

Ln(III)-cored Complexes Based on Boron Dipyrromethene (Bodipy) Ligands for NIR Emission

Jung Ho Ryu¹, Yu Kyung Eom¹, Jean-Claude G. Bünzli^{*1,2} and Hwan Kyu Kim^{*1}

¹Department of Advanced Materials Chemistry and WCU Center for Next Generation
Photovoltaic Systems, Korea University, Jochiwon, Chungnam 339-700, Korea

²École Polytechnique Fédérale de Lausanne (EPFL), Institute of Chemical Sciences and
Engineering BCH 1401, 1015 Lausanne, Switzerland
hkk777@korea.ac.kr & jean-claude.bunzli@epfl.ch

Supplementary Information

9 Pages

Reagents

Pyrrole, 1,3-dibromo-5,5-dimethylhydantoin, tributylamine (Bu_3N), sodium hydride (NaH , 60% in mineral oil), trifluoroacetic acid (TPA), boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), *N*-bromosuccinimide (NBS), 2,2':6',2''-terpyridine, erbium(III) chloride (anhydrous, 99%), gadolinium(III) chloride (anhydrous, 99%), ytterbium(III) chloride (anhydrous, 99%) were used as received from Sigma-Aldrich. Methyl 4-formylbenzoate was purchased from Fluka, Inc. Tetrakis(triphenylphosphine)palladium(0), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *p*-toluenesulfonyl chloride, were purchased from TCI Co. NaHCO_3 , NaOH , MgSO_4 , 2,2'-azobisisobutyronitrile (AIBN), triethylamine, and Na_2CO_3 were purchased from Samchun pure chemical Co. Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone under N_2 . Diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) and CH_2Cl_2 were freshly distilled from CaH_2 (Sigma-Aldrich, coarse granules, ~20mm, 95%) under a nitrogen atmosphere.

Characterization

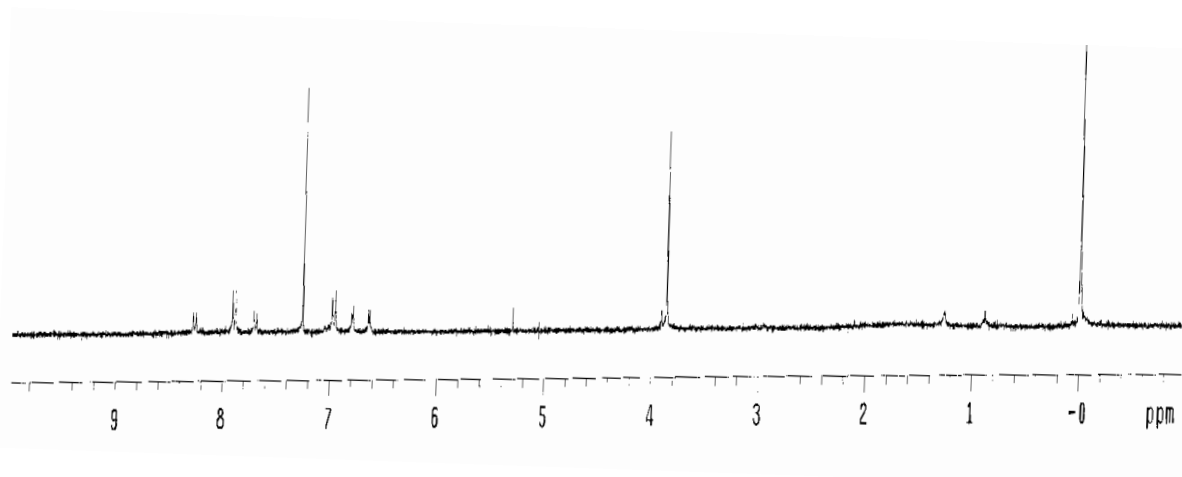


Figure S1. ^1H -NMR spectrum of **L1**.

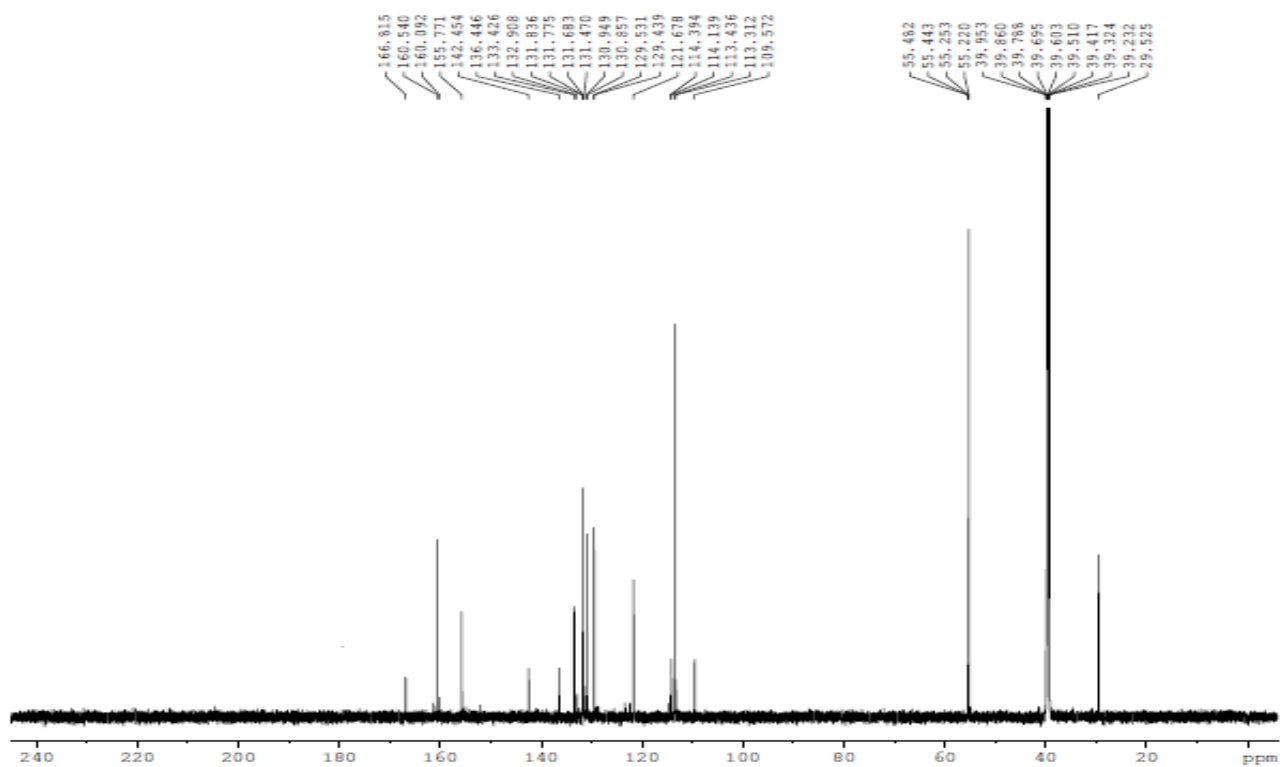


Figure S2. ^{13}C -NMR spectrum of L1.

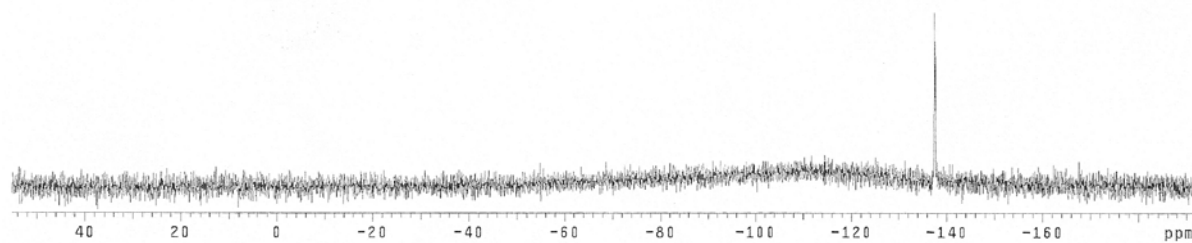


Figure S3. ^{19}F -NMR spectrum of L1.

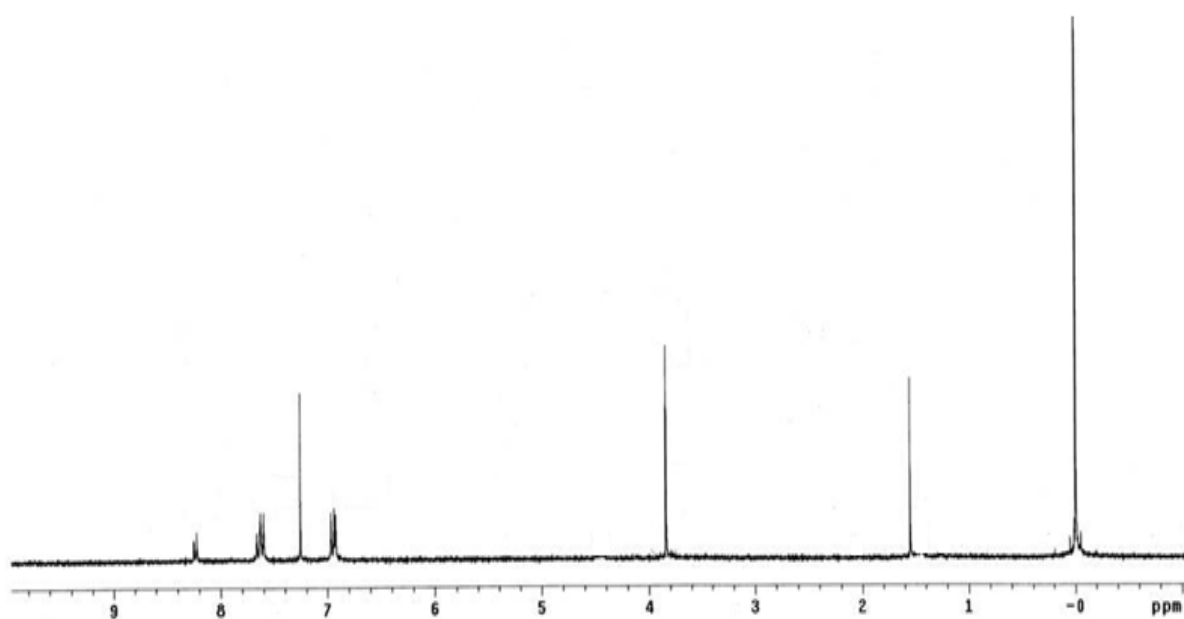


Figure S4. ¹H-NMR spectrum of L2.

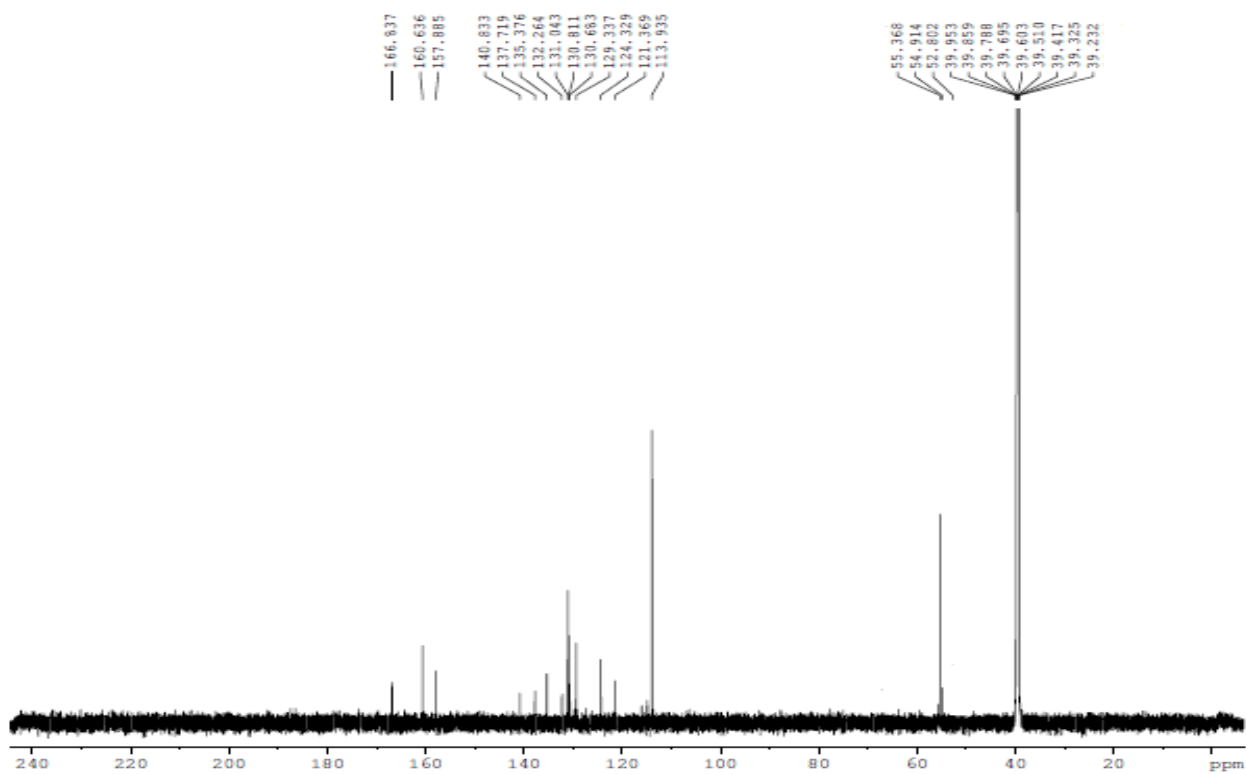


Figure S5. ¹³C-NMR spectrum of L2.

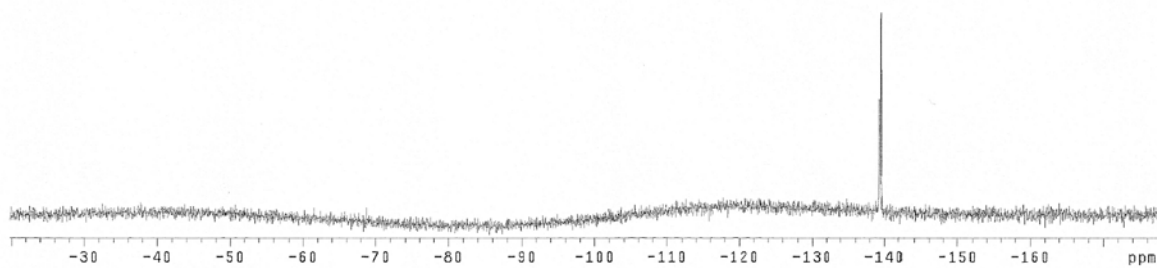


Figure S6. ^{19}F -NMR spectrum of L2.

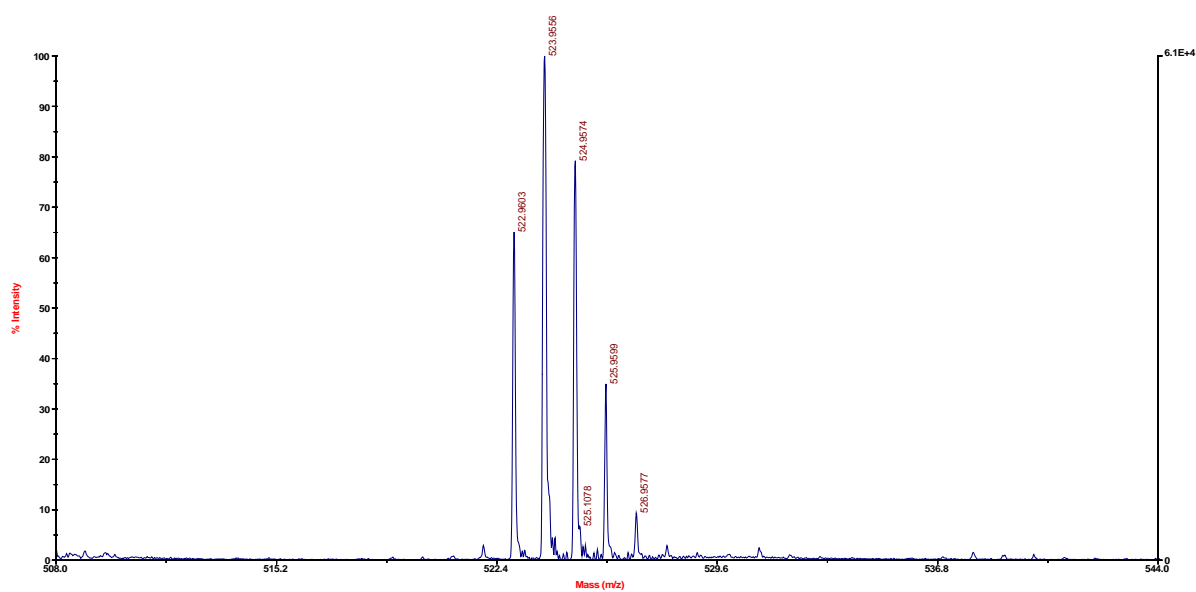


Figure S7. EI-mass spectrum of L1.

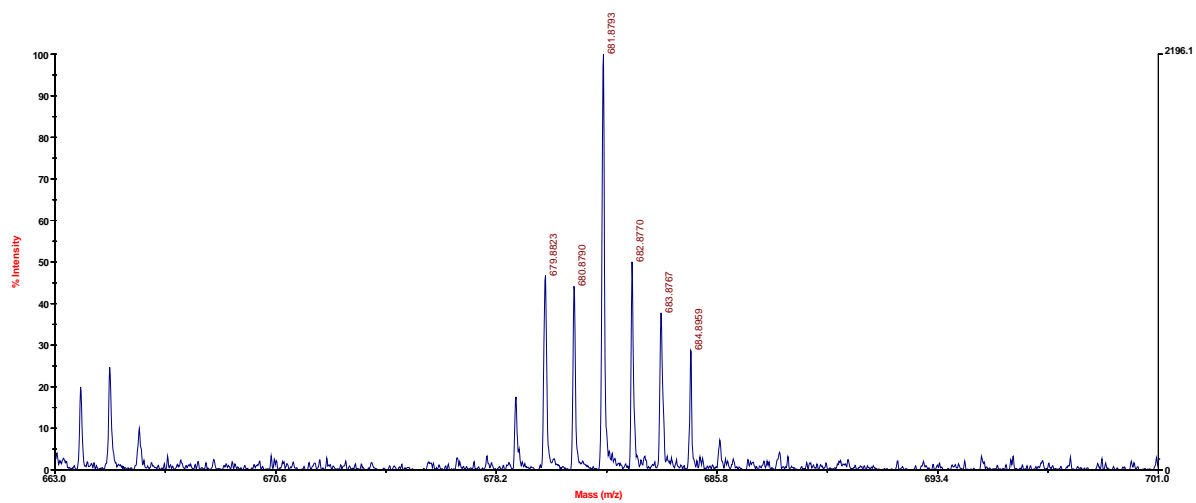


Figure S8. EI-mass spectrum of L2.

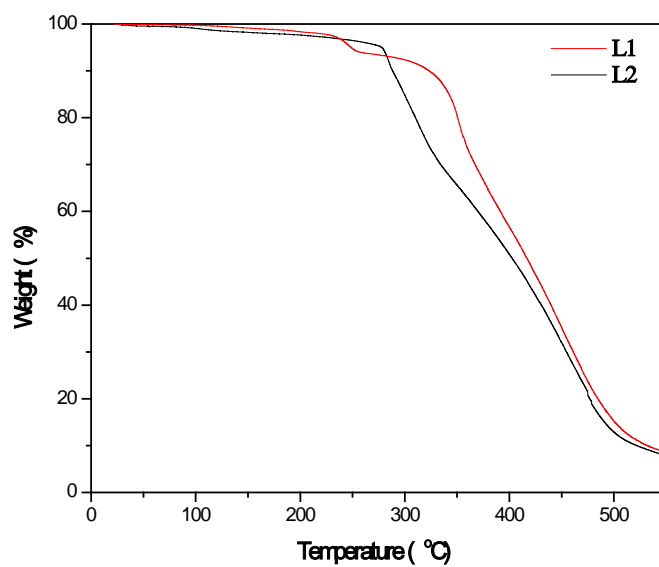


Figure S9. Thermogravimetric analysis of the ligands

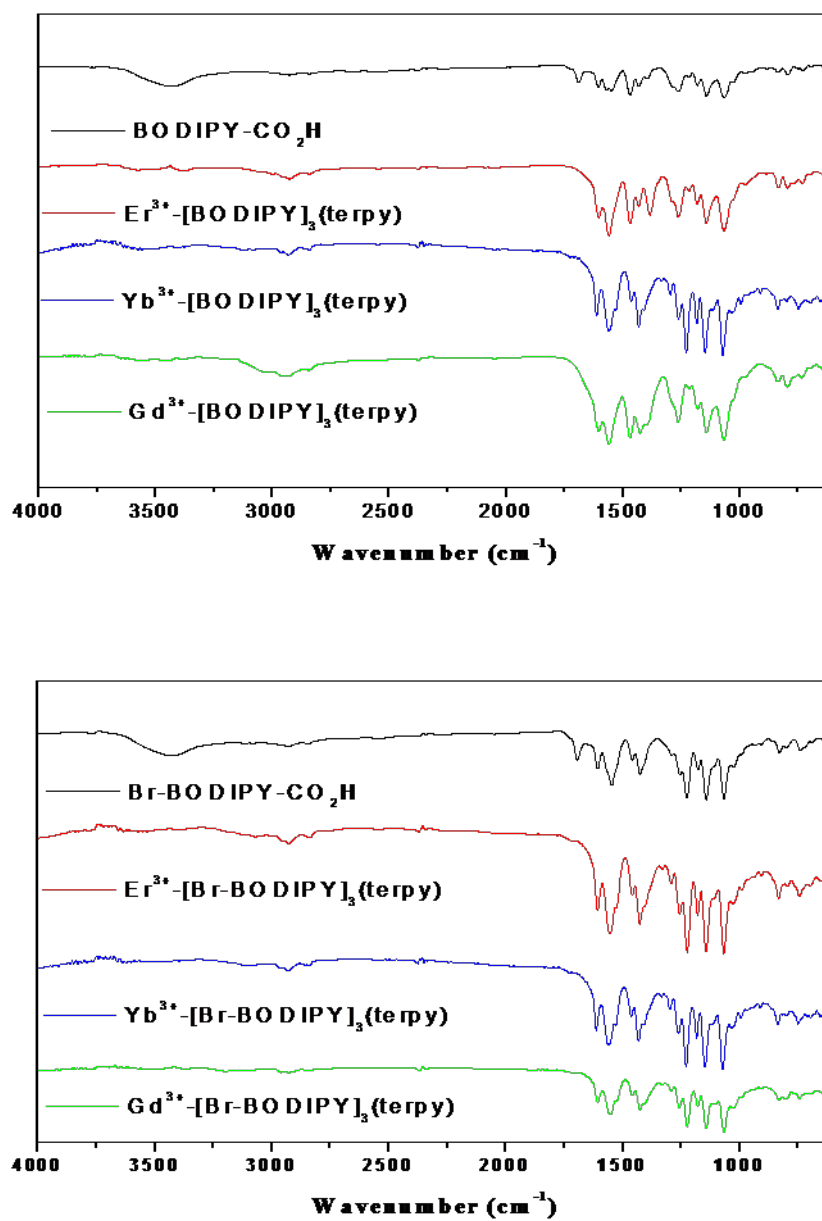


Figure S10. FT-IR spectra of the ligands and their complexes with Gd, Er, and Yb.

Photophysical data

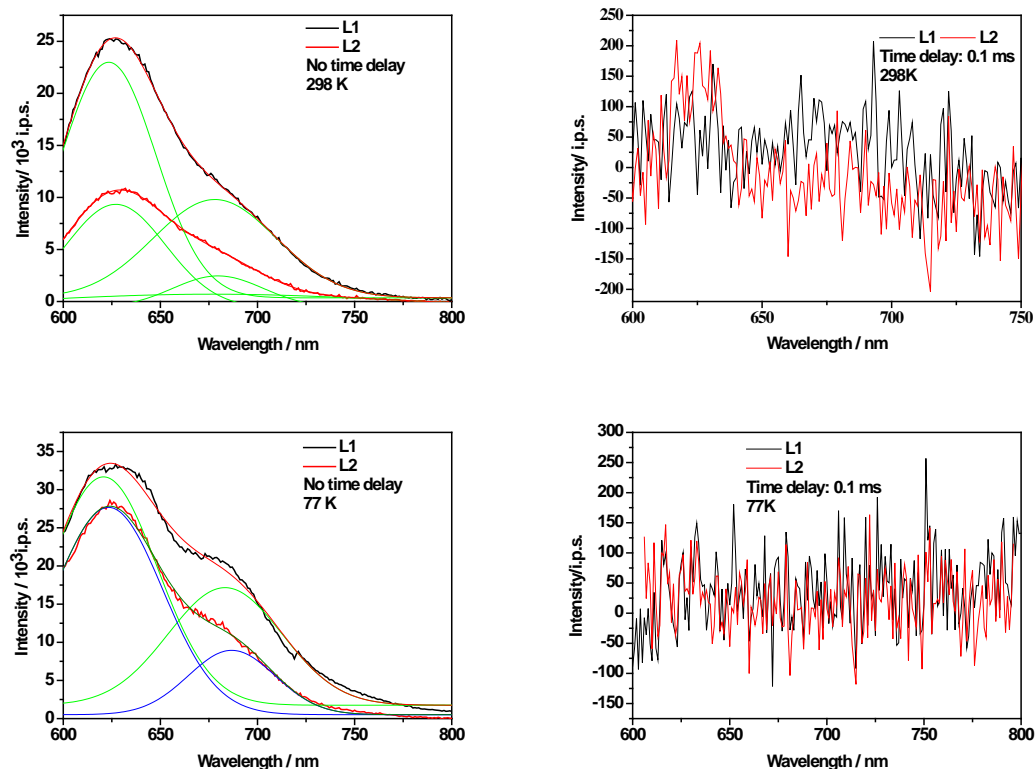


Figure S11. Fluorescence (left, with Gaussian analysis) and phosphorescence (right) spectra of the ligands in *m*-THF.

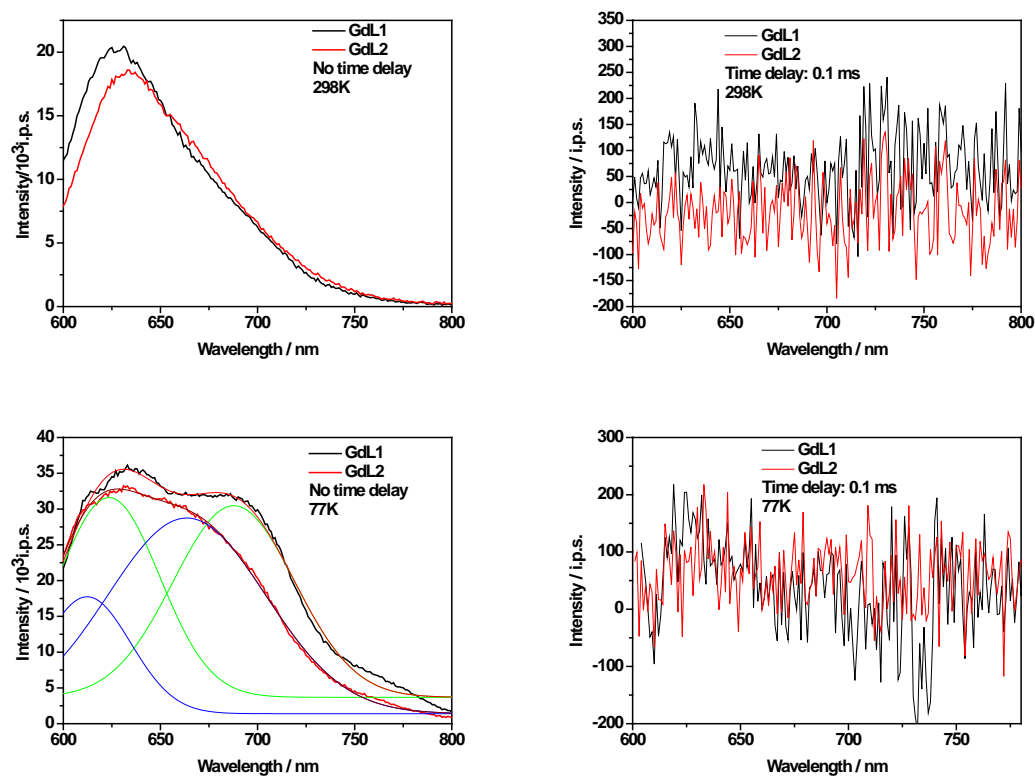


Figure S12. Fluorescence (left, with Gaussian analysis) and phosphorescence (right) spectra of the Gd^{III} complexes in *m*-THF.

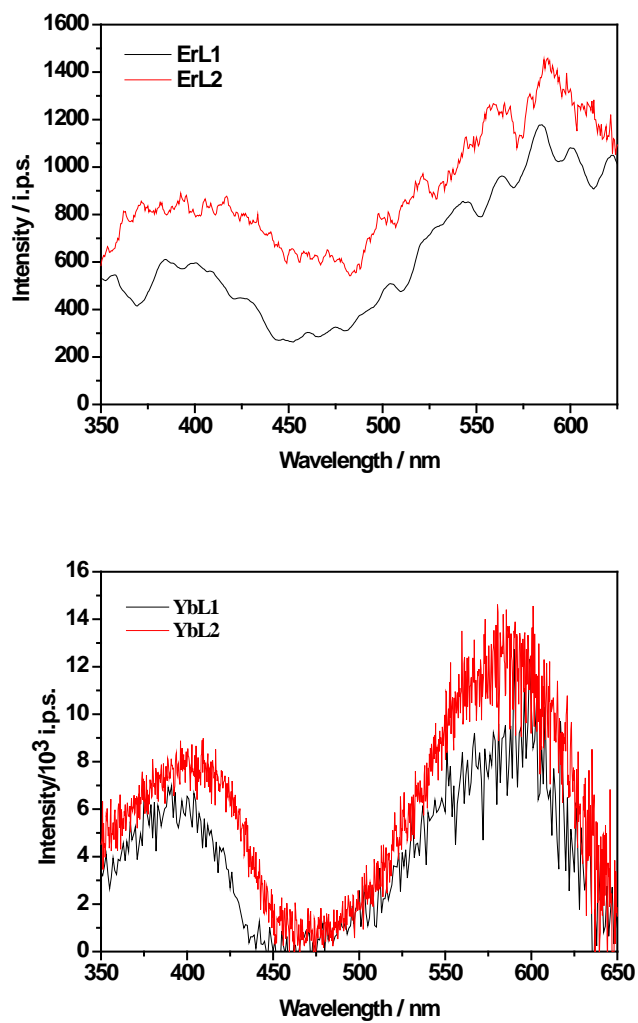


Figure S13. Excitation spectra of **ErLi** (top, $\lambda_{em} = 1530$ nm) and **YbLi** (bottom, $\lambda_{em} = 978$ nm) with the concentration of 1×10^{-5} M in THF at room temperature.