

Supporting Information

Synthesis and crystal structure of bis(9,10-dihydro-9-mesityl-10-aza-9-borabenz[*h*]quinolinato- κ^2N^1,N^{10})zinc(II)

Yannik Appiarius^{1,2}, Pim Puylaert³ and Anne Staubitz^{1,2,*}

¹ University of Bremen, Institute for Organic and Analytical Chemistry, 28359 Bremen, Germany.

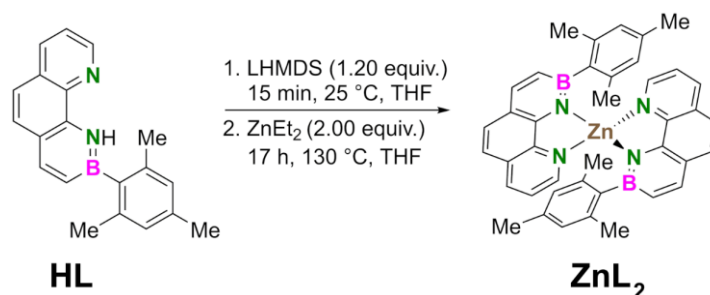
² University of Bremen, MAPEX Center for Materials and Processes, 28359 Bremen, Germany.

³ University of Bremen, Institute for Inorganic Chemistry and Crystallography, 28359 Bremen, Germany.

* Correspondence: staubitz@uni-bremen.de.

Abstract: The title compound, $C_{40}H_{36}B_2N_4Zn$ (**ZnL₂**), is an overall uncharged chelate that consists of two units of an *NH*-deprotonated 10-aza-9-borabenz[*h*]quinoline ligand (L) per Zn(II) center. It was synthesized in two steps by treating protonated ligand **HL** with lithium bis(trimethylsilyl)amide and further conversion with diethylzinc. Its asymmetric unit comprises one ZnL fragment; the molecule is completed by application of inversion symmetry at Zn. Due to the fourfold coordination with nitrogen atoms, the zinc(II) ion is located in a distorted tetrahedral environment. Besides the relatively short N–Zn bonds, **ZnL₂** is characterized by the significant protrusion of the central ion from the plane of the ligand backbone. The crystal structure is consolidated by intra- and intermolecular π – π stacking interactions, while the polarized B–N bond is barely involved in any close atom contacts.

1. Experimental Details



9,10-Dihydro-9-mesityl-10-aza-9-borabenzoh]quinoline (**HL**) was prepared according to a reported procedure (Appiarius *et al.*, 2021). For the synthesis of **ZnL₂**, **HL** (29.8 mg, 100 μmol , 1.00 equiv.) was dissolved in THF (1.5 mL) in a pressure resistant reaction vial under an argon atmosphere at 298 K. Under stirring, a solution of lithium bis(trimethylsilyl)amide (Sigma Aldrich, 1.0 M in THF, 120 μL , 1.20 equiv.) was added *via* a syringe. A small aliquot was taken under inert conditions and by ^1H NMR spectroscopy, a full conversion into **LiL** was confirmed. ^1H NMR (600 MHz, THF-*d*₈): δ = 8.60 (dd, 3J = 4.4 Hz, 4J = 1.7 Hz, 1H, C3-*H*), 8.20 (dd, 3J = 8.0 Hz, 4J = 1.7 Hz, 1H, C5-*H*), 7.97 (d, 3J = 10.8 Hz, 1H, C10-*H*), 7.64 (d, 3J = 8.4 Hz, 1H, C8-*H*), 7.38 (dd, 3J = 8.0, 4.4 Hz, 1H, C4-*H*), 7.11 (d, 3J = 8.4 Hz, 1H, C7-*H*), 6.80 (d, 3J = 10.8 Hz, 1H, C11-*H*), 6.72 (s, 2H, C14-*H*, C16-*H*), 2.24 (s, 6H, C19-*H*), 2.15 (s, 12H, C18-*H*, C20-*H*) ppm. Under argon, a solution of diethylzinc (Alfa Aesar, 15% w/w in hexanes, 230 μL , 2.00 equiv.) was added to **LiL** *via* a syringe. While stirring, the mixture was heated to 428 K for 17 h. The reaction vessel was transferred into a nitrogen-filled glove box. The volatiles were removed under reduced pressure (up to 353 K, 5 mbar). The dark violet slurry was extracted with *n*-hexane (3 \times 2 mL) and the solvents were removed. The crude product was dissolved in THF (500 μL) and *n*-hexane was allowed to diffuse into this solution over the course of 3 d to separate any remaining side-product, which remained at the bottom of the vial. The product was obtained as light yellow, air-sensitive crystals (6.4 mg, 19%) by repeating this process twice. These crystals were also suitable for structural analysis by X-ray diffraction and NMR spectroscopy. ^1H NMR (600 MHz, THF-*d*₈): δ = 8.37 – 8.32 (m, 4H, C3-*H* + C5-*H*), 8.07 (d, 3J = 11.0 Hz, 2H, C10-*H*), 7.79 (d, 3J = 8.7 Hz, 2H, C8-*H*), 7.38 – 7.35 (m, 2H, C4-*H*), 7.33 (d, 3J = 8.7 Hz, 2H, C7-*H*), 6.90 (d, 3J = 11.0 Hz, 2H, C11-*H*), 6.04 (s, 2H, C14-*H*), 5.61 (s, 2H, C16-*H*), 1.83 (s, 6H, C19-*H*), 1.79 (s, 6H, C18-*H*), 1.40 (s, 6H, C20-*H*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, THF-*d*₈): δ = 147.3 (C3), 145.8 (C1), 143.3 (C2), 143.0 (C10), 139.2 (C17), 139.2 (C5), 139.1 (C13), 134.8 (C15), 134.5 (C11), 131.2 (C8), 129.0 (C6), 127.1 (C14), 126.4 (C16), 126.1 (C9), 122.3 (C4), 116.1 (C7), 24.0 (C18), 23.8 (C20), 21.3 (C19) ppm. C12 was not detected due to its quaternary nature and the quadrupolar moment of the neighboring boron nucleus. $^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, THF-*d*₈): δ = 38.6 ppm. **MS** (EI, 70 eV, $R \approx 10\ 000$): m/z 658.3 (3%) [ZnL_2]⁺, 298.2 (100%) [**HL**]⁺. **HR-MS** (EI, 70 eV, $R \approx 10\ 000$): m/z calcd. for $\text{C}_{40}\text{H}_{36}\text{B}_2\text{N}_4\text{Zn}^+$ 658.24259, found 658.24253 (Dev.: 0.06 mu, 0.09 ppm). **UV/Vis**: λ_{abs} = 296, 343, 358 nm. **Fluorescence**: λ_{fl} = 488 nm (λ_{exc} = 350 nm). Solvents (THF, VWR, 99.7%; *n*-hexane, Honeywell, 97%) were dried and degassed with a solvent purification system, stored over activated molecular sieves (3 Å) and handled under inert conditions.

2. Crystallography

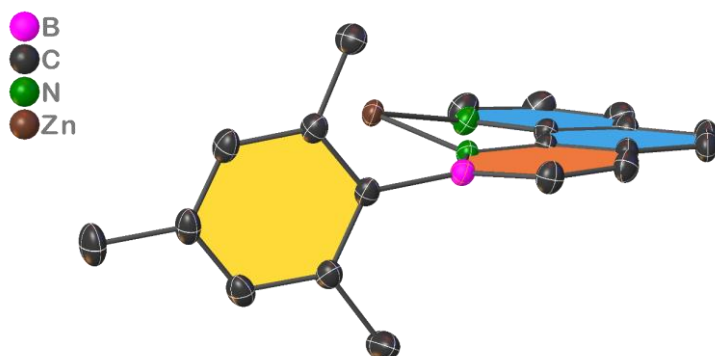


Figure S1. Asymmetric unit (ZnL), highlighting the off-plane position of the Zn(II) cation. BN-rings shown in orange, mesityl-rings in yellow, phenyl- and pyridyl-rings in blue.

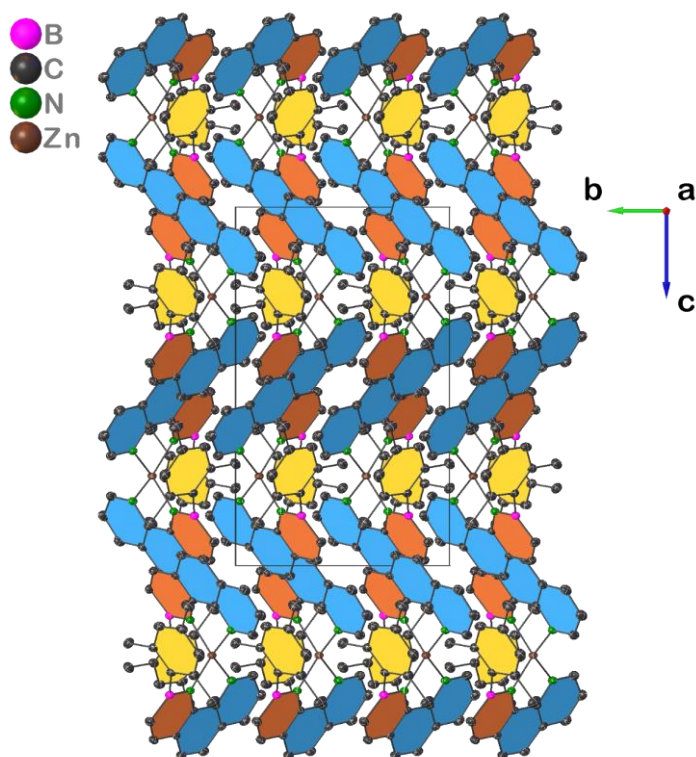


Figure S2. Unit cell packing view of a ZnL₂ crystal along the *a*-axis. BN-rings shown in orange, mesityl-rings in yellow, phenyl- and pyridyl-rings in blue.

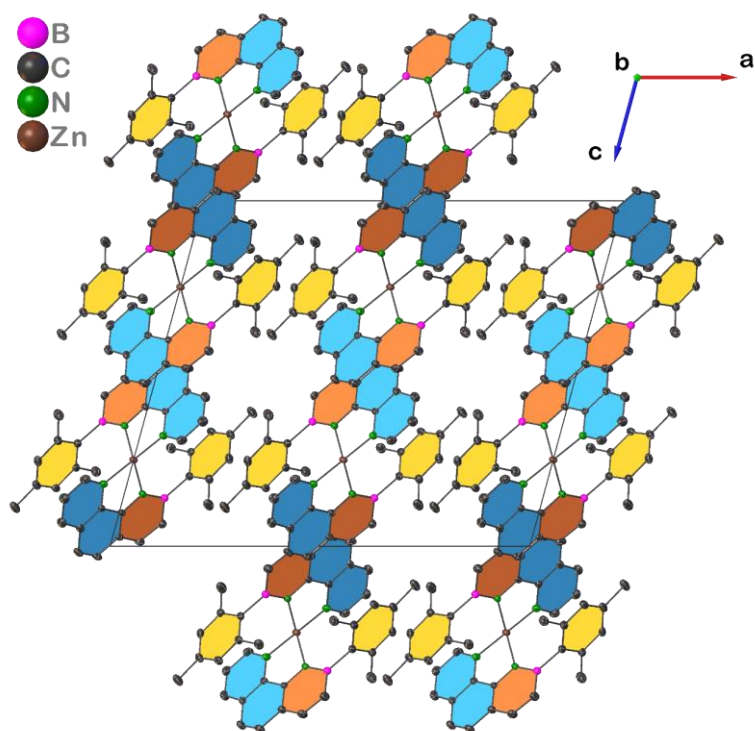


Figure S3. Unit cell packing view of a ZnL_2 crystal along the b -axis. BN-rings shown in orange, mesityl-rings in yellow, phenyl- and pyridyl-rings in blue.

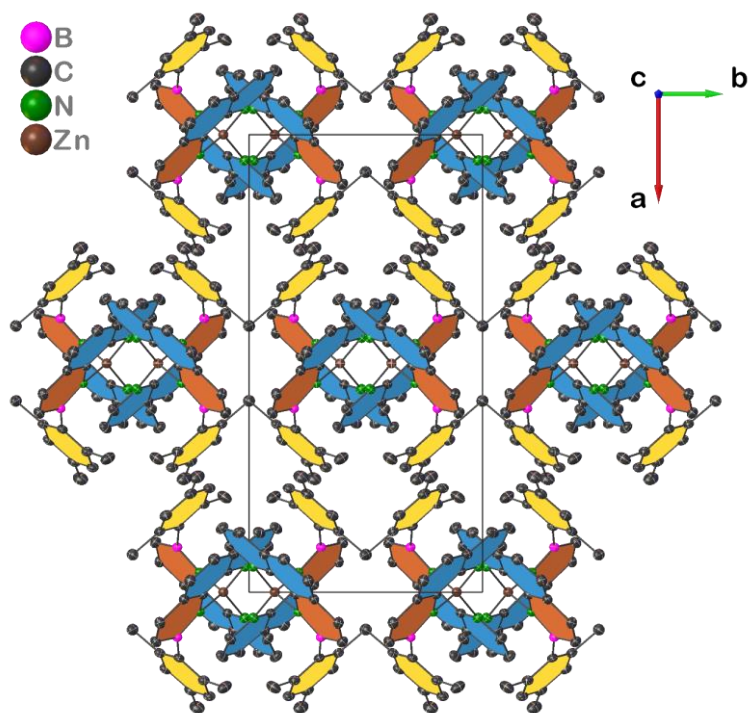
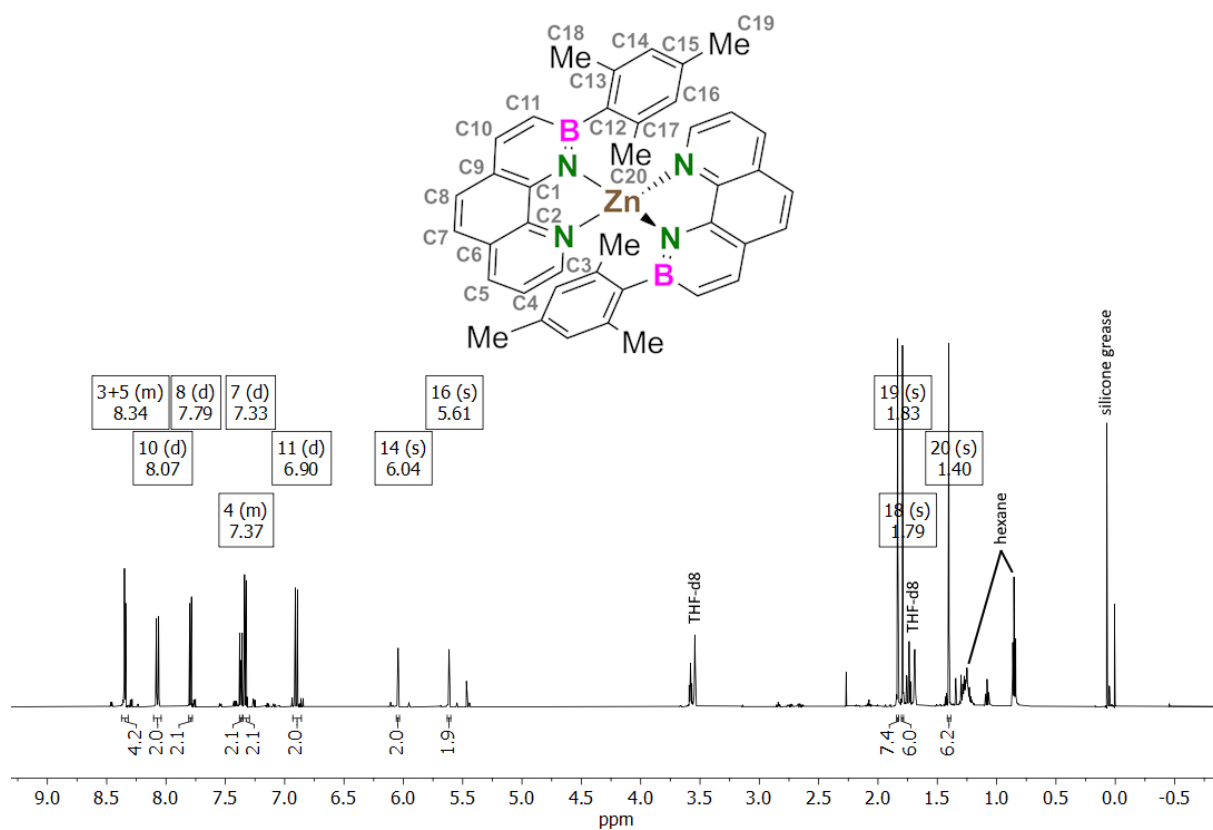


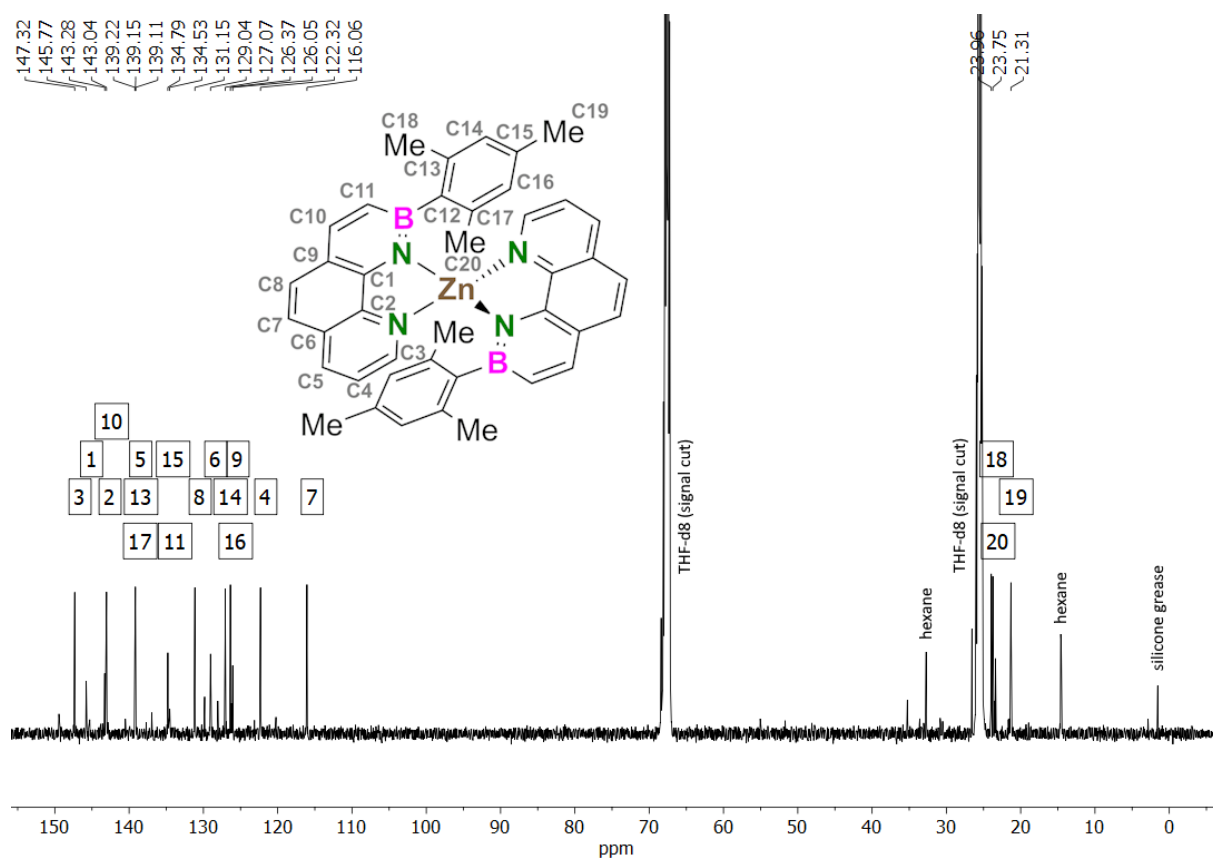
Figure S4. Unit cell packing view of a ZnL_2 crystal along the c -axis. BN-rings shown in orange, mesityl-rings in yellow, phenyl- and pyridyl-rings in blue.

3. NMR Spectra

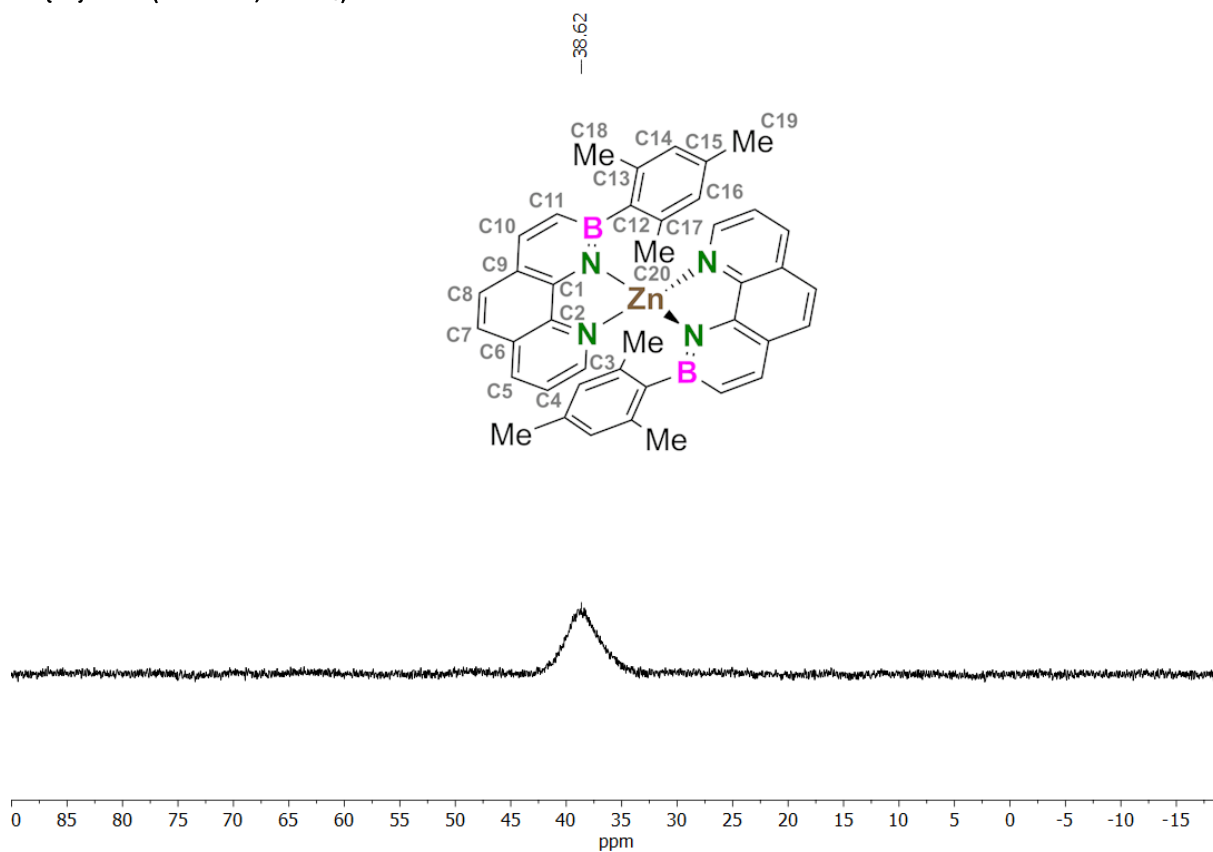
^1H NMR (600 MHz, THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, THF- d_8)



$^{11}\text{B}\{^1\text{H}\}$ NMR (193 MHz, $\text{THF-}d_6$)



4. Optical Spectroscopy

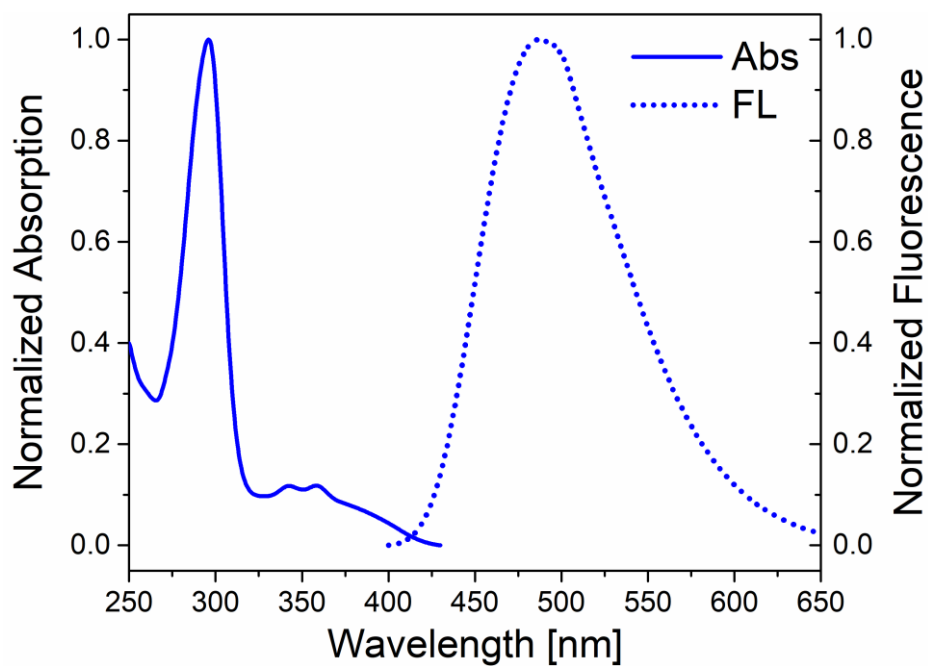


Figure S5. Normalized absorption (continuous) and fluorescence (dotted) spectra of ZnL_2 .