Boron-Dipyrromethene Dyes for Ion Recognition Studies

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Porphyrrins: Pigments of LIFE

Photosynthesis

O₂ and CO₂ Transport

18π system

e transfer

Metabolism

Chlorophyll a

Heme C (in c-type cytochromes)

B-12

Catalysis
Photosynthesis
Photodynamic Therapy (PDT)

The photosensitiser is given by injection. After time the photosensitiser concentrates in the tumour. The photosensitiser is activated by light. The tumour is selectively destroyed.

Current efforts are aimed to produce a photosensitiser which:

- Is a single compound
- Has increased absorbance in the red region of visible light
- Gives a high quantum yield of triplet formation
- Has good cytotoxic oxygen species generation
- Shows increased selectivity for malignant tissue over normal tissue
- Exhibits no dark toxicity

Photofrin® (Haematoporphyrin)
Porphyryins and their analogues

**Porphyryin**

**Corrole**

**Expanded porphyryin**

**Heteroporphyryin**

\[ X = S, O, Se, Te \]

\[ Y = NH \]

\[ X = S, O, Se, Te \]

\[ Y = S, O, Se, Te \]
Singlet state energy levels of porphyrins with various cores

Comparison of Fluorescence Spectra of ZnN$_4$–N$_3$S Porphyrin Dyad and its Corresponding 1:1 Mixture of Monomers

Covalently linked unsymmetrical porphyrin pentads containing three different porphyrin sub-units

Modified photonic wire

Energy Transfer

Input

Output

\( \lambda_{\text{em}} = 535 \text{ nm} \)

\( \lambda_{\text{em}} = 650 \text{ nm} \)

\( \lambda_{\text{em}} = 678 \text{ nm} \)

\( \lambda_{\text{em}} = 685 \text{ nm} \)

\( \lambda_{\text{em}} = 706 \text{ nm} \)

S. Punidha and M. Ravikanth, (Unpublished Results)
Porphyrin and its applications

- Catalysts
- Non-linear optics
- Molecular electronics\Devices
- Biomimetic models for several enzymes
- Supramolecular chemistry
- Nanomaterials
- Sensors\Biosensors
- Medicine
Boron-Dipyrromethene Dyes

**INTRODUCTION**

- First reported by Triebs and Kreuzer in 1968
- High fluorescent quantum yield
- Negligible triplet state formation
- Intense absorption profile
- Thermal and photochemical stability

**Boron-Dipyrromethene Dyes**

- **Focused positions on BODIPY**
- **Alters electronic properties**

**Boron-Dipyrromethene Dyes**

- **Nucleophilic substitution**
- **Electrophilic substitution**
- **Modification at the boron center**
- **Active methyl groups**
- **Metal catalysed cross coupling**
- **Extending the degree of \( \pi \)-conjugation**
Synthesis of Brominated BODIPYs 1-6

Lakshmi, V.; Ravikanth, M. *Dalton Trans.* 2012, 41, 5903-5911
Photophysical and Electrochemical properties

\[ \Delta E = 80-100 \text{ mV} \]

Absorption and Emission Spectra

V. Lakshmi and M. Ravikanth *Dyes and pigments*, 2013, 3, 665-671
Synthesis of Polyarylated BODIPYs

V. Lakshmi and M. Ravikanth *J. Org. Chem. 2011, 76, 8466-8471*
Synthesis of Polyarylated BODIPYs

Lakshmi, V.; Ravikanth, M. *Chem. Phys. Lett.* 2013, 564, 93-97
Lakshmi, V.; Ravikanth, M. *Indian Patent* (2468/MUM/2011)
Contd...

2+4 Combination:

\[ \text{Reactions representations for 2+4 combination.} \]

3+3 Combination:

\[ \text{Reactions representations for 3+3 combination.} \]

4+2 Combination:

\[ \text{Reactions representations for 4+2 combination.} \]

Multiply Polyarylated BODIPYs

Scheme:

\[
\begin{align*}
16 & \xrightarrow{3 \text{ equiv. NBS}} 24 \ (30\%) \\
& \xrightarrow{\text{B(OH)}_2, \text{Pd(PPh}_3)_4} 25 \ (78\%) \\
& \xrightarrow{5 \text{ equiv. Br}_2} 26 \ (82\%) \\
& \xrightarrow{\text{Pd(PPh}_3)_4, \text{Na}_2\text{CO}_3, \text{THF:Toluene:H}_2\text{O} (1:1:1)} \\
& 13 \ (80\%)
\end{align*}
\]

Lakshmi, V.; Ravikanth, M. RSC Adv. 2014, 4, 44327-44336
Synthesis of 3,5-Diformyl BODIPYs: pH Sensor


**Scheme 1** Synthesis of BODIPYs 3,5-diformyl derivatives

\[ \text{NaHCO}_3, \text{Reflux} \quad \rightarrow \quad \text{OHC} \]

A) Absorption and B) emission spectra of compound 9 in acetate buffer solution as a function of pH
3, 5-Diformyl-BODIPY for Selective Detection of Cyanide Anion

**Position of the formyl group** plays an important role in designing sensor

\[ \text{O} \quad \text{H}_c \]

\[ \text{CN}^- \]

1 equiv. CN⁻

\[ \text{CD}_3\text{CN} \]

\[ \text{N} \quad \text{B} \quad \text{N} \]

\[ \text{F}^- \quad \text{F}^- \]

\[ \text{CN}^- \]

\[ \text{F}^- \quad \text{F}^- \]

\[ \text{N} \quad \text{B} \quad \text{N} \]

\[ \text{CN}^- \]

\[ \text{O} \quad \text{H}_c \]

a) Absorption, b) emission spectra of compound 1; c) emission spectrum of compound 2 titration with varying concentration of CN⁻ (TBACN) ion

Meso-Salicylaldehyde Substituted BODIPYs: Chemodosimetric Sensor for Cyanide Anion

3,5-Bis(Dipyrromethanyl) BODIPY as F⁻ Sensor

Fluorescence, Cyclic Voltammogram of compound 5 during the titration with F⁻ (TBAF)

Benzimidazole substituted BODIPY: Sensing of Hg$^{+2}$ ion

Detection of Hg$^{2+}$ in the cells by spatially resolved fluorescence spectroscopy

- BODIPY dye 1 labeled human breast adenocarcinoma cells (MDA-MB-231) in the absence of Hg$^{2+}$ (A) and in presence of 10 µM (B) and 30 µM (C) of Hg$^{2+}$. 
Synthesis of Phenylhydrazone Substituted BODIPYs

Uv-Visible spectra under various anions

Titration with fluoride anion

Lakshmi, V.; Ravikanth, M. *J. Mater. Chem. C* 2014, 2, 5576-5586
Cation Sensing Studies for Phenylhydrazone Substituted BODIPYs

Lakshmi, V.; Ravikanth, M. *J. Mater. Chem. C* 2014, 2, 5576-5586
Changes in (a) absorption, (b) fluorescence spectra of BODIPY 2 (5 μM) upon titration with Picric acid (0 to 30 equiv.) in CH₃CN/H₂O (9:1; v/v) solution. (λₑₓ = 488 nm).
Absorption, (b) emission spectral changes of BODIPY 2 (5 μM) upon titration with Cys (0-35 equiv.) in pH 7.4 PBS/CH$_3$CN (9:1, v/v). The spectra were recorded after incubation of the probe with Cys for 30 min ($\lambda_{ex} = 510$ nm).

Synthesis of 3-Amino BODIPY and its Derivatives

Smaragdyrin-BF$_2$ complex

Extinction coefficients
- Smaragdyrin: 14100 M$^{-1}$ (695 nm)
- Smaragdyrin-BF$_2$ complex: 52400 M$^{-1}$ (702 nm)

**B(OH)₂ Smaragdyrin as a Anion Sensor**

Sapphyrin-BF$_2$-Smaragdylrin Dyad as Anion Sensor

HSO₄⁻ ion sensing phenomenon of Calixoxasmaragdyrin

\[
\text{HSO}_4^- \text{ ion sensing phenomenon of Calixoxasmaragdyrin}
\]

\[
\text{R} = -\text{H} : 5 \\
\text{R} = -\text{CH}_3 : 6
\]

\[
\text{R} = -\text{H}; 2a (12\%) \\
\text{R} = -\text{CH}_3; 2b (11\%)
\]

**Absorption Titration**

**Job's Plot**

Isosbestic points at 431, 545, 778 nm

Binding constants \(1.4 \times 10^3 \text{ M}^{-1}\)

Tamal, C.; Avijit, G.; Madhu, S.; Ravikanth, M. *Dalton Trans.* 2014, 43, 6050-6058
**Hg^{2+}** ion sensing phenomenon of Calixazasmaragdyrin

Isosbestic points at 600, 616, 740 nm

Binding constants $1.1 \times 10^5$ M$^{-1}$

Summary

- A series of brominated BODIPYs were synthesized and used as precursors to prepare different types of polyarylated BODIPYs.

- 3,5-Diformyl BODIPYs were synthesized in good yields using simple reaction conditions and used extensively to prepare different types of BODIPY derivatives for ion sensing applications.

- Highly fluorescent Boron-smaragdyrin complexes were synthesized and used for sensor applications.

- Calixsmaragdyrins were readily synthesized and demonstrated their specificity for cation and anion sensing applications.
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