

Supplementary Information

Sisters together: co-sensitization of near-infrared emission of ytterbium (III) by BODIPY and porphyrin dyes

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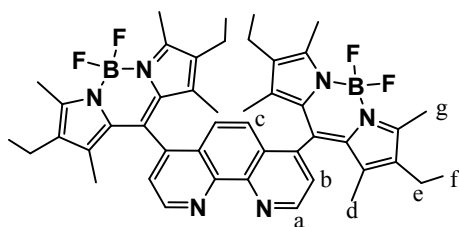
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General

All solvents were treated by standard methods prior to use. 4,7-dimethyl-1,10-phenanthroline monohydrate was purchased from GFS Chemicals and used directly with further purification. The 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was supplied by Biosynth International, Inc. All other chemicals were from Acros and used directly. All chemicals were analytical grade. 4,7-diformyl-1,10-phenanthroline was prepared according to the literature. Its purity was confirmed by ¹H NMR. The [Yb(TPP)(OAc)(MeOH)₂] was prepared as we described previously.

The column chromatography was conducted using a 200 or 230-400 mesh silica gel from Dynamic Adsorbents, Inc. NMR spectra were taken by a 400 MHz Bruker Avance II-NMR spectrometer, using ACROS Organics chloroform-d 99.8% D, containing 0.03% (v/v) TMS. All ¹H NMR signals were referenced to TMS. NMR spectra were processed using Bruker's TopSpin software and recorded using a 400 MHz Bruker NMR spectrometer. TMS was employed as the internal standard. Deuterated chloroform was used as the NMR solvent with a sample quantity of 4-6 mg depending on the sample molecular weight. 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.

1. Synthesis of BDP-Phen



To a dry dichloromethane (150 mL) solution of 4,7-diformyl-1,10-phenanthroline (0.476 g, 2 mmol) was added 3-ethyl-2, 4-dimethylpyrrole (0.492 mg, 4 mmol) under nitrogen. A drop of trifluoroacetic acid (~ 0.25 mL) was added and the resulting solution was stirred magnetically at room temperature for 12h. To this solution 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (0.45 g, 2 mmol) in dichloromethane (20 mL) was added. The solution became deep purple immediately. After stirring for 2h, triethylamine (4 mL) and $\text{BF}_3 \cdot \text{OEt}_2$ (4 mL) was added sequentially. After the solution was magnetically stirred for another 6h, water (100 mL) was added. The volume of the organic layer was reduced to 5 mL on a rotorevaporator. The solution was loaded on silica column and eluted with chloroform. The major band was collected. Yield: 0.54 g, 70%. Anal Calcd (Found) for $\text{C}_{46}\text{H}_{50}\text{B}_2\text{F}_4\text{N}_6$: C, 67.54 (66.73); H, 5.15 (5.35); N, 10.74 (10.88); ^1H NMR (CDCl_3 , ppm): 9.34 (d, 2H), 7.83 (s, 2H), 7.66 (d, 2H), 2.53 (s, 12H), 2.21 (dd, 8H), 0.97 (s, 12H), 0.91 (t, 12H).

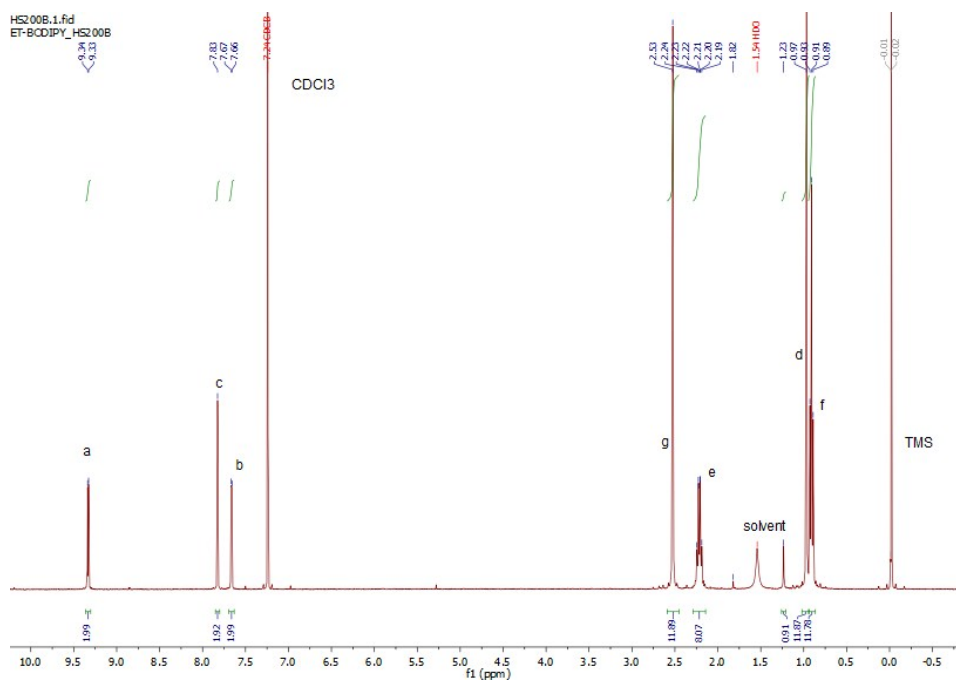


Figure S1. ^1H NMR spectrum of BDP-Phen in CDCl_3 .

2. Preparation of [Yb(TPP)(OAc)(BDP-Phen)]

To a solution of [Yb(TPP)(OAc)(MeOH)₂] (19.6 mmol, 22 mmol) in toluene (20 mL) was added BDP-Phen (15.6 mg, 22 mmol). The resulting solution was magnetically stirred overnight at room temperature. Then the solvent was removed and the residue was re-dissolved in 5 mL of dichloromethane and loaded on column (silica gel) for purification. Dichloromethane/methanol (100:5) was used as a solvent to elute the column. Due to the dissociation of the BDP-Phen from the complex, only the very first fraction of the major band (the first band) was collected to ensure the purity of the product. The product was stable in chloroform, dichloromethane, toluene, and hexane and decomposed slowly in the presence of methanol. Its purity was confirmed by thin layer chromatography (TLC). Yield: 15.1 mg.

3. **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 K α radiation ($\lambda = 1.54178 \text{ \AA}$). 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. 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. The structures were refined on F^2 using the SHELX97. Crystal data for BDP-Phen: C₄₆H₅₀B₂F₄N₆, MW = 784.54, monoclinic, space group = C2/c, a = 23.0197(7), b = 10.7450(3), c = 17.5896(5) \AA , $\beta = 112.737(2)^\circ$, V = 4012.5(2) \AA^3 , Z = 4, $\rho_{\text{calcd.}} = 1.299 \text{ Mgm}^{-3}$, $\mu = 0.726 \text{ mm}^{-1}$, F(000) = 1656, T = 100 (2) K. 42274 reflections were measured, of which 3677 were unique ($R_{\text{int}} = 0.0588$). Final $R_1 = 0.043$ and $wR_2 = 0.0992$ were obtained for 3677 observed reflections and $R_1 = 0.0365$ and $wR_2 = 0.0942$ with $I > 2\sigma(I)$, 268 parameters, and GOF = 1.023.

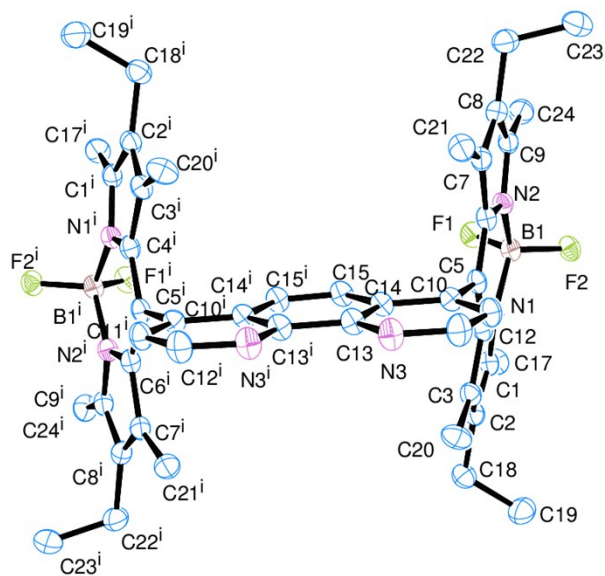


Figure S2. ORTEP diagram of the molecule with 50% thermal ellipsoid probability.

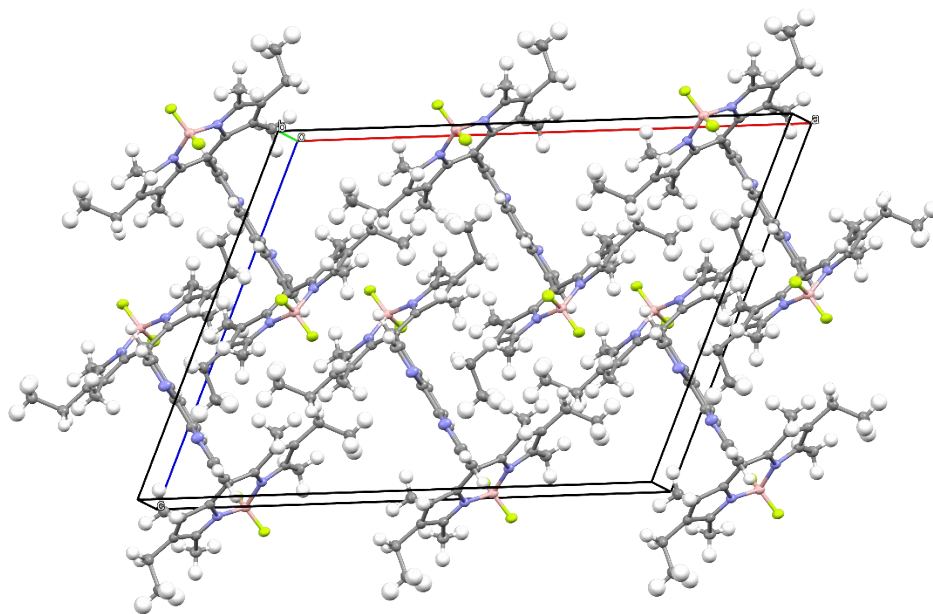


Figure S3. Packing diagram of BDP-Phen in a unit cell.

4. Photophysical measurements

Absorption spectra were obtained on an HP Agilent 8543 UV-visible spectrophotometer in CH_2Cl_2 at room temperature. The steady state fluorescence spectra were obtained on FS5 fluorimeter (Edinburg

Instruments, Inc) with Xenon arc lamp as light source. The decay curves of the samples were also measured on FS5 (Edinburg Instrument, Inc.) with time-correlated single photon counting. The laser diode EPL 375 (Edinburg Instrument, Inc) with wavelength at 375 nm was used as light source. The pulse repetition frequency was 20MHz. The lifetimes were obtained by exponential tail fitting of decay data.

The quantum yield in the visible region was measured using following equation:

$$\Phi_X = \Phi_r \left[\frac{Grad_X}{Grad_{ST}} \right] \left[\frac{n_X}{n_{ST}} \right]^2$$

where Φ_X is the fluorescence quantum yield of the sample, Φ_r the fluorescence quantum yield of the reference, Grad the gradient from the plot of integrated fluorescence intensity vs absorbance of five samples with different concentrations, and n the refractive index of the solvents. The Rhodamine 6G in ethanol ($\Phi = 0.95$, $\lambda_{ex} = 480$ nm) was used as a reference.²

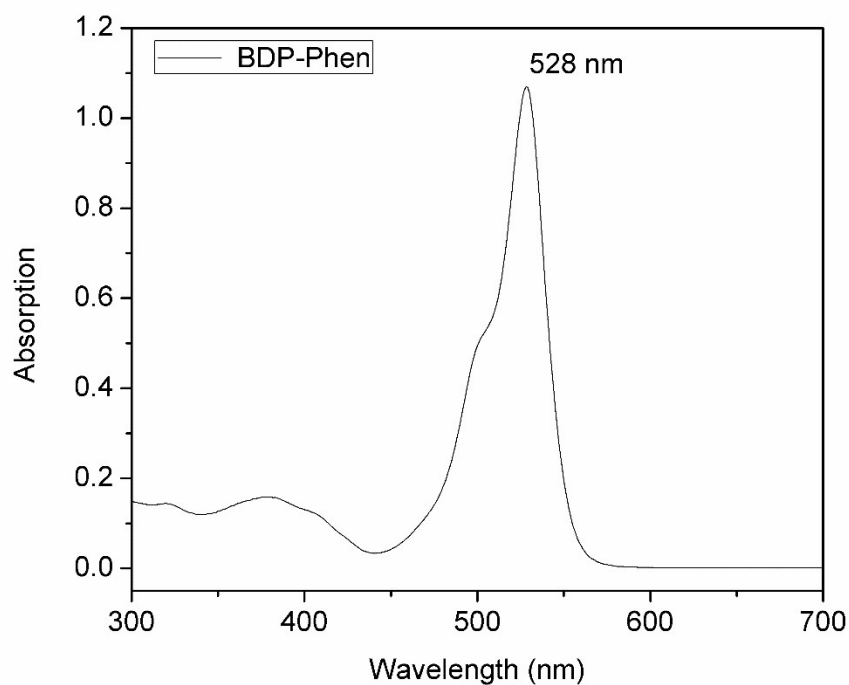


Figure S4. Absorption spectrum of BDP-Phen in DCM

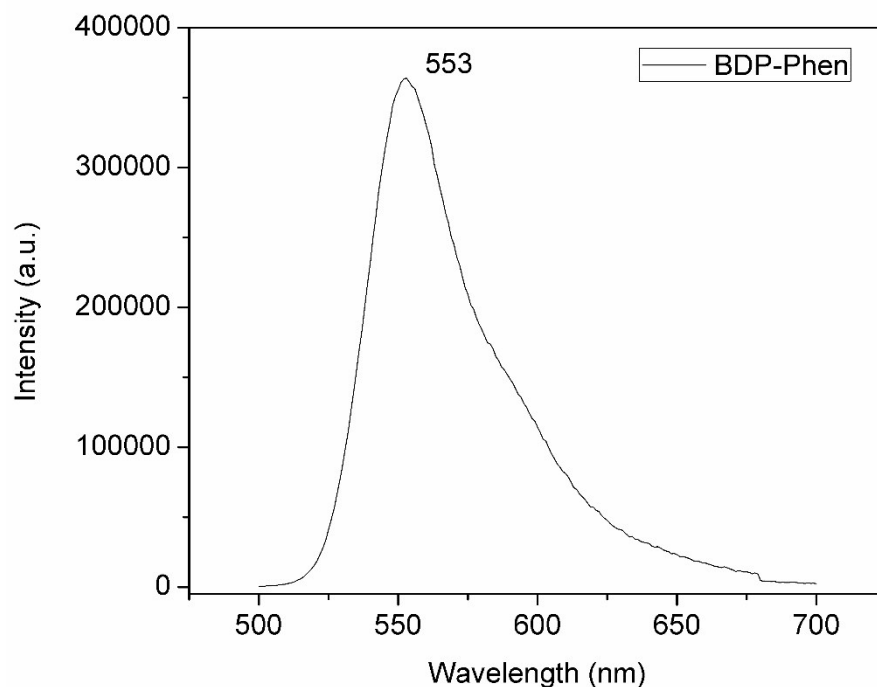


Figure S5. Fluorescence spectrum of BDP-Phen in DCM (excitation wavelength = 488 nm)

5. Theoretical Calculations. Theoretical calculations were performed at a density functional theory (DFT) level using Gaussian 09 software. 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. For complexes, Yb was replaced by Y and basis set of LAND2Z was used. All other parameters were default set. 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.

Table S1. Frontier molecular orbital electron density distribution profiles of BDP-Phen, [Y(TPP)(OAc)(Me-Phen)] and [Y(TPP)(OAc)(BDP-Phen)]

	BDP-Phen	[Y(TPP)(OAc)(Me-Phen)]	[Y(TPP)(OAc)(BDP-Phen)]
LUMO+1			

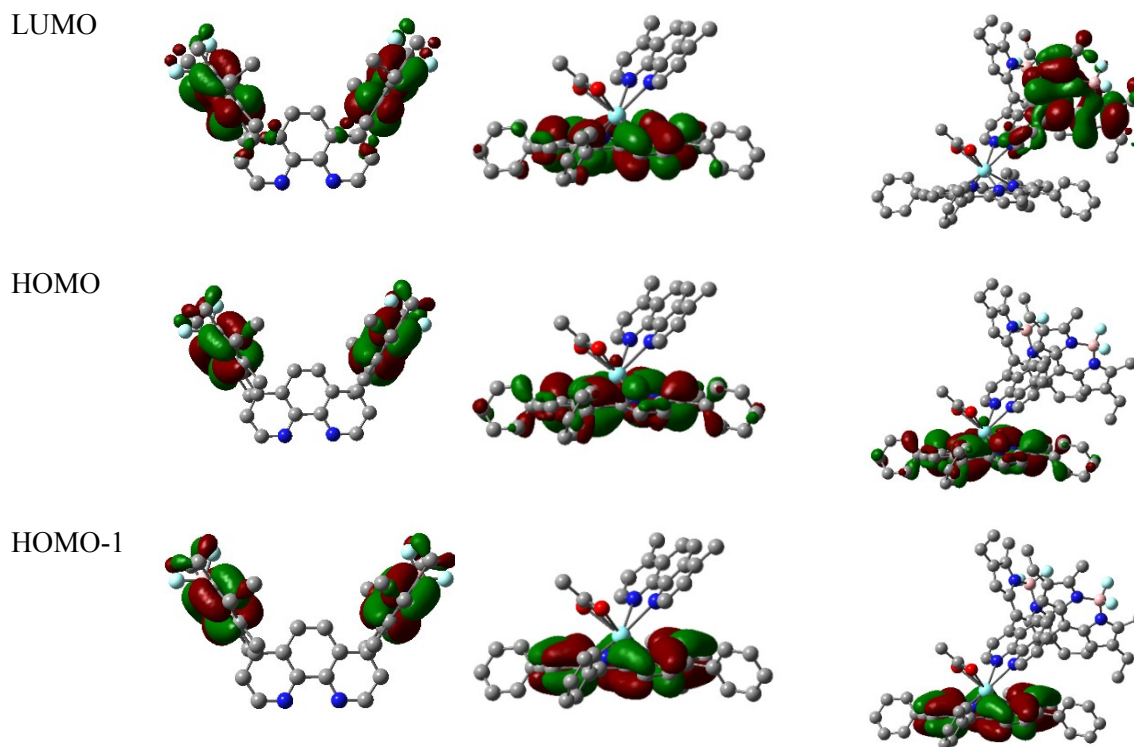


Table S2 Major transitions of BDP-Phen and their oscillation strength (f).

Transition	f	Compositions (percentage)	Character
808.4	0.00	H-1->L+1 (47%), HOMO->LUMO (53%)	Triplet
532.0	0.0179	HOMO->L+2 (100%)	Singlet
528.8	0.075	H-1->L+3 (100%)	Singlet
480.2	0.5714	H-3->LUMO (20%), H-2->L+1 (14%), H-1->L+1 (33%), HOMO->LUMO (32%)	Singlet
448.0	0.0165	H-7->LUMO (89%) H-3->LUMO (5%), H-2->L+1 (5%)	Singlet
423.9	0.7804	H-7->LUMO (10%), H-3->LUMO (26%), H-2->L+1 (28%), H-1->L+1 (18%), HOMO->LUMO (18%)	Singlet
417.7	0.0297	H-6->LUMO (22%), H-5->L+1 (47%), H-4->LUMO (20%) H-3->L+2 (7%), H-2->L+3 (3%)	Singlet

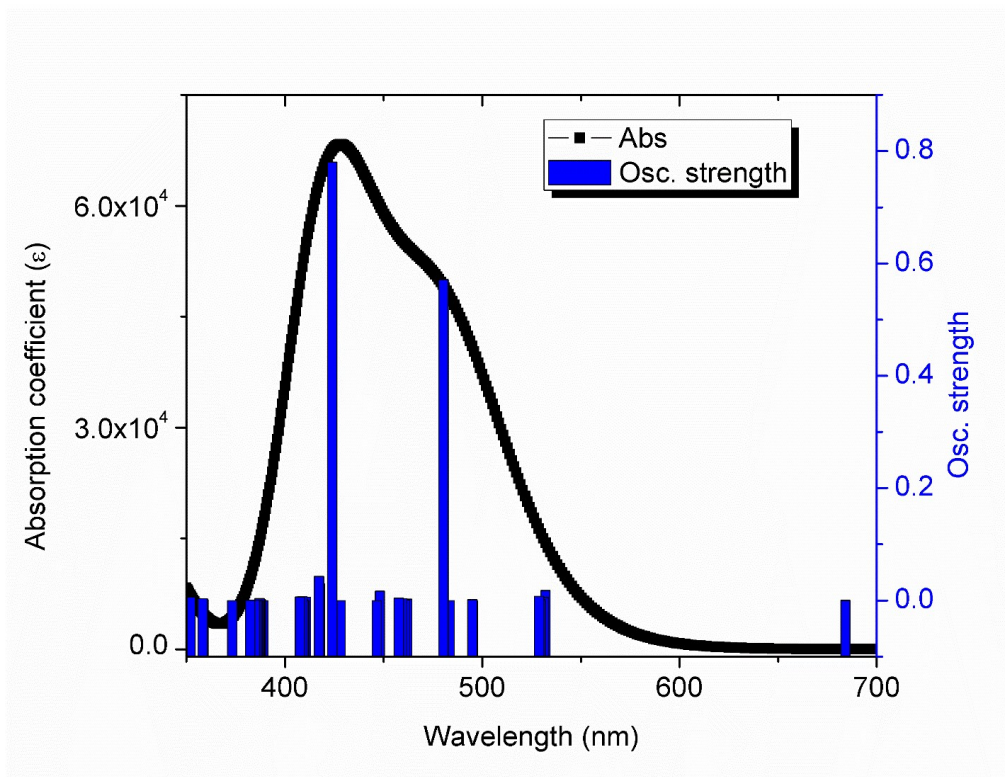


Figure S6. Predicted absorption spectra of BDP-Phen in DCM