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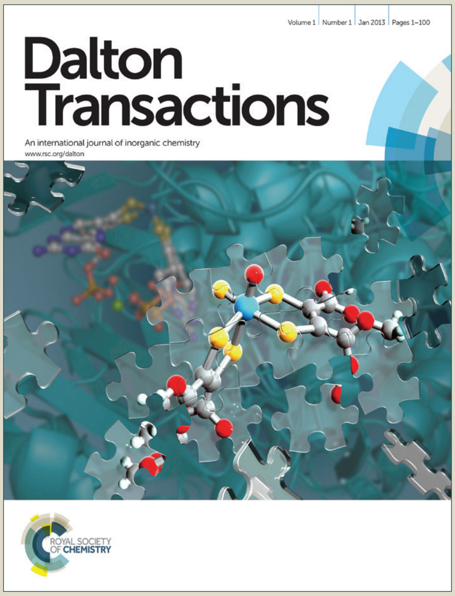

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Pyridyl-1,2,4-triazole diphenyl boron complexes as efficient tuneable blue emitters

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The detection of nuclear radiation necessitates the availability of new generations of tunable blue emitting fluorophores with high emission quantum yields. Here we show that pyridyl-1,2,4-triazole based diphenyl boron complexes can provide for highly tuneable emission through facile modification of the C5 position of the 1,2,4-triazolato ring. The series of complexes prepared show a wide range of emission from near-UV to green enabling fine control over the spectral overlap with detectors used in scintillator technology.

Introduction

The detection of nuclear radiation, specifically neutrons represents a major technical challenge, not least in the vicinity of potentially hazardous environments such as nuclear power reactors. Liquid scintillator cocktails (LSC) are a key component of scintillation based detection methods.[1] They comprise of an aromatic solvent to capture radiation and transfer the energy released to a fluorophore and subsequently a wavelength shifter (WLS), with POPOP (1,4-*bis*(5-phenyloxazol-2-yl)benzene), which emits at 410 nm, one of the most used WLS. Surprisingly the compositions used currently are largely unchanged from those developed in the 1950s despite the fantastic progress made in the development of novel fluorophores for applications as diverse as imaging, blue emitting OLEDs, etc. A primary reason for this may lie in the requirement that the fluorophores used in LSC emit in the blue region of the visible spectrum in order to achieve optimum overlap with the range of maximum responsivity of the fluorescence detectors used, in particular with photomultiplier tubes (PMT) where responsivity is typically at a maximum at ca. 420 nm.[2] Furthermore they must be available in sufficient amounts for detector volumes in excess of 1 m^3. The recent surge in interest blue emitters for OLED technologies has in large part focused on iridium based complexes, which are uneconomic in regard to neutron detection.

The application of boron compounds in thermal neutron detection is of particular note due to the unusually large cross-section of the ^{10}B isotope towards thermal neutron capture.[3] Boron containing fluorophores have attracted intensive interest over the last decades, not least of which has been the BODIPY class of complexes.[4] Tuning of the basic dipyrole ligand structure enables tuning of the relatively narrow absorption and emission bands over a wide range of wavelengths. In addition to enhancing the quantum yield of fluorescence of the ligands, the BF_2 moiety imparts considerable chemical stability to the dipyrole unit also enabling application in areas as diverse as materials, luminescent bioprobes etc.[5]

Several aspects, however preclude the application of Bodipy compounds in scintillator technology. The first is that the shortest wavelength reported, to the best of our knowledge, for emission from a bodipy derivative is 490 nm, achieved with the use of strongly electron withdrawing groups.[6] Secondly, the overlap with the wavelengths of optimum efficiency with currently used PMTs is low.[7] A third limitation is that intense absorption in the UV region is essential to provide maximum efficiency of transfer of the energy released by radiation capture from the solvent to the fluorophore. Finally, the cross section for nuclear capture, although high, nevertheless requires high mass content of boron and hence high BODIPY concentrations (>1 M), which can present challenges with regard to inner filter effects, where the Stokes shift of the emission is negligible, as is often the case with Bodipy dyes.

However, four-coordinate boron complexes have received increasing interest in OLED applications in recent years, as highlighted in recent reviews by Li *et al.* and Frath *et al.*,[8] in particular, for applications where emission in the blue region of the spectrum is of interest. In 2003, Cheng *et al*. reported a pyridylpyrazolate boron complex with its lowest energy absorption band between 315 and 350 nm and emission at 375 to 460 nm.[9] More recently, Suresh et al. have reported iminopyrrolyl based BPh_2 complexes for application in OLEDs with emission at ca. 450 to 520 nm.[10]

Surprisingly, 1,2,4-triazole based boron complexes have not yet been explored despite that the properties of the 1,2,4-triazoles (Fig. 1) can be tuned readily by substituents at the C5 position and the extensive application of 1,2,4-triazole complexes of Ru(II), Os(II)[11] and more recently Ir(III).[12] Furthermore the synthesis of substituted pyrid-2'-yl-1,2,4-triazoles can be carried out readily on large scale and these ligands are chemically robust. These attributes are essential in their application as fluorophores in scintillation detectors, where detector volumes are typically of the order of m^3 and radiation induced degradation of fluorophores is a challenge.

Here we report the synthesis, photophysical and electrochemical characterisation of a series of tetracoordinate $[LB(Ph)_2]$ complexes, where L is a substituted pyrid-2'-yl-

1,2,4-triazoles (Fig. 1). The complexes formed show readily tuneable luminescence properties with emission showing a strong dependence on the nature of the substituent at the C5 position of the 1,2,4-triazole moiety and emission quantum yields of up to 0.7 at room temperature in solution. Furthermore, we demonstrate the potential of using these complexes as fluorophores in liquid organic scintillators for nuclear radiation detection.

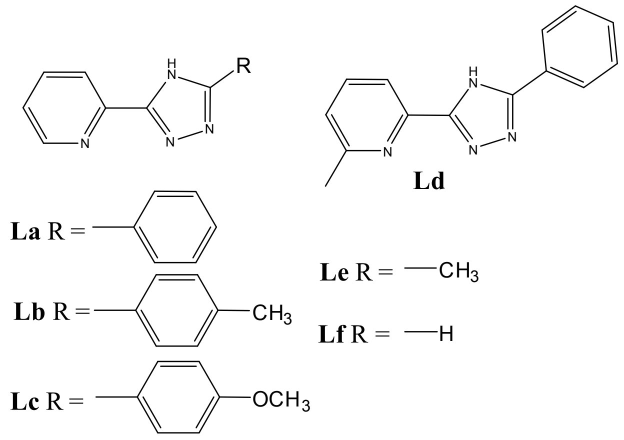
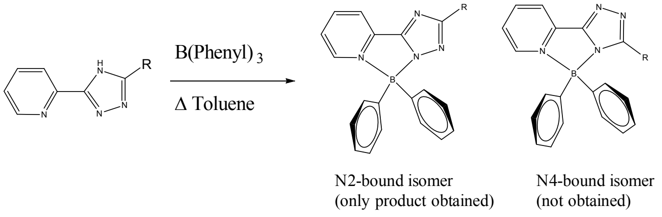


Fig. 1 Structure of ligands **La-Lf**

Results and discussion

The synthesis of the ligands **La-Lf** were carried out using methods reported elsewhere.[13] Initial attempts to prepare the corresponding boron complexes using $BF_3{\cdot}OEt_2$ were unsuccessful, however, reaction of the ligands with $B(Ph)_3$ at reflux in toluene, (or THF in the case of **Le**) provided complexes of the type $(L)B(Ph)_2$ in 25-40% isolated yields (Scheme 1). In the case of **Lf**, although an obvious increase in fluorescence intensity was apparent (*i.e.* an emission band at 535 nm) after heating with $B(Ph)_3$ at reflux in toluene, isolation of the corresponding boron complex by crystallisation or column chromatography was unsuccessful, most probably due to the acidity of the C(5)-H of the 1,2,4-triazole (pKa ca. 10).[14] The boron complexes of ligands **La-Le** were characterised by elemental analysis, ^1H, ^{13}C and ^{11}B NMR spectroscopy and mass spectrometry (see the electronic supporting information). In all cases only a single signal is observed by ^{11}B NMR spectroscopy.



Scheme 1 Synthesis of 5-R-(pyridine-2'-yl)-1,2,4-triazolato $B(Ph)_2$ complexes. The N2 and N4 coordination isomers are shown.

The FTIR and Raman spectra of ligands and complexes confirm deprotonation of the ligands by $B(Ph)_3$ to yield $LB(Ph)_2$ (see ESI for spectra). In particular, the pyridyl based mode at ca. 1594 cm^{-1} undergoes a shift of 30-40 cm^{-1} to higher wavenumbers upon complexation.

Coordination of the 1,2,4-triazole moiety to the boron atom can, in principle be via either the N2 or N4 nitrogen (Scheme 1). The ^1H NMR spectra indicate that only a single coordination isomer is obtained, however definitive assignment cannot be made on the bases of the spectra alone. Nevertheless the presence of a substituent at the C5 position introduces steric interactions that disfavour coordination via the N4 nitrogen as found earlier for octahedral Ru(II),[15] Os(II)[16], La(III)[17] Ir(III) complexes,[18] as well as square planar complexes.[19]

Single crystal X-ray crystallography of 1

Single crystal X-ray structural analysis of **1e** confirmed the N2 coordination of the 1,2,4-triazolato moiety (Fig. 2)

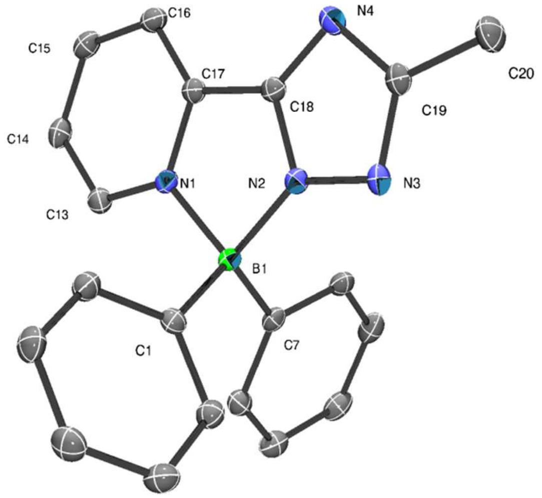


Fig. 2 Ortep plot for **1e**. The ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. {CCDC 1001413}

The boron atom binds to the triazolato ring via the nitrogen in the N2 position (B(1)-N(2) = 1.5652(16) Å) and to the pyridyl nitrogen (B(1)-N(1) = 1.6332(15) Å). The difference between the two B-N bond lengths is consistent with other tetrahedral $LBPh_2$ complexes.[9,10] The tetrahedral coordination environment around the boron atom is completed by the two phenyl rings with bond lengths of 1.6053(17) (B(1)-C(1)) and 1.6081(17) Å (B(1)-C(7)). The phenyl rings are essentially orthogonal to the plane of the ligand (88.08(14)°, planes through B(1)-C(1)-C(7) and B(1)-N(1)-N(2)). The 5-methyl-(pyrid-2'-yl)-1,2,4-triazolato ligand deviates slightly from planarity with a dihedral angle of 3.27(13)° (N(1)-C(17)-C(18)-N(2)).

UV/vis absorption spectra of ligands and complexes

The ligands **La-Lf** show absorbance in the UV region of the UV/vis absorption spectrum at ca. 250 nm. Coordination to diphenylborane results in the appearance of a new absorption band at ca. 350 nm for all complexes and an increase in molar absorptivity at 250 nm due to the additional contribution of absorption by the phenyl rings (Table 1).

The UV/vis absorption spectra of **1a-e** are generally similar with absorption maxima at ca. 250 and 340 nm (Fig. 3). Complex **1e** shows the most blue shifted absorbance with a maximum at 325 nm. For the aryl substituted ligands **1a-c**, a 15 nm red shift (-H, -Me, -OMe) is observed, which is consistent with destabilisation of the largely triazole based HOMO orbital by electron donating groups (*vide infra*). Notably, the presence of a methyl group at the 6'-position, which would be expected to cause steric hindrance and thereby affect the B-N(pyr) bonding has a negligible effect on the absorption spectrum.

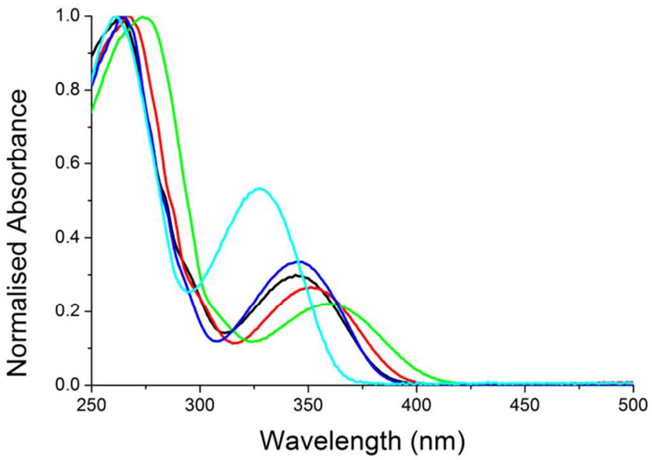


Fig 3. Normalised absorption spectra of **1a** (black), **1b** (red), **1c** (green), **1d** (dark blue) and **1e** (light blue) in dichloromethane

Emission and excitation spectroscopy

Variation of the substituent at the C5 position of the triazole affects the emission spectrum, quantum yield and lifetime also. Ligand **La** emits at 350 nm, which shifts bathochromically to 451 nm when complexed to $B(Ph)_2$, together with a substantial increase in emission quantum yield (Table 1).

Table 1. Photophysical properties of **1a-e** and ligands **La** and **Lb**

	λ_{abs}/nm (log(ε M^{-1} cm^{-1}))		λ_{em} /nm	Φ	τ (ns)
1a	263 (4.38)	344 (3.86)	451	0.72	9.52
1b	267 (4.34)	351 (3.70)	461	0.71	10.7
1c	274 (4.38)	360 (3.73)	494	0.49	12.5
1d	265 (4.43)	345 (3.95)	441	0.75	7.77
1e	261 (4.01)	327 (3.74)	397	0.77	8.64
La	235 (4.24)		345	0.03	< 0.4
Lb	253		354	0.08	< 0.4

In CH_2Cl_2 at 20 °C

As for the UV/vis absorption spectra of complexes **1a-1e**, the emission spectra show a similar dependence on the substituent at the C5 position of the 1,2,4-triazole (Fig. 4). Complexes **1a**, **1b** and **1d** emit at ca. 450 nm and exhibit a small shoulder at the blue side of their spectra, which is most pronounced for **1d**. Introduction of the *para*-methoxy group in **1c** results in a considerable bathochromic shift in emission to 494 nm, which corresponds with the bathochromic shift of its lowest absorption band compared with **1a**. In the case of **1e**, which bears a methyl group at the C5 position of the triazole moiety, the emission is shifted hypsochromically to 397 nm. These data demonstrate the ease with which the emission spectrum of this class of boron complexes can be tuned by relatively minor peripheral variations in ligand structure. An important aspect with regard to application, however, is that such tuning should not impact negatively on the quantum yield of emission or emission lifetimes. In both regards, variation of the substituents on the ligand has a relatively minor effect, with the exception of complex **1c**, which shows a small decrease in emission quantum yield and an increase in emission lifetime compared with **1a**. The increase in emission lifetime and decrease in quantum yield, observed on going from **1a** to **1c** indicates that a decrease in the radiative decay rate occurs.

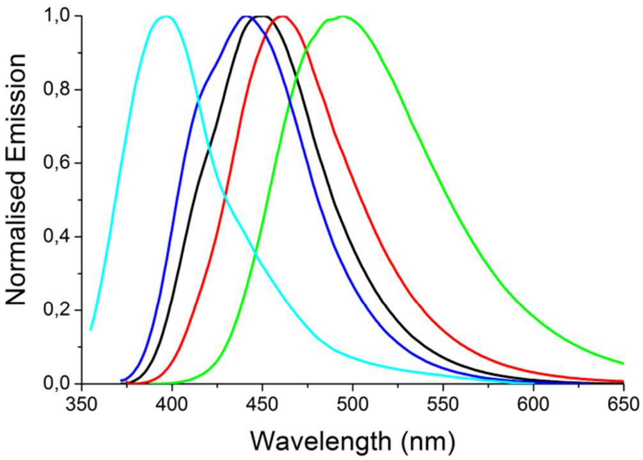


Fig 4 Normalised emission spectra of **1a** (black), **1b** (red), **1c** (green), **1d** (dark blue) and **1e** (light blue) in dichloromethane

Cyclic voltammetry

The redox properties of **1a-e** were determined by cyclic voltammetry in dichloromethane at room temperature (see ESI Fig. S26). For complexes **1a**, **1b** and **1d** the oxidation occurs at potentials close or at the onset potential for solvent oxidation. Complex **1c** however shows an irreversible oxidation at $E_{p,a}$ +1.37 V, which is > 200 mV less positive than for the other complexes, indicating destabilisation of the HOMO orbital by the electron donating methoxy substituent. All complexes showed an irreversible reduction ($E_{p,c}$) at ca. -1.85 V vs SCE, with the exception of **1d**, which is reduced cat -1.92 V. The irreversibility for both oxidation and reduction is ascribed to chemical instability of the oxidised and reduced species respectively. Indeed reduction results in the appearance of a new oxidation wave at ca. -0.5 V.

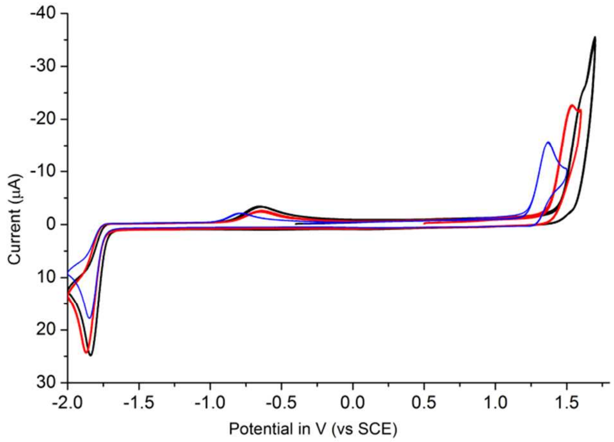


Fig. 5 Cyclic voltammetry of **1a** (black), **1b** (red) and **1c** (blue) in CH_2Cl_2 with 0.1 M $TBAPF_6$ at a GC electrode, 0.1 V s^{-1}.

1d bears an electron donating methyl group in the *ortho* position of the pyridyl ring and potentially introduces steric strain between the pyridine and the $B(Ph)_2$ unit. The localization of the LUMO on the pyridyl ring (vide infra) is consistent with the effect of a methyl substituent on the pyridyl ring in **1d** to shift the reduction potential negatviely. Overall, however, the HOMO/LUMO gaps estimated from the difference in the oxidation and reduction potentials (3.1 to 3.3 eV) are consistent with the lowest energy absorption band (3.1-3.2 eV).

Density functional theory

Calculation of the frontier molecular orbitals of **1e** was carried out using DFT methods (see ESI for details) in order to rationalise the effect of substitution at the C5 position of the 1,2,4-triazole unit. The calculated length for the B(1)-N(2) bond is 1.564 (from X-ray analysis = 1.5652(16) Å) and B(1)-N(1) is 1.652 (from X-ray analysis = 1.6332(15) Å) and the calculated dihedral angle for (N(1)-C(17)-C(18)-N(2) is 1.067° (compared with 3.27(13)° as determined by X-ray structural analysis).

The HOMO to HOMO-5 orbitals are localised on the triazolato and $B(Ph)_2$ moieties with negligible electron density on the pyridyl rings. The lowest virtual orbitals (LUMO to LUMO+2) are localised across the triazole-pyridyl ligand with no distribution of the orbitals on the phenyl rings until the LUMO+3 level. TDDFT was carried also (see ESI for details) and confirms the assignment of the electronic spectrum. Hence, the perturbation of the redox and electronic properties of the complexes by the C5 substitutions can be understood through inductive perturbation of electron density on the triazole ring.

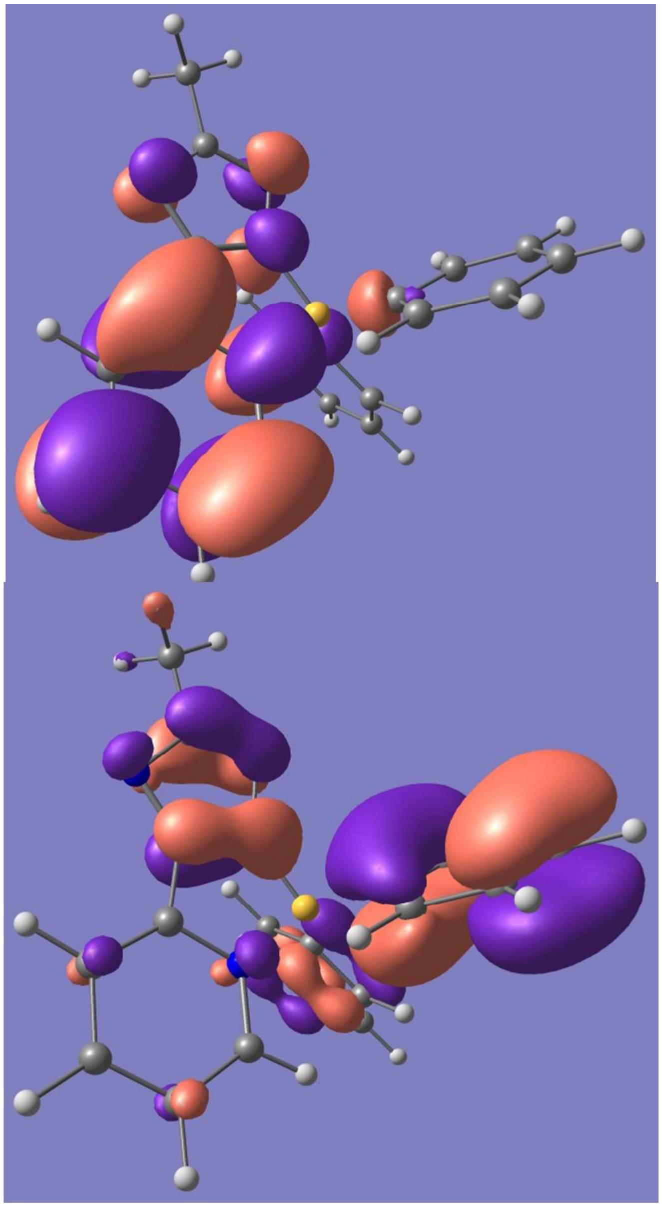


Fig. 6 HOMO (lower) and LUMO (upper) orbitals calculated for **1e**

Application of complexes in Liquid Scintillation

In radiation detection, the energy released upon capture excites the solvent, which is typically a polyaromatic hydrocarbon, followed by energy transfer to the wavelength shifter (WLS), which emits visible light capable of penetrating the solvent and reach the detectors. Di-isopropylnaphthalene (DIN) is used widely as solvent in such applications together with fluorophores (WLS) such as POPOP. Complex **1a** was mixed with DIN to determine its efficiency in this application using ^{133}Ba as a source of radiation. As the concentration of **1a** is increased, it approaches the measured transformed Spectral Index of the External Standard (tSIE) value (the closer this tSIE value is to 1000 the better the fit to the theoretical ^{133}Ba energy spectrum).[20] The best result is obtained at 8.7 mM above which concentration **1a** is not soluble.

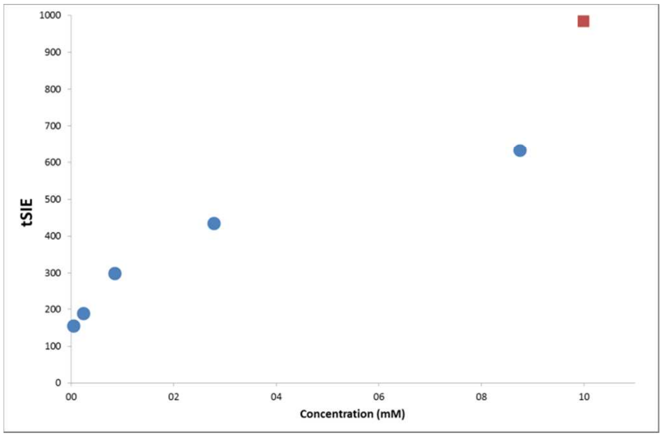


Fig 7. Transformed-Spectral Index of the External Standard (tSIE) versus concentration of **1a**. The molarity of the control is set arbitrarily at 10 mM.

Conclusions

The drive for new fluorophores that show spectral overlap of their emission spectrum with the range of optimum responsivity of the detector technology used for liquid scintillators must face demands in regard to cost and the avoidance of scarce elements and non-scalable syntheses. In this contribution, we demonstrate that boron complexes of the well-known pyridyl-1,2,4-triazole based ligand system can allow for high quantum yield emission in the blue region of the spectrum with facile control over emission wavelength achieved by substitution at the C5 position of the triazole. The complexes described here hold further potential in other applications where blue emission is required, not least in OLEDs.

Experimental

Materials. All reagents were commercially available and used without further purification unless stated otherwise. Dichloromethane, diethyl ether, THF, toluene were dried using a MBraun solvent purification system. Ligands **La-e** were prepared according to previously reported methods.

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian Avance {400MHz} NMR spectrometer, ^{11}B NMR spectra were recorded on a Varian Avance NMR spectrometer. Spectra were referenced to residual solvent peak.[21] FT-Infrared spectra were recorded as solids on a PerkinElmer Spectrum400 FTIR spectrpometer equipped with an ATR accessory. UV/vis absorption spectra were recorded on a Specord600 UV/vis absorption spectrometer (AnalytikJena) in 1 cm pathlength quartz cuvettes. Fluorescence spectra were recorded using a JASCO FP7200 spectrofluorimeter, and were corrected for instrument response. Quantum yields were determined relative to a diphenylanthracene in ethanol.[22] Fluorescence decay lifetimes were measured using a Picoquant 300 TCSPC. Melting points were determined using a BUCHI Melting Point B-545 apparatus with open glass capillaries. Mass spectra were recorded using a Xevo G2-S QTof equipped with Ion Sense DART SVP. Elemental analysis was determined using a EuroVector Euro EA. For details of single crystal X-ray diffraction, see ESI. Scintillator cocktails consisting of di-isopropylnaphthalene (DIN) and complex were made at concentrations ranging from 0.57 to 87 μM. The samples were introduced into a PerkinElmer Tricarb 2910 TR and measured with a ^{133}Ba source.

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Notes and references

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Electronic Supplementary Information (ESI) available: Details of synthesis and characterisation of complexes, voltammetry, DFT calculations. See DOI: 10.1039/b000000x/

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1 J. B. Birks, *The theory and practice of scintillation counting*, Macmillan, New York, 1964; D. L. Horrocks, *Application of Liquid scintillation counting* (Academic Press, Inc, New York, **1974**).

2 Photomultipliers: data handbook. PC04, Philips Components, London, 1990; G. F. Knoll, *Radiation detection and measurement*, Edition John Wiley & Sons USA, 1989.

3 S. Wang, C. C. Hsu, R. W. S. Leung, S. L. Wang, C. Y. Chang, C. P. Chen, K. C. Cheng, T. I. Ho, W. P. Lai, H. M. Liu, Z. P. Mao, I. C. Shih, H. T. Wong and Z. Q. Yu, *Nucl Instrum Meth A*, 1999, **432**, 111-121; United States Government Accountability Office, Neutron Detectors: Alternatives to Using Helium-3, GAO-11-753, 2011.

4 R. Ziessel, G. Ulrich, and A. Harriman, *New J. Chem.* 2007, **31**, 496; G. Ulrich, R. Ziessel, and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184.

5 A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.,* 2013, **42**, 77; N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.,* 2012, **41**, 1130; F. Cheng and F. Jaekle, *Polym. Chem.,* 2011, **2**, 2122.

6 C. F. A. Gomez-Duran, I. Garcia-Moreno, A. Costela, V. Martin, R. Sastre, J. Banuelos, F. L. Arbeloa, I. L. Arbeloa and E. Pena-Cabrera, *Chem. Commun.,* 2010, **46**, 5103.

7 J. B. Birks, *The theory and practice of scintillation counting*, Macmillan, New York, 1964; P. Dijkstra, H. J. Wortche, and W. R. Browne, *AIP Conf. Proc.* 2011, **1338**, 221.

8 (a) D. Li, H. Zhang, and Y. Wang, *Chem. Soc. Rev.,* 2013, **42,** 8416; (b) D. Frath, J. Massue, G. Ulrich and R. Ziessel, *Angew. Chem. Int. Ed.*, 2014, **53**, 2290

9 C. C. Cheng, W. S. Yu, P. T. Chou, S. M. Peng, G. H. Lee, P. C. Wu, Y. H. Song and Y. Chi, *Chem., Commun.,* 2003, 2628.

10 D. Suresh, C. S. B. Gomes, P. T. Gomes, R. E. Di Paolo, A. L. Macanita, M. J. Calhorda, A. Charas, J. Morgado and M. T. Duarte, *Dalton Trans.* 2012, **41**, 8502.

11 W. R. Browne, R, Hage, J. G. Vos, *Coord. Chem. Rev.*, 2006, **250**, 1653.

12 E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Frohlich, R. Frtshlich, L. De Cola, A. van Dijken, M. Buchel and H. Borner, *Inorg. Chem.,* 2007, **46**, 11082-11093.

13 R. Prins, R. A. G. de Graaff, J. G. Haasnoot, C. Vader and J. Reedijk, *J. Chem. Soc., Chem. Commun*., 1986, 1430.

14 S. Fanni, C. Di Pietro, S. Serroni, S. Campagna and J. G. Vos, *Inorg. Chem. Commun*. 2000, **3**, 42

15 R. Hage, J. G. Haasnoot, H. A. Nieuwenhuis, J. Reedijk, D. J. A. Deridder and J. G. Vos, *J. Am. Chem. Soc.* 1990, **112**, 9245;

16 B. E. Buchanan, R. Y. Wang, J. G. Vos, R. Hage, J. G. Haasnoot, J. Reedijk, *Inorg. Chem*., **29**, 3263.

17 M. G. B. Drew, M. J. Hudson, P. B. Iveson, C. Madic and M. L. Russell, *J. Chem. Soc. - Dalton Trans* 1999, 2433

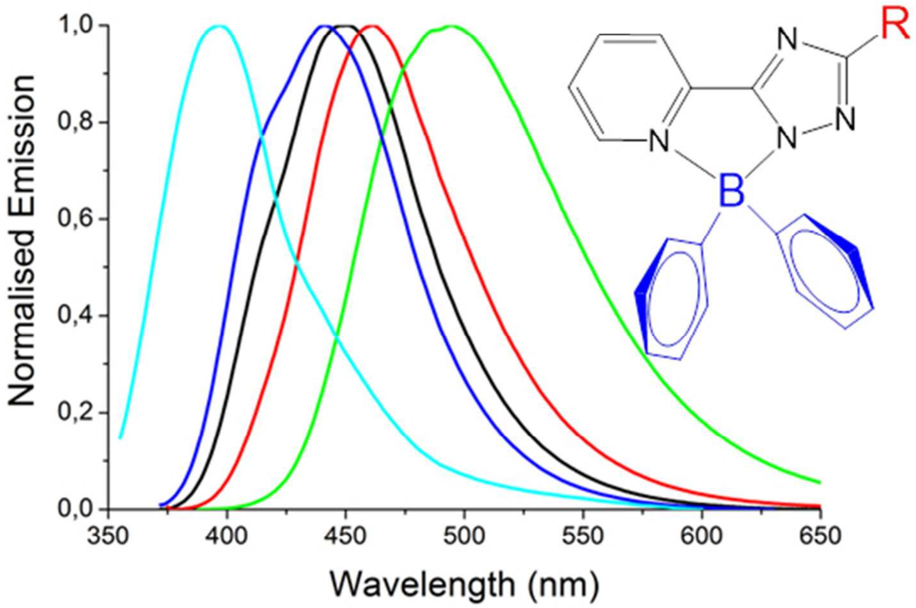
18 S. Soman, J. C. Manton, J. L. Inglis, Y. Halpin, B. Twamley, E. Otten, W. R. Browne, L. De Cola, J. G. Vos and M. T. Pryce, *Chem. Commun*., 2014, DOI: 10.1039/C4CC02249A

19 S.-Y. Chang, J. Kavitha, S.-W. Li, C.-S. Hsu, Y. Chi, Y.-S. Yeh, P-T. Chou, G.-H. Lee, A. J. Carty, Y.-T. Tao and C.-H. Chien, *Inorg. Chem.*, 2006, **45**, 137

20 Gamma radiation and fast neutrons are both detected in the scintillation systems employed here, with pulse shape discrimination used to distinguish the two radiation types. Gamma radiation detection is used for an initial assessment of the functionality of a detection system for practical reasons.

21 H. E. Gottlieb, V. Kotlyar, and A. Nudelman, *J. Org. Chem.* 1997, **62**, 7512.

22 Montalti, M., Credi, A., Prodi, L., & Gandolfi, M. T. (2006). Handbook of photochemistry. CRC press.



1,2,4-triazole based boron complexes are readily tunable blue emitters

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