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Synthesis, characterization and photophysical properties of an acenaphthalene fused-ring-expanded NIR absorbing aza-BODIPY dye

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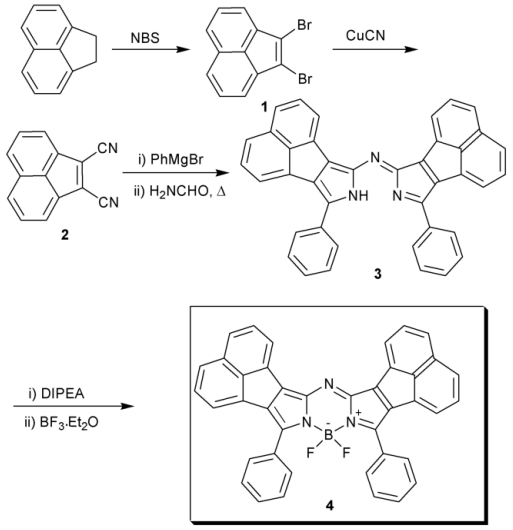
The synthesis and characterization of an NIR absorbing acenaphthalene fused-ring-expanded aza-BODIPY dye is reported. In contrast with its naphtho-fused analogue, a stable complex is obtained when the corresponding phthalonitrile is used as the precursor. A comparison is made with the photophysical properties of 3,5-diphenyl-aza-dibenzoBODIPY.

Introduction

In recent years there has been considerable interest in the synthesis of new organic chromophores with strong absorption and fluorescence bands in the near-infrared (NIR) region due to their possible applications in optical imaging, microarrays, electrophoresis and the need to develop labels and optical sensors for biological and medical applications.[1] A key advantage of NIR dyes is that the scattering of light, autofluorescence and absorption by tissues and cells is minimized.[2] Traditionally, cyanine dyes such as Cy3 or Cy5 were used in these contexts, but their flexible structures result in relatively poor photostability and low fluorescence quantum yields.[3] There has been increasing interest in the use of boradiazaindacene (BODIPY) dyes for these applications,[4] since they often have superior spectral characteristics to those of fluoresceins and rhodamines. BODIPYs have already started to be used in some of these contexts.[5]

The BODIPY π-system typically absorbs and emits in the 480 – 540 nm region.[6] Marked red shifts of the absorption and emission maxima have been achieved through aryl or styryl substitution at the 1, 3, 5 and/or 7 positions, aromatic ring fusion, by incorporating an oxygen atom into the π-system to coordinate the boron or by replacing the *meso*-carbon with an aza-nitrogen to form an aza-BODIPY.[6,7] A further advantage of aza-BODIPY dyes[8] is that a marked red shift of the absorption and emission bands relative to conventional BODIPY dyes can be achieved without modifying the key properties of BODIPY dyes, such as their high molar absorption coefficients, narrow and structured absorption and emission bands, small Stokes shifts, high fluorescence quantum yields and photostability.

The use of NIR absorbing aza-BODIPY dyes in practical applications is only likely to become feasible when a facile and commercially viable synthetic method has been developed. In recent years, a novel synthetic method has been reported for obtaining 3,5-diaryl-aza-dibenzoBODIPYs in moderate yield through a two-step reaction of phthalonitrile and an arylmagnesium bromide.[9] Phthalonitrile is commercially available, while arylmagnesium bromides are easily prepared. A marked red shift of the absorption and emission bands was observed relative to the spectra of conventional 1,3,5,7-tetraaryl aza-BODIPY dyes.[9,10] The introduction of additional substituent groups on the precursors is straightforward so the spectral properties of the aza-BODIPY product can be further fine tuned. Since phthalonitriles are the main precursors used for the synthesis of phthalocyanines, the synthesis and properties of substituted phthalonitriles have already been studied in depth.[11] Subsequent progress on benzo-fused aza-BODIPYs has been limited by issues with the stability of the compounds and further expansion of the π-system to form naphtho-fused compounds proved impossible.[12] We report the synthesis, characterization and photophysical properties of a significantly fused-ring-expanded 3,5-diphenyl-aza-



Scheme 1 Synthesis of the acenaphthalene fused-ring-expanded aza-BODIPY **4**.

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† Electronic Supplementary Information (ESI) available: Experimental details for **1** and **2**, NMR spectra for **1**-**4**. See DOI: 10.1039/x0xx00000x

diacenaphthoBODIPY compound by using 1,2-dicyanoacenaphthylene as a precursor.[13] To our knowledge, despite this phthalonitrile analogue being reported over 40 years ago, it has not been used previously to synthesize phthalocyanine or aza-BODIPY compounds.

Experimental section

Theoretical Calculations

The Gaussian 09 software package[14] was used to carry out density functional theory (DFT) geometry optimizations and time dependent-DFT (TD-DFT) calculations by using the B3LYP functional with 6-31G(d) basis sets, so that the optical properties of **4** can be compared to its naphtho- and benzo-fused analogues (**5** and **6**) and the unsubstituted 3,5-phenyl-aza-dibenzoBODIPY (**7**) parent complex.

Materials and reagents

All chemicals were analytically pure and were used as received. Solvents were dried and distilled prior to synthesis.

Synthesis and characterization data

1 and **2** were prepared using the methods of Trost and Britelli,[15] and Rieke and co-workers,[13] respectively, and 3,5-Diphenyl-aza-dibenzoBODIPY (**6**) was derived from phthalonitrile using the standard literature methods.[9,12]

Synthesis of 3,5-diphenyl-aza-diacenaphthoBODIPY (4)

A freshly prepared diethyl ether solution (50 mL) of phenylmagnesium bromide prepared from magnesium (4 g, 168 mmol), bromobenzene (15.70 mL, 150 mmol) and catalytic amount of iodine was added dropwise at –20°C under nitrogen atmosphere to a vigorously stirred absolute diethyl ether solution (60 mL) of 1,2-dicyanoacenaphthylene **2** (5.06 g, 25 mmol). After complete addition, the resultant mixture was allowed to warm to room temperature and further stirred for 3 h. The solvents from the dark reaction mixture were removed with a rotary evaporator and rapidly heated with formamide (3 × 100 mL) until gas evolution was observed. The reaction mixture was further heated for 5 min, cooled to room temperature and then poured onto water. The precipitate was purified by column chromatography (silica gel, eluted with 100:4 $CHCl_3$-MeOH (v/v)) to yield **3** as a dark brownish green solid. Yield: 2.64 g, 19%. MALDI-TOF-MS m/z: calcd for $[C_{40}H_{23}N_3]$: 545.63 $[M]^+$; found: 545.20.

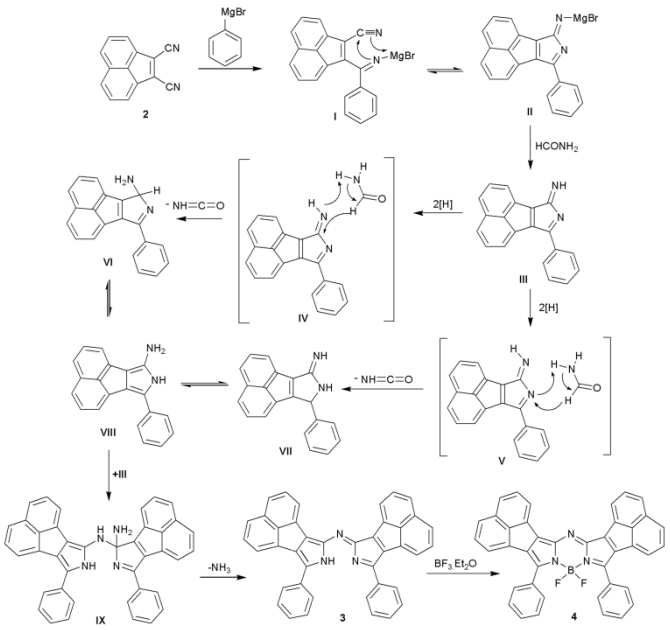
The 3,5-diphenyl-aza-diacenaphthodipyrromethene precursor was used for the final step of the synthesis of **4** prior to its complete purification. Distilled diisopropylethylamine (DIPEA) (1.15 mL, 6.6 mmol) was added to a solution of **3** (327 mg, 0.6 mmol) in distilled CH_2Cl_2 (60 mL). The solution was stirred for 1 h at rt and $BF_3.Et_2O$ (1.18 mL, 9.6 mmol) was added dropwise. The solution was stirred for 24 h at rt. The reaction mixture was quenched with water and the organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, first eluted with 100:4 $CHCl_3$-MeOH (v/v) then with 3:1 EtOAc-hexane (v/v) to give **4** as a bluish green solid. Yield: 193 mg, 54%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65-7.58 (m, 8H), 7.52-7.46 (m, 8H), 7.25 (d, 2H, J = 6 Hz), 6.80 (d, 2H, J = 12 Hz), 6.68 (d, 2H, J = 6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.57, 143.90, 131.36, 130.77, 130.63, 130.09, 130.02, 129.61, 129.00, 128.96, 128.90, 128.84, 128.11, 127.71, 124.57, 119.30, 118.51, 117.45, 116.73, 115.17, 111.74, 104.10. Anal. calcd for $[C_{40}H_{22}BF_2N_3 + 2C_4H_8O_2 + C_6H_{14}]$: C, 75.78; H, 6.12; N, 4.91. Found: C, 75.50; H, 5.97; N, 4.82.

Analytical measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 600 spectrometer at 600 and 150 MHz, respectively, ($CDCl_3$ as solvent, TMS as standard. Mass spectra were determined on a Bruker AutoFLEX III Smartbeam TOF MALDI-TOF mass spectrometer. Elemental analyses were carried out on a Vario EL III MicroCube CHNS instrument and was in agreement with the calculated values within ±0.4%. Absorption spectra were recorded on a Shimadzu UV-Vis 2550 spectrophotometer. Fluorescence spectra were measured on a Varian Eclipse spectrofluorimeter. Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). The excitation source was a diode laser (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, 44 ps pulse width, Picoquant GmbH. Fluorescence quantum yields were measured with compound **6** as standard (14% in CH_2Cl_2).[12] The optical parametric oscillator unit of an Ekspla NT 342B-20-AW laser (2.0 mJ/5 ns, 20 Hz) Ekspla was used to provide beams of monochromatic laser light in the 600–700 nm range to carry out singlet oxygen quantum yield (Φ_Δ) measurements in $CHCl_3$ by using 1,3-diphenylisobenzofuran (DPBF) as a $^1O_2$ scavenger.

Results and discussion

Initially, the synthesis of aza-dipyrromethene **3** was attempted by reacting 1,2-dicyanoacenaphthylene with phenylmagnesium bromide in dry benzene at room temperature adopting the procedures reported in literature.[12,16] After steam distillation none of the anticipated aza-dipyrromethene **3** was obtained. This can be attributed to the low reactivity of the reactants at room temperature in the reaction system. By implementing a modified procedure reported by Gresser et al., the slurry obtained from the reaction of 1,2-dicyanoacenaphthylene with phenymagnesium bromide was heated with formamide to give the aza-dipyrromethene **3** as the main product (**Scheme 1**). The yield of the aza-dipyrromethene **3** varies markedly depending on the manner that phenylmagnesium bromide Grignard reagent is added to the 1,2-dicyanoacenaphthylene **2**, so the reaction conditions had to be optimized by changing the temperature, solvent, and the molar ratios of the Grignard reagents. The addition of phenylmagnesium bromide to 1,2-dicyanoacenaphthylene **2** in benzene and THF at room temperature, followed by heating above room temperature under an aerobic atmosphere resulted in a negligible yield of aza-dipyrromethene **3**. Increasing the temperature above room temperature and varying phenylmagnesium bromide from 1 to 3 equiv. drastically increased the quantity of side products resulting in a tedious workup of the reaction mixture.



Scheme 2 Proposed mechanism for the formation of aza-BODIPY **4**.

The best results were achieved by adding phenylmagnesium bromide to 1,2-dicyanoacenaphthylene **2** in diethyl ether at ca. –20°C under a nitrogen atmosphere. Subsequently the reaction mixture was evaporated directly to dryness and the magnesium salt of the intermediate was heated with formamide to form the aza-dipyrromethene **3** target compound. BF_2 complexation of **3** in CH_2Cl_2 in the presence of diisopropylethylamine (DIPEA) formed the aza-BODIPY **4** (**Scheme 1**). The molecular structure of **4** was confirmed by ^1H NMR (**Fig S4** in ESI). The absence of a peak in the upfield region (δ = –1 to –3 ppm) due to the shielding of the inner core protons of pyrrole confirms the formation of the 3,5-diaryl-aza-diacenaphthoBODIPY target compound instead of the analogous phthalocyanine or one of its partially aza-substituted structural analogues.

The reaction mechanism involves the initial nucleophilic attack of the phenylmagnesium bromide at the carbon atom of the nitrile moiety forming magnesium derivative **I** which on subsequent ring cyclization forms the magnesium salt of isoindolylimine **II** (**Scheme 2**). The conversion of **III** to **3** is ambiguous and follows Leuckart–Wallach reaction process involving reduction of **III** by formamide via either of the intermediate **VI** or **VII**. Both of these intermediates can tautomerize to form **VIII**, which ultimately reacts with **III** to give **3** via **IX** followed by loss of ammonia.

The absorption maxima for aza-BODIPY **4** was observed in the NIR region at 673 nm (ε = 50 000 $M^{-1}.cm^{-1}$ in $CHCl_3$) with a high energy shoulder at 628 nm (**Table 1** and **Fig 1**). When spectra are measured over a wide range of concentrations, it becomes clear that there are no significant aggregation effects. The main absorption band can be assigned to the HOMO–LUMO transition, based on the TD-DFT calculations at the B3LYP/6-31G(d) level (**Table 2** and **Fig 2**). The high energy shoulder band may be either vibronic or electronic in origin, since a relatively intense transition to the S_2 state is predicted

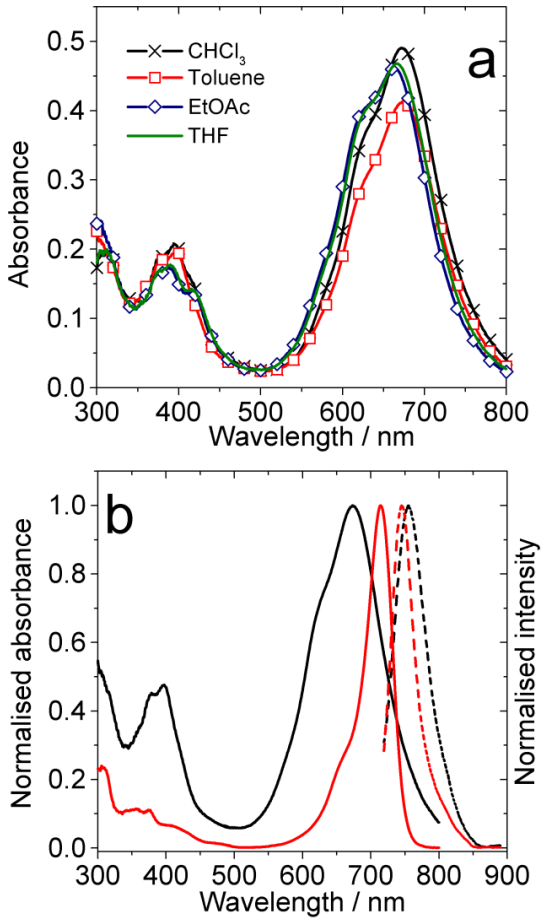


Fig 1 (a) UV-visible absorption spectra of aza-BODIPY **4** in different solvents; (b) Normalized absorption spectra (solid line) and fluorescence spectra (dash line) of aza BODIPY **4** (black) and aza BODIPY **6** (red) (λ_{ex} = 700 nm, c = 1.0×10^{-5} M).

Table 1 Spectroscopic data of aza-BODIPY **4** at 298 K[a]

	λ_{max} [nm]	ε [$M^{-1}.cm^{-1}$]	λ_{em} [nm]	Stokes Shift [nm]	Φ_F[b]	τ_f[ns][c]
Toluene	674	41 300	755	81	0.01	2.87
$CHCl_3$	673	50 000	774	101	0.005	2.42
EtOAc	664	46 200	780	---[d]	---[d]	---[d]
THF	667	46 800	---[d]	---[d]	---[d]	---[d]

[a]c = 1.0 × 10^{-5} M. [b]Fluorescence quantum yields with aza-BODIPY **6** (Φ_F = 14% in CH_2Cl_2)[12]. [c]Fluorescence lifetimes under an air atmosphere. [d]not determined.

Table 2 Calculated and observed electronic excitation wavelengths of **4-7**, and calculated oscillator strengths and wavefunctions.

		λ_{max} [nm] Exp	Calc	f[a]	Wavefunction =[b]
4	$S_0 \rightarrow S_1$	674	659	0.66	H→L (87%); H–1→L (14%); …
	$S_0 \rightarrow S_2$	---[c]	562	0.38	H–1→L (84%); H→L (15%); …
	$S_0 \rightarrow S_{10}$	385	392	0.36	H→L+1 (61%); …
5	$S_0 \rightarrow S_1$	---[c]	677	0.91	H→L (100%); …
6	$S_0 \rightarrow S_1$	714	590	0.75	H→L (100%); …
7	$S_0 \rightarrow S_1$	---[c]	517	0.67	H→L (100%); …

[a]Calculated oscillator strength. Only bands predicted to have oscillator strengt greater than 0.2 to the red of 350 nm are included. [b]The wavefunctions bas on the eigenvectors predicted by a TD-DFT calculation for the B3LYP optimiz geometries of **4-7** calculated with 6-31G(d) basis sets. H and L are used t denote the HOMO and LUMO, respectively. [c]not determined

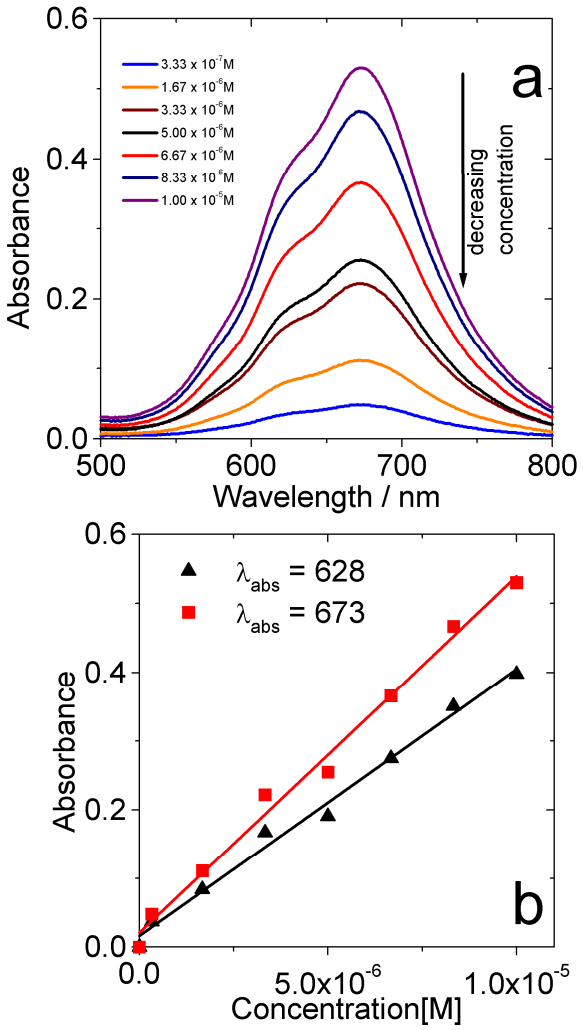


Fig 2 (a) Absorption spectra of aza-BODIPY **4** in $CHCl_3$ at different concentrations; (b) Beer-Lambert plot for **4** in $CHCl_3$.

in this spectral region (**Table 2**). A blue shift of the main absorption band is observed relative to the analogous band of the benzo-fused aza-BODIPY **6** (λ_{max} = 712 nm)[12] (**Fig 1b** and **Table 2**).

The energies of the HOMO and LUMO of the naphtho- and benzo-fused aza-BODIPYs **5** and **6** are destabilized relative to the frontier MOs of aza-BODIPY **4** (**Table 2** and **Fig 3**). Since the destabilization of the HOMO is greater than that of the LUMO for the naphtho-fused aza-BODIPY **5** there is a narrowing of the HOMO–LUMO band gap (ΔE = 1.91 for **4**, 1.71 eV for **5**) (**Fig 3**), which is reflected in the wavelengths of the corresponding aza-dipyrromethenes.[12] A red shift of the main absorption band is predicted for **5** and **6** due to a marked decrease in the HOMO–LUMO gap. The HOMO of the aza-BODIPY π-system is directly comparable to that of the a_{1u} HOMO of tetraazaporphyrins, since it also has nodal planes on the bridging aza- and pyrrole nitrogens.[12,18] This means that the effect of incorporating fused-ring moieties is broadly similar in both cases due to antibonding interactions at the points of attachment on the β-carbons of the pyrrole rings (**Fig 3**). In contrast, there is a stabilization of the HOMO of the π-system of **4** relative to that of **6**, despite the further expansion of the π-system. This makes **6** more stable towards oxidation, which was the key problem that made the synthesis of the naphtho-fused **5** complex problematic.[12]

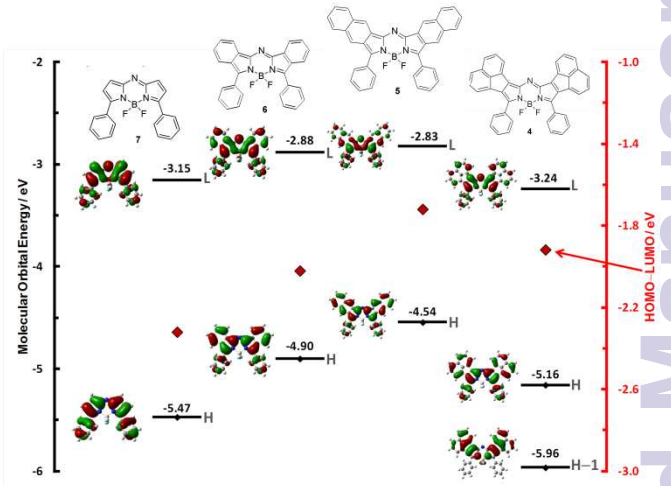


Fig 3 Energy-level diagram for the frontier π-MOs of aza-BODIPYs **4-7**. Electron density maps of the frontier π-MOs at an isosurface of 0.02 a.u. in TD-DFT calculations for the B3LYP optimized geometries by using the B3LYP functional with 6-31G(d) basis sets. The HOMO–LUMO energy gap values are plotted against a secondary axis and are denoted with red diamonds. Dark gray L and H labels refer to the LUMO and HOMO respectively.

In TD-DFT calculations, the main absorption band of **4** is predicted to lie to the red of that of 3,5-diaryl-aza-dibenzoBODIPY **6** (**Table 2**), due primarily to a stabilization of the LUMO that results in a marked narrowing of the HOMO–LUMO gap. The maximum of the experimentally observed band lies well to the red, however (**Fig 1b**). The much larger Stokes Shift observed for **4** suggests that this is due to vibrational intensity and the main electronic origin may lie to the red of that of **6**. In marked contrast with what is observed for 3,5-diphenyl-aza-dibenzoBODIPY where the reported Φ_F values range from 0.14–0.24 in CH_2CH_2, acetonitrile and hexane,[12] the emission intensity of **4** is very weak in non-polar toluene and is completely quenched in polar ethyl acetate (EtOAc) and tetrahydrofuran (THF) (**Table 1**). The emission band is not a mirror image of the absorption band, which is also consistent with there being marked differences in the vibrational levels of the ground and excited states. The most probable explanation is that the presence of a second close-lying excited S_2 state (**Table 2**) modifies the photophysical properties of the core aza-BODIPY moiety. It is noteworthy, that while the main absorption bands of **5-7** are predicted to be associated 100% with the HOMO → LUMO transition (**Table 2**), a significant contribution from the HOMO–1 → LUMO transition is predicted for the main absorption band of **4**. A slight blue shift was observed in the main absorption band of **4** on increasing the solvent polarity (**Table 1** and **Fig 1a**), which suggests that the low Φ_F values are related to an intramolecular charge-transfer process that results in a non-emissive decay channel. The HOMO–1 of **4**

has the same symmetry as the HOMO and is localized mainly on the acenaphthalene moieties (**Fig 3**), while the LUMO is mainly associated with the aza-BODIPY core. Similar photophysical properties have been reported for BODIPY dyes that are predicted to have S_1 states with significant charge transfer character.[19]

In future, the use of phthalonitriles and arylmagnesium bromides could provide a facile method for bulk synthesis, which would facilitate the use of fused-ring-expanded aza-BODIPYs in a wide range of practical applications, since it has been demonstrated that NIR-absorbing BODIPY and aza-BODIPY dyes are potentially suitable for use in photodynamic therapy (PDT) and bioimaging,[8f,20] and in solar cells.[7h,21] Attempts were made to determine a Φ_Δ value for **4** by using DPBF as a $^1O_2$ scavenger in $CHCl_3$. Negligible changes were observed in the intensity of the main absorption band of DPBF upon irradiation with red region laser light, so **4** has a near zero Φ_Δ value. The incorporation of heavy atoms such as bromine and iodine atoms is known to significantly enhance the rate of intersystem crossing and hence the Φ_Δ values of aza-BODIPY dyes, however, so there may be scope for PDT related research in future by carrying out further structural modifications.[10,22] In a similar manner to 1,2-dicyanobenzene, functionalization is possible at the peripheral positions of 1,2-dicyanoacenaphthylene and other fused-ring expanded precursors in a manner that can fine-tune the optical and redox properties, and enable conjugation to nanoparticles.

Conclusion

The synthesis, characterization and theoretical analysis of an acenaphtho-fused aza-BODIPY dye has been successfully achieved. In contrast with its naphtho-fused analogue,[6] a stable complex was readily obtained, due to the differing effects of the fused ring moieties on the energies of the frontier π-MOs. The Φ_F values obtained for **4** are relatively low in a range of solvents of differing polarity, limiting the utility of this compound for sensor and bioimaging applications, but the relatively broad absorption band at the red end of the visible region may make the compound suitable for use in solar cells. Further studies are now under way to investigate in depth, which types of fused-ring-expanded phthalonitriles can be used to form NIR absorbing aza-BODIPYs, which retain more of the favourable photophysical properties observed for 3,5-diphenyl-aza-dibenzoBODIPY.

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