Dyes and Pigments 94 (2012) 496–502

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

A novel Bodipy-Dipyrrin fluorescent probe: Synthesis and recognition behaviour towards Fe (II) and Zn (II)

Ahmed Nuri Kursunlu [a], Ersin Guler [a], Halil Ismet Ucan [a], Ross W. Boyle [b],*

[a] Department of Chemistry, University of Selcuk Campus, 42075 Konya, Turkey
[b] Department of Chemistry, University of Hull, Kingston-upon-Hull, East Yorkshire HU6 7RX, UK

ARTICLE INFO

Article history:
Received 8 December 2011
Received in revised form
6 February 2012
Accepted 7 February 2012
Available online 16 February 2012

Keywords:
Bodipy
Florescent probe
Dipyrrin
Metal complex
Fluorophore
Photophysical property

ABSTRACT

We present the design, synthesis, characterization and spectral studies for a new Zn (II) and Fe (II) selective fluorescent probe, 4,4-Difluoro-8-{3-[(4-phenoxy-dipyrromethene)propoxy]}-4-bora-3a,4a-diazaindacene (DPYBODPY). DPBODPY consists of a terminal fluorophore and a selective ligand and was designed to detect significant changes in absorbance and/or fluorescence on metal ion binding. The fluorophore is based on the Bodipy unit due to its excellent photophysical properties, while the dipyrrin unit has specific recognition abilities for Fe^{2+} and Zn^{2+} ions. The combination of these two structures is optimised to achieve significant spectral changes in the presence of Fe^{2+} and Zn^{2+} ions.

1. Introduction

The design of fluorescent probes for metal cations is an important field in organic chemistry, bioinorganic chemistry and the life sciences due to their relatively high sensitivity, selectivity and short response time [1–4]. Most fluorescent probes are designed to incorporate either a structure wherein the receptor is part of the π-electron system of the fluorophore, or a structure consisting of a fluorophore and a receptor separated by a short alkyl chain [5,6]. In the last decade, a range of Bodipy (borondifluorodipyrromethene) fluorophores have been developed with excellent stability, high fluorescence quantum yields, negligible triplet state formation, intense absorptions, good solubility, and chemical robustness [7–11]. Some similarities between Bodipys and porphyrins, which are often assembled from dipyrromethane or dipyrromethene building blocks, have been noted [12]. Due to these similarities, novel Bodipy complexes (which can be converted into an energy transfer cassette) have been synthesized in order to creating a large Stoke shift [13]. Energy transfer cassettes typically rely on PET (photoinduced electron transfer) and ICT (internal charge transfer) processes for their activity. Bodipy compounds also show reduced fluorescence due to an active quenching process (PET or ICT) in the presence of some metal ions [14,15].

Dipyrrins, which are closely structurally related to Bodipys, are also efficient ligands for the formation of charge-neutral metal complexes. Derivatives of dipyrrins complexed with a variety of metal cations have been extensively investigated due to favourable electrochemical and fluorescent properties [16,17]. Generally, the dipyrrins have had a widespread impact on coordination chemistry, and the first reports in the area date back to early last century [18,19]. Examples include the work of Baudronet et al., who reported homo- and hetero-metallic dipyrrin compounds [20] and Catherine et al. who have shown that four cyclo-metallated Pd and Pt complexes coordinated simultaneously to a dipyrrin derivative could be synthesized [21].

In this article, we investigate the binding properties of metal ions [Fe (II), Co (II), Ni (II), Cu (II), Zn (II), Pb (II), Hg (II)] towards DPYBODPY in methanol and describe a new fluorescent probe, DPYBODPY, for Zn (II) and Fe (II).

2. Experimental

2.1. Instruments and chemicals

NMR spectra were recorded on a Jeol JNM ECP 400 spectrometer, with TMS $\delta_H = 0$ as the internal standard or residual protic

---

* Corresponding author.
E-mail address: r.w.boyle@hull.ac.uk (R.W. Boyle).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2012.02.006

solvent. [$CDCl_3$, $\delta_H = 7.26$]. Chemical shifts are given in ppm (δ) and coupling constants (J) are given in Hertz (Hz). NMR measurements were recorded at 400 MHz. UV–vis spectra were obtained on a Perkin Elmer Lambda 25 UV–vis spectrophotometer. The percentages of carbon, hydrogen and nitrogen in all compounds were determined using a *TruSpec* elemental analyser. Fluorescence spectra were measured using a PerkinElmer LS 55 Fluorescence spectrometer with a right angle illumination method. Compact UV Lamps – UVGL-25 Compact UV Lamp was used to the visualization of thin-layer chromatography (TLC).

4-Hyroxybenzaldehyde, was purchased from Merck. Pyrrole, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 3-bromo-1-chloropropane and sodium iodide, were purchased from Acros Organics. All metal acetate salts were purchased from Fluka and used as received. Other chemicals were purchased from Sigma Aldrich or Alfa Aesar. All chemicals were used as received with the exception of pyrrole, which was distilled before use. All solvents were purchased from Fisher Scientific with the exception of butanone, which was purchased from Acros Organics.

TLC was performed with using Merck aluminium plates coated with silica gel 60 F254 and visualized under UV light (254 nm or 372 nm). Column chromatography was performed with using MP Silica 32-63, 60 Å. All solvent mixtures are given in v/v ratios.

2.2. Synthesis

2.2.1. Synthesis of 4-(3-chloropropyloxy)benzaldehyde (*1*)

1-Bromo-3-chloropropane (4.71 g, 30.00 mmol, 1.5 equiv.) was added to a solution of 4-hydroxybenzaldehyde (2.44 g, 20.00 mmol, 1.0 equiv.) and K_2CO_3 (5.52 g, 40.00 mmol, 2.0 equiv) in acetonitrile (100 mL). The mixture was refluxed for 18 h, then cooled to r.t. and filtered through diatomaceous earth. The filtrate was concentrated and the residue was purified by column chromatography (silica gel, ratio: 1:10, 1:9 and 1:8, ethyl acetate/hexanes) to afford 2.58 g (65%) of 4-(3-chloropropyloxy)benzaldehyde. ^1H NMR [400 MHz, $CDCl_3$]: 9.88 (s, 1H, CHO), 7.84 (d, 2H, ArH), 6.99 (d, 1H, ArH), 4.19 (t, 2H, CH), 3.59 (t, 2H, CH), 2.36 (m, 2H, CH). ^{13}C NMR [100 MHz, $CDCl_3$]: 191.2, 164.0, 132.0130.1, 115.5, 66.3, 32.1, 29.8. Anal. Calc. for (%) $C_{10}H_{11}ClO_2$ C, 60.46; H, 5.58; Found: C, 60.79; H, 5.92.

2.2.2. Synthesis of 4-(3-iodopropyloxy)benzaldehyde (*2*)

1 (1.99 g, 10 mmol) and 1.2-equivalent sodium iodide (1.8 g, 12 mmol) were heated in DMF (50 mL) at 80 °C for 18 h. The mixture was cooled to r.t. and water was added. The aqueous mixture was extracted with ethyl acetate (three times) and the combined extracts were dried ($MgSO_4$), filtered, and concentrated. The pale oil was obtained. Yield: 99% (2.88 g). ^1H NMR [400 MHz, $CDCl_3$]: 9.87 (s, 1H, CHO), 7.84 (d, 2H, ArH), 7.04 (d, 1H, ArH), 4.19 (t, 2H, CH), 3.48 (t, 2H, CH), 2.36 (m, 2H, CH). ^{13}C NMR [100 MHz, $CDCl_3$]: 191.2, 164.1, 132.1, 129.9, 115.5, 66.0, 29.5, 2.1. Anal. Calc. for (%) $C_{10}H_{11}IO_2$; C, 41.40; H, 3.82; Found:C, 41.62; H, 3.92.

2.2.3. Synthesis of 5-[4-((3-iodopropoxy)phenyl)]dipyrromethane (*3*)

2 (1.45 g, 5 mmol) was dissolved in freshly distilled pyrrole (100 mL) and degassed with nitrogen for 15 min. Then TFA (0.1 ml) was added and the solution stirred at r.t. under nitrogen for 30 min. The excess pyrrole was then removed by evaporation *in vacuo* and the green oily residue was purified by column chromatography eluting with 1:10 ethyl acetate:dichloromethane to give an oil. The oil was triturated with hexanes and the material was obtained as an off-white solid. The solid was dried under vacuum. The resulting solid was recrystallized from methanol to yield the pure product as an off-white dust. Yield: 76% (1.54 g) ^1H NMR [400 MHz, $CDCl_3$]: 7.90 (b, 2H, NH), 7.12 (d, 2H, ArH), 6.86 (d, 2H, ArH), 6.69 (d, 2H, PyH), 6.16 (d, 2H, PyH), 5.91 (d, 2H, PyH), 5.42 (s, 1H, meso-H), 4.08 (t, 2H, CH) 3.60 (t, 2H, CH), 2.30 (m, 2H, CH). ^{13}C NMR [100 MHz, $CDCl_3$]: 161.4, 143.3, 134.8, 132.8, 131.4, 126.3, 118.3, 114.9, 65.0, 48.2, 28.5, 0.9. Anal. Calc. for (%)$C_{18}H_{19}IN_2O$; C, 53.22; H, 4.71; N, 6.90; Found; C, 53.41; H, 4.92; N, 6.81.

2.2.4. Synthesis of 5-[4-((3-iodopropoxy)phenyl)]dipyrromethene (*4*)

To a solution of **3** (0.81 g, 2.00 mmol) in ether (35 mL), was added DDQ (470 mg, 2.00 mmol) in ether/methanol (6 mL:4 mL), the reaction was allowed to proceed at room temperature-dark ambient under an inert atmosphere for 15 min. The solution was then filtered and treated four times with ether (apart, 25 mL), followed by filtration to yield a dark brown microcrystalline solid (0.8 g, 99%). ^1H NMR [400 MHz, CD_3OD]: 8.00 (b, 1H, NH), 7.93 (d, 2H, PyH), 7.55 (d, 2H, ArH), 7.07 (d, 2H, ArH), 6.98 (d, 2H, PyH), 6.56 (d, 2H, PyH), 4.22 (t, 2H, CH) 3.65 (t, 2H, CH), 2.37 (m, 2H, CH). ^{13}C NMR [100 MHz, CD_3OD]: 161.4, 143.2, 134.8, 132.5, 131.4, 126.2, 118.7, 115.2, 65.1, 48.2, 28.5, 1.2. Anal. Calc. for (%)$C_{18}H_{17}IN_2O$; C, 53.48; H, 4.24; N, 6.93; Found; C, 53.52; H, 4.43; N, 6.77.

2.2.5. Synthesis of 4,4-difluoro-8-[4-((3-iodopropoxy)phenyl)]-4-bora-3a,4a-diazaindacene (*5*)

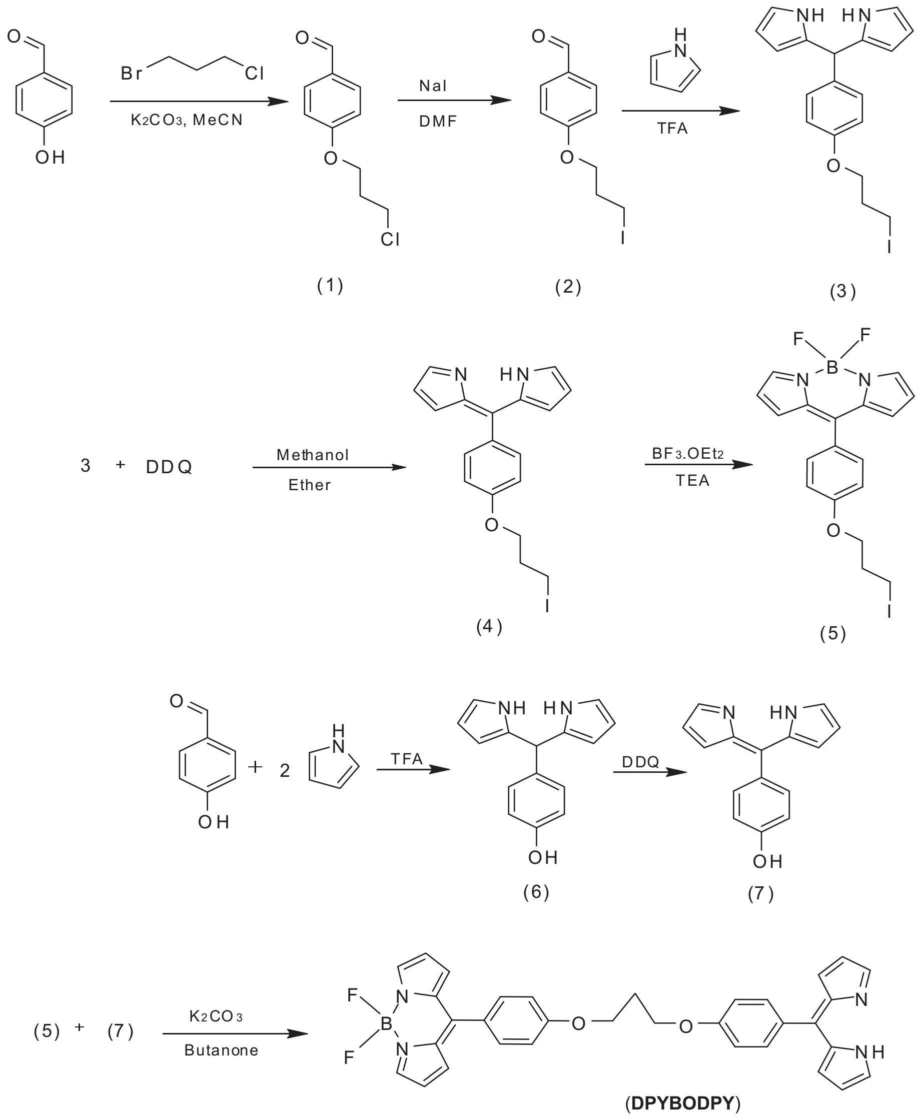
Toluene (100 mL) was degassed for 30 min with nitrogen. To this was added **4** (0.8 g, 2.00 mmol), and 8 equivalents triethylamine. The solution was heated to 70 °C for 30 min after which 5 equivalents boron triflouride etherate was added in four portions with 3 min between each addition. Intensive white fume was occurred and the reaction was stirred at reflux for 3 h. The solution was concentrated by evaporation and the black residue re-dissolved in a minimal amount of dichloromethane and carefully purified by column chromatography (SiO_2 dichlormethane:ethyl acetate 7:1) a single red-orange band was observed which yielded a vermilion solid. Yield; 40% (0.36 g). ^1H NMR [400 MHz, $CDCl_3$]: 7.93 (bs, 2H, PyH), 7.56 (d, 2H, ArH), 7.07 (d, 2H, ArH), 6.98 (d, 2H, PyH), 6.55 (t, 2H, PyH), 4.23 (t, 2H, CH), 3.65 (t, 2H, CH), 2.37 (m, 2H, CH). ^{11}B-NMR [128.3 MHz, $CDCl_3$]: −0.44 (s, 1B); ^{19}F NMR [376.83 MHz, $CDCl_3$]: −145.0 (dd, 2F) −144.85 (dd,1F); ^{13}C NMR [100 MHz $CDCl_3$]: 180.7, 174.3, 146.8, 137.1, 133.9, 132.0, 127.8, 110.7, 104.3, 77.0, 33.6, 1.9. Anal. Calc. for (%) $C_{18}H_{16}BF_2IN_2O$; C, 47.83; H, 3.57; N, 6.20; Found; C, 47.78; H, 3.77; N, 6.12.

2.2.6. Synthesis of 5-(4-Hydroxyphenyl)dipyrromethane (*6*)

To a solution of freshly distilled and degassed pyrrole (150 mL) was added 4-hydroxybenzaldehyde (2.44 g, 20.00 mmol) and trifluoroacetic acid (0.15 mL, 2.00 mmol). The reaction was allowed to proceed protected from light and under nitrogen for 15 min at room temperature, yielding a red-orange solution. The excess pyrrole was removed under reduced pressure to yield a black/brown oil, which was purified by gravity percolation chromatography (silica, eluent: dichloromethane:ethylacetate 19:1). The resulting ruby coloured oil was triturated with hexanes yielding a white solid. The solid was dried under vacuum to yield a pale pink solid [21]. Yield: 99% ^1H NMR [400 MHz, $CDCl_3$]: 7.92 (b, 2H, NH), 7.25 (bs, 2H, PyH), 7.06 (d, 2H, ArH), 6.76 (d, 2H, ArH), 6.68 (d, 2H, PyH), 6.15 (m, 2H, PyH), 5.90 (bs, 1H, ArOH), 5.41 (s, 1H, meso-H). ^{13}C NMR [100 MHz, $CDCl_3$]: 156.2, 143.2, 138.8, 135.3, 133.7, 127.1, 118.7, 118.2, 102.4. Anal. Calc. for (%); $C_{15}H_{14}N_2O$; C, 75.61; H, 5.92; N, 11.76; C, 75.72; H, 6.15; N, 11.71.

2.2.7. Synthesis of 5-(4-Hydroxyphenyl)dipyrromethene (*7*)

To a solution of **6** (480 mg, 2.00 mmol) in ether (25 mL), was added DDQ (470 mg, 2.00 mmol) in ether/methanol (3 mL:2 mL), the reaction was allowed to proceed at room temperature under an inert atmosphere for 8 min. The solution was then filtered and triturated with ether (35 mL), followed by filtration to yield a dark



Scheme 1. Synthesis of DPYBODPY.

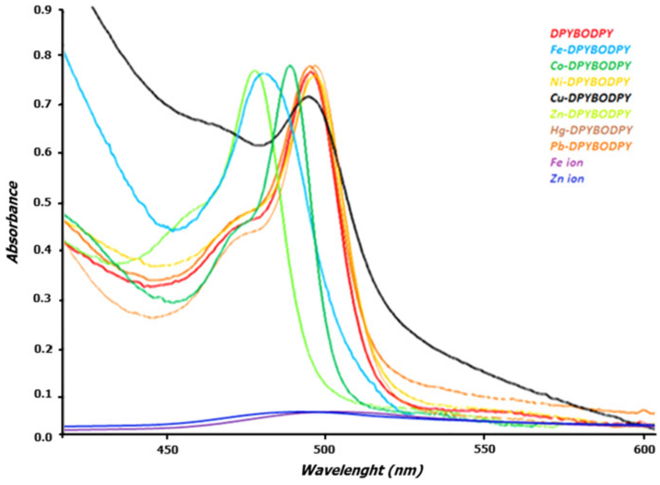


Fig. 1. Absorption spectra of DPYBODPY-metal ion mixtures.

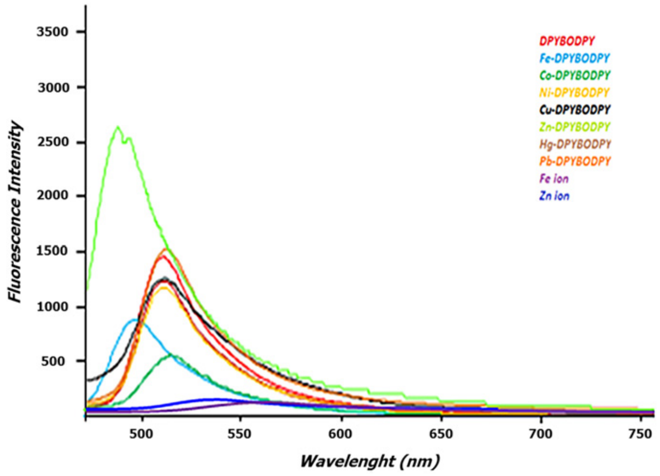


Fig. 2. Fluorescence spectra of DPYBODPY-metal ion mixtures.

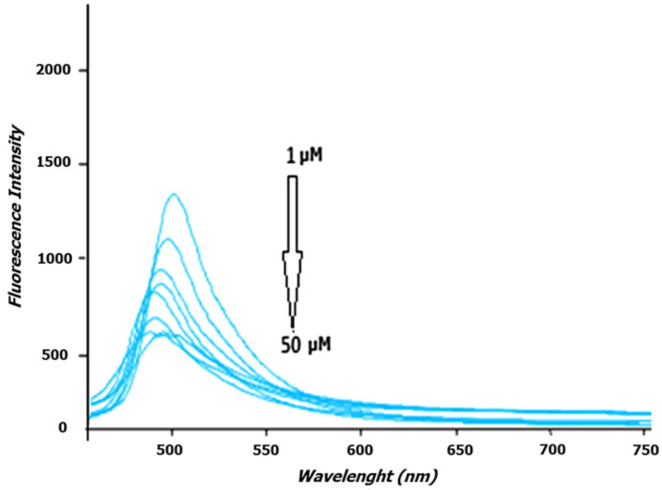


Fig. 3. Emission spectra (λ_{ex} = 450 nm) of DPYBODPY (1 μM) upon addition of Fe^{2+} (1 μM, 10 μM, 20 μM 30 μM, 35 μM, 40 μM, 45 μM, 50 μM) in MeOH.

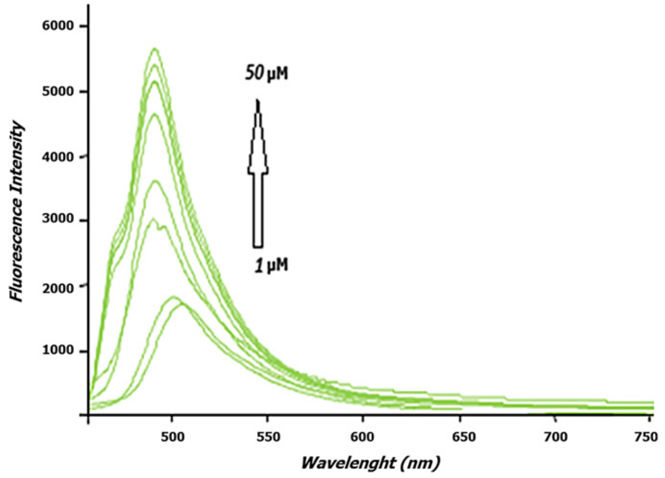


Fig. 4. Emission spectra (λ_{ex} = 450 nm) of DPYBODPY (1 μM) upon addition of Zn^{2+} (1 μM, 10 μM, 20 μM 30 μM, 35 μM, 40 μM, 45 μM, 50 μM) in MeOH.

brown microcrystalline solid (475 mg, 99%) [21]. ^1H NMR [400 MHz, CD_3OD]: 8.32 (b, 1H, NH), 7.94 (bs, 2H, PyH), 7.51 (d, 2H, ArH), 7.25 (d, 2H, PyH), 7.04 (d, 2H, ArH), 6.83 (m, 2H, PyH), 5.90 (bs, 1H, ArOH). ^{13}C NMR [100 MHz, CD_3OD]: 154.7, 141.9, 139.6, 135.3, 133.7, 127.1, 118.9, 118.3, 102.0. Anal. Calc. for (%), $C_{15}H_{12}N_2O$; C, 76.25; H, 5.12; N, 11.86; Found; C, 76.55; H, 5.33; N, 11.71.

2.2.8. Synthesis of DPYBODPY

5 (0.452, 1.00 mmol, 1 equiv.) was dissolved in butanone (70 mL), **7** was added to this solution (0.354 g, 1.5 mmol, 1.5 equiv.) followed by 5 equivalents K_2CO_3 as solid. The mixture was stirred at 60 °C for 96 h. The butanone was then removed *in vacuo* and dichloromethane (150 mL) was added to the residue. The solution was extracted with dichloromethane (200 mL) and water (2 × 200 mL) and brine (1 × 200 mL). The organic layer was collected and dried over anhydrous sodium sulphate. Then, the solvent of the filtration was removed, following the residue was purified through a column eluting with 10:1; dichloromethane:ethyl acetate. The relevant fractions were collected and the solvent was removed by evaporation. A crimson crystalline material was obtained. Yield; 58% (0.325 g). ^1H NMR [400 MHz, $CDCl_3$]: 8.15 (b, 1H, NH), 7.83 (d, 4H, PyH), 7.58 (d, 4H, ArH), 7.33 (d, 2H, PyH), 7.10 (d, 2H, ArH), 6.96 (d, 2H, ArH), 6.87 (d, 4H, PyH), 6.55 (t, 2H, PyH), 4.20 (t, 2H, CH), 4.18 (t, 2H, CH), 2.32 (m, 2H, CH). ^{11}B-NMR [128.3 MHz, $CDCl_3$]: −0.4891 (s, 1B). ^{19}F NMR [376.83 MHz, $CDCl_3$]: −144.59 (dd, 2F), −144.74 (dd, 1F). ^{13}C NMR [100 MHz $CDCl_3$]: 161.3, 159.3, 143.4, 140.2, 136.0, 133.7, 132.9, 131.4, 129.3, 127.0, 125.0, 123.8, 119.1, 118.4, 117.4, 115.1, 66.3, 31.3. Anal. Calc. for (%); $C_{33}H_{27}BF_2N_4O_2$; C, 70.73; H, 4.86; N, 10.00; Found; C, 70.64; H, 4.77; N, 9.90.

3. Results and discussion

3.1. Synthesis and spectroscopic studies of DPYBODPY

Bodipy complexes have a strong chemical and photochemical stability with excellent electron-transfer properties [22,23]. The novel Bodipy-dipyrrin derivative (DPYBODPY) was synthesized by an eight-step protocol as shown in Scheme 1. The DPYBODY dye was prepared from Bodipy (**5**) and dipyrrin (**7**) containing a phenolic −OH with halo-alkane as the solvent in good to excellent yield. DPYBODPY and intermediates were characterized by ^1H NMR,

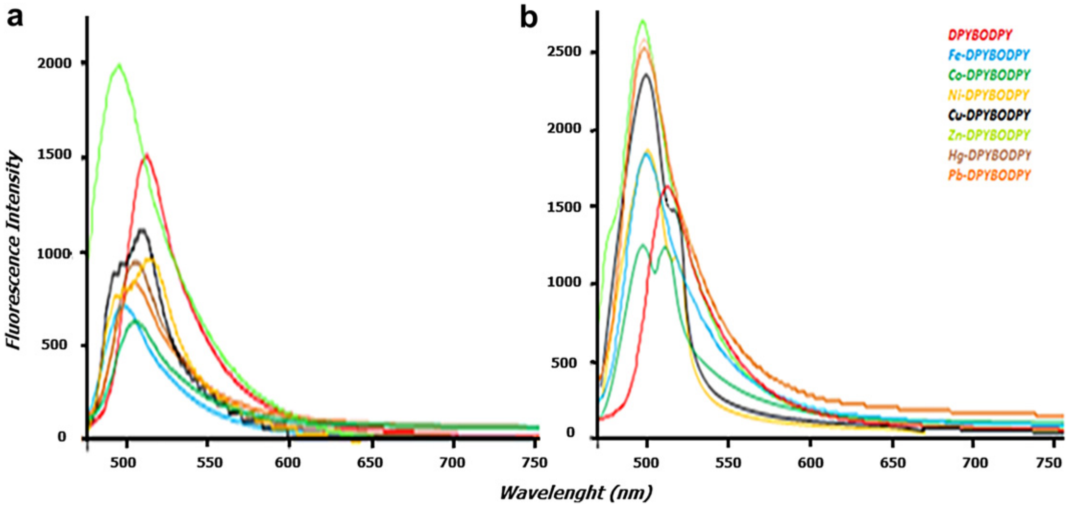


Fig. 5. a) The selectivity of DPYBODPY (1 μM) towards iron ions (20 equiv.) in the presence of other metal ions on fluorescence spectra (in methanol). b) The selectivity of DPYBODPY (1 μM) towards zinc ions (20 equiv.) in the presence of other metal ions on fluorescence spectra (in methanol).

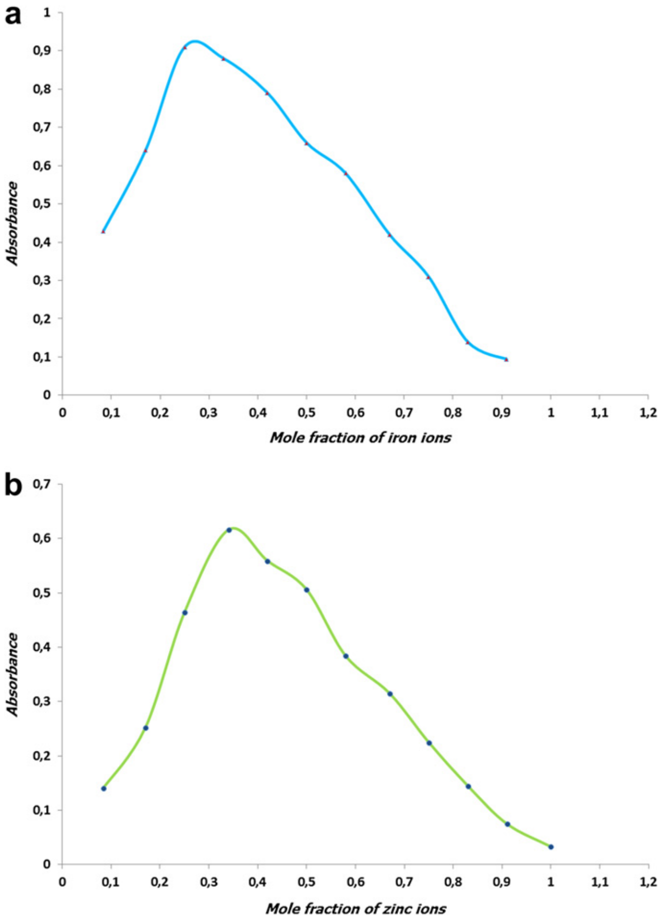


Fig. 6. Job's plot for DPYBODPY/metal ions, 0.1 mM in CH_3OH.

^{13}C NMR, ^{19}F NMR, ^{11}B NMR (as appropriate) [NMR data in supporting information].

UV–vis absorption and fluorescence spectra were recorded at room temperature in methanol, although the target DPYBODPY has good solubility in a range of organic solvent. To investigate the application of DPBODPY as a fluorescence probe, the effect of metal ions was performed at 1 μM concentration. In this way complexation reactions of DPYBODPY and the binding properties of the metal ions (Fe, Co, Ni, Cu, Zn, Pb, Hg) were studied. From this data it was concluded that Zn (II) and Fe (II) are the ions most successfully detected by DPYBODPY.

3.2. UV–vis absorption spectra of DPYBODPY with metal ions

The recognition behaviour of DPYBODPY towards various metal ions was investigated. Briefly methanolic solutions of DPYBODPY (1 μM) and metal acetate salt (20 μM) were prepared. UV–visible absorption spectra were then obtained. DPYBODPY and DPYBODPY-metal ion complexes, present a strong absorption transition in the 475–500 nm range, which can be attributed to the S_0–S_1 transition of the Bodipy component (Fig. 2) [24,25]. The Zn and Fe complexes were detected at 472 nm and 479 nm, respectively; although the wavelength of metal free DPYBODPY was observed at 495 nm in the absorption spectra, representing hyspsochromic shifts of 23 nm for DPYBODPY-Zn (II) and 16 nm for DPYBODPY-Fe (II) relative to metal free DPBODPY. DPYBODPY-metal ion mixtures showed no significant changes relative to metal free DPYBOPPY, with the exception of Co (II). The remarkable hypsochromic shift of the maximum absorption wavelengths of DPYBODPY were attributed to the complexation between the electron-donating nitrogen of dipyrrin group and metal ions in solution medium [20]. As the inset in Fig. 1 clearly shows, above 20 equivalents of Zn (II) or Fe (II), the change in the absorption wavelengths fall off very quickly, indicating a strong affinity between the DPYBODPY (ligand) and the Zn (II), Fe (II) ions (or Co (II)) in methanol. Additionally, no remarkable change in maximum absorption intensities or wavelengths was observed with other DPYBODPY-metal cations (Ni, Cu, Pb, Hg).

Table 1
Chemical shifts of 1H-NMR signals of DPYBODPY [in $(CD_3)_2SO$] in the free form and in the presence of Zn^{2+}.

Chemical shift (ppm)		
	DPYBODPY	DPYBODPY + Zn^{2+}
Py-H_1	7.83	7.64
Py-H_2	6.87	6.92
Py-H_3	6.55	6.65
Py-NH	8.15	–

3.3. Fluorescence spectra of DPYBODPY with metal ions

The fluorescence spectra of DPYBODPY and DPYBODPY-Metal ion mixtures were similarly measured in methanol at an excitation wavelength of 450 nm and are shown in Fig. 2. The fluorescence peak of the free dye was observed at 515 nm in methanol. By addition of Fe (II) and Zn (II) solution, the maximum peak shifted towards the blue with a concomitant increasing or quenching in emission intensity.

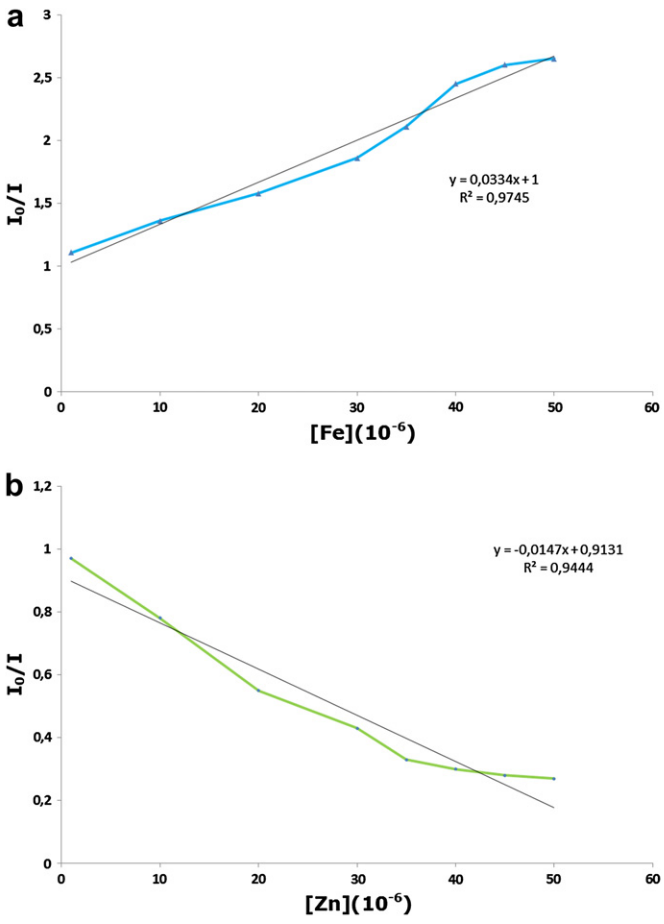


Fig. 7. Stern–Volmer plot for the fluorescence quenching and enhancement of metal ions by DPYBODPY in CH_3OH.

The bands shifted 25 nm and 21 nm for Zn (II) and Fe (II) respectively. In addition, the fluorescence emission intensity of DPYBODPY is remarkably enhanced upon the addition of Zn (II) and quenched upon the addition of Fe (II) which is attributed to the formation of complex (1:2 or 1:3; metal:ligand) [21].

In contrast, the emission of DPYBODPY-Co (II) mixture occurred at lower intensity and other transition metal ions such as Hg (II), Ni (II), Cu (II) and Pb (II) gave only a minor quenching of the fluorescence of DPYBODPY. This quenching effect is often attributed to electron transfer from ligand to metal cations (generally for heavy metal cation).

The enhancement or decrease in fluorescence intensity can be ascribed to the planarity and stability of the dipyrrin group induced by chelation of Zn (II) or Fe (II). The geometry of Zn (II) complex is slightly distorted tetrahedral [26] and the geometries of Fe (II) – Fe (II) are distorted tetrahedral-octahedral, respectively. There, the valance of iron depends on the stability of the ion in solution. It has been generally reported that iron complexes have an octahedral geometry. Similarly, cobalt complexes have the same geometry and coordination as iron complexes [27,28]. In summarily, the basis of the selectivity and affinity depends on the match between the valence of the metal cation and the electron donating ability of the nitrogen on the dipyrrin. Moreover, it can be considered that the expected trends between ligand and metal ion are observed as hard–soft acid–base effects.

The gradual addition of Fe (II) and Zn (II) to DPYBODPY resulted in significant quenching or enhancement, respectively as shown Figs. 3 and 4. Due to the interaction between DPYBODPY and metal ions, suggesting that DPYBODPY could be used as a quantitative chemosensor for Fe (II) and Zn (II).

Fig. 3 indicates that starting with a 1 μM concentrations of Fe (II), a decrease in the fluorescence intensity occurred with a 10–12 nm bathochromic shift. In order to ascertain the selectivity of DPYBODPY for Fe (II), we repeated the experiments for Zn (II). In contrast to DPYBODPY + Fe (II) mixtures, the wavelength of DPYBODPY + Zn (II) mixtures is hypsochromically shifted and the fluorescence intensity increases with increasing Zn (II) concentration.

To confirm DPYBODPY as an ion-selective fluorescence probe for iron and zinc ions the effect of competing metal ions was determined. DPYBODPY 1 μM was treated with 20 equiv. iron and zinc metals in the presence of other metal ions (20 equiv), respectively. As shown in Fig. 5, the presence of other metal ions on the detection of Zn^{2+} and Fe^{2+}had little effect, except in the case of Co^{2+} which showed a significant perturbation.

3.4. Determination of complex stoichiometry

In order to determine the stoichiometry of the Zn (II) and Fe (II)/Fe (III) complexes, the Job's plot method of continuous variation was also used. The total concentration of the compound DPYBODPY and metal ions were constant (0.1 mM), with a continuous variable molar fraction of guests. Fig. 5 shows the Job plot of DPYBODPY with metal ions. The DPYBODPY/Zn and DPYBODPY/Fe complex concentrations approach a maximum when the molar fraction of iron and zinc ions are 0.27and 0.34, respectively, (which means DPYBODPY with complex forms ∼1:3 and 1:2,respectively).

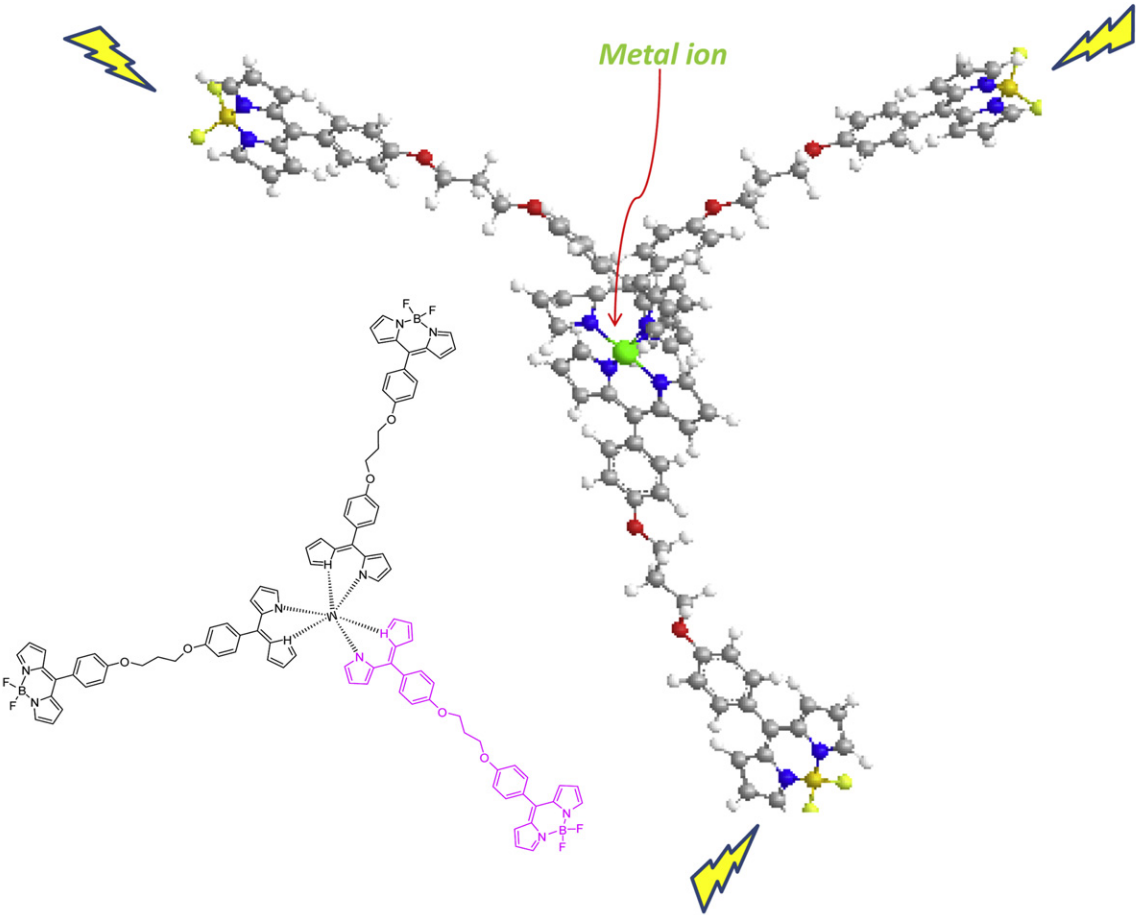


Fig. 8. The estimated perspective of DPYBODPY-metal ions combination with four or six coordination.

3.5. Stern–Volmer analysis

Stern–Volmer analysis was utilized to probe the nature of the quenching or enhancement process in the complexation of metal ions. The plots obtained emission intensities (I_0/I) against metal ion concentration and showed a linear graph (Fig. 6).

$$I_0/I = 1 + K_{sv}[\mathrm{M}]$$

In Eq., I_0; the fluorescence intensity of DPYBODPY in the absence metal ion; I; in the presence metal ion, K_{sv} static quenching constant. For both metal ion, linear behaviour was shown in both graphics. But, while the line of slope to upward in iron ion; towards down in zinc ion. The static quenching constants (K_{sv}) are calculated 3.27×10^5 and -1.9×10^5, respectively.

3.6. Analysis of ^{1}H-NMR spectrum of Zn complex

We carried out the ^{1}H-NMR experiments of DPYBODPY in the absence of zinc ions in order to understand the binding behaviour. The data of complex obtained are shown in supporting information. The two proton signals of dipyrrin were shifted to downfield and one proton signal was shifted to up field (see Table 1 and support. info). Accordingly, the mechanism of complex formation was estimated between DPYBODPY and metal ions in Figs. 7 and 8.

4. Conclusion

In conclusion, a novel selective fluorescent probe for Zn (II) and Fe (II) with high selectivity has been reported. The Bodipy-dipyrrin conjugate presented in this work give a rapid, sensitive and selective response to Fe (II) and Zn (II), but gives little response when associated with a range of other metal cations. We believe the BPYBODPY probe therefore has a number of potential applications for the qualitative and quantitative detection of Zn (II) and iron (II) ions in solution.

Acknowledgement

This work was supported by the Scientific Research Projects Foundation of Selcuk University (SUBAP-Grant Number 2011-11601191 and 11601195).

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2012.02.006.

References

[1] Wang Huan-Huan, Xue Lin, Yu Cai-Lan, Qianb Yuan-Yu, Jiang Hua. Rhodamine-based fluorescent sensor for mercury in buffer solution and living cells. Dyes Pigm 2011;91:350–5.

[2] Guney O, Cebeci FC. Molecularly imprinted fluorescent polymers as chemosensors for the detection of mercury ions in aqueous media. J Appl Polm. Sci 2010;117:2373–9.

[3] Topal SZ, Gurek AG, Ertekin K, Atilla D, Yenigul B, Ahsen V. Fluorescent probes for silver detection employing phthalocyanines in polymer matrices. Sensor Lett 2010;8:336–43.

[4] Zhang Z, Xu B, Su J, Shen L, Xie Y, Tian H. Color-tunable solid-state emission of 2,2'-biindenyl-based fluorophores. Angew Chem Int Ed 2011; 50:11654–7.

[5] Georgiev NI, Sakr AR, Bojinov VB. Design and synthesis of novel fluorescence sensing perylene diimides based on photoinduced electron transfer. Dyes Pigm 2011;91:332–9.

[6] Erten-Ela S, Ozcelik S, Eren E. Synthesis and photophysical characterizations of thermal-stable naphthalene benzimidazoles. J Fluoresc 2011;21:1565–73.

[7] Crawford SM, Thompson A. Conversion of 4,4-difluoro-4-bora-3a, 4a-diaza-s-indacenes (F-BODIPYs) to dipyrrins with a microwave-promoted deprotection strategy. Org Lett 2010;12:1424–7.

[8] Bura T, Ziessel R. Design, synthesis and redox properties of a fluorene platform linking two different bodipy dyes. Tetrahedron Lett 2010;51: 2875–9.

[9] Sharma A, Neibert K, Sharma R, Hourani R, Maysinger D, Kakkar A. Facile construction of multifunctional nanocarriers using sequential click chemistry for applications in biology. Macromolecules 2011;44:521–9.

[10] Kowada T, Yamaguchi S, Fujinaga H, Ohe K. Near-infrared BODIPY dyes modulated with spirofluorene moieties original research article. Tetrahedron 2011;67:3105–10.

[11] Ziessel R, Harriman A. Artificial light-harvesting antennae: electronic energy transfer by way of molecular funnels. Chem Commun 2011;47:611–31.

[12] Bozdemir OA, Cakmak Y, Sozmen F, Ozdemir T, Siemiarczuk A, Akkaya EU. Synthesis of symmetrical multichromophoric Bodipy dyes and their facile transformation into energy transfer cassettes. Chem Eur J 2010;16: 6346–51.

[13] Barin G, Yilmaz MD, Akkaya EU. Boradiazaindacene (Bodipy)-based building blocks for the construction of energy transfer cassettes. Tetrahedron Lett 2009;50:1738–40.

[14] Bozdemir OA, Sozmen F, Buyukcakir O, Guliyev R, Cakmak Y, Akkaya EU. Reaction-based sensing of fluoride ions using built-in triggers for intramolecular charge transfer and photoinduced electron transfer. Org Lett 2010; 12:1400–3.

[15] Ding Y, Xie Y, Li X, Hill JP, Zhanga W, Zhua W. Selective and sensitive "turn-on" fluorescent Zn^{2+} sensors based on di- and tripyrrins with readily modulated emission wavelengths. Chem Commun 2011;47:5431–3.

[16] Palma A, Gallagher JF, Muller-Bunz H, Wolowska J, McInnes EJL, O'Shea DF. Co(II), Ni(II), Cu(II) and Zn(II) complexes of tetraphenylazadipyrromethene. Dalton T 2009;2:273–9.

[17] Mei Y, Frederickson CJ, Giblin LJ, Weiss JH, Medvedeva Y, Bentley PA. Sensitive and selective detection of zinc ions in neuronal vesicles using PYDPY1, a simple turn-on dipyrrin. Chem Commun 2011;47:7107–9.

[18] Rio Y, Sanchez-Garcia D, Seitz W, Torres T, Sessler JL, Guldi DM. A bisfullerene-bis(dipyrrinato)zinc complex: electronic coupling and charge separation in an easy-to-assemble synthetic system. Chem Eur J 2009;15:3956–9.

[19] Baudron SA. Dipyrrin based homo- and hetero-metallic infinite architectures. Cryst Eng Comm 2010;12:2288–95.

[20] Bronner C, Baudron SA, Hosseini MW, Strassert CA, Guenet A, De Cola L. Dipyrrin based luminescent cyclometallated palladium and platinum complexes. Dalton T 2010;39:180–4.

[21] Rao MR, Bolligarla R, Butcher RJ, Ravikanth M. Hexa boron-dipyrromethene cyclotriphosphazenes: synthesis, crystal structure, and photophysical properties. Inorg Chem 2010;49:10606–16.

[22] Pochorovski I, Breiten B, Schweizer WB, Diederich F. FRET studies on a series of BODIPY-dye-labeled switchable resorcin[4]arene cavitands. Chem Eur J 2010;16:12590–602.

[23] Ziessel R, Ulrich G, Olivier JH, Bura T, Sutter A. Carborane-Bodipy scaffolds for through space energy transfer. Chem Commun 2010;46:7978–80.

[24] Gresser R, Hummert M, Hartmann H, Leo K, Riede M. Synthesis and characterization of near-infrared absorbing benzannulated Aza-BODIPY dyes. Chem Eur J 2011;17:2939–47.

[25] Baudron SA, Salazar-Mendoza D, Hosseini MW. Combination of primary amide and dipyrrin for the elaboration of extended architectures built upon both coordination and hydrogen bonding. Cryst Eng Comm 2009;11: 1245–54.

[26] Telfer SG, McLean TM, Waterland MR. Exciton coupling in coordination compounds. Dalton Trans 2011;40:3097–108.

[27] Hall JD, McLean TM, Smalley SJ, Waterland MR, Telfer SG. Chromophoric dipyrrin complexes capable of binding to TiO_2: synthesis, structure and spectroscopy. Dalton Trans 2010;39:437–45.

[28] Filarowski A, Kluba M, Cieslik-Boczula K, Koll A, Kochel A, Pandey L, et al. Generalized solvent scales as a tool for investigating solvent dependence of spectroscopic and kinetic parameters. Application to fluorescent BODIPY dyes. Photochem Photobiol Sci 2010;9:996–1008.