Electronic Supplementary Information

BODIPY functionalized 1,10-phenanthrolines as efficient sensitizers for near-infrared emission of ytterbium (III) ion

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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-pheanthroline was prepared according to the literature. Its purity was confirmed by ^{1}H NMR.

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 ^{1}H NMR signals were referenced to TMS. NMR spectra were processed using Bruker's TopSpin software and recorded using a 400 MHz ruker 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

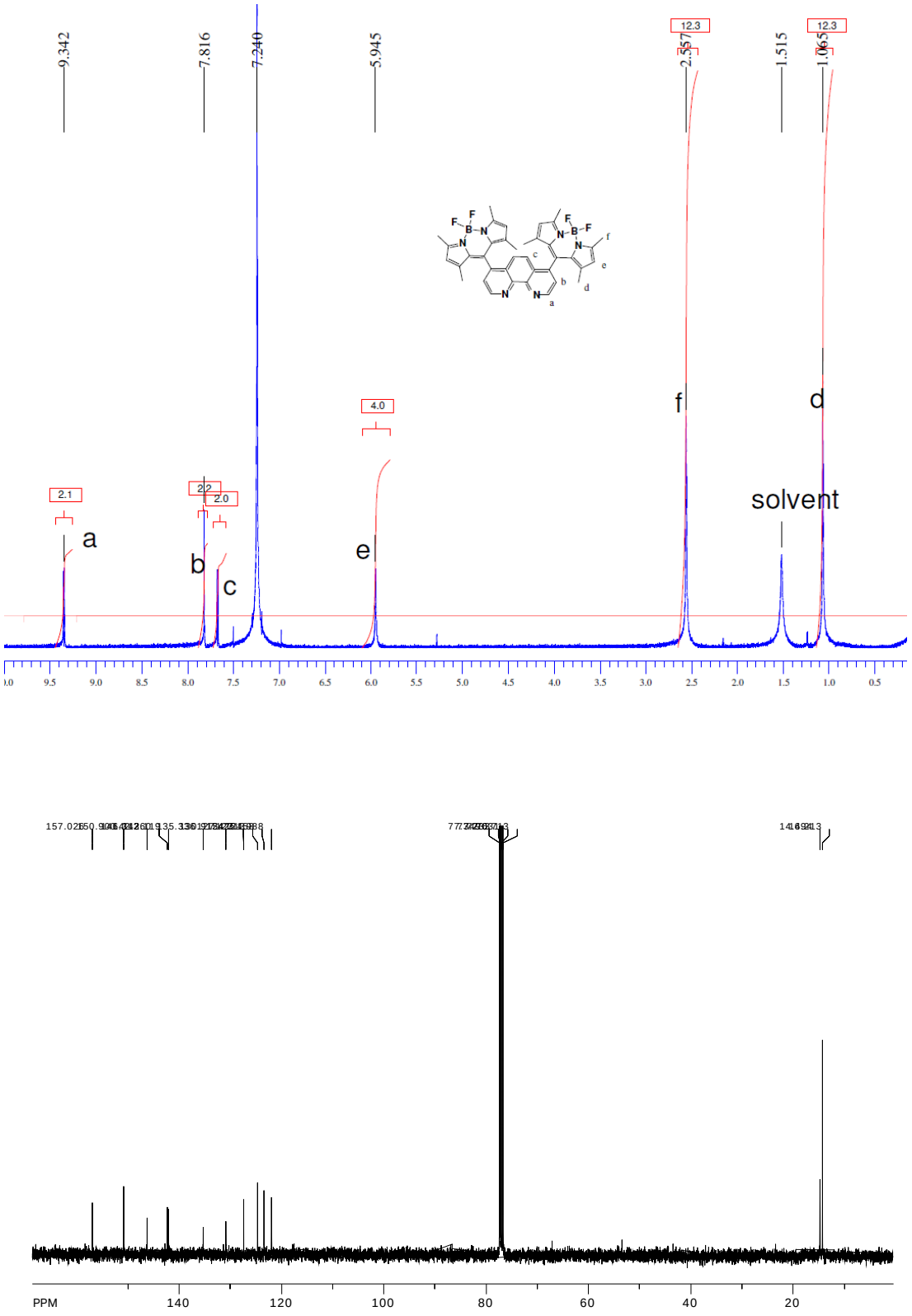


Figure S1 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of BODIPY-Phen (**L1**) in $CDCl_3$. s: solvent

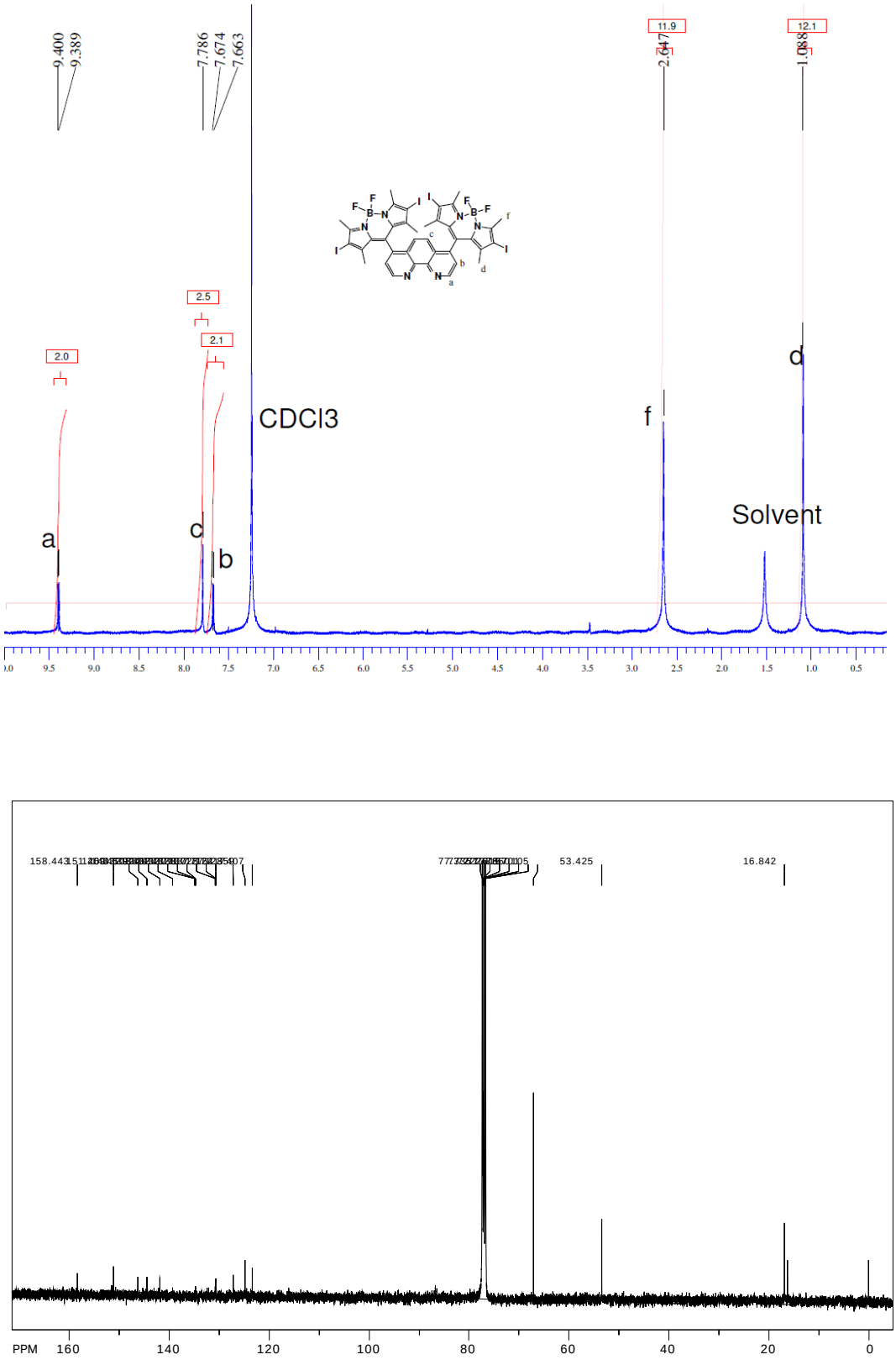


Figure S2. ^{1}H NMR (top) and 13C NMR (bottom) spectra of 4I-BODIPY-Phen (**L2**) in $CDCl_3$.

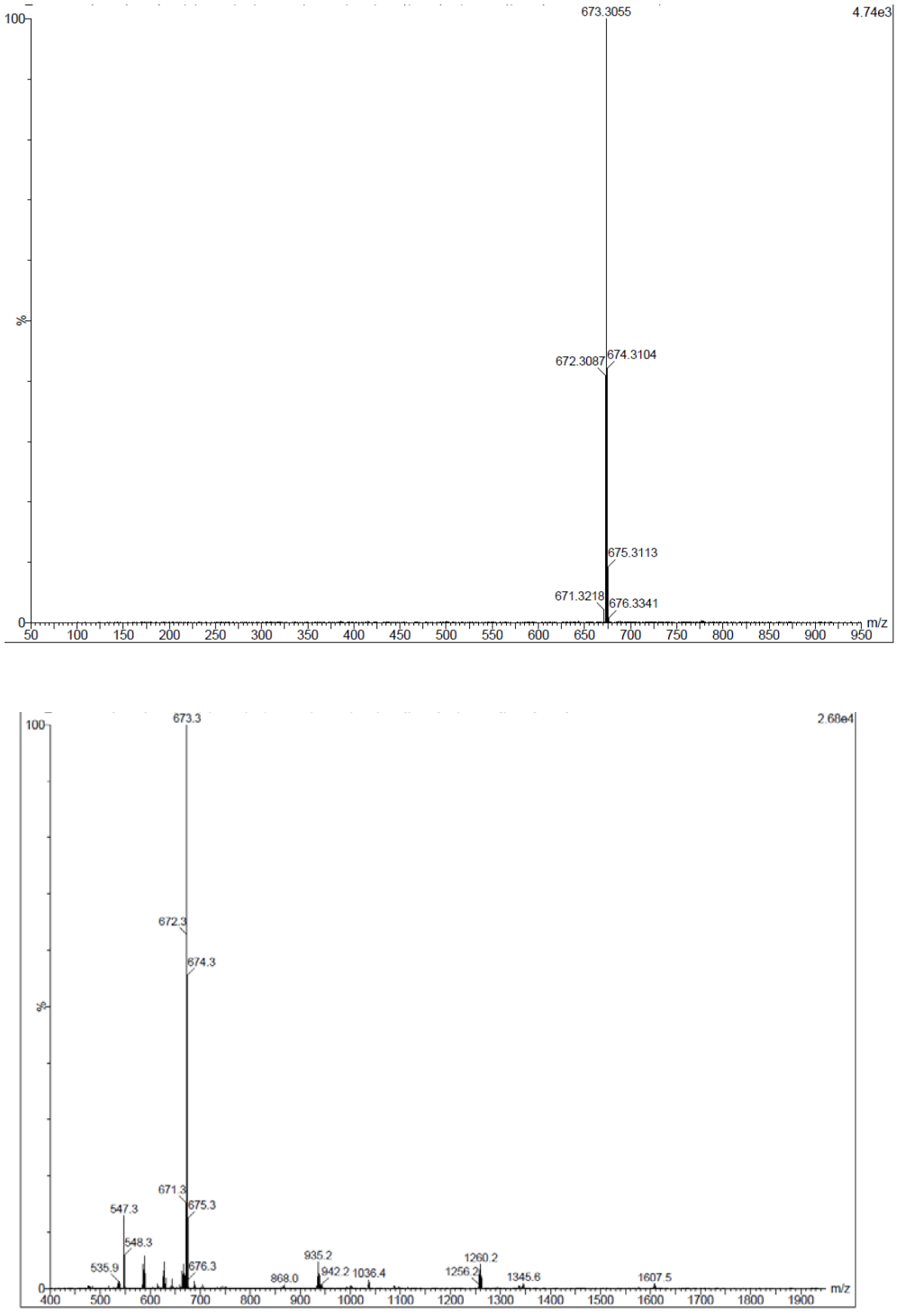


Figure S3. MS for L1 (top) and L1-Yb (bottom).

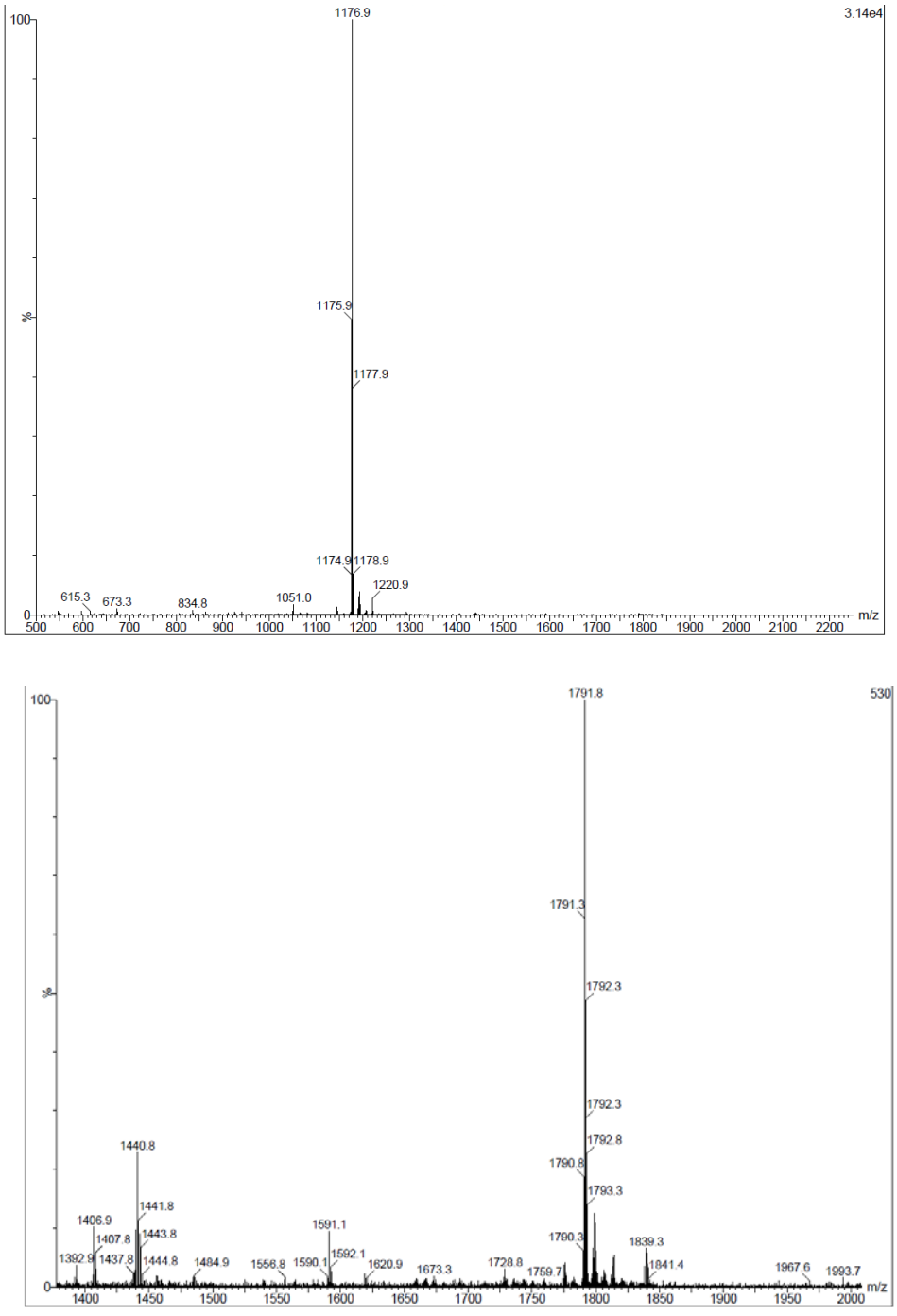


Figure S4. MS for L2 (top) and L2-Yb (bottom).

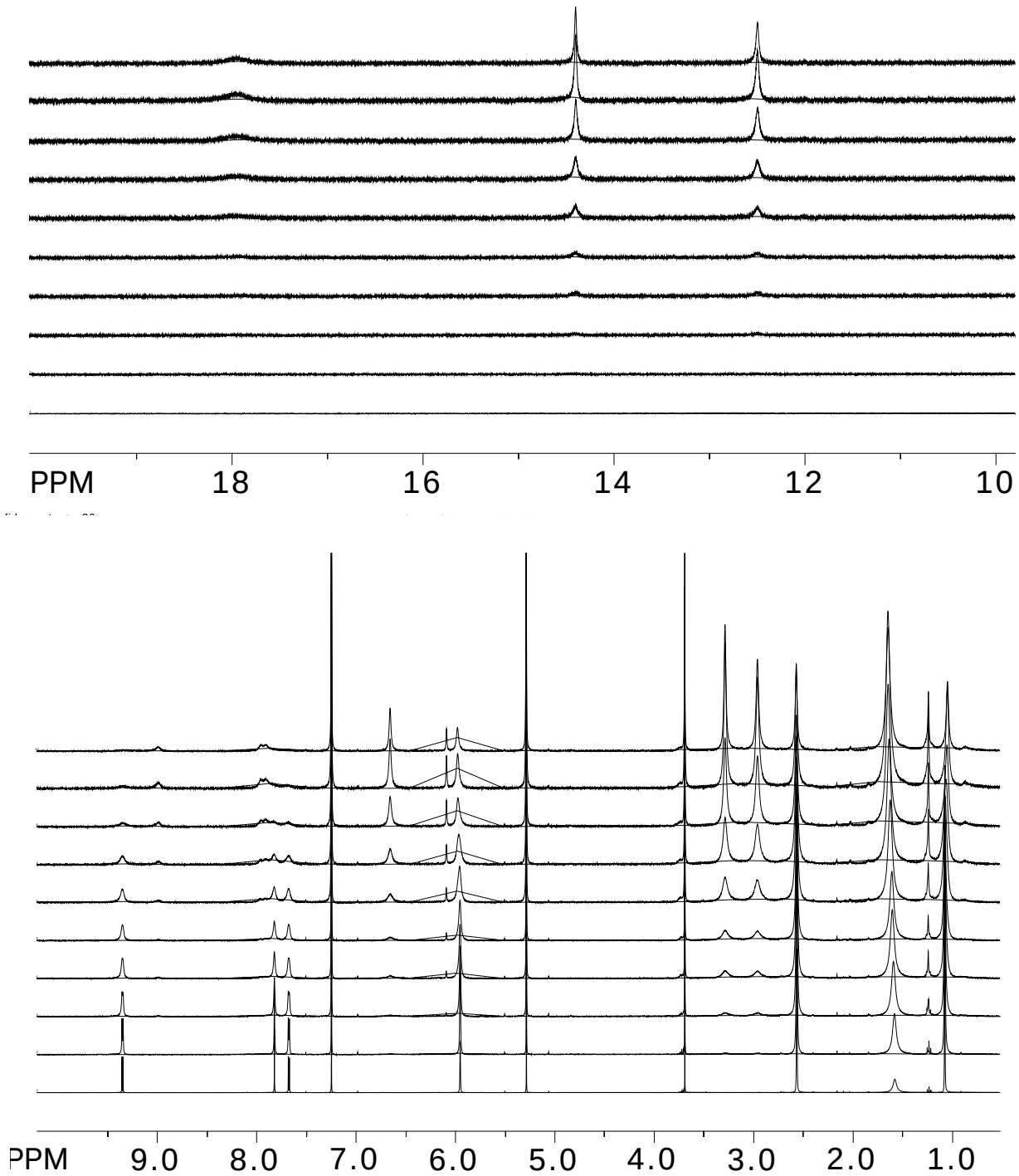


Figure S5. The ^{1}H NMR spectral changes in the range of 20 - 10 ppm (top) and 10 - 0 ppm (bottom) of L1and $[Yb(HFA)_3(H_2O)_2]$ in $CDCl_3$ during their reaction. Spectrum 1 to 10 corresponded to the molar ratio of Yb/L1 from 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.65, 0.75, 0.85 and 1.0. The top spectra were enlarged to better show the spectral changes.

Photophysical Measurements

FT-IR spectra were performed on a Nicolet 6700 spectrometer with ATR mode using a diamond crystal. Absorption spectra were obtained on an HP Agilent 8543 UV-visible spectrophotometer at room temperature. Steady state fluorescence spectra were obtained on an FS920 fluorimeter (Edinburg Instrument, Inc) with Xenon arc lamp as a light source. The slits (for both emission and excitation arms) were set to 1.0 nm and 8.0 nm for all measurements for VIS and NIR measurements, respectively. A filter with a cut-off of 645 nm was used to remove any possible high order. Quantum yield in the visible region was measured using following equation:

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

where Φ is the fluorescence quantum yield, Grad 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 ($\Phi = 0.95$, $\lambda_{ex} = 480$ nm) was used as a reference. The decay curves of the samples were measured on a LifeSpec II (Edinburg Instrument, Inc.) spectrometer. A laser diode EPL 375 (Edinburg Instrument, Inc) with wavelength of 375 nm was used as light source. The lifetimes were obtained by exponential fitting of deconvoluted decay data and tail fitting of data for visible and NIR emission respectively. The rate constants of fluorescence (k_f) ($k_f = \phi/\tau$, where ϕ is the fluorescence efficiency and τ is the decay lifetime).

Table S1. Photophysical data of BODIPY-Phen (**L1**) in different solvents at room temperature.

Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ (%)	k_f (10^8 s^{-1})
$CHCl_3$	506	525	88.9	1.14
CH_2Cl_2	508	524	84.6	1.07
CH_3CN	502	518	11.6	0.87
EtOH	502	522	25.5	1.01
MeOH	501	522	15.4	0.93
DMF	502	523	8.7	0.95
THF	502	522	78.9	1.03

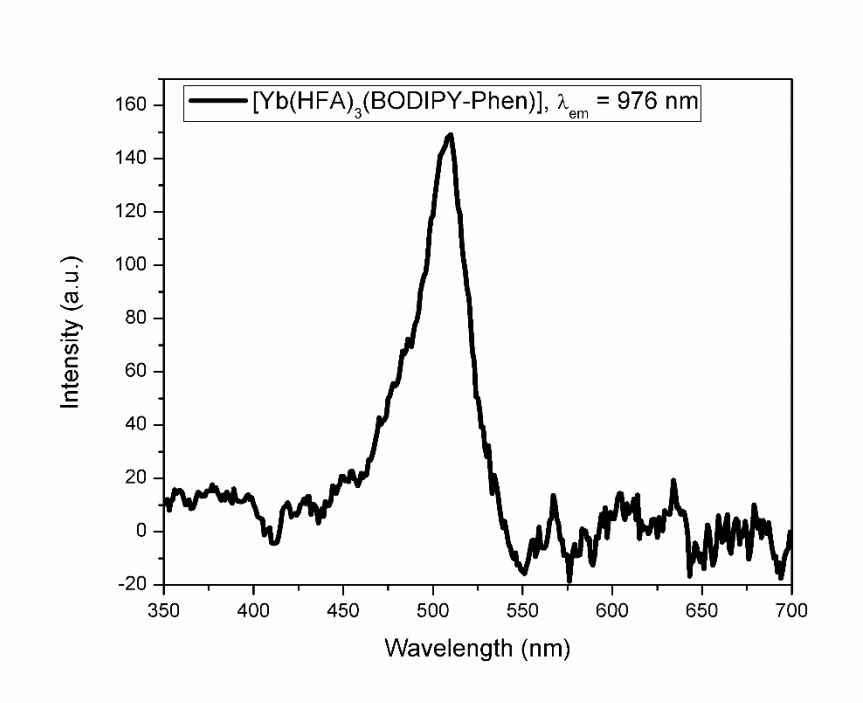


Figure S6. The excitation spectrum of **L1-Yb** in dichloromethane. λ_{em} = 976 nm.

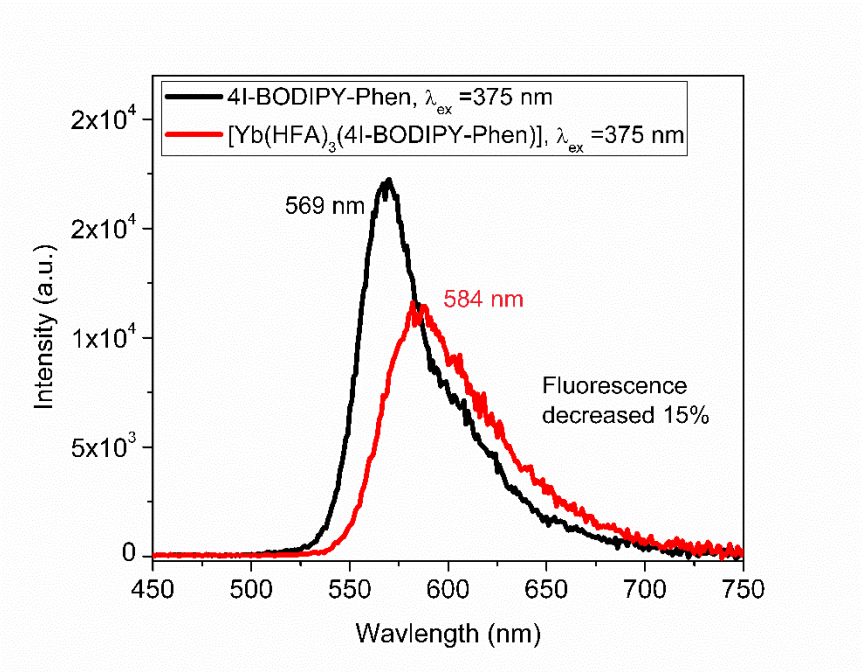


Figure S7. VIS emission of 4I-BODIPY-Phen (**L2**) and [Yb(HFA)$_3$(4I-BODIPY-Phen)] (**L2-Yb**) in dichloromethane (concentration = 5.18×10^{-6} M). λ_{ex} = 375 nm.

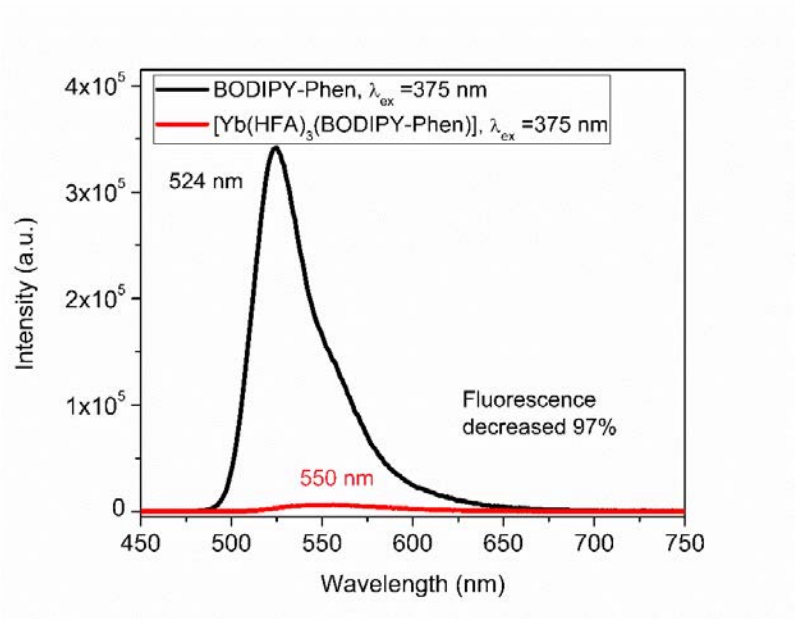


Figure S8. VIS emission of BODIPY-Phen (**L1**) and [Yb(HFA)$_3$(BODIPY-Phen)] (**L2**) in dichloromethane (concentration = 5.18×10^{-6} M). λ_{ex} = 375 nm.

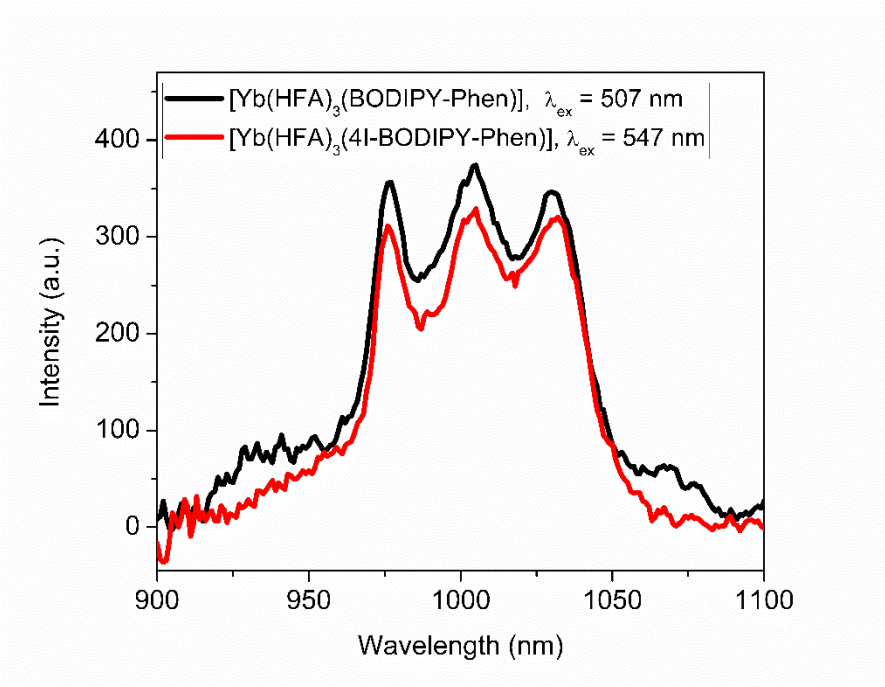


Figure S9. NIR emission of [Yb(HFA)$_3$(BODIPY-Phen)] (**L1-Yb**) and [Yb(HFA)$_3$(4I-BODIPY-Phen)] (**L2-Yb**) with the same absorbance at their peak positions (Abs = 0.316) in dichloromethane.

Theoretical Calculation

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 B3LYP as functional and 6-31G as basis set for C, H, N, B, F, Midix for I and MWB28 for Yb in dichloromethane. No negative frequency was found in the final optimized structures. The same basis sets were also used for the time-dependent (TD) DFT calculations. The SMD model was used for mimicking the solvent effect.

Table S2. Frontier molecular orbital electron density distribution profiles of BODIPY-Phen (**L1**) and 4I-BODIPY-Phen (**L2**).

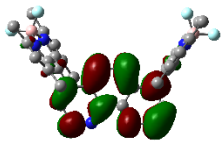
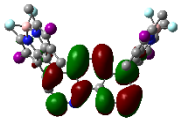
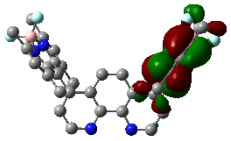
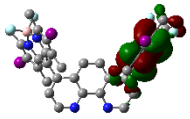
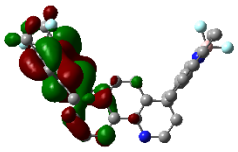
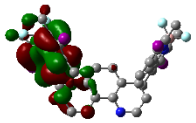
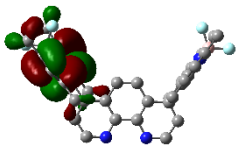
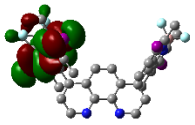
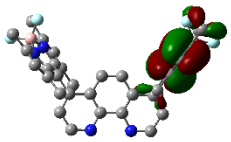
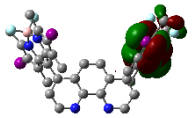
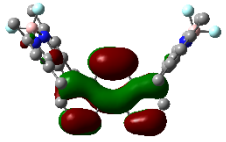
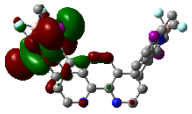
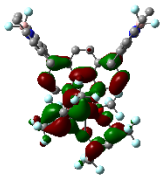
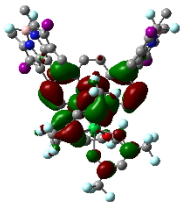
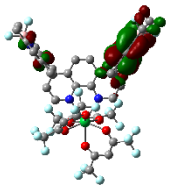
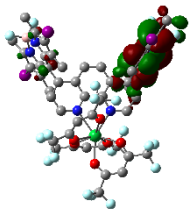
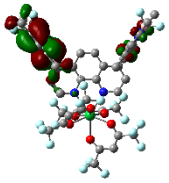
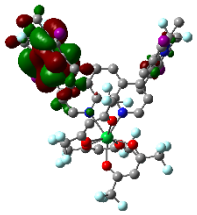
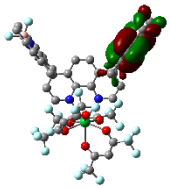
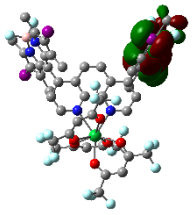
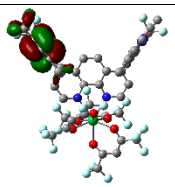
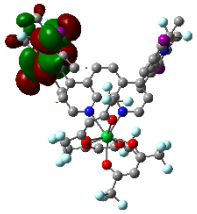
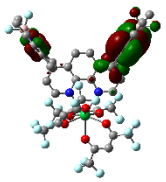
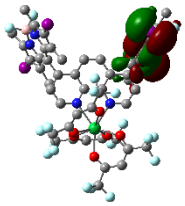
	BODIPY-Phen (L**1**)	4I-BODIPY-Phen (L**2**)
LUMO+2		
LUMO+1		
LUMO		
HOMO		
HOMO-1		
HOMO-2		

Table S3. Frontier molecular orbital electron density distribution profiles of [Yb(HFA)$_3$(BODIPY-Phen)] and [Yb(HFA)$_3$(BODIPY-Phen-4I)]. BODIPY-Phen and BODIPY-Phen-4I refer to L1 and L2, repsectively

	[Yb(HFA)$_3$(L1)]	[Yb(HFA)$_3$(L2)]
LUMO+2		
LUMO+1		
LUMO		
HOMO		
HOMO-1		
HOMO-2		

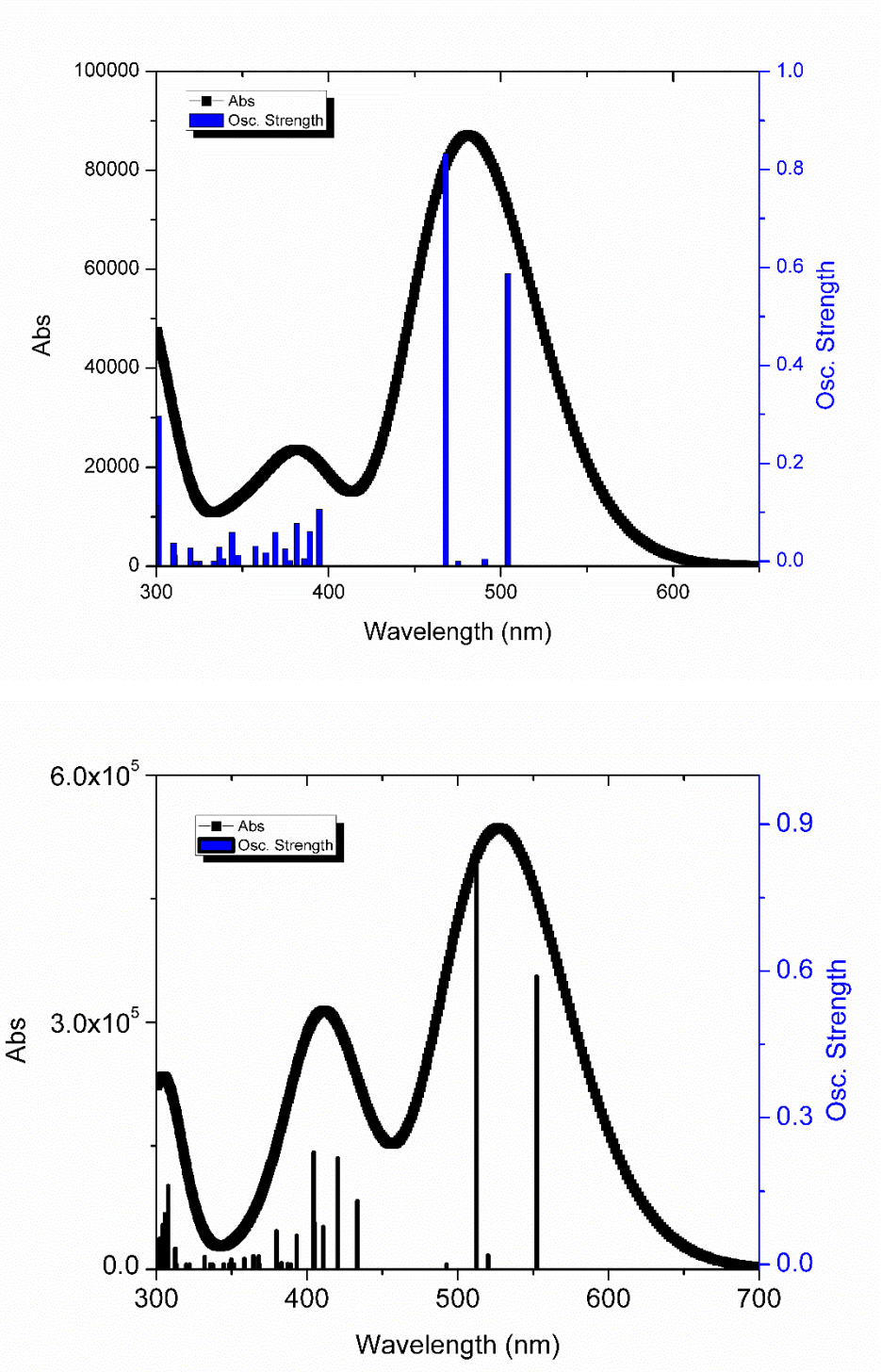


Figure S7. Predicted absorption spectra of **L1** (top) and **L2** (bottom).