Alnoman RB, Stachelek P, Knight JG, Harriman A, Waddell PG.
Synthesis of 2-aminoBODIPYs by palladium catalysed amination.
Organic and Biomolecular Chemistry (2017)
DOI: <https://doi.org/10.1039/C7OB01767G>

Copyright:

This is the authors' accepted manuscript of an article that has been published in its final definitive form by the Royal Society of Chemistry, 2017.

DOI link to article:

<https://doi.org/10.1039/C7OB01767G>

Date deposited:

18/08/2017

Embargo release date:

31 August 2018

Synthesis of 2-aminoBODIPYs by palladium catalysed amination

Rua B. Alnoman,^{a,b} Patrycja Stachelek,^a Julian G. Knight,^{*a} Anthony Harriman,^a and Paul G. Waddell^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Palladium catalysed coupling of the 2-iodoBODIPY **3** with a range of anilines and a primary alkylamine succeeds in generating the corresponding 2-aminoBODIPYs. These 2-aminoBODIPY derivatives are non-emissive and quantum chemical calculations and electrochemistry are consistent with charge transfer from the amine substituent. Attenuation of this charge transfer pathway by conversion of the 1,2-phenylenediamine derivative **9** into the corresponding benzimidazolone **10** restores the fluorescence and has been used as the basis for a fluorescence sensor for phosgene.

Introduction

The 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes (BODIPYs, Fig. 1) are a class of organic dyes typically characterised by sharp absorption and emission spectra, excitation and emission wavelengths in the visible/near infra red region, high molar absorption coefficients, high quantum yields of fluorescence, high photostability and resistance to chemical degradation. The synthetic accessibility of BODIPYs enables elaboration of the core structure in order to tune the photophysical properties.¹ BODIPYs have consequently found widespread application including use as fluorescence sensors,² as biomolecular imaging agents,³ in photodynamic therapy,⁴ as laser dyes,⁵ in electroluminescence,⁶ and in electron-transfer applications such as dye-sensitized solar cells.⁷

Figure 1 Numbering scheme for 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes (BODIPY)

There is a growing number of amine-functionalised BODIPYs in which the strongly electron donating amino group results in fluorescence quenching by intramolecular charge transfer (ICT) or photoelectron transfer (PET) to the excited state. This

electron donation can be attenuated by coordination of the nitrogen lone pair to a Lewis or Brønsted acid, leading to restoration of the BODIPY fluorescence, and this property has been frequently employed in the design of 'switch-on' fluorescence sensors.^{2,3,8}

In these systems the amino group is typically appended to a substituent. The direct attachment of amine nitrogen to the BODIPY core is less common and such systems have been the focus of detailed structural and photophysical investigations motivated by the high level of current interest in elucidating the effects of substituents on the properties of these fluorophores.⁹ Synthesis of directly-aminated BODIPYs relies almost exclusively on nucleophilic substitution (S_NAr) of BODIPY electrophiles carrying a suitable nucleofuge (halogen, ether, thioether, or hydrogen under oxidative conditions).^{9,10} Nucleophilic amination (S_NAr) is electronically restricted to the 1, 3, 5, 7 and 8 positions of the BODIPY (Fig. 1) because attack at these positions allows the resulting intermediate anion to be delocalised onto one of the nitrogen atoms.

The effect of amino substituents on the energy of absorption is known to be dependent on the position of substitution: 8-amino substitution is reported to lead to a significant blue-shift due to LUMO destabilisation by an antibonding interaction between nitrogen and C8^{9d} and the size of the blue-shift is reduced in systems in which coplanarity between the amine and BODIPY core is sterically disfavoured;^{9k} 3-amino substitution of an 8-methyl BODIPY leads to red-shifted absorption which has been ascribed simply to an increase in the length of the conjugated system.^{9g} The effect of direct 2-amino substitution on the photophysical properties of BODIPY is therefore of some interest. We were therefore interested in accessing 2-aminoBODIPY derivatives, which have been relatively neglected presumably because of the lack of convenient synthetic routes. Amino substitution has been introduced by electrophilic nitration followed by reduction but this approach is limited to the parent 2-NH₂ substituent.^{9g,j} The resulting α -unsubstituted 2-NH₂ derivative was also reported to be very unstable and so no photophysical data was reported.^{9g} The 2-NH₂ group has also

^a School of Chemistry, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU
E-mail: julian.knight@ncl.ac.uk

^b Present Address: Department of Chemistry, College of Science, Taibah University, Yanbu, Saudi Arabia.

† Electronic Supplementary Information (ESI) available: Modified synthetic procedures for previously reported compound **4**; overlay of the two independent in the X-ray crystal structure of compound **6d**; absorption spectra in terms of the molar absorption coefficient (ϵ) for **6a** in various solvents; copies of NMR spectra for all compounds; and the CIF file giving details of crystal data, structure solution, and refinement, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for compound **6d**. CCDC 1562614. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

been introduced by palladium-catalysed substitution of a 2-bromoBODIPY with benzophenone imine followed by hydrolysis of the resulting 2-iminoBODIPY.^{9e,f} This approach is also structurally limited and uses a rather high palladium loading (5 – 40 mol%). The presence of phenyl substituents in the 3,5-positions or a 4-nitrophenyl group in the BODIPY 6-position was reported to stabilise the resulting 2-NH₂-substituted BODIPYs but no photophysical data was reported for these compounds. Attempted palladium catalysed amination of a 2-bromoBODIPY has been reported to fail, instead giving a complex mixture from which a 2-aminoBODIPY was not isolated.¹¹

We report herein the synthesis of 2-alkyl- and 2-aryl-amino BODIPYs by palladium catalysed Buchwald-Hartwig amination of the corresponding 2-iodoBODIPY derivatives. The potential utility of such compounds is demonstrated by synthesis of an off-on fluorescent probe for the detection of phosgene.

Results and discussion

Palladium catalysed amination of 2-iodoBODIPYs

We recently reported the copper catalysed amination of 2-iodoBODIPY **1** which produces the 3-aminoBODIPY derivatives **2** by a vicarious nucleophilic substitution (Scheme 1).¹²

Scheme 1 Copper-catalysed vicarious nucleophilic amination of 2-iodoBODIPYs.¹²

This mode of reaction should be denied to systems in which the 3- (and 5-) position is blocked by substitution. The ‘fully-blocked’ BODIPY **3** was synthesised by zinc oxide catalysed Friedel-Crafts acylation¹³ of 2,4-dimethylpyrrole to give the 2-ketopyrrole **4**. BF₃-mediated condensation¹⁴ with 3-ethyl-2,4-dimethylpyrrole followed by electrophilic iodination of the resulting BODIPY **5** with *N*-iodosuccinimide¹⁵ gave the 2-iodoBODIPY **3** (Scheme 2).

Attempted copper catalysed amination of the 2-iodoBODIPY **3** under our previously reported¹² conditions did not produce any of the corresponding 2-aminoBODIPY; instead the only product to be identified was the protodehalogenated BODIPY **5**, which may well result from protonation of an intermediate organocopper species. Inspection of the literature reveals that, apart from cases in which the aryl ring is strongly activated by electron withdrawing groups *ortho*- or *para*- to the halogen, there are very few reports of successful copper-catalysed intermolecular coupling of alkyl- or aryl-amines with aromatic halides carrying two *ortho* substituents and these generally require very forcing conditions.¹⁶ In contrast to this, the corresponding palladium-catalysed amination of highly hindered doubly *ortho*-substituted aromatic halides is more

common.¹⁷ Table 1 shows the results of our initial screening of conditions for the amination of the 2-iodoBODIPY **3** with 4-methoxyaniline.

Scheme 2 Synthesis of the 1,3-dialkylated-2-iodoBODIPY **3**. Reagents: (a) ZnO (25 mol%), rt, 5 min (55%); (b) 3-ethyl-2,4-dimethylpyrrole, BF₃.OEt₂, rt, 2 h; (c) BF₃.OEt₂, *i*-Pr₂NEt, CH₂Cl₂, rt, 4 h (86% over two steps); (d) NIS, CH₂Cl₂, rt, 4 h (80%). (Ar = 4-MeC₆H₄).

Table 1 Variation of conditions for amination of 2-iodoBODIPY **3**

Entry ^a	Ligand	Pd source	%Pd ^b	Base	Yield ^c
1	XantPhos	Pd ₂ (dba) ₃	10	Cs ₂ CO ₃	36
2	BINAP	Pd ₂ (dba) ₃	10	Cs ₂ CO ₃	5
3	XPhos	Pd ₂ (dba) ₃	10	Cs ₂ CO ₃	71
4	SPhos	Pd ₂ (dba) ₃	10	Cs ₂ CO ₃	80
5	SPhos	Pd(OAc) ₂	10	Cs ₂ CO ₃	19
6	SPhos	(LPdOMs) ₂ ^d	10	Cs ₂ CO ₃	96
7	SPhos	(LPdOMs) ₂ ^d	5	Cs ₂ CO ₃	94
8	SPhos	(LPdOMs) ₂ ^d	2.5	Cs ₂ CO ₃	92
9	SPhos	(LPdOMs) ₂ ^d	1.2	Cs ₂ CO ₃	81
10	SPhos	(LPdOMs) ₂ ^d	0.5	Cs ₂ CO ₃	10
11	SPhos	(LPdOMs) ₂ ^d	0.1	Cs ₂ CO ₃	n.r. ^e
12	SPhos	(LPdOMs) ₂ ^d	1.2	KF	n.r. ^e
13	SPhos	(LPdOMs) ₂ ^d	1.2	K ₃ PO ₄	60
14	SPhos	(LPdOMs) ₂ ^d	1.2	Cs ₂ CO ₃	13 ^f
15	SPhos	(LPdOMs) ₂ ^d	1.2	Cs ₂ CO ₃	4 ^g
16	SPhos	(LPdOMs) ₂ ^d	1.2	Cs ₂ CO ₃	n.r. ^{e,h}

^a Reagents and conditions: BODIPY **3** (0.203 mmol), 4-MeOC₆H₄NH₂ (1.01 mmol), Pd source, ligand (1.1 mol per mol Pd), base (0.345 mmol), 1,4-dioxane (2 mL), 95 °C, 16 h. ^b Total palladium loading (mol%). ^c Isolated yield (%). ^d Di-μ-mesylbis[2'-(amino-*N*)[1,1'-biphenyl]-2-yl-C]dipalladium(II) **7**.¹⁸ ^e No reaction. ^f Reaction at 60 °C. ^g Reaction at 30 °C. ^h Reaction at 20 °C.

The palladium catalysed reaction of the 2-iodoBODIPY **3** with 4-methoxyaniline was first attempted using the conditions reported by Hiroto and Shinokubo for substitution of a 2-bromoBODIPY with benzophenone imine (Scheme 3 and Table 1, entry 1).^{9e,f} This reaction did produce the desired 2-aminoBODIPY **6a** albeit in low yield (36%). Replacement of the chelating diphosphine XantPhos with *rac*-BINAP resulted in a lower yield (5%, entry 2) but the use of the bulky, electron-rich biarylmonophosphine XPhos produced a much improved 71% yield (entry 3). The related ligand SPhos improved the yield further to 80% (entry 4). Changing the metal precursor from Pd₂(dba)₃ to palladium diacetate led to a lower yield (19%, entry 5) but the use of the cyclometalated biphenylamine palladium mesylate dimer **7**, developed by Buchwald,¹⁸ produced an excellent yield of the 2-aminoBODIPY **6a** (96%, entry 6). Reduction of the palladium loading from 10 mol% down to 1.2 mol% resulted in a slight drop in yield (from 96% to 81%, entries 6 – 9) but further reduction to 0.5 mol% and 0.1 mol% was unsuccessful (entries 10 and 11). Changing the base from caesium carbonate to either tripotassium phosphate or potassium fluoride resulted in lower yields (entry 9 vs entries 12 and 13) as did lowering the reaction temperature from 95 °C (entry 9 vs entries 14 – 16).

The conditions which represented the best compromise between producing the highest yield and requiring the lowest loading of palladium precursor and ligand were those in Table 1, entry 8 (2.75 mol% SPhos, 1.25 mol% mesylate dimer **7**, 1.5 eq. Cs₂CO₃, 1,4-dioxane, 95 °C, 16 h). These conditions were applied to the reaction of the 2-iodoBODIPY **3** with a range of amines (Scheme 3).

Scheme 3 Amination of 2-iodoBODIPY **3**^a

^a BODIPY **3** (0.203 mmol), amine (1.01 mmol), **7** (1.25 mol%), SPhos (2.5 mol%), Cs₂CO₃ (0.345 mmol), 1,4-dioxane (2 mL), 95 °C, 16 h.

Good yields were obtained with a range of anilines bearing electron donating (**6a,d**), electron withdrawing (**6b,c,e**), and sterically hindering substituents (**6d,e**). A rather low yield was obtained with a primary alkylamine (**6f**) and attempts to use secondary alkyl amines (pyrrolidine, morpholine) were unsuccessful, leading principally to protodehalogenation.

Spectroscopic properties of 2-aminoBODIPYs **6a-f**

The absorption data for the parent 2-unsubstituted BODIPY **5** and the 2-aminoBODIPYs **6a-f** are summarized in Table 2 (left). All of the 2-aminoBODIPY derivatives **6a-f** are essentially non-fluorescent. Absorption data for the 4-methoxyaniline derivative **6a** in different solvents are shown in Table 2 (right). For the 2-aminoBODIPY **6a** the solvent dependence of the absorption maximum is weak; being blue-shifted by only 185 cm⁻¹ when the solvent is changed from toluene to acetonitrile (Table 2 and Fig. S2). The absorption spectra are unlike those of a conventional BODIPY dye^{1a} and, in particular, feature a pronounced low energy tail which becomes more significant as the solvent polarity increases. To clarify this situation, the absorption spectrum was deconstructed into a series of Gaussian-shaped components (Figure 2), each Gaussian representing the vibronic component associated with an electronic transition. The low energy absorption envelope is best described as a progression of narrow (full-width at half-maximum (FWHM) = 750 cm⁻¹) peaks that closely resembles that observed for conventional BODIPY derivatives. This progression is assigned to the corresponding π,π^* absorption transition. The 0,0 band is located at 18,000 cm⁻¹ (i.e., 556 nm). Superimposed over the π,π^* transition is a series of broad (FWHM = 3,600 cm⁻¹) peaks, with the 0,0 band also appearing at 18,000 cm⁻¹. This latter transition has the characteristics of an intramolecular charge-transfer transition;¹⁹ such transitions have been reported for other BODIPY dyes in polar solvent.²⁰

Table 2. Absorption data for compounds **5**, **6a-f** in THF (left) and for compound **6a** in different solvents (right).

^a	λ_{abs}^b (max) /nm	ϵ /10 ⁴ M ⁻¹ cm ⁻¹	BODIPY 6a solvent	λ_{abs} (max) /nm	ϵ /10 ⁴ M ⁻¹ cm ⁻¹
5	512	9.3	toluene	525	4.0
6a	523	3.0	CH ₂ Cl ₂	523	4.5
6b	524	2.5	THF	523	3.0
6c	520	3.6	EtOH	522	3.4
6d	523	2.9	MeCN	520	3.5
6e	522	5.1			
6f	524	2.4			

^a BODIPY compound number. ^b Spectrum recorded in THF.

Figure 2. Deconvolution of reduced experimental absorption spectrum for **6a** in MeCN into Gaussian components. The major components are interpreted as: -- **peak 1** (charge transfer band); ---- **peak 2** (BODIPY S_0-S_1 transition); -- **peak 3** (0-1 vibrational band of S_0-S_1); -- **peak 4** (a higher energy vibrational band, such as NH stretching).

The absence of fluorescence from the amino-substituted derivatives is explained as follows: The coincidental matching of the 0,0 transitions masks the real situation. The peak of the absorption band can be approximated²¹ as the sum of the excited-state energy (E_S) and the corresponding re-organization energy (λ_T). The latter is small for a π, π^* state, typically being a few hundred wavenumbers, but substantial for a charge-transfer state. In the latter case, important contributions arise from both nuclear and solvent terms.²⁰ It is possible to estimate λ_T for the charge-transfer state from the corresponding half-width in the appropriate solvent.²² This gives a value for λ_T of 0.69 eV. Taking this value together with the excitation energy of 2.36 eV (i.e., 19,000 cm^{-1}), we reach an estimate for the excited state energy of 1.67 eV (i.e., 740 nm). This value can be compared with the difference between oxidation and reduction potentials (see later) of 1.81 eV; this gives a crude estimate of the HOMO-LUMO gap.

Continuing this exercise, we note that the magnitude of the Stokes shift²³ is twice that of the reorganization energy. Thus, the fluorescence peak for the π, π^* excited state is expected at around 575 nm while that for the charge-transfer state is anticipated to peak at around 1,265 nm. Conventional fluorescence spectrophotometers have no sensitivity in this spectral range. Furthermore, the emission profile will resemble that of the corresponding absorption transition (i.e., broad, featureless and low intensity) and would be difficult to resolve from the baseline. To exacerbate the situation, the low energy of the projected charge-transfer emission will favour²⁴ rapid nonradiative charge recombination to restore the ground state but disfavour²⁵ the radiative process. Hence the quantum yield should be very low. This position is illustrated pictorially by way of Chart 1.

Hybridisation of the amino N atom, via protonation or amide formation, will raise the energy of the charge-transfer state while having minimal effect on the π, π^* state (chart 1). Consequently, fluorescence is expected to appear in the 550-

600 nm region. At the same time, the absorption spectrum should sharpen because of loss of the broad charge-transfer transition and the spectrum will take on the characteristics of a conventional BODIPY dye.^{1a} The absorption maximum of the 2-amino substituted BODIPYs **6a-f** is red-shifted (by 300 – 450 cm^{-1}) compared to that of the parent system **5** (Table 2).

Chart 1. Pictorial representation of the energy-level positioning for the π, π^* and charge-transfer (CT) states relative to the ground state (GS). Panel (a) refers to the amino-substituted BODIPY while panel (b) is intended to mimic the situation following hybridisation of the amino N atom. IC = internal conversion; CR = charge recombination.

Quantum chemical calculations of 2-aminoBODIPYs

Ground state geometries were optimised using the Gaussian 09 software²⁶ by DFT calculations at the B3LYP/6-31G(d) level,²⁷ applying the polarizable continuum model²⁸ (IEFPCM, with solvent=THF). Figure 3 shows the HOMO and LUMO orbitals and energies for the 2-unsubstituted BODIPY **5**, the 2-aminoBODIPYs **6a** and **8** (as a model for alkylamine substitution).

As expected for 1,3-dimethylated systems, the amine (NHR) and the BODIPY core are predicted to be non-coplanar which reduces conjugation between the nitrogen and the BODIPY. Consequently the nitrogen in the alkyl amine derivative **8** is significantly pyramidalized (the sum of bond angles at the nitrogen is 336.4°). Inspection of the orbitals (Fig. 3) indicates that the 2-amino substituent has minimal effect on the energy and topology of the LUMO whereas the HOMO is substantially delocalised onto the substituent and raised in energy, particularly in the case of the aniline derivative **6a**.

Figure 3 HOMO and LUMO molecular orbitals and energies (eV) for **5**, **6a**, and the 2-NHMe model BODIPY **8** (Ar = 4-MeC₆H₄).

Crystal structure determination of **6d**

Slow diffusion of hexane into a dichloromethane solution of the *ortho*-toluidine derivative **6d** succeeded in producing a crystalline sample suitable for analysis by X-ray diffraction (Figure 4).

Figure 4 One of the two crystallographically independent molecules in the asymmetric unit of the structure of the 2-aminoBODIPY **6d**. Hydrogen atoms have been omitted for clarity. The two independent molecules are similar hence only one is shown.

The compound crystallised with $Z' = 2$ where the two crystallographically independent molecules differ only slightly in their conformation (RMSD 0.219 Å, Fig. S1 shows an overlay of the two molecules) and hence there are two values for each geometric parameter quoted. The bond lengths between the nitrogen atoms and the benzene rings of the aniline moiety (N3-C12 = 1.392(2) Å; N6-C42 = 1.392(2) Å) are typical of a

conjugated aniline, whilst the corresponding distances from nitrogen to the BODIPY 2-position (N3-C2 = 1.4136(19) Å; N6-C32 = 1.406(2) Å) are slightly longer as would be expected on the basis of reduced π -overlap due to the non-coplanarity of the amine and the pyrrolic plane of the BODIPY core [torsion angles C12-N3-C2-C1 = 105.9(2)°; C42-N6-C32-C31 = 113.9(2)°].

Electrochemical properties of the 2-aminoBODIPY **6a**

A representative cyclic voltammogram of the 2-anilino BODIPY **6a** is shown in Figure 5.

Figure 5 Cyclic voltammogram of the 2-aminoBODIPY **6a** in MeCN with 1.0 M tetrabutylammonium hexafluorophosphate at 20 °C, referenced to Ag/Ag⁺. Scan rate 0.2 Vs⁻¹.

The reversible one electron reduction with $E_{1/2} = -1.48$ V is as expected for a BODIPY system. In contrast, at positive potentials the reversible oxidation with $E_{1/2} = +0.33$ V is much too low to be related to the BODIPY and is presumably due to oxidation of the aniline and confirms that the lowest energy absorption transition should be of strong charge transfer character. The subsequent irreversible oxidation ($E_p = +0.56$ V) is also due to oxidation of the aniline. A final irreversible oxidation at $E_p = +1.26$ V may be due to oxidation involving the BODIPY but cannot sensibly be used to calculate an electrochemical band gap due to the multiple preceding oxidations.

The spectroscopic, computational and electrochemical data are consistent with intramolecular charge transfer from the amine substituent.

Design of a fluorescence sensor for phosgene

Phosgene (COCl₂) is a highly toxic,²⁹ colourless gas which has been used in the past as a chemical warfare agent. Due to its high reactivity with many organic nucleophiles, phosgene has a number of industrial uses such as in polymer, pesticide and dye production.³⁰ Reports of fluorescence-based sensors for phosgene are limited to systems based on: a FRET-induced response resulting from triphosgene induced coupling of donor and acceptor coumarins (limit of detection 50 μM);^{31a} cyclisation of an *ortho*-hydroxycinnamic acid to produce a fluorescent coumarin (LOD 1 nM);^{31b} and ring opening of a rhodamine spiropyrone lactam (LOD 50 nM).^{31c} There are no

reports of a BODIPY-based phosgene sensor. For this proof of principle study we utilised triphosgene $[(\text{Cl}_3\text{CO})_2\text{CO}]$ as a safer phosgene equivalent. Sequential nucleophilic attacks on the carbonyl of triphosgene lead to the liberation of two further equivalents of phosgene.

We envisaged that nucleophilic attack of a 2-aminoBODIPY on phosgene would decrease the electron-donor ability of the substituent. In turn, this effect would push the corresponding intramolecular charge-transfer transition to higher energy (Chart 1). At a certain point, the energy of the charge-transfer state would exceed that of the π, π^* transition. The absorption spectrum would lose the broad, featureless band and acquire the sharp, structured profile characteristic of the π, π^* state. Once the energy gap exceeds the amount of thermal energy available to the molecule, charge transfer will no longer be an option and fluorescence from the π, π^* state would be observed. This description nicely summarises the situation found following treatment of the aniline derivative **9** with triphosgene. We expect the other 2-amino derivatives to show similar behaviour. Since the LUMO energy remains fairly insensitive to the nature of the substituent, the energy of the charge-transfer state is set by the HOMO energy. The substituent will have only a minor effect on the energy gap for the π, π^* excited-singlet state. To investigate this proposal the 2-nitroaniline derivative **6e** was hydrogenated to give the corresponding 2-aminoaniline **9** (Scheme 4). Reaction of this compound with triphosgene gave the corresponding benzimidazolone-substituted BODIPY **10** in excellent yield.

Scheme 4 Synthesis of the benzimidazolone **10**. Reagents: (a) H_2 (1 atm), 10% Pd/C, $\text{MeOH}-\text{CH}_2\text{Cl}_2$, rt, 2 h (95%); (b) $(\text{Cl}_3\text{CO})_2\text{CO}$, Et_3N , CH_2Cl_2 , rt, 10 min (98%). (Ar = 4-MeC₆H₄).

The aminoaniline derivative **9** is non-emissive, in line with the other 2-aminoBODIPYs **6a-f**. In contrast the benzimidazolone **10** is strongly fluorescent ($\lambda_{\text{abs}} = 515 \text{ nm}$, $\epsilon = 64,000 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda_{\text{em}} = 539 \text{ nm}$, $\Phi_f = 0.97$ in THF, determined vs rhodamine 6G in ethanol,³² $\lambda_{\text{ex}} = 490 \text{ nm}$). Figure 6 shows the absorption and emission spectra of compounds **9** and **10** together with optical images of a solution of the aminoBODIPY **9** before and after the addition of triphosgene. Figure 7 shows the fluorescence emission spectra of a solution of the aminoaniline **9** on treatment with varying concentrations of triphosgene. On the basis of the fluorescence titration (Fig. 7, inset) the Limit of

Detection³³ for phosgene was found to be 160 nM (recalculated from a concentration of triphosgene = 53 nM).

Figure 6. Absorption spectrum (solid lines) in terms of the molar absorption coefficient (ϵ) for **9** (—) and **10** (—) and emission spectrum (dashed lines) of **10** (---) in THF. Optical images inset: solution of the BODIPY **9** (50 μM in CH_2Cl_2 containing 3% Et_3N) before (left) and after (right) addition of triphosgene (25 μM). A visible light illumination; B illumination with hand-held lamp at 365 nm.

Figure 7. Fluorescence emission spectra of the aminoaniline **9** (0.01 mg mL^{-1} , 21 μM) in the presence of triphosgene (0 to 3.4 μM) in MeCN containing 3% Et_3N . Graphical inset: fluorescence emission intensity at 534 nm vs triphosgene concentration ($\lambda_{\text{ex}} = 490 \text{ nm}$).

The sensitivity is determined by the initial concentration of the BODIPY aniline and the amount of phosgene; consequently this system should also be useful at high concentrations of phosgene. Although sensors based on reversible complexation enable dynamic reporting of analyte concentrations, a potential

advantage of the irreversible nature of the present reaction with phosgene is that it should enable use over a very wide range of phosgene concentrations. In order to develop a practical phosgene sensor, determination of the sensitivity towards potential competing analytes such as aldehydes and acid chlorides would need to be undertaken. Incorporation of this system into a thin-film might also enable fabrication of a practical solid-state sensor.

Conclusions

Palladium catalysed coupling of the 2-iodoBODIPY **3** with a range of anilines and a primary alkylamine succeeds in generating the corresponding 2-aminoBODIPY derivatives. The non-emissive behaviour of these compounds is believed to be the consequence of introducing a low-energy, intramolecular charge-transfer state where the 2-amino group is the donor and the dipyrin unit is the acceptor. The energy of this state, and the energy gap between π, π^* and charge-transfer states, is controlled by the energy of the HOMO. Attenuation of this charge transfer pathway by conversion of the 1,2-phenylenediamine derivative **9** into the corresponding benzimidazolone **10** restores the fluorescence and has been used to demonstrate the potential for use as a fluorescence sensor for phosgene.

Experimental

General

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen in flame-dried glassware. CHCl_3 , CH_2Cl_2 and NEt_3 were distilled from CaH_2 ; MeOH and EtOH from magnesium; 1,4-dioxane, Et_2O and THF from Na/benzophenone; toluene from sodium; and MeCN from K_2CO_3 , under an atmosphere of nitrogen. DMF was dried over activated 4 Å molecular sieves and stored under nitrogen. All other chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on either a JEOL ECS 400 or a Bruker Avance 300 instrument. All NMR were referenced relative to CDCl_3 ($\delta_{\text{H}} = 7.26$, $\delta_{\text{C}} = 77.16$). IR spectra were recorded on a Varian 800 FT-IR Scimitar Series infrared spectrometer. Mass spectra were recorded on Waters ACQUITY UPLC LCT premier MS in positive ion mode. UV-vis and fluorescence spectra were recorded at 20 °C on a Shimadzu UV-1800 and Hitachi F2500 machines respectively. Relative fluorescence quantum yields (Φ_{f}) were determined using dilute solutions with an absorbance below 0.1 at the excitation wavelength and using Rhodamine 6G ($\Phi_{\text{f}} = 0.95$)³² in ethanol as standard. TLC was carried out on glass plates pre-coated with silica gel 60F₂₅₄ and flash column chromatography was performed on Fluorochem LC3025 (40–63 μm) silica gel. Compound **4**,^{34,13} was prepared by a modification to the reported procedure (see Electronic Supplementary Information).

X-ray crystal structure analysis

Single crystals were prepared by slow diffusion of hexane into a solution of the compound in chloroform. Crystal structure data were collected at 150 K on an Rigaku Oxford Diffraction Gemini A Ultra using $\text{CuK}\alpha$ radiation ($\lambda = 1.54184$ Å) and equipped with an Oxford Cryosystems Cryostream open-flow N_2 cooling device. Cell refinement, data collection, reduction and absorption correction were carried out using Rigaku Oxford Diffraction CrysAlisPro.³⁵ The intensities were corrected for absorption semi-empirically based on repeated, symmetry-equivalent reflections.

The structure was solved *via* direct methods and refined on F^2 values for all unique data. Refinements were performed using SHELXL³⁶ within the Olex2 program.³⁷ All non-hydrogen atoms were modelled as anisotropic. Hydrogen atoms were positioned geometrically and defined as riding on their parent atoms except for those bound to heteroatoms, which were located using peaks in the Fourier difference map.

Materials

2-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene 5. (3,5-Dimethyl-1H-pyrrol-2-yl)(p-tolyl)methanone **4** (2.11 g, 9.88 mmol) was taken in dry CH_2Cl_2 (60 mL). 3-Ethyl-2,4-dimethyl-1H-pyrrole (1.73 mL, 12.8 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (1.20 mL, 12.0 mmol) were added and the resulting solution was stirred at room temperature for 2 h. The mixture was then neutralized with *N,N*-diisopropylethylamine (7.66 g, 59.3 mmol) and treated with $\text{BF}_3 \cdot \text{OEt}_2$ (9.10 g, 79.1 mmol) and then the mixture was stirred at room temperature for 4 h. The crude mixture was washed with water (200 mL). The aqueous layer was back extracted with CH_2Cl_2 (2×100 mL). The combined organic layers were dried (MgSO_4) and the solvent was removed under reduced pressure. The resulting orange crude product was purified by column chromatography (CH_2Cl_2 :petroleum ether 1:3) to give the title compound **5** as an orange solid (3.13 g, 86%), mp 141–142 °C. $R_{\text{f}} = 0.3$ (CH_2Cl_2 :petroleum ether 1:3). ^1H NMR (300 MHz, CDCl_3) δ 7.19 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 7.9$ Hz, 2H), 5.85 (s, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 2.35 (s, 3H), 2.22 (q, $J = 7.5$ Hz, 2H), 1.29 (s, 3H), 1.24 (s, 3H), 0.90 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 155.16, 153.64, 141.98, 141.33, 139.41, 138.70, 133.34, 132.33, 131.43, 131.14, 129.75, 127.91, 120.46, 21.45, 17.09, 14.59, 14.48, 14.41, 12.62, 11.82. ^{11}B NMR (96 MHz, CDCl_3) δ 0.77 (t, $J_{\text{B-F}} = 33.1$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -146.02 (q, $J_{\text{F-B}} = 33.1$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 2966, 1713, 1539, 1516, 1310, 1191, 1053, 974, 754. HRMS-ES Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2^{11}\text{BF}_2 + \text{H}^+$: 367.2157, found: 367.2162.

6-Ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene 3. 2-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **5** (2.16 g, 5.92 mmol) was taken in dry CH_2Cl_2 (35 mL). *N*-Iodosuccinimide (1.39 g, 5.92 mmol) in CH_2Cl_2 (40 mL) was added to the mixture dropwise. The mixture was stirred at room temperature for 4 h. The crude product mixture was washed with H_2O (3×100 mL). The aqueous layer was back extracted with CH_2Cl_2 (2×30 mL). The combined organic layers were dried (MgSO_4) and the solvent was removed under reduced pressure. The resulting orange crude product was purified by column chromatography (CH_2Cl_2 :petroleum ether 1:1) to give the title compound **3** as an orange solid (2.35 g, 80%), mp 220–221 °C. $R_{\text{f}} = 0.5$ (CH_2Cl_2 :petroleum ether 1:1). ^1H NMR (300 MHz, CDCl_3) δ 7.22 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 7.9$ Hz, 2H), 2.54 (s, 3H), 2.48 (s, 3H), 2.37 (s, 3H), 2.24 (q, $J = 7.5$ Hz,

2H), 1.30 (s, 3H), 1.25 (s, 3H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 157.80, 152.75, 141.92, 141.03, 140.98, 139.06, 134.52, 132.14, 131.92, 130.68, 129.91, 127.85, 83.38, 21.49, 17.13, 16.64, 15.69, 14.43, 12.87, 12.04. ^{11}B NMR (96 MHz, CDCl_3) δ 0.68 (t, $J_{\text{B-F}} = 32.8$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -145.74 (q, $J_{\text{F-B}} = 32.8$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 2966, 2931, 1532, 1401, 1310, 1179, 1070, 976, 754. HRMS-ES Calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2^{11}\text{BF}_2^{127}\text{I} + \text{H}^+$: 493.1124, found: 493.1131.

General procedure for palladium catalysed amination.

2-Ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol), the amine (1.01 mmol), di((2-(2'-amino-1,1'-biphenyl))palladium(II) methanesulfonate dimer **7** (1.87 mg, 2.50 μmol , 1.25 mol%) SPhos (2.30 mg, 5.50 μmol , 2.75 mol %), and Cs_2CO_3 (0.11 g, 0.35 mmol) were taken in a flame-dried Schlenk tube and flushed with N_2 several times. Dry 1,4-dioxane (2 mL) was then added and the mixture was stirred at 95 °C for 16 h. The mixture was diluted with ethyl acetate (30 mL) and washed with water (2 $\times$ 100 mL). The organic layer was dried (MgSO_4) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (ethyl acetate:petroleum ether mixtures).

6-Ethyl-4,4-difluoro-2-((4-methoxyphenyl)amino)-8-(4-methylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene 6a. According to the general procedure for palladium catalysed amination, 2-ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol) was reacted with *p*-anisidine (0.12 g, 1.01 mmol). The crude product was purified by column chromatography (ethyl acetate:petroleum ether 1:7) to give the title compound **6a** as a dark purple solid (0.09 g, 92%), mp 240–241 °C. $R_f = 0.25$ (ethyl acetate:petroleum ether 1:7). ^1H NMR (300 MHz, CDCl_3) δ 7.20 (d, $J = 7.9$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 6.65 (d, $J = 8.9$ Hz, 2H), 6.40 (d, $J = 8.9$ Hz, 2H), 3.65 (s, 3H), 2.48 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.24 (q, $J = 7.5$ Hz, 2H), 1.26 (s, 3H), 1.15 (s, 3H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.50, 152.52, 151.71, 141.13, 140.86, 139.59, 138.84, 136.73, 133.31, 132.44, 131.75, 131.56, 129.84, 129.30, 128.03, 114.89, 114.31, 55.83, 21.53, 17.15, 14.67, 12.72, 11.95, 11.19. ^{11}B NMR (96 MHz, CDCl_3) δ 0.78 (t, $J_{\text{B-F}} = 32.2$ Hz); ^{19}F NMR (282 MHz, CDCl_3) δ -145.93 (q, $J_{\text{F-B}} = 32.2$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3399, 2962, 2927, 2360, 1541, 1508, 1477, 1184, 1005, 798. HRMS-ES Calcd for $\text{C}_{29}\text{H}_{32}\text{N}_3^{11}\text{BF}_2\text{O} + \text{H}^+$: 488.2686, found: 488.2685.

2-((4-Chlorophenyl)amino)-6-ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene 6b. According to the general procedure for palladium catalysed amination, 2-ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol) was reacted with 4-chloroaniline (0.13 g, 1.01 mmol). The crude product was purified by column chromatography (ethyl acetate:petroleum ether 1:7) to give the title compound **6b** as a dark purple solid (0.09 g, 85%), mp 270–271 °C. $R_f = 0.37$ (ethyl acetate:petroleum ether 1:7). ^1H NMR (300 MHz, CDCl_3) δ 7.21 (d, $J = 7.9$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 6.37 (d, $J = 8.6$ Hz, 2H), 4.77 (s, 1H), 2.49 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 2.25 (q, $J = 7.6$ Hz, 2H), 1.27 (s, 3H), 1.13 (s, 3H), 0.92 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 156.51, 150.89, 145.55, 141.34, 140.12, 138.88, 137.01, 133.70, 132.20, 131.82, 130.03, 129.82, 129.10, 127.87, 124.83, 122.55, 114.17, 21.47, 17.08, 14.55, 12.74, 12.76, 11.94, 11.09. ^{11}B NMR (96 MHz, CDCl_3) δ 0.69 (t, $J_{\text{B-F}} = 33.0$ Hz). ^{19}F NMR

(282 MHz, CDCl_3) δ -146.05 (q, $J_{\text{F-B}} = 33.0$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3357, 2962, 2923, 2360, 1661, 1597, 1539, 1490, 1259, 1074, 1009, 796. HRMS-ES Calcd for $\text{C}_{28}\text{H}_{29}\text{N}_3^{11}\text{B}^{19}\text{F}_2^{35}\text{Cl} + \text{Na}^+$: 514.2009, found: 514.2012.

2-((4-Cyanophenyl)amino)-6-ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene 6c. According to the general procedure for palladium catalysed amination, 2-ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol) was reacted with 4-cyanoaniline (0.12 g, 1.01 mmol). The crude product was purified by column chromatography (ethyl acetate:petroleum ether 1:7) to give the title compound **6c** as a dark red solid (0.05 g, 51%), mp 282–286 °C. $R_f = 0.25$ (ethyl acetate:petroleum ether 1:7). ^1H NMR (300 MHz, CDCl_3) δ 7.32 (d, $J = 8.6$ Hz, 2H), 7.22 (d, $J = 7.9$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 6.45 (d, $J = 8.6$ Hz, 2H), 5.25 (s, 1H), 2.50 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 2.29 – 2.18 (m, 2H), 1.28 (s, 3H), 1.12 (s, 3H), 0.93 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.91, 150.61, 149.58, 141.59, 140.82, 139.05, 136.71, 134.29, 133.79, 132.25, 132.00, 129.89, 128.79, 127.94, 127.80, 120.16, 112.90, 99.97, 21.45, 17.08, 14.45, 12.84, 11.99, 11.64, 11.03. ^{11}B NMR (96 MHz, CDCl_3) δ 0.67 (t, $J_{\text{B-F}} = 32.5$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -145.91 (q, $J_{\text{F-B}} = 32.5$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3386, 2964, 2928, 2212, 1668, 1606, 1537, 1515, 1314, 1261, 1200, 1074, 1005, 800. HRMS-ES Calcd for $\text{C}_{29}\text{H}_{29}\text{N}_4^{11}\text{B}^{19}\text{F}_2 + \text{Na}^+$: 505.2351, found: 505.2355.

6-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-((2-methylphenyl)amino)-4-bora-3a,4a-diaza-s-indacene 6d. According to the general procedure for palladium catalysed amination, 2-ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol) was reacted with *o*-toluidine (0.11 g, 1.01 mmol). The crude product was purified by column chromatography (ethyl acetate:petroleum ether 1:7) to give the title compound **6d** as a dark purple solid (0.09 g, 90%), mp 201–202 °C. $R_f = 0.37$ (ethyl acetate:petroleum ether 1:7). ^1H NMR (300 MHz, CDCl_3) δ 7.20 (d, $J = 7.9$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 2H), 6.98 (d, $J = 7.3$ Hz, 1H), 6.96 – 6.89 (m, 1H), 6.59 (td, $J = 7.4$, 1.1 Hz, 1H), 6.24 (dd, $J = 8.0$, 0.9 Hz, 1H), 4.54 (s, 1H), 2.49 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.25 (q, $J = 7.6$ Hz, 2H), 2.17 (s, 3H), 1.27 (s, 3H), 1.14 (s, 3H), 0.92 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 155.70, 151.54, 144.76, 141.18, 139.69, 138.79, 137.01, 133.36, 132.34, 131.56, 130.94, 130.25, 129.78, 129.23, 127.94, 127.07, 121.52, 117.85, 111.59, 21.47, 17.52, 17.09, 14.60, 12.68, 11.90, 11.82, 11.11. ^{11}B NMR (96 MHz, CDCl_3) δ 0.74 (t, $J_{\text{B-F}} = 32.5$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -146.13 (q, $J_{\text{F-B}} = 32.5$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3410, 2962, 2972, 2868, 1535, 1475, 1323, 1303, 1179, 1054, 977, 750. HRMS-ES Calcd for $\text{C}_{29}\text{H}_{32}\text{N}_3^{11}\text{B}^{19}\text{F}_2 + \text{Na}^+$: 494.2555, found: 494.2561.

6-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-(2-nitrophenyl)amino)-4-bora-3a,4a-diaza-s-indacene 6e. According to the general procedure for palladium catalysed amination, 2-ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol) was reacted with 2-nitroaniline (0.14 g, 1.01 mmol). The crude product was purified by column chromatography (ethyl acetate:petroleum ether 1:9) to give the title compound **6e** as a dark red solid (0.08 g, 67%), mp 220–222 °C. $R_f = 0.25$ (ethyl acetate:petroleum ether 1:9). ^1H NMR (300 MHz, CDCl_3) δ 8.72 (s, 1H), 8.10 (dd, $J = 8.6$, 1.5 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.63 (ddd, $J = 8.4$, 7.0, 1.2 Hz, 1H), 6.55 (dd, $J = 8.6$, 1.1 Hz, 1H), 2.51 (s, 3H), 2.36 (s, 3H),

2.34 (s, 3H), 2.26 (q, $J = 7.6$ Hz, 2H), 1.29 (s, 3H), 1.14 (s, 3H), 0.94 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 158.17, 149.08, 144.97, 141.65, 140.93, 139.07, 136.36, 136.10, 134.39, 132.32, 132.34, 131.97, 129.91, 128.90, 127.80, 127.13, 126.55, 116.75, 115.74, 21.46, 17.09, 14.46, 12.88, 12.02, 11.68, 11.02. ^{11}B NMR (96 MHz, CDCl_3) δ 0.71 (t, $J_{\text{B-F}} = 32.6$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -146.06 (q, $J_{\text{F-B}} = 32.6$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3439, 3362, 2920, 1910, 1642, 1595, 1527, 1503, 1313, 1257, 1089, 938, 734. HRMS-ES Calcd for $\text{C}_{28}\text{H}_{29}\text{N}_4^{11}\text{B}^{19}\text{F}_2\text{O}_2 + \text{Na}^+$: 525.2249, found: 525.2256.

6-Ethyl-4,4-difluoro-2-(hexylamino)-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene 6f. According to the general procedure for palladium catalysed amination, 2-ethyl-4,4-difluoro-2-iodo-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene **3** (0.10 g, 0.20 mmol) was reacted with hexylamine (0.10 g, 1.01 mmol). The crude product was purified by column chromatography (ethyl acetate:petroleum ether 1:7) to give the title compound **6f** as a dark purple solid (0.03 g, 31%), mp 200–201°C. $R_f = 0.49$ (ethyl acetate:petroleum ether 1:7). ^1H NMR (300 MHz, CDCl_3) δ 7.19 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 2.81 (t, $J = 7.4$ Hz, 2H), 2.50 (s, 3H), 2.46 (s, 3H), 2.37 (s, 3H), 2.26–2.18 (m, 2H), 1.24–1.20 (m, 8H), 1.19–1.15 (m, 6H), 0.91 (t, $J = 7.6$ Hz, 3H), 0.82–0.76 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.81, 149.75, 140.03, 139.56, 138.53, 137.95, 132.70, 132.12, 130.76, 129.78, 129.61, 128.56, 128.17, 50.02, 31.69, 30.80, 26.71, 22.62, 21.44, 17.06, 14.67, 14.04, 12.41, 12.09, 11.72, 10.85. ^{11}B NMR (96 MHz, CDCl_3) δ 0.70 (t, $J_{\text{B-F}} = 32.5$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -146.13 (q, $J_{\text{F-B}} = 32.5$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3290, 2962, 2359, 1544, 1411, 1260, 1017, 797. HRMS-ES Calcd for $\text{C}_{28}\text{H}_{38}\text{N}_3^{11}\text{B}^{19}\text{F}_2 + \text{H}^+$: 466.3205, found: 466.3205.

6-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-((2-aminophenyl)amino)-4-bora-3a,4a-diaza-s-indacene 9. 6-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-((2-nitrophenyl)amino)-4-bora-3a,4a-diaza-s-indacene **6e** (0.05 g, 0.10 mmol) was dissolved in CH_2Cl_2 (1 mL) and MeOH (3 mL). 10% Pd/C (0.05 g) was added. The mixture was stirred under nitrogen for 15 min and the nitrogen line was replaced with a hydrogen-filled balloon. The mixture was stirred at room temperature for 2 h and then filtered through Celite, washing with CH_2Cl_2 . The solvent was removed under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2) to give the title compound **9** as a dark purple solid (0.05 g, 95%), mp 215–218°C. $R_f = 0.25$ (CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3) δ 8.72 (s, 1H), 8.10 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.31–7.25 (m, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.63 (ddd, $J = 8.4, 7.0, 1.2$ Hz, 1H), 6.55 (dd, $J = 8.6, 1.1$ Hz, 1H), 2.51 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.26 (q, $J = 7.6$ Hz, 2H), 1.29 (s, 3H), 1.14 (s, 3H), 0.94 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 157.90, 150.61, 149.57, 141.58, 140.82, 139.05, 136.72, 134.29, 133.79, 132.24, 131.99, 129.90, 128.78, 127.92, 127.79, 120.19, 112.90, 99.92, 21.46, 17.08, 14.47, 12.85, 12.00, 11.65, 11.04. ^{11}B NMR (96 MHz, CDCl_3) δ 0.77 (t, $J_{\text{B-F}} = 32.4$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -146.00 (q, $J_{\text{F-B}} = 32.4$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3440, 3362, 2921, 2360, 1642, 1595, 1527, 1503, 1413, 1312, 1257, 1090, 733. HRMS-ES Calcd for $\text{C}_{28}\text{H}_{31}\text{N}_4^{11}\text{B}^{19}\text{F}_2 + \text{H}^+$: 473.2688, found: 473.2690.

2-((2-Benzimidazolinon-1-yl)-6-ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene 10. 6-Ethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-methylphenyl)-2-((2-aminophenyl)amino)-4-bora-3a,4a-diaza-s-indacene **9** (0.02 g, 0.09 mmol) was dissolved in dry CH_2Cl_2 (10

mL). A solution of triethylamine (0.09 g, 0.71 mmol) and triphosgene (8.70 mg, 0.29 mmol) in CH_2Cl_2 (1 mL) was added. The mixture was stirred at room temperature for 10 min. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2 :ethyl acetate 10:1) to give the title compound **10** as an orange solid (0.04 g, 98%), mp 205–206°C. $R_f = 0.25$ (CH_2Cl_2 :ethyl acetate 10:1). ^1H NMR (300 MHz, CDCl_3) δ 10.37 (s, 1H), 7.21 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 7.07–7.04 (m, 1H), 7.02–6.90 (m, 2H), 6.64 (d, $J = 7.0$ Hz, 1H), 2.53 (s, 3H), 2.34 (s, 6H), 2.27 (q, $J = 7.5$ Hz, 2H), 1.30 (s, 3H), 1.13 (s, 3H), 0.95 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 158.98, 155.23, 148.65, 142.04, 141.26, 139.05, 136.73, 134.71, 132.67, 131.89, 131.01, 129.92, 129.80, 128.90, 128.17, 128.00, 127.73, 122.69, 122.12, 121.55, 109.99, 108.91, 21.44, 17.11, 14.40, 12.97, 12.07, 11.87, 11.24. ^{11}B NMR (96 MHz, CDCl_3) δ 0.78 (t, $J_{\text{B-F}} = 32.0$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -145.24 (dq, $J_{\text{F-F}} = 107.0$, $J_{\text{F-B}} = 32.0$ Hz), -146.10 (dq, $J_{\text{F-F}} = 107.0$, $J_{\text{F-B}} = 32.0$ Hz). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$: 3440, 3362, 3233, 2917, 2274, 2119, 1707, 1641, 1594, 1569, 1531, 1503, 1387, 1257, 1089, 820, 734. HRMS-ES Calcd for $\text{C}_{29}\text{H}_{29}\text{N}_4^{10}\text{B}^{19}\text{F}_2 + \text{Na}^+$: 520.2336, found: 520.2337.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgements

We gratefully acknowledge the Department of Chemistry, Faculty of Science, Taibah University, Saudi Arabia for a scholarship (R.B.A.). We thank Newcastle University and EPSRC (EP/K503885/1) for the award of a Research Scholarship to P.S.

Notes and references

- (a) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.*, 2008, **47**, 1184; (b) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891.
- (a) N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, 2012, **41**, 1130; (b) X. Li, X. Gao, W. Shi and H. Ma, *Chem. Rev.*, 2014, **114**, 590; (c) Y. Jeong and J. Yoon, *Inorg. Chim. Acta*, 2012, **381**, 2; (d) M. Vendrell, D. Zhai, J. C. Er and Y.-T. Chang, *Chem. Rev.*, 2012, **112**, 4391; (e) M. J. Culzoni, A. Muñoz De La Peña, A. MacHuca, H. C. Goicoechea and R. Babiano, *Anal. Methods*, 2013, **5**, 30.
- (a) T. Kowada, H. Maeda and K. Kikuchi, *Chem. Soc. Rev.*, 2015, **44**, 4953; (b) K. Umezawa, D. Citterio and K. Suzuki, *Anal. Sci.*, 2014, **30**, 327; (c) Y. Ni and J. Wu, *Org. Biomol. Chem.*, 2014, **12**, 3774; (d) L. Yuan, W. Lin, K. Zheng, L. He and W. Huang, *Chem. Soc. Rev.*, 2013, **42**, 622.
- (a) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.*, 2013, **42**, 77; (b) S. G. Awuah and Y. You, *RSC Adv.*, 2012, **2**, 11169.
- (a) I. Esnal, G. Duran-Sampedro, A. R. Agarrabeitia, J. Bañuelos, I. García-Moreno, M. A. Macías, E. Peña-Cabrera, I. López-Arbeloa, S. De La Moya and M. J. Ortiz, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8239; (b) Y. Yang, L. Zhang, B. Li, L. Zhang and X. Liu, *RSC Adv.*, 2013, **3**, 14993; (c) I. Esnal, I. Valois-Escamilla, C. F. A. Gómez-Durán, A. Urías-Benavides, M. L. Betancourt-Mendiola, I. López-Arbeloa, J. Bañuelos, I. García-Moreno, A. Costela and E. Peña-Cabrera, *ChemPhysChem*, 2013, **14**, 4134.

- 6 (a) A. B. Nepomnyashchii and A. J. Bard, *Acc. Chem. Res.*, 2012, **45**, 1844; (b) S. Xiao, Q. Cao and F. Dan, *Curr. Org. Chem.*, 2012, **16**, 2970; (c) L. Bonardi, H. Kanaan, F. Camerel, P. Jolinat, P. Retailleau and R. Ziessel, *Adv. Functional Materials*, 2008, **18**, 401.
- 7 (a) A. Harriman, *Chem. Commun.*, 2015, **51**, 11745; (b) J. F. Lefebvre, X. Z. Sun, J. A. Calladine, M. W. George and E. A. Gibson, *Chem. Commun.*, 2014, **50**, 5258; (c) E. M. Sánchez-Carnerero, L. Gartzia-Rivero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, J. Bañuelos, I. López-Arbeloa and S. De La Moya, *Chem. Commun.*, 2014, **50**, 12765; (d) B. Kim, B. Ma, V. R. Donuru, H. Liu and J. M. J. Fréchet, *Chem. Commun.*, 2010, **46**, 4148.
- 8 For some recent examples see: (a) A. Vanessa Saura, M. Isabel Burguete, F. Galindo and S. V. Luis, *Org. Biomol. Chem.*, 2017, **15**, 3013; (b) W. Mao, L. Xia and H. Xie, *Angew. Chem. Int. Ed.*, 2017, **56**, 4468; (c) M. Vedamalai, D. Kedaria, R. Vasita, S. Mori and I. Gupta, *Dalton Trans.*, 2016, **45**, 2700; (d) M. Ren, B. Deng, X. Kong, K. Zhou, K. Liu, G. Xu and W. Lin, *Chem. Commun.*, 2016, **52**, 6415; (e) C. Yu, Q. Wu, J. Wang, Y. Wei, E. Hao and L. Jiao, *J. Org. Chem.*, 2016, **81**, 3761; (f) L. Zhang, J. C. Er, H. Jiang, X. Li, Z. Luo, T. Ramezani, Y. Feng, M. K. Tang, Y.-T. Chang and M. Vendrell, *Chem. Commun.*, 2016, **52**, 9093; (g) B. Sui, X. Liu, M. Wang and K. D. Belfield, *Chem. Eur. J.*, 2016, **22**, 10351; (h) H. Agarwalla, P. S. Mahajan, D. Sahu, N. Taye, B. Ganguly, S. B. Mhaske, S. Chattopadhyay and A. Das, *Inorg. Chem.*, 2016, **55**, 12052; (i) Q. Lin, J. J. Gruskos and D. Buccella, *Org. Biomol. Chem.*, 2016, **14**, 11381.
- 9 Examples of the synthesis and photophysical properties of directly aminated BODIPYs: (a) C. S. Gutsche, B. F. Hohlfield, K. J. Flanagan, M. O. Senge, N. Kulak and A. Wiehe, *Eur. J. Org. Chem.*, 2017, 3187; (b) C. Ray, E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, I. López-Arbeloa, J. Bañuelos, K. D. Cohovi, J. L. Lunkley, G. Muller and S. de la Moya, *Chem. Eur. J.*, 2016, **22**, 8805; (c) X. Shao, R. Kang, Y. Zhang, Z. Huang, F. Peng, J. Zhang, Y. Wang, F. Pan, W. Zhang and W. Zhao, *Anal. Chem.*, 2015, **87**, 399; (d) N. Boens, L. Wang, V. Leen, P. Yuan, B. Verbelen, W. Dehaen, M. Van Der Auweraer, W. D. De Borggraeve, L. Van Meervelt, J. Jacobs, D. Beljonne, C. Tonnelé, R. Lazzaroni, M. J. Ruedas-Rama, A. Orte, L. Crovetto, E. M. Talavera and J. M. Alvarez-Pez, *J. Phys. Chem. A*, 2014, **118**, 1576; (e) H. Yokoi, N. Wachi, S. Hiroto and H. Shinokubo, *Chem. Commun.*, 2014, **50**, 2715; (f) H. Yokoi, S. Hiroto and H. Shinokubo, *Org. Lett.*, 2014, **16**, 3004; (g) I. Esnal, J. Bañuelos, I. López Arbeloa, A. Costela, I. García-Moreno, M. Garzón, A. R. Agarrabeitia and M. José Ortiz, *RSC Adv.*, 2013, **3**, 1547; (h) I. Esnal, I. Valois-Escamilla, C. F. A. Gómez-Durán, A. Urías-Benavides, M. L. Betancourt-Mendiola, I. López-Arbeloa, J. Bañuelos, I. García-Moreno, A. Costela and E. Peña-Cabrera, *ChemPhysChem*, 2013, **14**, 4134; (i) R. I. Roacho, A. Metta-Magaña, M. M. Portillo, E. Peña-Cabrera and K. H. Pannell, *J. Org. Chem.*, 2013, **78**, 4245; (j) M. Gupta, S. Mula, M. Tyagi, T. K. Ghanty, S. Murudkar, A. K. Ray and S. Chattopadhyay, *Chem. Eur. J.*, 2013, **19**, 17766; (k) C. A. Osorio-Martínez, A. Urías-Benavides, C. F. A. Gómez-Durán, J. Bañuelos, I. Esnal, I. López Arbeloa and E. Peña-Cabrera, *J. Org. Chem.*, 2012, **77**, 5434; (l) W. Qin, V. Leen, W. Dehaen, J. Cui, C. Xu, X. Tang, W. Liu, T. Rohand, D. Beljonne, B. Van Averbeke, J. N. Clifford, K. Driesen, K. Binnemans, M. D. Van Auweraer and N. Boens, *J. Phys. Chem. C*, 2009, **113**, 11731.
- 10 (a) N. Zhao, M. G. H. Vicente, F. R. Fronczek and K. M. Smith, *Chem. Eur. J.*, 2015, **21**, 6181; (b) J. C. Er, C. Leong, C. L. Teoh, Q. Yuan, P. Merchant, M. Dunn, D. Sulzer, D. Sames, A. Bhinge, D. Kim, S. M. Kim, M. H. Yoon, L. W. Stanton, S. H. Je, S. W. Yun and Y. T. Chang, *Angew. Chem. Int. Ed.*, 2015, **54**, 2442; (c) J. R. Lin, C. J. Chu, P. Venkatesan and S. P. Wu, *Sensors and Actuators, B: Chemical*, 2014, **207**, 563; (d) X. He, J. Zhang, X. Liu, L. Dong, D. Li, H. Qiu and S. Yin, *Sensors and Actuators, B: Chemical*, 2014, **192**, 29; (e) E. Ganapathi, S. Madhu, T. Chatterjee, R. Gonnade and M. Ravikanth, *Dyes and Pigments*, 2014, **102**, 218; (f) M. De Lourdes Betancourt-Mendiola, E. Peña-Cabrera, S. Gil, K. Chulvi, L. E. Ochando and A. M. Costero, *Tetrahedron*, 2014, **70**, 3735; (g) R. Misra, B. Dhokale, T. Jadhav and S. M. Mobin, *Organometallics*, 2014, **33**, 1867; (h) A. M. Lifschitz, R. M. Young, J. Mendez-Arroyo, V. V. Roznyatovskiy, C. M. McGuirk, M. R. Wasielewski and C. A. Mirkin, *Chem. Commun.*, 2014, **50**, 6850; (i) X. Yu, X. Jia, X. Yang, W. Liu and W. Qin, *RSC Adv.*, 2014, **4**, 23571; (j) X. Li, Y. Gong, K. Wu, S. H. Liang, J. Cao, B. Yang, Y. Hu and Y. Han, *RSC Adv.*, 2014, **4**, 36106; (k) M. R. Martínez-Gonzalez, A. Urías-Benavides, E. Alvarado-Martínez, J. C. Lopez, A. M. Gómez, M. Del Rio, I. García, A. Costela, J. Bañuelos, T. Arbeloa, I. L. Arbeloa and E. Peña-Cabrera, *Eur. J. Org. Chem.*, 2014, **2014**, 5659; (l) Y. A. Volkova, B. Brizet, P. D. Harvey, A. D. Averin, C. Goze and F. Denat, *Eur. J. Org. Chem.*, 2013, 4270; (m) L. Y. Niu, H. Li, L. Feng, Y. S. Guan, Y. Z. Chen, C. F. Duan, L. Z. Wu, Y. F. Guan, C. H. Tung and Q. Z. Yang, *Anal. Chim. Acta*, 2013, **775**, 93; (n) X. Jia, X. Yu, X. Yang, J. Cui, X. Tang, W. Liu and W. Qin, *Dyes and Pigments*, 2013, **98**, 195; (o) M. J. Ortiz, A. R. Agarrabeitia, G. Duran-Sampedro, J. Bañuelos Prieto, T. A. Lopez, W. A. Massad, H. A. Montejano, N. A. García and I. Lopez Arbeloa, *Tetrahedron*, 2012, **68**, 1153; (p) L. Jiao, W. Pang, J. Zhou, Y. Wei, X. Mu, G. Bai and E. Hao, *J. Org. Chem.*, 2011, **76**, 9988; (q) S. C. Dodani, S. C. Leary, P. A. Cobine, D. R. Winge and C. J. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 8606; (r) J. Bañuelos, V. Martín, C. F. A. Gómez-Durán, I. J. A. Córdoba, E. Peña-Cabrera, I. García-Moreno, A. Costela, M. E. Pérez-Ojeda, T. Arbeloa and I. L. Arbeloa, *Chem. Eur. J.*, 2011, **17**, 7261; (s) C. F. A. Gómez-Durán, I. García-Moreno, A. Costela, V. Martin, R. Sastre, J. Bañuelos, F. López Arbeloa, I. López Arbeloa and E. Peña-Cabrera, *Chem. Commun.*, 2010, **46**, 5103; (t) D. W. Domaille, L. Zeng and C. J. Chang, *J. Am. Chem. Soc.*, 2010, **132**, 1194; (u) L. Li, B. Nguyen and K. Burgess, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 3112; (v) O. Dilek and S. L. Bane, *Tetrahedron Lett.*, 2008, **49**, 1413; (w) T. Rohand, M. Baruah, W. Qin, N. Boens and W. Dehaen, *Chem. Commun.*, 2006, 266; (x) V. Goud, A. Tutar and J. F. Biellmann, *Tetrahedron*, 2006, **62**, 5084; (y) M. Baruah, W. Qin, R. A. L. Vallée, D. Beljonne, T. Rohand, W. Dehaen and N. Boens, *Org. Lett.*, 2005, **7**, 4377.
- 11 Y. Zhang, R. F. Ma, H. J. Lv, H. M. Fang, C. Y. Xue, G. J. Zhang, X. Y. Wang and G. W. Xing, *Tetrahedron Lett.*, 2016, **57**, 4624.
- 12 J. G. Knight, R. B. Alnoman and P. G. Waddell, *Org. Biomol. Chem.*, 2015, **13**, 3819.
- 13 S. Zhang, C. Feng, J. Cai, J. Chen, H. Hu and M. Ji, *J. Chem. Res.*, 2013, **37**, 480.
- 14 H. Shimogawa, H. Mori, A. Wakamiya and Y. Murata, *Chem. Lett.*, 2013, **42**, 986.
- 15 C. Zhang, J. Zhao, S. Wu, Z. Wang, W. Wu, J. Ma, S. Guo and L. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 10566.
- 16 For typical examples see: (a) D. Wang, D. Kuang, F. Zhang, Y. Liu and S. Ning, *Tetrahedron Lett.*, 2014, **55**, 7121; (b) Y. Xie, Y. Ding, X. Li, C. Wang, W. Zhang, W. Zhu, J. P. Hill and K. Ariga, *Chem. Commun.*, 2012, **48**, 11513; (c) T. L. Andrew and T. M. Swager, *J. Org. Chem.*, 2011, **76**, 2976; (d) M. Shen, W. Zhang, K. Nomura and W.-H. Sun, *Dalton Trans.*, 2009, 9000; (e) C. Ran, Q. Dai and R. G. Harvey, *J. Org. Chem.*, 2005, **70**, 3724; (f) G. E. Job and S. L. Buchwald, *Org. Lett.*, 2002, **4**, 3703; (g) D. Ma, *J. Am. Chem. Soc.*, 1998, **120**, 12459; (h) S. Sasaki, F. Murakami and M. Yoshifuji, *Tetrahedron Lett.*, 1997, **38**, 7095.
- 17 For typical examples see: (a) P. Ruiz-Castillo, D. G. Blackmond and S. L. Buchwald, *J. Am. Chem. Soc.*, 2015, **137**, 3085; (b) G.-D. Roiban, G. Mehler and M. T. Reetz, *Eur. J. Org. Chem.*, 2014, **2014**, 2070; (c) S. M. Raders, J. N. Moore, J. K. Parks, A. D. Miller, T. M. Leissing, S. P. Kelley, R. D. Rogers and K. H. Shaughnessy, *J. Org. Chem.*, 2013, **78**, 4649; (d) S. Meiries, A.

- Chartoire, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2012, **31**, 3402; (e) S. Rodriguez, B. Qu, N. Haddad, D. C. Reeves, W. Tang, H. Lee, D. Krishnamurthy and C. H. Senanayake, *Adv. Synth. Catal.*, 2011, **353**, 533; (f) R. Kuwano, Y. Matsumoto, T. Shige, T. Tanaka, S. Soga and Y. Hanasaki, *Synlett*, 2010, 1819; (g) A. Dumrath, X.-F. Wu, H. Neumann, A. Spannenberg, R. Jackstell and M. Beller, *Angew. Chem. Int. Ed.*, 2010, **49**, 8988; (h) Q. Shen, T. Ogata and J. F. Hartwig, *J. Am. Chem. Soc.*, 2008, **130**, 6586.
- 18 N. C. Bruno, M. T. Tudge and S. L. Buchwald, *Chem. Sci.*, 2013, **4**, 916.
- 19 A. C. Benniston, A. Harriman, P. Y. Li, J. P. Rostron, H. J. van Ramesdonk, M. M. Groeneveld, H. Zhang and J. W. Verhoeven, *J. Am. Chem. Soc.*, 2005, **127**, 16054.
- 20 (a) A. C. Benniston, G. Copley, A. Harriman, D. Howgego, R. W. Harrington and W. Clegg, *J. Org. Chem.*, 2010, **75**, 2018; (b) A. C. Benniston, S. Clift and A. Harriman, *J. Mol. Struct.*, 2011, **985**, 346.
- 21 N. S. Hush, *Coord. Chem. Rev.*, 1985, **64**, 135.
- 22 A. C. Benniston, A. Harriman, P. Y. Li, C. A. Sams and M. D. Ward, *J. Am. Chem. Soc.*, 2004, **126**, 13630.
- 23 P. Vath, M. B. Zimmt, P. V. Matyushov and G. A. Voth, *J. Phys. Chem. B*, 1999, **103**, 9130.
- 24 R. Englman and J. Jortner, *Mol. Phys.*, 1970, **18**, 145.
- 25 M. Bixon, J. Jortner and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1994, **116**, 7349.
- 26 Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.
- 27 A. D. Becke, *Phys. Rev. A*, 1986, **33**, 2786.
- 28 B. Mennucci, E. Cancès, and J. Tomasi, *J. Phys. Chem. B*, 1997, **101**, 10506.
- 29 W. F. Diller, *Toxicol. Ind. Health*, 1985, **1**, 7.
- 30 H. Babad and A. G. Zeiler, *Chem. Rev.*, 1973, **73**, 75.
- 31 (a) H. Zhang and D. M. Rudkevich, *Chem. Commun.*, 2007, 1238; (b) P. Kundu and K. C. Hwang, *Anal. Chem.*, 2012, **84**, 4594; (c) X. Wu, Z. Wu, Y. Yang and S. Han, *Chem. Commun.*, 2012, **48**, 1895.
- 32 M. Fischer and J. Georges, *Chem. Phys. Lett.*, 1996, **260**, 115.
- 33 The Limit of Detection is defined as $3s_B/m$, where s_B is the standard deviation of the blank measurement (dye solution in the absence of analyte) and m is the slope of the calibration curve (Fig. 6). See: G. L. Long and J. D. Winefordner, *Anal. Chem.*, 1983, **55**, 712A.
- 34 A. R. Katritzky, K. Suzuki, S. K. Singh and H.-Y. He, *J. Org. Chem.*, 2003, **68**, 5720.
- 35 CrysAlisPro, Rigaku Oxford Diffraction, Tokyo, Japan.
- 36 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.
- 37 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 229.