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Dual Emissive Ytterbium (III) Complexes with π-Conjugated BODIPY-Bipyridine Ligands

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Abstract

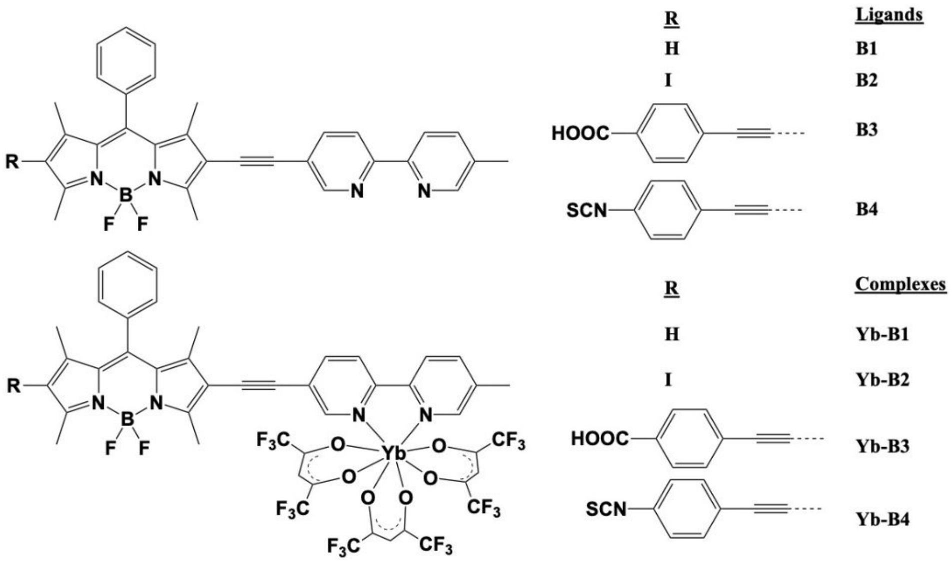
Four BODIPY-functionalized bipyridine ligands (B1, B2, B3 and B4) were synthesized for sensitizing the near-infrared emission of Yb (III) ions. In these ligands, a BODIPY moiety was conjugated to 2,2′-bipyridine through an acetylene spacer at its C2 position, whereas its C6 position was substituted by H (B1), iodine (B2), 4-carboxylphenylacetylene (B3) or 4-thiocyanophenylacetylene (B4). The ligands exhibit strong absorption in the visible region and readily form stable complexes with ytterbium (III) trishexafluoroacetylacetonate ($hfac^-$) hydrate in dichloromethane. Single-crystal X-ray diffraction analysis for Yb-B2 showed that the BODIPY unit almost falls into the bipyridine plane with Yb (III) being coordinated by six O from $hfac^-$ and two N atoms from bipyridine. All complexes exhibit strong absorption between 530 and 570 nm and can sensitize the ytterbium (III) for its emission at 980 nm under the UV-VIS light illumination. Interestingly, the visible emission from the complex increased when excited at 375 nm, making the complexes dual emissive, which is due to the increased absorption of the complex at 375 nm and inefficient energy transfer from BODIPY moiety to the Yb(III) ion.

Keywords: BODIPY, 2,2′-bipyridine, ytterbium, near-infrared, emission, complexes

Introduction

Near-infrared (NIR) emission of lanthanide ions is characterized by its sharp peaks, long lifetime, and almost fixed frequency due to the nature of the emission from inner *f* - *f* transition. [1-3] For example, ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition in ytterbium (III) usually gives emission at 980 nm with a lifetime in μs ranges.[4] Such optical properties make lanthanide materials promising alternatives to conventional organic dyes as fluorescent labels for medical diagnosis. [4-13] They can be integrated with time-gated technology or high-sensitive near-infrared detectors to reduce or even eliminate the autofluorescence, and therefore increase the sensitivity. [14] The sensitivity can be further increased by large Stokes shifts, which is difficult to achieve in conventional organic dyes. However, it is difficult to initiate luminescence by direct excitation of lanthanide ions due to the poor absorption of light in the visible region.[1] An effective way is to use organic chromophores as antennas to sensitize the emission, a phenomenon that was reported by Weissman in 1942. [15] In this process the organic chromophores absorb photons and transfer energy from their excited states to the excited states of the lanthanide *via* a Förster or a Dexter mechanism. [1] The strategy provides a convenient way to use the UV or the visible light instead of high intensity coherent light sources like laser to produce NIR emission. Over the years, numerous complexes have been constructed based upon this concept and NIR emission has been achieved mostly under short wavelength excitation, [16, 17] which is problematic as far as the photobleaching is concerned. It is quite challenging to obtain strong NIR emission under a longer wavelength excitation. [9, 18-24] Ouahab *et al* [25] developed a 4-tetrathiafulvalene-2,6-pyridinecarboxylic acid dimethyl ester (L) as a sensitizer and synthesized [Er(hfac)$_3$(L)] complex and a characteristic emission at 1530 nm was observed under excitation at ~ 500 nm. Rigaut *et al* [26] used a ruthenium acetylide functionalized 2,2′-bipyridine (L), which has a broad absorption in the visible region. Its ytterbium (III) and neodymium (III) complexes exhibit characteristic emission in the NIR region upon excitation at 450 nm. Zhang *et al* studied a series of porpholactonate ytterbium (III) complexes that can be sensitized by the visible light. [27-29] A recent report [30] on perfluorinated porphyrinate ytterbium (III) complex with emission efficiency ~ 25% in dichloromethane demonstrated the possibility of higher emission efficiency through structural modifications of the complexes.

BODIPY dyes have been explored as strong visible light sensitizers for NIR emission of lanthanides. [31] BODIPY is a family of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene compounds with unique characteristics, including tunable spectral coverage in the visible region, high absorption coefficients, and exceptional chemical and photostability. Bunzli *et al* first reported [32] that a BODIPY functionalized terpyridine can sensitize the NIR emission of ytterbium (III) and neodymium (III) complexes of nitrates under excitation at 514 nm, though the emission efficiency was quite low (0.31% and 0.0016% for ytterbium and neodymium, respectively). In a follow up study, these authors linked a BODIPY dye to a benzoic acid and prepared nine-coordinate Er and Yb complexes, which can be excited at 583 nm but the sensitization is inefficient (20-60%). [33] In our previous studies, it was found that the BODIPY moiety that is attached to 8-hydroxylquinoline or 1,10-phenanthroline through its *meso* position is an excellent green light sensitizer for the near-infrared emission of ytterbium (III). [34-36] The dramatic quenching of fluorescence from BODIPY in these complexes indicate the excellent energy transfer. We also conjugated a BODIPY unit to a porphyrin through an acetylene spacer. The resulting ligand showed red-shifted absorption at 610 nm and the Yb(III) complex exhibited characteristic NIR emission was obtained under the excitation of this wavelength.[22] In this study, we report four BODIPY-functionalized 2,2′-bipyridine ligands and their Yb(III) complexes Yb-B*i* (*i* = 1 - 4) as shown in **Scheme 1**. The introduction of an iodine atom to the ligand (B2) in the 6-position of the BODIPY dyes enhanced the NIR emission compared its parent complex. It was found that the π-conjugation ligands (B3 and B4) effectively enable the red-shift of the absorption and characteristic emission from Yb(III) in the NIR region was observed with a broader range of excitation wavelength from the UV region up to 575 nm. The further inclusion of an SCN group for potential labeling to the biological molecule had minimal impact on the photophysical properties; however, the absorption and fluorescence of the ligand (B3) were split, most likely due to the formation of intermolecular H-bonding formation between carboxylic acid group.



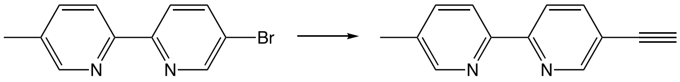
Scheme 1. Chemical structures of ligands and their ytterbium (III) complexes.

Experimental

General

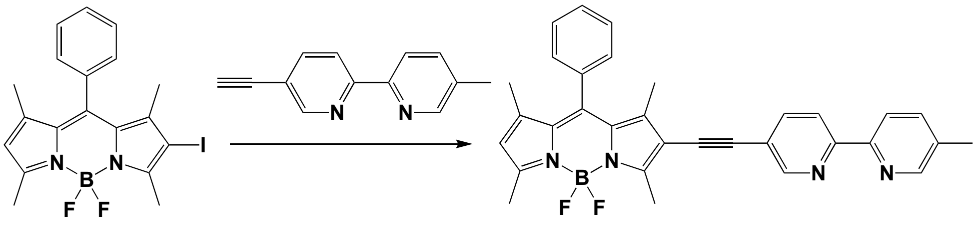
All reagents and solvents were purchased from commercial sources and employed without further purification unless otherwise stated. The 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was supplied by Biosynth International, Inc. Extra dry tetrahydrofuran (THF), dimethylformamide (DMF), deuterated chloroform ($CDCl_3$), N-iodosuccinimide (NIS), copper(I) iodide (CuI), tetrakis(triphenylphosphine) palladium (0), boron trifluoride diethyl etherate (48%), 2,4-dimethylpyrrole, and benzaldehyde, ytterbium tris(hexafluoroacetylacetonate) dihydrate were purchased from ACROS Organics. The 200 or 230-400 mesh silica gel was purchased from Dynamic Adsorbents, Inc. NMR spectra were obtained on a 400 MHz Bruker Avance II-NMR spectrometer, using ACROS Organics chloroform-d 99.8% D, containing 0.03% (v/v) TMS. All ^{1}H NMR signals were referenced to TMS. The chemical shifts were reported in parts per million (ppm). For the signal splitting, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; bs, broad singlet. UV-Vis absorption spectra were performed on a Cary 100 Series UV-Vis Dual Beam Spectrophotometer over a range of 200-800 nm. BDP was prepared from the reaction between benzaldehyde and 2,4-dimethylpyrrole, which was converted to its monoiodinated derivative (I-BDP) as we described previously.[36] 5-bromo-5′-methyl-2.2′-bipyridine was prepared according to the literature method.[37]

Synthesis of EN-BPY



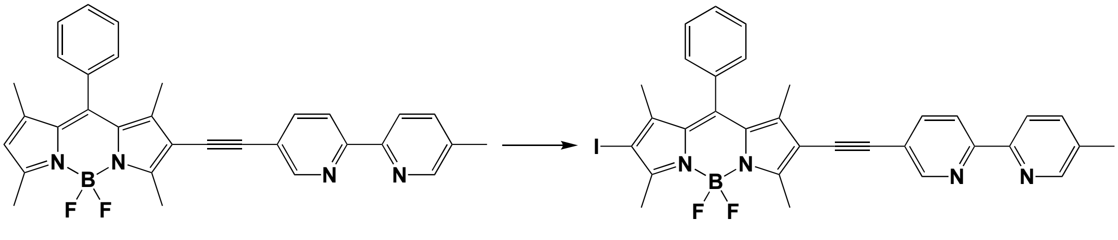
Triethylamine (10.0 mL, 71.60 mmol) and dry THF (30.0 mL) were added to [Pd(PPh$_3$)$_2$Cl$_2$] (0.422 g, 0.60 mmol), CuI (0.190 g, 0.99 mmol), and 5-bromo-5′-methyl-2.2′-bipyridine (1.00 g, 4.0 mmol) under a nitrogen atmosphere. Ethynyltrimethylsilane (1.4 mL, 10.02 mmol) was added, and the resulting solution was stirred overnight at room temperature. Reaction mixture was filtered, and the final product was extracted using Soxlet extraction method and hexane was used as a solvent. Solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel, CH$_2$Cl$_2$) to give product as a pale brown color powder. Yield: 0.890 g, 82.8%. The product (0.264 g, 0.99 mmol) was then combined with K$_2$CO$_3$ (0.250 g, 1.80 mmol) in methanol (50.0 mL) and stirred for one hour at room temperature. The suspended K$_2$CO$_3$ was decanted, and solvent was removed *in vacuo* and observed pale yellow color powder as EN-BPY. Yield: 0.182 g, 95 %. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.75 (s, 1H, H), 8.51 (s, 1H, H), 8.36 (d, J = 8.1 Hz, 1H, H), 8.30 (d, J = 8.1 Hz, 1H, H), 7.89 (d, J = 8.3 Hz, 1H, H), 7.87 (d, 8.3 Hz, 1H, H), 3.28 (s, 1H, H), 2.40 (s, 3H, H).

Synthesis of B1



Compound I-BDP (0.107 g, 0.240 mmol), 5-ethynyl-5′-methyl-2,2′-N-bipyridine (0.046 g, 0.234 mmol), CuI (0.0041 g, 0.024 mmol) and [PdC(PPh$_3$)$_2$Cl$_2$] (0.016 g, 0.024 mmol) were dissolved in THF (30 mL) and Et$_3$N (10 mL) in a pressure tube under argon. The tube was sealed, and the mixture was then stirred at 50°C for two days. The solvent was then removed under reduced pressure and crude product was purified by a column chromatography (silica gel, DCM:MeOH 10:1,v/v) to give B1 as dark purple solid. Yield: 0.127 g, 52.0%. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.51 (s, 1H), 8.32 (d, 1H), 8.31 (s, 1H), 7.84 (d, 1H), 7.63 (s, 1H), 7.52-7.51 (m, 3H), 7.24 (d, 2H), 6.05 (s, 1H), 2.72 (s, 3H), 2.59 (s, 3H), 2.39 (s, 3H), 1.51 (s, 3H), 1.41 (s, 3H).

Synthesis of B2

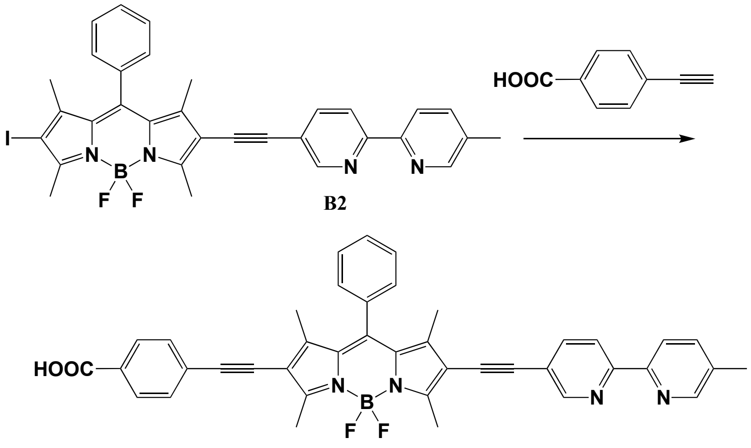


PH1

B2

To a compound B1 (0.085 g, 0.35 mmol) dissolved in dichloromethane (100 mL) in an ice-bath was added N-iodosuccinamide (0.078 g, 0.35 mmol) in dichloromethane (40 mL) dropwise within 30 min. Reaction mixture was then stirred over night at room temperature. After solvent was removed under reduced pressure, the crude product was purified on a column chromatography (silica gel, $CHCl_3$) to give B2 as dark purple color powder. Yield: 0.186 g, 83%. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 8.71 (s, 1H), 8.51 (s, 1H), 8.37 (d, 1H), 8.31 (s, 1H), 7.84 (d, 1H), 7.63 (d, 1H), 7.54-7.51 (m, 3H), 7.30 (m, 2H), 2.73 (s, 3H), 2.67 (s, 3H), 2.40 (s,3H), 1.52 (s, 3H), 1.42 (s, 3H)

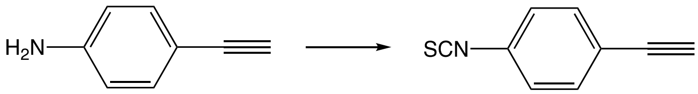
Synthesis of B3



B3

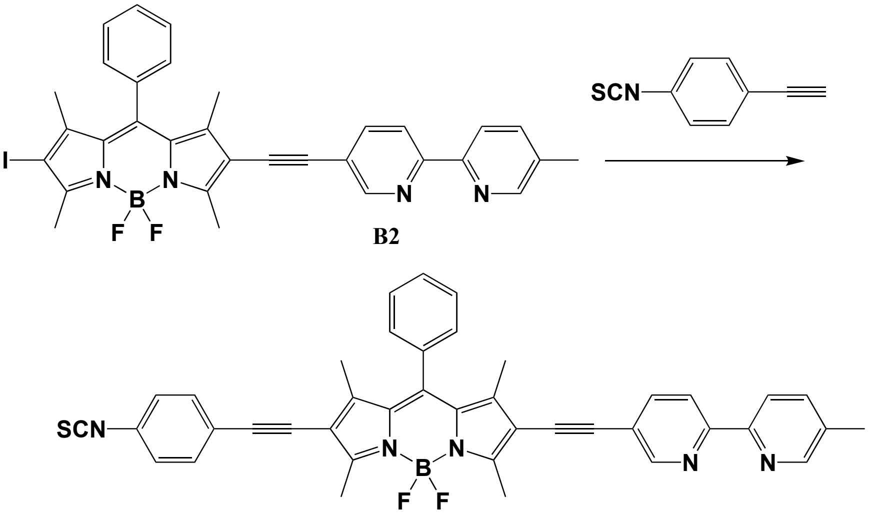
4-Ethynylbenzoic acid (0.015 g, 0.1 mmol), compound B2 (0.065 g, 0.1 mmol), CuI (0.02 g, 0.01 mmol), and $[Pd(PPh_3)_2Cl_2]$ (0.007 g, 0.005 mmol) were dissolved in THF (30 mL) and Et_3N (10 mL) in a pressure tube under argon. The tube was sealed and was magnetically stirred at 50 °C for 24 h. Then the solvent was removed under reduced pressure. The crude product was purified on a column chromatography (silica gel, $CHCl_3$:MeOH 10:2) to give B3 as dark purple solid. Yield: 0.025 g, 38%. ^1H NMR (400MHz, $CDCl_3$) δ (ppm) %. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.71 (s, 1H), 8.51(s, 1H), 8.36 (d, 2H), 7.84 (d, 1H), 7.72 (d, 1H), 7.65 (d, 1H), 7.54 (m, 5H), 7.48 (d, 1H), 7.29 (m, 2H), 2.73 (s, 3H), 2.67 (s, 3H), 2.40 (s, 3H), 1.52 (s, 3H), 1.42 (s, 3H).

Synthesis of SCN-EN



4-ethynylbenzenamine (1.0 g, 17.1 mmol) and trimethylamine (5 mL, 71.6 mmol) in 15 mL $CHCl_3$ were placed in a flask under an atmosphere of N_2. A solution of thiophosgene (3 mL, 38.6 mmol) in 20 mL $CHCl_3$ was added drop wise at room temperature for 1h. The mixture was heated under reflux for 2h, and then cooled to room temperature. The mixture was quenched by addition of 20 mL cold water and extracted with 300 mL (3×100 mL) $CHCl_3$. The organic layer was washed with H_2O (3×50 mL), dried on Na_2SO_4 and concentrated to dryness to give yellow residue. The crude product was purified using column chromatography (silica gel, Hexane: CH_2Cl_2 3:1) to give SCN-EN as pale-yellow solid. Yield: 0.87 g, 64%. ^1H NMR (400MHz, $CDCl_3$) δ (ppm) 7.47 (d, 2H), 7.18 (d. 2H), 3.16 (s, 1H).

Synthesis of B4

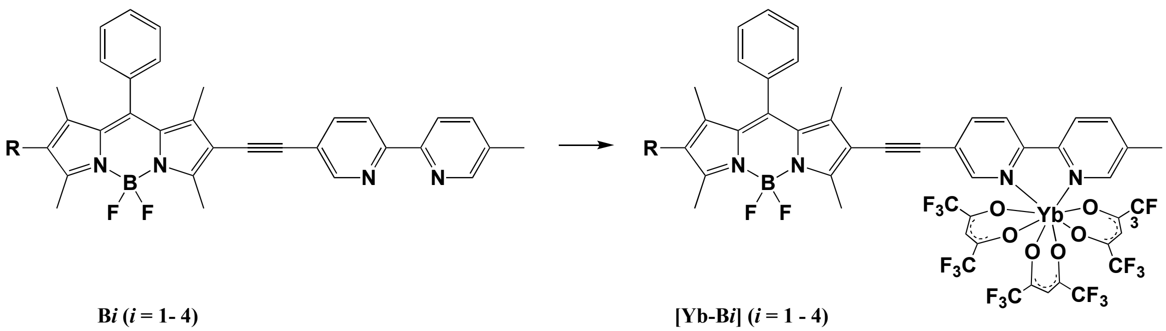


B2

B4

1-Ethynyl-4-isothiocyanatobenzene (0.016 g, 0.1 mmol), compound B2 (0.065g, 0.1 mmol), CuI (0.002 g, 0.01mmol), and [Pd(PPh_3)$_2$$Cl_2$] (0.0035 g, 0.005 mmol) were dissolved in THF (30 mL) and Et_3N (10 mL). Reaction was stirred for 24 h at 50°C. Then reaction mixture was concentrated under reduced pressure and crude product was purified using column chromatography (silica gel, $CHCl_3$: MeOH 10:2) to give B4 as dark purple solid. Yield: 0.027 g, 40%. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.50 (s, 1H), 8.35 (d, 2H), 7.84 (d, 1H), 7.70 (d, 1H), 7.63 (d, 1H), 7.54 (m, 5H),7.40 (d, 1H), 7.30 (m, 2H), 2.73 (s, 3H), 2.67 (s, 3H), 2.40 (s, 3H,), 1.52 (s, 3H), 1.42 (s, 3H).

Synthesis of Yb(III) complexes [Yb(hfac)$_3$(B*i*)] (*i* = 1 - 4)



B*i* (*i* = 1- 4)

[Yb-B*i*] (*i* = 1 - 4)

All four ytterbium complexes were synthesized following a similar method. A typical procedure is described here for [Yb(hfac)$_3$(B1)]. The B1 ligand (0.052 g, 0.10 mmol) was dissolved in CH_2Cl_2

(50.0 mL), then [Yb(hfac)$_3$·(H$_2$O)$_2$] (0.079 g, 0.10 mmol) in CH_2Cl_2 (15.0 mL) was added to the ligand solution. The resulting mixture was magnetically stirred for 1 h at room temperature, and then concentrated under reduced pressure. The crude product was recrystallized using CH_2Cl_2 and hexane. Yields: Yb-B1, 0.120 g 95%; Yb-B2, 0.132 g, 94%; Yb-B3b, 0.135 g, 95%; Yb-B4, 0.133 g, 93%. Elemental Analysis: Yb-B1: $C_{47}H_{30}BF_{20}N_4O_6Yb$, Calc.: C, 43.07; H, 2.31; N, 4.27. Found: C, 43.12; H, 2.25; N, 4.32. Yb-B2: $C_{47}H_{29}BF_{20}IN_4O_6Yb$, Calc.: C, 39.30; H, 2.03; N, 3.90. Found: C, 39.42; H, 2.10; N, 4.05; Yb-B3: $C_{56}H_{34}BF_{20}N_4O_8Yb$. Calc. C, 46.24; H, 2.36; N, 3.85. Found: C, 46.38; H, 2.21; N, 3.92. Yb-B4: $C_{56}H_{33}BF_{20}N_5O_6SYb$, Calc.: C, 45.82; H, 2.27; N, 4.77. Found: C, 45.67; H, 2.18; N, 4.93.

Photoluminescence measurement

Steady-state fluorescence spectra in the UV-VIS and NIR regions were obtained on an FS5 fluorimeter (Edinburgh Instrument, Inc.) with a 150 W Xenon arc lamp as the light source. The decay curves of the samples in the visible region were also acquired on the FS5 using single-photon-counting technology at emission maximum. A pulsed laser diode EPL 375 (Edinburg Instrument, Inc) with wavelength of 375 nm was used as light source. The lifetimes in the visible region were obtained from exponential fitting of data. Quantum yield in the visible region was measured using following equation:

$$\Phi\mathrm{x} = \emptyset_{ST}\left[\frac{Grad_X}{Grad_{ST}}\right]\left[\frac{n_X}{n_{ST}}\right]^2$$

where Φ is the fluorescence quantum yield, X and ST stand for sample and reference, respectively. Grad is the gradient from the plot of integrated fluorescence intensity *vs* absorbance of five samples with different concentrations, and n is the refractive index of the solvents. Rhodamine 6G in ethanol (Φ_{ST} = 0.94, λ_{ex} = 488 nm) was used as a reference.[38] The decay curves of complexes in the NIR region were recorded as we described previously. [35, 39]

Single-crystal x-ray diffraction analysis.

The crystals were mounted on glass fiber for data collection. Diffraction measurements were made on a CCD-based commercial X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å). The frames were collected at ambient temperature with a scan width 0.3° in ω and integrated with the Bruker SAINT software package using the narrow-frame integration algorithm. [40] The unit cell was determined and refined by least squares upon the refinement of *XYZ*-centeroids of reflections above $20\theta(I)$. The data were corrected for absorption using SADABS program.[41] The structures were refined on F^2 using the SHELX97. [42] Crystal data for [Yb(hfac)(B2)].CH_2Cl_2: $C_{48}H_{31}BCl_{12}F_{20}IN_4O_6Yb$, MW = 1521.42, monoclinic, space group = P2(1)/c, a = 12.6619(5), b = 18.7236(8), c = 22.661(1) Å, β = 91.456(2)°, V = 5370.7(4) Å^3, Z = 4, $\rho_{calcd.}$ = 1.882 Mgm^{-3}, μ = 9.759 mm^{-1}, $F(000)$ = 2948, T = 100 (2) K. 81326 reflections were measured, of which 9827 were unique (R_{int} = 0.0824). Final R_1 = 0.0840 and wR_2 = 0.1320 values were obtained for 9827 observed reflections with I>2σ(I), 755 parameters, and GOF = 1.023. Detailed crystal parameters and xyz coordinates can be found at the end of the SI.

Theoretical calculations

Theoretical calculations were performed at a density functional theory (DFT) level using Gaussian 09 software. [43] The initial input structures were built using structure builder tools. The ground state geometries of ligands were optimized using 6-31G as basis set and B3LYP as functional in vacuum. No negative frequency was found in the final optimized structures. The time-dependent (TD) DFT calculations were carried out using 6-31G as basis set and B3LYP as functional in dichloromethane. The continuum (CPCM) model was used for mimicking the solvent effect. The data were analyzed using GaussView 6.

Results and Discussion

Synthesis and Characterization. Scheme 1 shows the synthetic procedure of four ligands, B*i* (I = 1 – 4), and their complexes. The B1 and B2 each has a bipyridine conjugated to the BODIPY core through an ethynyl group at C2 position, whereas its opposite C6 position has either an H (B1) or an I atom (B2). Synthesis of B1 started from the preparation of BDP. 2,4-dimethylpyrrole and benzaldehyde were reacted in dry dichloromethane under an inert atmosphere at room temperature, followed by addition of DDQ for oxidation and $BF_3.OEt_2$ to insert an BF_2 unit in the presence of Et_3N. The BDP was then iodinated to convert to I-BDP using NIS at low temperature. The EN-BPY was prepared according to the literature method.[44] The I-BDP was then reacted with EN-BPY to form B1 under Sonogashira cross-coupling reaction conditions. The B2 was then coupled respectively with 4-ethynylbenzoic acid and 1-ethynyl-4-isothiocyanatobenzene under Sonogashira coupling conditions to give the ligands B3 and B4. All four ligands were purified on column chromatography using DCM/MeOH as elute. In general, the product showed a more pinkish color that is different from the reactants and therefore it is relatively easy to identify the desired band. Purity of all samples was validated by running a series of thin-layer chromatography in DCM/MeOH with different polarity ^1H NMR in $CDCl_3$.

The complexes were prepared by direct substitution reaction between $[Yb(hfac)_3(H_2O)_2]$ and ligand B*i* (*i* = 1- 4) in dichloromethane at room temperature. The final product was obtained by precipitation from dichloromethane/hexane. The compositions of the complexes were confirmed by elemental analysis. The structure of Yb-B2 was further ascertained by single-crystal X-ray diffraction analysis. The crystals were obtained by slow diffusion of hexane into a solution of Yb-B2 in dichloromethane. A perspective view of the complex is shown in **Figure 1.** It showed that the central Yb^{3+} ion is eight-coordinate, surrounded by two N atoms from the bipyridine unit and six O atoms from three hfac$^-$ ligands. The Yb-O distances are slightly longer than that of Yb-N. The Yb ion is well shielded by six CF$_3$ units and bipyridine. The coordination geometry around Yb atom can be described as a distorted square antiprisim. Such a coordination environment has been observed in several analogues of [Ln(hfac)$_3$(L)] complexes.[26, 45, 46] It should be mentioned that BODIPY moiety and bipyridine unit do not fall into a same plane; instead, a torsion angle of 17.87° was observed. The phenyl group on the *meso* position is almost perpendicular (84.47°) to the BODIPY core.

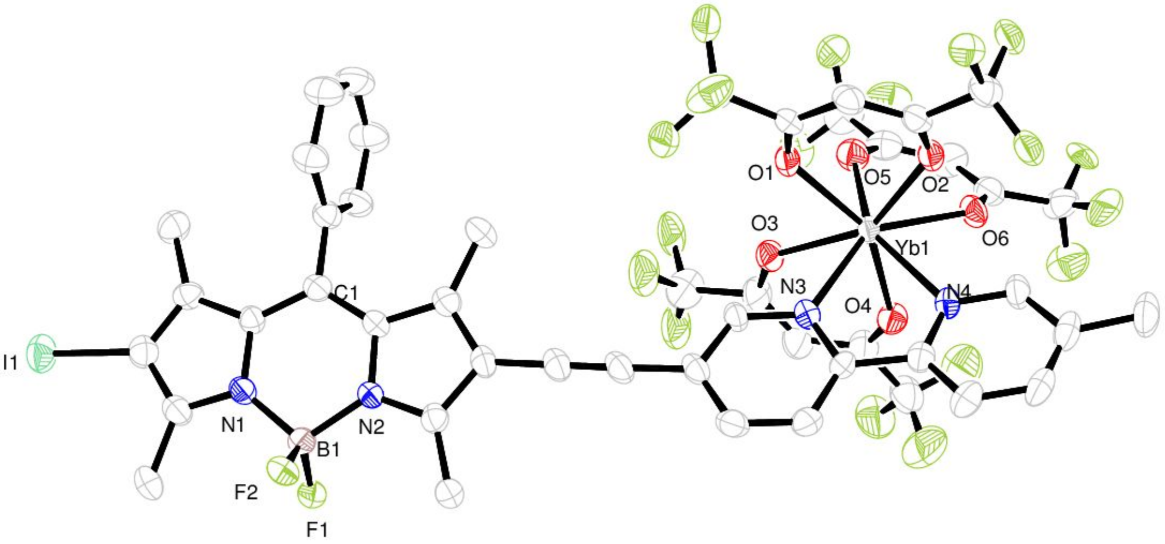


Figure 1. ORTEP diagram of a single-crystal structure of Yb-B2 with 50% thermal ellipsoid probability. Hydrogen atoms were omitted for clarity. All F atoms on hfac$^-$ were disordered and only one set of disordered F atoms was shown for clarity.

Photophysical Properties of Ligands. The absorption spectra of ligands in dichloromethane are shown in **Figure 2** and physical data are summarized in **Table 1**. Each ligand shows a strong peak between 537 and 573 nm. Compared to BDP having no substituent at C2 and C6 positions, four dyes exhibited red-shifted absorption and significantly decreased absorption coefficients due to the extended π-conjugation system in the dyes. The absorption maximum of iodinated derivative B2 shifted about 15 nm (～ 477 cm^{-1}) toward the red region. The B3 has a much larger π– conjugation and exhibited a 36 nm red shift of absorption in respect to the B1. The B4 is also bearing a similar π– conjugation to B3, however, only 16 nm (~ 543 cm^{-1}) red shift was observed. This could be due to the strong electron withdrawing property of -NCS group. It has been reported that the similar group will lead to the blue shift of the absorption.[47, 48]

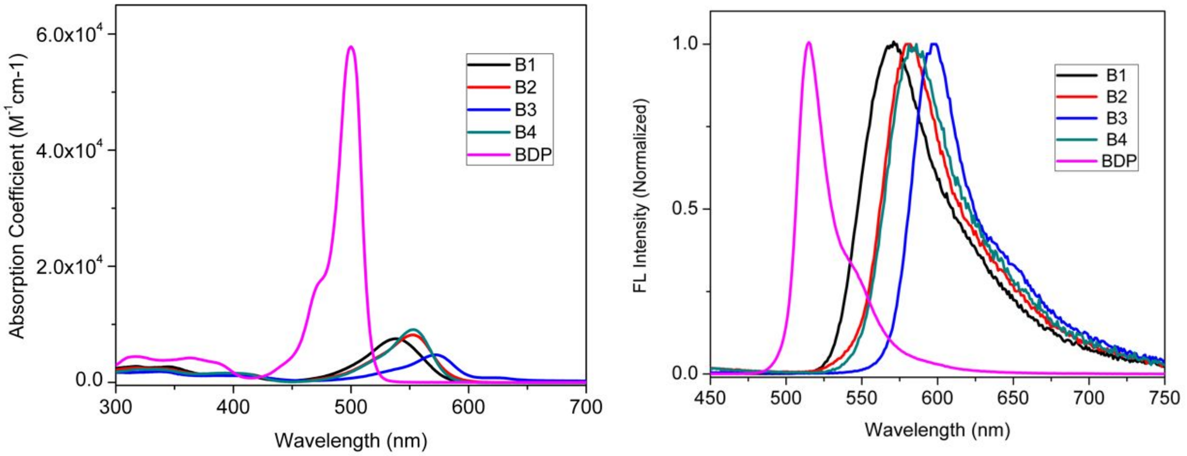


Figure 2. Left: UV/vis absorption spectra of ligands in DCM with a concentration of 3.9 ×10^{-5} *M* for all four ligands and the concentration for BDP was 5.0 × 10^{-6} *M*. Right: Normalized emission spectra (λ_{ex} = 375 nm) of ligands in DCM.

Table 1. Spectroscopic data for ligands in dichloromethane at room temperature.

Compound	Absorption (λ in nm, ε in $M^{-1}cm^{-1}$)	Emission [a] (λ in nm, τ in ns)	QY[b]	Excitation[c] (λ in nm)	k_r [d] (s^{-1})	k_{nr} [e] (s^{-1})	ϕ_{ISC} [f]
BDP	500 (5.3 × 10^4)	516 (4.5)	0.76 ± 0.03	502	5.9×10^9	0.05×10^9	0.24
B1	535 (7.43 × 10^3)	572 (3.7)	0.47 ± 0.02	533	0.13×10^9	0.14×10^9	0.53
B2	549 (8.05 × 10^3)	580 (2.7)	0.21 ± 0.01	552	0.07×10^9	0.29×10^9	0.79
B3	569 (4.74 × 10^3), 620	597 (3.4)	0.31 ± 0.04	571	0.09×10^9	0.20×10^9	0.69
B4	551 (9.04 × 10^3)	583 (3.5)	0.11 ± 0.01	551	0.03×10^9	0.25×10^9	0.89

a: λ_{ex} = 375 nm. b: λ_{ex} = 488 nm for quantum yield measurement. c: λ_{em} = 620 nm. d: calculated using $k_r = \phi_F / \tau$, in which τ refers to lifetimes in the visible region. e: calculated using $k_{nr} = (1-\phi_F)/\tau$, in which τ refers to lifetimes in the visible region. f: calculated using $\phi_{ISC} = 1-\phi_F$.

The emission spectra for B1-B4 ligands in DCM are also shown in **Figure 2**. Emission wavelength has increased from B1, B2 to B4 whereas B3 ligand is exhibiting the longest emission wavelength. Consistent with the absorption spectra, B2 and B4 showed very similar emission maximum at ~ 572 nm and excitation spectra (**Figure S1**). All four ligands show a small Stokes shift (~ 20 nm, 790 cm^{-1}), which is quite typical for most BODIPY dyes. The emission efficiencies are lower than that of BDP as shown by the measured quantum yields in DCM. The lower emission efficiency of B2 is due to the "heavy atom" effect of I atom.[49] The fluorescence decay curves of four ligands at their emission peak positions are quite similar (**Figure S2**), therefore their lifetimes are quite close to each other (3.0 to 3.7 ns).

The emission efficiency of B3 is poor in DCM but strong in DCM/MeOH as shown in **Figure 3**. The compound showed two absorption peaks (569 nm and 620 nm) in DCM. When a small amount of MeOH was added dropwise, the longer peak slowly decreased with a simultaneous increase of the peak at 569 nm. When a large excess of MeOH was added, the peak at 620 nm disappeared completely with a significant enhancement of emission at 592 nm. We also monitored the absorbance and fluorescence of B3 in DCM under different concentrations (**Figure S3**). It was found that its absorbance at 620 nm slowly increased and surpassed the absorption at 569 nm upon increasing the concentration, whereas the emission intensity almost reached a plateau under the same conditions. Adding MeOH dramatically enhanced the absorption at 569 nm and emission. This observation could be due to the breakdown of polymeric species formed between benzoic acid and bipyridine groups through H-Bonding by MeOH. [50-52]

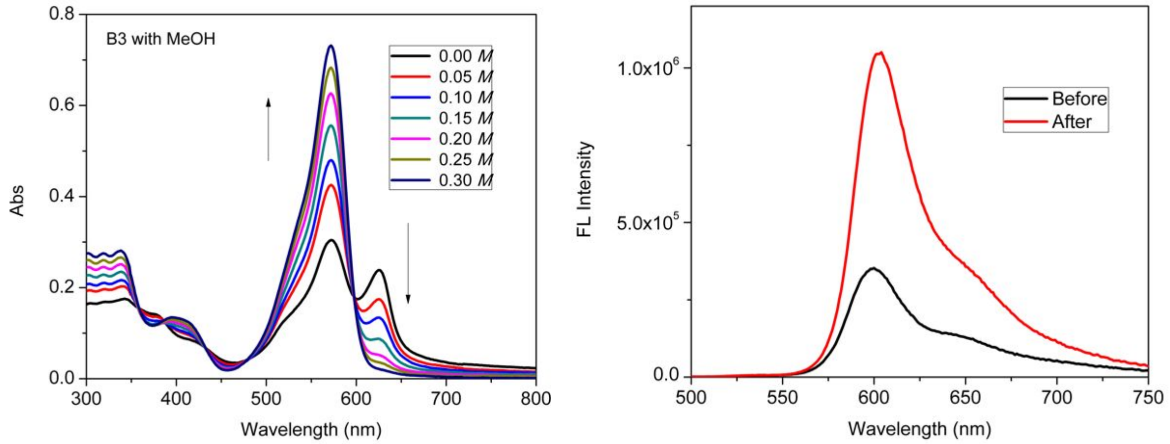


Figure 3. Left: Changes of absorption of B3 with different concentrations of MeOH. Right: Changes of fluorescence of B3 in DCM with and without adding methanol. The excitation wavelength λ_{ex} = 375 nm. The concentration of B3 in DCM was 3 $\times 10^{-6}$ *M*. The concentration of added MeOH increased from 0.05 mol/L - 0.30 *M*.

Photophysical Properties of Complexes. The absorption and emission spectra of the complexes as shown in **Figure 4** were measured in CH_2Cl_2 at room temperature. Spectroscopic data are tabulated in **Table 2**. The complexes have absorption in the 350 nm – 650 nm range. It is worth pointing out that the strong peak at about 620 nm from ligand B3 did not appear in its complex, which is consistent with the proposed breakdown of intermolecular H-bonding after the formation of the complex. All complexes gave characteristic emission at 976, 1005, and 1031 nm as shown in **Figure 5** and they can be assigned to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.[53] The peak intensities at 1005 and 1031 nm are higher than that of 976 nm, which is indicative of an eight-coordinate environment as we observed in porphyrinated ytterbium (III) complexes.[9, 54] All complexes showed similar single exponent decay behavior of emission in the NIR region and the decay curve for Yb-B1 is also shown in **Figure 5** and **Figure S4**. The calculated lifetimes are about 11 µs.[55] The estimated ϕ_{Yb} yield is about 0.55% using the equation $\phi_{Yb} = \tau_{obs}/\tau_{rad}$,[1] where τ_{rad} = 2.0 ms,[24, 56, 57] which is comparable to the calculated values from other similar complexes.[24]

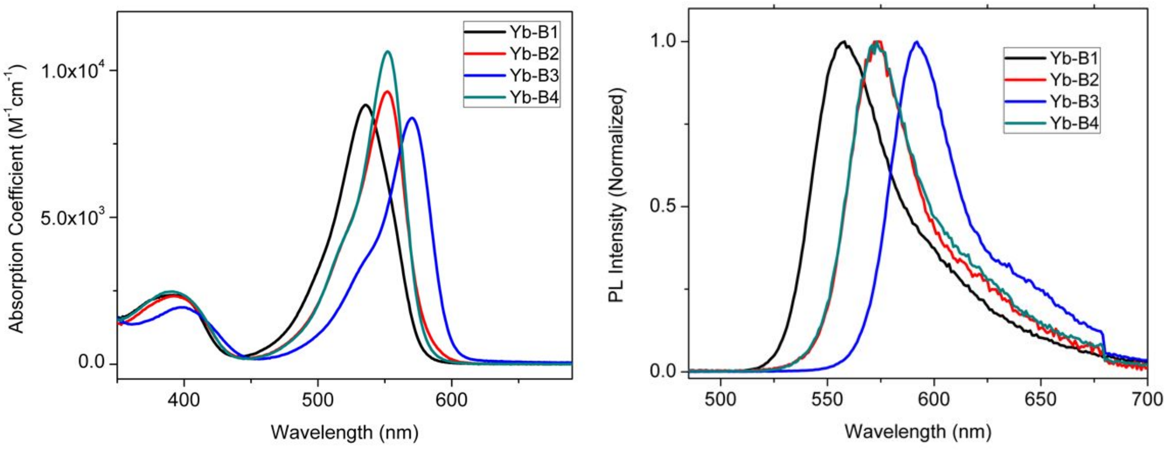


Figure 4. Left: UV/vis absorption spectra of the complexes in DCM with a concentration of 3.9 $\times 10^{-5}$ *M*. Right: Normalized emission spectra of the complexes in DCM with a concentration of 1.6 $\times 10^{-6}$ *M*. The excitation wavelength λ_{ex} = 375 nm. The sharp drop of emission at around 680 nm was due to the second order scatter of the sample.

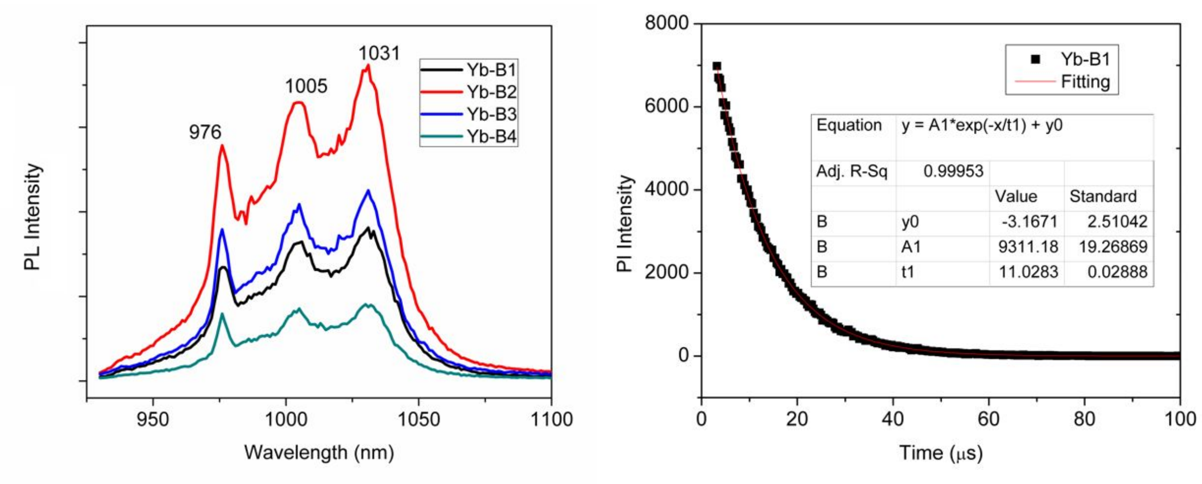


Figure 5. Left: NIR emission spectra of four ytterbium (III) complexes. The excitation wavelength λ_{ex} = 375 nm. Right: Decay of NIR emission of Yb-B1 in DCM (λ_{em} = 980 nm). The concentration of the complex ~2.5 $\times 10^{-4}$ *M*.

Table 2. Spectroscopic data for complexes in dichloromethane at room temperature.

Compound	Absorption (λ in nm, ε in $M^{-1}cm^{-1}$)	Emission ^{a} (λ in nm)	$\phi_F{}^{b}$	Excitation^{c} (λ in nm)	$k_r{}^{d}$ (s^{-1})	$k_{nr}{}^{e}$ (s^{-1})	$\phi_{ISC}{}^{f}$	$\phi_{Yb.}{}^{g}$ (%)
Yb-B1	533 (8.69×10^3)	558 (3.8 ns), 977 (11μs), 1001, 1028	0.42±0.02	542	0.11×10^9	0.16×10^9	0.58	0.55
Yb-B2	545 (9.51×10^3)	574 (2.2 ns), 978 (11μs), 1002, 1029	0.07±0.03	562	0.15×10^9	0.42×10^9	0.93	0.55
Yb-B3	569 (8.33×10^3)	592 (3.2 ns), 975 (11μs), 1001, 1025	0.53±0.06	570	0.16×10^9	0.14×10^9	0.47	0.55
Yb-B4	550 (10.51×10^3)	574 (3.1 ns), 975 (11μs), 1001, 1027	0.13±0.03	551	0.04×10^9	0.29×10^9	0.87	0.55

a: λ_{ex} = 375 nm. b: λ_{ex} = 488 nm for quantum yield measurement. c: λ_{em} = 980 nm. d: calculated using $k_r = \phi_F / \tau$, in which τ refers to lifetimes in the visible region. e: calculated using $k_{nr} = (1-\phi_F)/\tau$, in which τ refers to lifetimes in the visible region. f: calculate using $\phi_{ISC} = 1-\phi_F$. g: determined using $\phi_{Yb} = \tau_{obs}/2.0$ ms.[24, 56, 57]

The observed NIR emission is most likely due to the sensitization of Yb(III) ions by BODIPY moiety via its triplet state. The excitation spectra (λ_{em} = 980 nm, **Figure S5**) were quite similar to their respective absorption spectra. The smaller k_r values and larger k_{nr} values of complexes compared to ligands are also consistent with this pathway. The further support includes the different NIR emission intensities in the presence and absence of oxygen, which was demonstrated in complexes Yb-B1 and Yb-B2. Yb-B2 showed stronger emission compared to other three due the addition of an I atom to the BODIPY. It is well-known that heavy atoms like I increased triplet yield of BODIPY.[49] **Figure 6** shows the NIR emission of Yb-B1 and Yb-B2 complexes in toluene in the absence and presence of oxygen. The NIR emission decreased dramatically in the presence of oxygen, most likely due to the quenched of triplet state through the formation of singlet oxygen.[58] The decrease is more pronounced in Yb-B1 (97% decrease) than in Yb-B2 (55%

decrease compared to the initial emission). Re-purging the nitrogen to the aerated solution brought up the NIR emission (not completely recovered, which could be due to the remaining oxygen after purging N_2). This clearly indicated that the triplet state is involved in the sensitization process. This also suggests that that energy transfer rate from the triplets state to the lanthanide is comparable to that to the singlet oxygen. This observation is in accordance with spectroscopic studies from Zhao et al. Zhao et al[59] studied a series of BODIPY dyes with and without an I atom and an ethylene group on the 2 and 6 positions of the BODIPY core structure. The results showed that iodination increases the triplet state lifetime dramatically with simultaneous increase of intersystem crossing yield. The triplet state peaks between 816 nm – 878 nm, which has some overlaps with the absorption of Yb(III).[60, 61] In a related study, Zhao et al[62] also revealed that a metal atom like Pt(II) increases the quantum yield of triplet state once it coordinates to the BODIPY core through a 2-ethynyl unit.

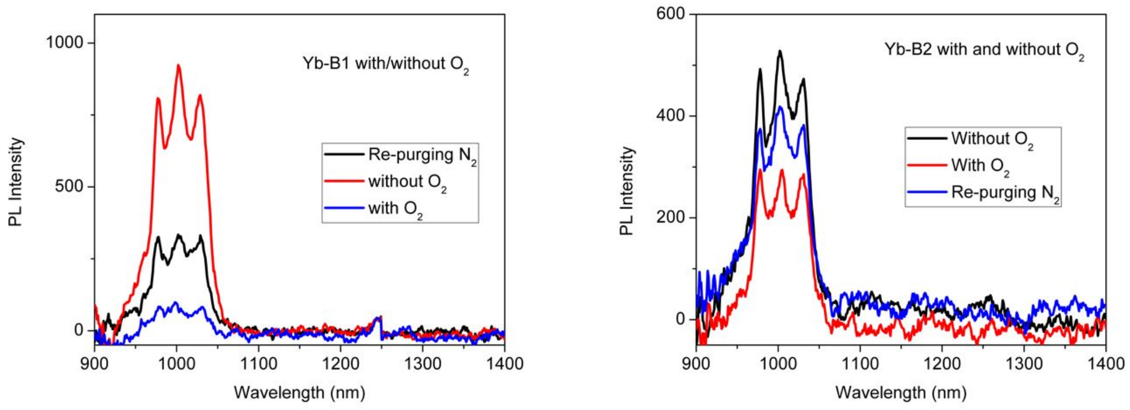


Figure 6. Effect of oxygen on the NIR emission of Yb-B1 (left) and Yb-B2 (right) in toluene at room temperature with a concentration $\sim 4 \times 10^{-5}$ *M*. $\lambda_{ex} = 375$ nm.

The complex also showed strong emission in the visible region. The measured quantum yields in DCM for all four complexes ($\lambda_{ex} = 488$ nm) are generally lower than those of free ligands but not dramatically quenched. Interestingly, the change of emission intensity compared to the respective ligands in the visible region is dependent upon the excitation wavelength, which was demonstrated by spectroscopic titration (absorption and fluorescence) of B1 solution by [Yb(hfac)$_3$(H$_2$O)$_2$] as shown in **Figure 7**. Upon excitation at 375 nm, the fluorescence increased till the ratio of Yb: B1 reached 1.0, which is expected due to the gradual substitution of H_2O by B1 to form [Yb(hfac)$_3$(B1)]. An 14% increase was observed. This increase is most likely due to the increase of absorbance at 375 nm. A similar increase was also observed when other three ligands were titrated by [Yb(hfac)$_3$(H$_2$O)$_2$] (**Figure S6, S7, S8** and **S9**). The estimated increase of emission was about 21%, 93% and 38% for B2, B3 and B4 at the end of titration, respectively. The increase for B3 is more pronounced, which could be due to the breakdown of aggregates during the formation of the complex. However, a 32% and 35% decrease of fluorescence upon excitation at 361 nm or 431 nm was observed, respectively. This is different from a 95% decrease of emission for a BODIPY-functionalized phenanthroline at the end of the titration by [Yb(hfac)$_3$(H$_2$O)$_2$], in which BODIPY-Phen stands for a 1,10-phenathroline ligand with two BODIPY units attached through their *meso* positions to the 4,7-positions of phenanthroline as we reported previosuely.[34, 36]

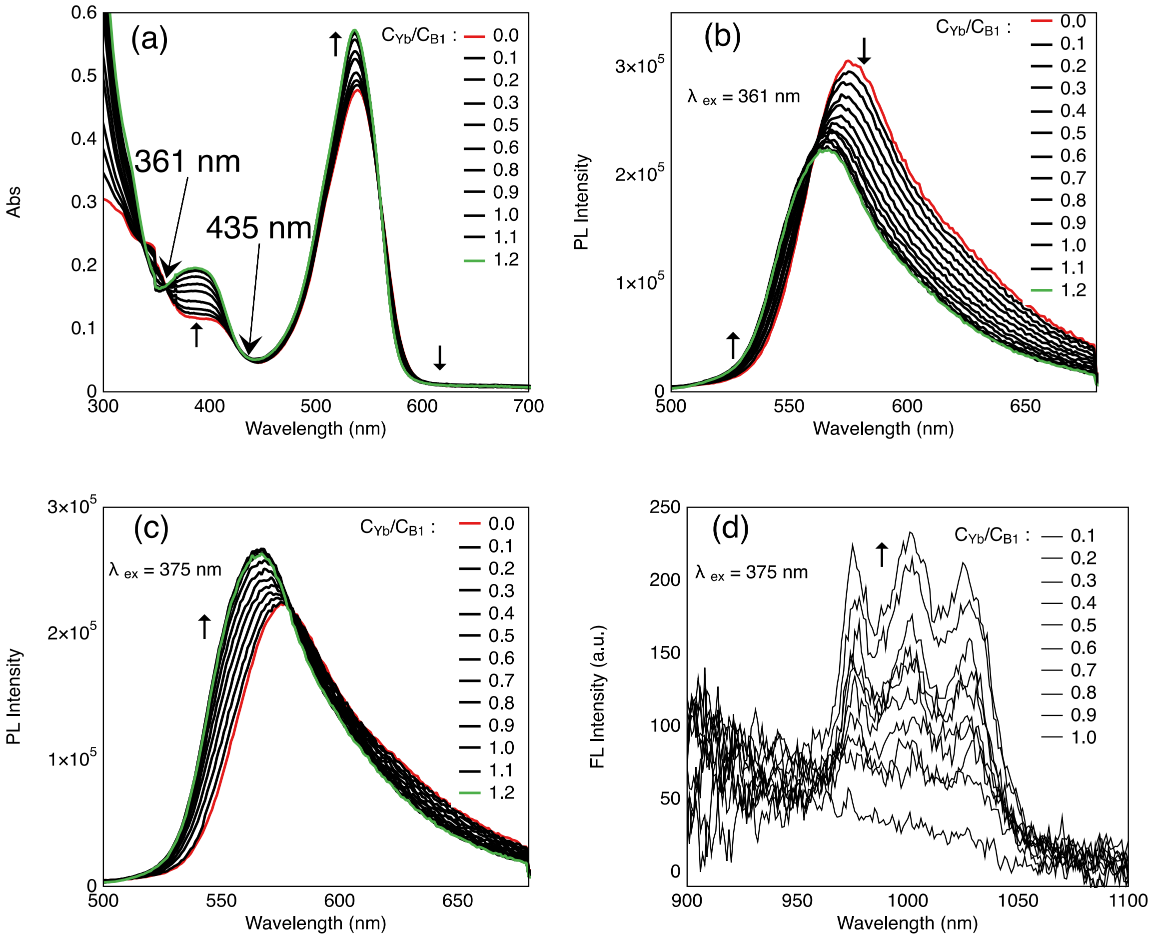


Figure 7. Spectral changes of (a) absorption, (b) VIS emission with λ_{ex} = 361 nm, (c) VIS emission with λ_{ex} = 375 nm, and (d) NIR emission with λ_{ex} = 540 nm of ligand B1 in DCM upon addition of $[Yb(hfac)_3(H_2O)_2]$. The concentration of ligand B1 was ~6.6×10^{-5} *M*.

The observed fluorescence in the visible region from complexes is indicative of inefficient sensitization process. As the sensitization efficiency is determined by ϕ_{ISC} and ϕ_{ET}, it is unlikely that the poor sensitization comes from the misalignment of energy levels between the triplet states of ligands and the excited states of Yb(III). Zhao *et al* studied a bipyridine conjugated BODIPY ligand and its iridium complex.[63] The ligand is very similar to B1 except no CH_3 group in 4 position. It was found the triplet state of the ligand is located at 742 nm (ca. 13477 cm^{-1}), which is higher than the emissive state of ytterbium (ca. 10250 cm^{-1}).[64] The measured lifetimes of triplet states in ethynyl-conjugated BODIPY analogues are ~50 -200 μs.[59] We also performed TD-DFT calculations for all four ligands (**Tables S1** and **S2** and **Figures S10** and **S11**) and found the triplet states are 834 nm, 832 nm, 848 nm, and 847 nm for B1, B2, B3 and B4, respectively. Considering the calculated energy levels are usually lower than the measured values, the triplet states are higher than the excited state of ytterbium (III). Therefore, both are favorable for a desired energy transfer. We were unable to determine the ϕ_{ISC} values for our complexes, however, studies from Zhao et al indicate that ϕ_{ISC} in either iodinated BODIPYs or ethynyl-conjugated BODIPYs is relatively high. Using Ermolev's rule,[59] the estimated ϕ_{ISC} (= $1-\phi_F$) values in all four complexes are 58, 93, 47 and 87%, respectively. Therefore, except Yb-B2 and Yb-B4, the internal system crossing is inefficient. The smaller k_r values and larger k_{nr} values of complexes compared to ligands are also consistent with the fluorescence quenching pathway via singlet to triplet. also demonstrating larger than those in ligands it is reasonable to believe that the dual emission of the complexes in the visible and NIR regions is most likely the result of the poor energy transfer between Yb (III) and BODIPY core in the four complexes. The distance between Yb(III) and the nearest C atom of the BODIPY core in Yb-B1 is about 8.1Å, which is shorter than the distance (~ 9 Å) in a BODIPY-functionalized terpyridine ytterbium (III) complex that showed 68% sensitization efficiency,[32] but longer than that (~ 7.0 Å) in [Yb(hfac)$_3$(BODIPY-Phen)]. It should be mentioned that dual Vis/NIR emission was also observed in several other systems.[65, 66]

Conclusion

Four bipyridine ligands with a BODIPY unit conjugated through a triple bond and their ytterbium complexes were synthesized and characterized. Their photophysical properties were investigated. The bipyridine coordinates to Yb^{3+} with three hexafluoroacetylacetonate forming eight-coordinate complexes. The ligands and complexes showed strong absorption around 550 nm due to the π-conjugation of BODIPY and bipyridine. Excitation of complexes with absorption maxima wavelength led to the characteristic emission at ~980 nm from ytterbium (III). It was found that VIS emission from ligands was not quenched completely, indicating an inefficient sensitization process due to the long distance between the BODIPY unit and Yb(III) center.

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Notes

Any additional relevant notes should be placed here.

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Data Statement

- The data supporting this article have been included as part of the Supplementary Information.
- Crystallographic data for Yb-PH2 has been deposited at the CCDC under 2269661 and can be obtained from https://www.ccdc.cam.ac.uk/