies involving simple 1,8-NI dyes establish that large red-shifts in absorption can be accomplished by altering the π-molecular orbital system of 1,8-NI from their usual electron deficient framework. These findings bode well for designing panchromatic dyes used in DSSC applications as well as fluorescent platforms such as Lucifer yellow anhydride, a commonly used NI based biological probe.

3. Experimental section

3.1. General

Reactions were typically run overnight for 16 h and thin layer was chromatography used to reveal reaction products. Merck precoated Silica gel 60 F_{254} on prescored glass was used for qualitative TLC. Spots were detected by UV-lamp. The solvent DMF was purified by filtration through silica gel 60. Other solvents such as acetone and dichloromethane were used directly from Fisher Scientific. Diethyl amine was obtained from Fisher Scientific and distilled prior to use. 1,3-Propane sultone was obtained from Sigma–Aldrich and used directly. For purification, a column was done using mixture of acetone and dichloromethane in different ratios for these different isomers. Finally, solvent was evaporated using rotary evaporator and a dry tan powder was obtained. IR spectra were recorded on a Nicolet Avatar 370 DTGS. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a JEOL Eclipse 300+ spectrometer. Elemental analyses were performed by Galbraith Laboratories. Melting points were measured on a hot plate melting apparatus and were uncorrected.

Compounds **1**–**3** were prepared previously and have been reported elsewhere. For experimental details see: Ref. 13.

*3.1.1. (4-Diethylamino-1,8-naphthaloyl)-2-aminopyridine (**4**)*

(4-Bromo-1,8-naphthaloyl)-2-aminopyridine (0.15 g, 0.42 mmol) and excess diethyl amine (5 mL) were taken in a 25 mL round bottom flask along with 5 mL DMF as a solvent. This mixture was refluxed at about 100 °C for overnight. Then, the solvent was evaporated by passing compressed air and the crude dry material was purified in a silica gel column (long) with 1:8 acetone and dichloromethane mixture and collected in test tubes. After evaporating the solvent, 0.104 g (69%) yellow powder was obtained: mp 141–144 °C.

^{1}H NMR ($CDCl_3$) δ 8.72–8.56 (m, 3H), 8.04–7.82 (m, 2H), 7.61 (t, J=7.5 Hz, 1H), 7.46–7.32 (m, 2H), 7.25 (t, J=7.5 Hz, 1H), 3.43 (q, J=6.6 Hz, 2H), 3.05 (t, J=6.6 Hz, 3H), 1.46 (t, J=6.6 Hz, 3H), 1.18 (t, J=6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 163.7, 150.2, 149.3, 138.7, 133.9, 132.5, 131.6, 131.3, 131.0, 129.5, 128.3, 125.3, 124.3, 123.9, 123.1, 122.2, 116.7, 47.4, 42.5, 12.4, 11.3. IR: ν=1695, 1646, 1560, 1360, 1241, 812, 767 cm^{-1}.

Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.0; H, 5.54; N, 12.2. Found: C, 72.84; H, 5.38; N, 11.83.

*3.1.2. (4-Diethylamino-1,8-naphthaloyl)-3-aminopyridine (**5**)*

(4-Bromo-1,8-naphthaloyl)-3-aminopyridine (0.15 g, 0.42 mmol) and excess diethyl amine (5 mL) were mixed in a 25 ml round bottom flask along with 5 mL DMF as a solvent and heated under reflux and stirring overnight at around 100 °C. Then, the DMF solvent and excess diethyl amine were evaporated by passing air and crude product was purified by running a silica gel column with 1:5 acetone and dichloromethane mixture and collected in test tubes. After evaporating the solvent, this reaction afforded 0.11 g (73%) yellow powder as product: mp 154–157 °C.

^{1}H NMR ($CDCl_3$) δ 8.67–8.43 (m, 3H), 8.06 (d, J=7.5 Hz, 1H), 7.82 (t, J=7.5 Hz, 1H), 7.67 (dd, J=7.0 Hz, 2H), 7.46 (dd, J=7.0 Hz, 1H), 7.22 (dd, J=7.0 Hz, 1H), 3.45 (q, J=6.6 Hz, 4H), 1.21 (t, J=6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 164.7, 164.0, 155.9, 150.0, 149.4, 136.7, 132.81, 132.7, 131.9, 131.8, 125.3, 123.9, 123.9, 122.8, 121.6, 116.7, 115.9, 47.5, 12.4. IR: ν=1654, 1572, 1368, 1245, 780, 694 cm^{-1} Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.0; H, 5.54; N, 12.2. Found: C, 72.80; H, 5.49; N, 11.96.

*3.1.3. (4-diethylamino-1,8-naphthaloyl)-4-aminopyridine (**6**)*

(4-Bromo-1,8-naphthaloyl)-4-aminopyridine (0.15 g, 0.42 mmol) and excess diethyl amine (5 mL) were mixed in a 25 mL round bottom flask along with 5 mL DMF as a solvent. This reaction was carried out under reflux at around 100 °C and stirring overnight. A TLC showed the product and the solvent DMF and diethyl amine were evaporated by passing compressed air. Then, the dry crude product was purified in a silica gel column with 1:4 acetone and dichloromethane mixture as solvent system. This reaction gave 0.107 g (71%) yellow powder mp 200–205 °C.

^{1}H NMR ($CDCl_3$) δ 8.85 (s, 2H), 8.58 (d, J=7.5 Hz, 1H), 8.49 (d, J=7.5 Hz, 2H), 7.67 (t, J=7.5 Hz, 2H), 7.35–7.19 (m, 2H), 3.46 (q, J=6.6 Hz, 4H), 1.19 (t, J=6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 164.1, 163.5, 156.0, 151.2, 143.8, 142.7, 132.9, 131.8, 130.8, 127.3, 125.3, 124.3, 122.8, 116.7, 114.8, 47.5, 12.4 IR: ν=1701, 1654, 1584, 1356, 1228, 773 cm^{-1} Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.0; H, 5.54; N, 12.2. Found: C, 72.79; H, 5.44; N, 11.91.

3.2. Sultonation reactions

*3.2.1. (4-Diethylamino-1,8-naphthaloyl)-2-aminopyridinium propanesulfonate (**4a**)*

(4-Diethylamino-1,8-naphthaloyl)-2-aminopyridine (0.05 g, 0.19 mmol) was taken in a 25 mL round bottom flask along with excess of 1,3-propane sultone (2 g or 16.4 mmol) as a reactant and a solvent as well. This mixture was refluxed for 5 h and then cooled. Then, this crude product was washed with diethyl ether for several times to remove the excess sultone. After that, the crude product was purified in a silica gel column with 1:1 acetone and methanol and collected in test tubes. After evaporating the solvent, the product was again washed with acetone and ether separately to get pure product. This reaction afforded 0.04 g (80%) orange colored crystals. The product seemed to be hygroscopic and collected under ether: mp>300 °C.

^{1}H NMR (MeOH-d_3) δ 9.53–8.13 (m, 9H), 5.99 (s, 2H), 4.32–3.45 (m, 6H), 2.75–1.96 (m, 4H), 1.19 (br s, 2H). TOF MS ES$^+$ m/z 527.1963 (M+1 requires 527.1942).

*3.2.2. (4-Diethylamino-1,8-naphthaloyl)-3-aminopyridinium propanesulfonate (**5a**)*

(4-Diethylamino-1,8-naphthaloyl)-3-aminopyridine (0.066 g, 0.25 mmol) was mixed with excess of 1,3-propane sultone (2 g or 16.4 mmol) in a 25 mL round bottom flask as a reactant. This mixture was heated for about 5 h under reflux and cooled. Then, it was washed with diethyl ether many times and then a silica gel column was run with acetone and methanol mixture. Again, the product was washed with acetone and ether separately. This reaction gave 0.053 g (80%) orange red crystalline solid as product and collected under ether: mp>300 °C.

^{1}H NMR (MeOH-d_3) δ 9.46 (br s, 1H), 9.23 (br s, 1H), 8.81–8.46 (m, 5H), 7.88 (br s, 1H), 7.46 (br s, 1H), 5.22 (br s, 2H), 4.67–3.48 (m, 6H), 2.73–1.99 (m, 4H), 1.18 (br s, 2H). TOF MS ES$^+$ m/z 527.1940 (M+1 requires 527.1942).

*3.2.3. (4-Diethylamino-1,8-naphthaloyl)-4-aminopyridinium propanesulfonate (**6a**)*

(4-Diethylamino-1,8-naphthaloyl)-4-aminopyridine (0.06 g, 0.225 mmol) was heated with excess of 1,3-propane sultone (2 g or 16.4 mmol) in a 25 mL round bottom flask for about 5 h under reflux and cooled. Then, it was washed with diethyl ether to remove excess sultone and after that, a silica gel column was done with methanol and acetone mixture. After evaporating the solvent, orange red solid was obtained, which was again washed with ether and acetone separately. This reaction provided 0.049 g (82%) orange red crystalline compound as a product and the product was kept under ether because it seemed to be hygroscopic: mp>300 °C.

^{1}H NMR (MeOH-d_3) δ 9.35 (br s, 1H), 8.72–8.22 (m, 6H), 7.84 (br s, 1H), 7.54 (br s, 1H), 4.89 (s, 2H), 4.44–3.45 (m, 6H), 2.76–1.96 (m, 4H), 1.25 (pseudo d, 2H). TOF MS ES$^+$ m/z 527.1940 (M+1 requires 527.1942).

Acknowledgements

We thank the National Institutes of Health for their continued support of this work.

Supplementary data

This section contains fluorescence spectral data and copies of NMR spectra. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.01.048.

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