An organic white light-emitting dye: very small molecular architecture displays panchromatic emission†

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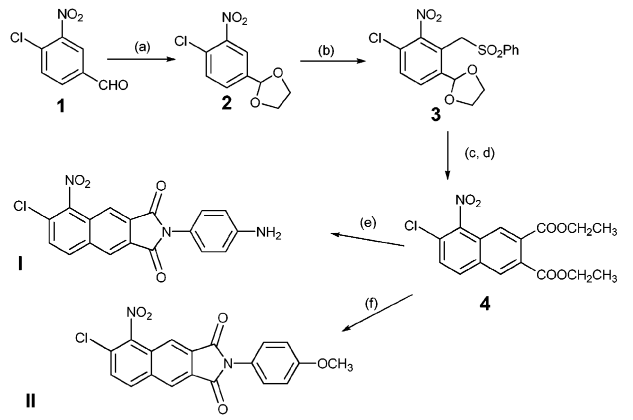
The synthesis and photophysical characterization of a new white-light fluorophore is described. The optimization of excitation wavelengths allows the naphthalimide (NI) dyes to display blue, green or white light emission depending on the excitation wavelength.

Organic fluorophores have at times been criticized for their wide band emission. In the rapidly developing field of white organic light-emitting devices (WOLEDs)[1] however, such features have become exalted in the search for dyes with panchromatic emission.[2] To date, very few small molecule dyes have been reported to display white light emission. Grätzel recently reported a cyclometallated iridium(III) complex emitting from an excited state of mixed character.[3] Among metal-free organic systems, Strongin and coworkers have developed a white-light emitting system composed of benzo[*a*]- and [*b*]xanthene derivatives.[4] Advantages of this system include water-solubility with simple synthetic design. More recently, Park and coworkers prepared a white-light emitting molecule utilizing excited state properties *via* so-called frustration of ESIPT relaxation mechanism.[5] Lastly, Hou demonstrated the brightest white-light organic dyes to date using π-conjugated carbazole-substituted phenyl enynes.[6] In solution, these dyes emit blue-green emission, however upon vapor deposition, an orange-red band appears that is attributed to excimer formation. Therefore, the synthesis of efficient and color-stable white-light emitting single molecules not affected by the environment represents a current challenge.

In an earlier report, we implemented a synthetic matrix approach to discover dual-fluorescent dyes[7] by preparing a nine element matrix of *N*-aryl-1,8-naphthalimides.[8] Based on those findings, we report the synthesis and optical measurements of two 2,3-NI systems I and II whereby a balance between two excited states is achieved *via* donation into the *N*-arene and electron withdrawal from the naphthalimide; a requirement for two-color spectra. A key hypothesis we sought to verify involves the alteration of structure with symmetry related 2,3-NI systems. This study allows us to probe the effects of the rotationally dynamic *N*-aryl-2,3-naphthalimide junction in comparison to similar 1,8 NI systems. The anticipated advantages of these new dyes over the aforementioned systems include (1) reduced molecular weight for improved vacuum deposition, (2) water solubility as an improvement with respect to environmental concerns during processing and (3) perhaps most importantly, a versatile synthetic plan giving several structural scaffolds for a variety of synthetic handles as well as photooptical properties.



Scheme 1 Synthesis of di-substituted-2,3-naphthalic anhydride. *Reagents and conditions*: (a) ethylene glycol, toluene, reflux, overnight, 95%; (b) dry DMSO, KOH, ClCH$_2$SO$_2$Ph, overnight, 24 °C, 75%; (c) AcOH/H$_2$O 4 : 1, reflux, 6 h, 95%; (d) diethyl maleate, 18-crown-6, K$_2$CO$_3$, CH$_3$CN, 24 °C, then reflux, 6 h, 70%; (e) *p*-phenylenediamine, pyridine, reflux, 12 h; (f) *p*-anisidine, pyridine, reflux, 12 h.

A synthesis that generates various 5- and 6-substituted 2,3-naphthalic anhydrides bearing electron-withdrawing substituents is critical for panchromatic emission. 6-Choloro-7-nitro-2,3-NI dyes can be obtained from 4-chloro-3-nitrobenzaldehyde as starting material (Scheme 1). Protection of this substrate (ketalization with ethylene glycol) is required for the key step known as "vicarious nucleophilic substitution of aromatic hydrogen" involving chloromethyl phenylsulfone.[9] This functionality along with the protected benzaldehyde undergoes basic elimination in order to react with diethylmaleate giving diethyl ester **4**. Simple condensation yields compounds **I** and **II**.

As shown in Fig. 1, compound **I** displays a three-color emission over the entire visible region. When excited at 423 nm dye **I** displays three-color peaks, blue, green and orange (450–700 nm) with high emission intensities (see inset Fig. 1 middle photo of white light emission). Upon shorter wavelength excitation (390 nm), **I** displays intense blue color emission whereas longer wavelength excitation at 450 nm, **I** displays intense green color emission. Although dye **II** displays dual fluorescence, it did not exhibit white light emission. Nevertheless, excitation of **II** at specific wavelengths promoted the fluorescence emission of colors similar to **I**. The origin of these bands in emission spectra, as fully described in a recent paper, results from a mix of π–π^* and n–π^* excited

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† Electronic supplementary information (ESI) available: Data in this section includes optical absorbance spectra, fluorescence spectra as well as NMR data for the reported compounds. See DOI: 10.1039/c0cc02598d

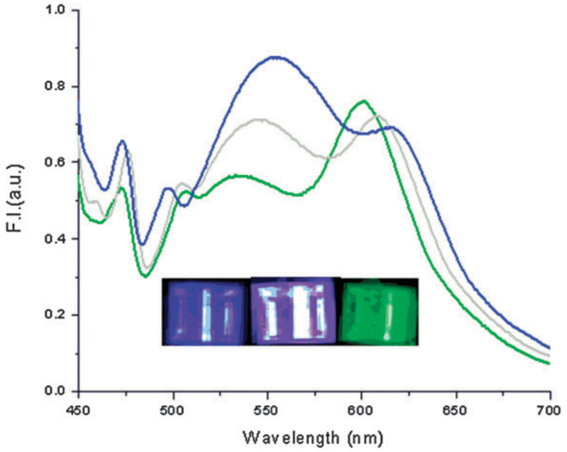

Fig. 1 The emission spectra of 20 μM compound **I** in water with 0.10% DMSO at different excitation wavelengths 390 nm, 423 nm and 450 nm, corresponding to blue, white and green photographs, respectively. Colored light of cuvette is due to output of excitation light.

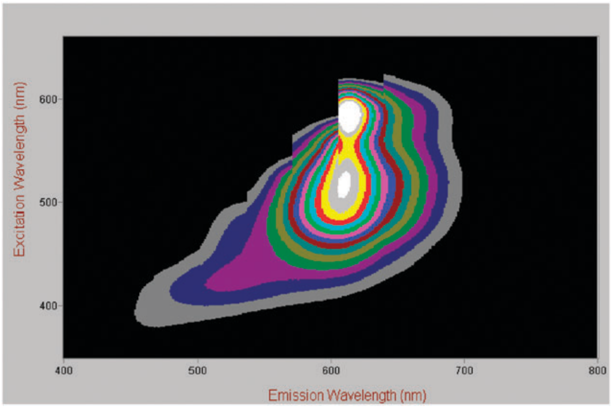

Fig. 2 Excitation–emission matrix of 20 μM compound **I** in DMSO with 0.25% phosphate buffer (35 mM, pH 7).

states.[8] An excitation–emission matrix of **I** in DMSO are shown in Fig. 2. This figure shows broad spectrum of wavelengths from 450 nm to 700 nm.

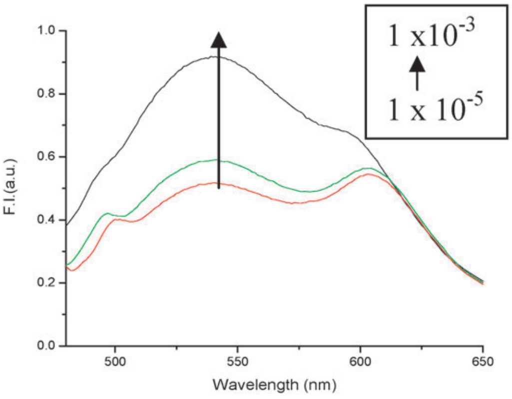

Fig. 3 Fluorescence spectra of **I** at different concentrations (1×10^{-5}, 6×10^{-5} and 1×10^{-3} M in water with 0.10% DMSO). The excitation wavelength was 423 nm.

Table 1 Summary of fluorescence, molar absorptivity and quantum yield *Φ*

Entry	Excitation/nm	Emission/nm	ε[a]		Φ[b]
			π → π*	n → π*	
I	423	450	6.5×10^4	3.4×10^4	0.46
II	390	405	1.4×10^5	5.5×10^4	0.36

[a] Molar absorptivity **I**: π–π* 350 nm, n–π* 422 nm; **II**: π–π* 390 nm, n–π* 422 nm. [b] Quantum yields are calculated based on quinine sulfate.

When we measured the fluorescence spectra at different concentrations (Fig. 3), the peak profiles and λ_{max} values did not change over a 100 fold increase in concentration. This observation lends evidence against any excimer formation as being responsible for the panchromatic features.[10] As shown in Table 1, both dyes exhibit high fluorescence quantum yields. In addition, the optical spectra for these dyes indicate high molar absorptivities. We tentatively assign the shortwave and more intense absorption as π–π* and the long wavelength less intense absorption as n–π*.[11]

In conclusion, we have synthesized two dual fluorescent 2,3-NI dyes using vicarious nucleophilic substitution at the aromatic C–H bond to deliver the required Diels–Alder synthons. Our hypothesis that 2,3-NI dyes would exhibit similar photophysics as symmetry related 1,8-NI proved to be a correct one with the added advantage that the 5-ring carboximide/6-ring N-aryl juncture permits broader fluorescence emission than the more restrictive 6-ring carboximide/6-ring N-aryl juncture of 1,8 NI. In addition these dyes exceeded our goals prescribed earlier such as water solubility, reduced chromophore size and molecular weight as well as a synthetic path that allows synthetic diversity of substituents within the 2,3-NI framework. Plans to utilize this synthetic approach for a variety of panchromatic fluorophores are currently underway. Lastly, experiments involving solid state optical properties using electroluminescence are planned in the near future.

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