Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information: Synthesis and complexes of a constrained cavity Schiff-base dipyrrin macrocycle

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Contents

1 General procedures

The syntheses of all air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under an atmosphere of dry argon. Vacuum Atmospheres and MBraun glove boxes were used to manipulate and store air- and moisture-sensitive compounds under an atmosphere of dried and deoxygenated dinitrogen. All glassware was dried in an oven at 160 °C, cooled under 10^{-3} mbar vacuum and then purged with argon. Prior to use, all Fisherbrand R 1.2 *m*m retention glass microfiber filters and stainless-steel cannulae were dried in an oven at 160 °C overnight. All solvents for use with air- and moisture-sensitive compounds were stored in Teflon-tapped ampoules containing pre-dried 4 Å molecular sieves. Solvents were collected from a solvent purification system (Innovation Technologies), where they had been passed over a column of molecular sieves for 24 hours prior to collection. Deuterated solvents were dried over potassium and degassed by three freeze-pump-thaw cycles. They were then degassed prior to use and subsequent storage. All chemicals were used as used as received without any purification, unless otherwise specified.

^{1}H NMR spectra were recorded on a Bruker AVA400 spectrometer operating at 399.90 MHz, a Bruker AVA500 or Bruker PRO500 operating at 500.12 MHz or a Bruker AVA600 spectrometer operating at 599.81 MHz. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVA500 or Bruker PRO500 operating at 125.76 MHz. ^{19}F{^{1}H} NMR spectra were recorded on a Bruker AVA500 spectrometer operating at 470.59 MHz. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to residual solvent resonances calibrated against an external standard, $SiMe_4$ (*d* = 0 ppm). ^{19}F{^{1}H} NMR spectra are referenced to an external standard, CCl_3F (*d* = 0 ppm). All spectra were recorded at 298 K unless otherwise specified. All data were processed using MestReNova 12.0.3.

X-ray crystallographic data were collected at 170 K on an Oxford Diffraction Excalibur diffractometer using graphite monochromated Mo-K*a* radiation equipped with an Eos CCD detector (λ = 0.71073 Å), or at 120 K on a Supernova, Dual, Cu at Zero Atlas diffractometer using Cu-Kalpha radiation (λ = 1.5418 Å). Structures were solved using ShelXT direct methods or intrinsic phasing and refined using a full-matrix least square refinement on $|F|^2$ using ShelXL.[1-3] All programs were used within the Olex suite.[4] All non-hydrogen atoms refined with anisotropic displacement parameters and H-parameters were constrained to parent atoms and refined using a riding model unless otherwise specified. All X-ray crystal structures were analysed and illustrated using Mercury 4.1.0.

DFT calculations were conducted using the Gaussian09[5] package on the Eddie server system at the University of Edinburgh. Initial starting geometries were either generated from X-ray crystal structures or from a drawn molecule using the Avogadro program (version 1.0.3). All structures discussed in the text were optimised and converged according to the criteria for maximum displacement and maximum force. Frequency calculations were conducted to confirm that the optimised structures represented minimum energy geometries, which was confirmed by having no imaginary frequencies. TD-DFT calculations were conducted on the first 100 excited stated using SCRF PCM solvent model (\Solvent=Dichloromethane), spanning the wavelength range measured experimentally. All optimisation, frequency and TD-DFT calculations were carried out using CAM-B3LYP functional and 6-311G(d,p) basis set unless otherwise specified.

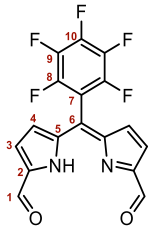
MALDI-TOF MS spectra were collected using an ultrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with 2 kHz Smartbeam II laser (355 nm) and operated in linear mode. The method employed to analyse the compounds used an m/z range of 200-3500 in positive and negative ion mode. A solution of the individual compound in THF was spotted on a polished/ground steel MTP 384 MALDI plate and allowed to dry prior to analysis. Air-sensitive HR-MS spectra were carried out by the Mass Spectrometry Facility at the University of Edinburgh.

Elemental analyses were carried out by Mr Stephen Boyer at the London Metropolitan University and Elemental Microanalysis Ltd., measured in duplicate. All FT-IR spectra were recorded using JASCO 410 or JASCO 460 plus spectrometers. All UV-vis absorption spectra were recorded on a Jasco V-670 spectrometer in a 10 mm quartz cuvette, fitted with a septum for air-sensitive compounds.

1,9-diformyl-(5-pentafluorophenyl)dipyrromethane[6] and of bis(*m*-aminoisopropyl)benzene[7] were synthesised according to published procedures.

2 Synthetic procedures

2.1 Synthesis of 1,9-diformyl-5(pentafluorphenyl)dipyrrin (**4^{ox}**)



4^{ox}

The synthesis was conducted under inert condition using a Schlenk set-up. A solution of 1,9-diformyl-(5-pentafluorophenyl)dipyrromethane (1.06 g, 2.8 mmol, 1.0 eq) in dry CH_2Cl_2 (20 mL) was treated with DDQ (832 mg, 3.6 mmol, 1.3 eq) at 0 °C, after which the reaction mixture was allowed to warm to room temperature. Subsequently, the reaction mixture was irradiated (420 nm Kessil H380 dual function lamp; output power: 90 W, 19.3 Wat 420 nm) for 48 h, filtered in air, and washed with CH_2Cl_2. The filtrate and washings were combined and evaporated to dryness under vacuum. The solid residues were recrystallised from hot CH_2Cl_2 giving 728 mg (72 %) of **4^{ox}** as dark red crystals. Crystals suitable for X-ray diffraction were grown by slow evaporation of CH_2Cl_2 at −30 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 12.41 (1H, s, bs, NH), 10.00 (2H, s, C(1)*H*), 7.01 (2H, d, *J* = 4.5 Hz, C(3)*H*), 6.62 (2H, d, *J* = 4.5 Hz, C(4)*H*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ_C 184.79 (*C*(1)), 153.85 (*C*(2)), 144.58 (d, $^1J_{CF}$ = 262.5 Hz,(*C*(10)F), 144.40 (*C*(5)), 142.31 (d, $^1J_{CF}$ = 258.4 Hz, *C*(8)F), 137.71 (d, $^1J_{CF}$ = 251.5 Hz, *C*(9)F), 132.88 (*C*(7)), 128.81 (*C*(3)H), 128.33 (*C*(6)), 122.71 (*C*(4)H). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ_F −136.88 - −138.63 (2F, m, Ar^F *ortho*-F), −149.68 (1F, ddd, *J* = 23.3, 21.1, 2.2 Hz, Ar^F *para*-F), −158.56 - −160.18 (2F, m, Ar^F *meta*-F). FTIR (film): **ν** 1671 cm^{-1} (C=O, conjugated aldehyde). UV-vis (CH_2Cl_2): **λ**$_{max}$ 275 nm, ε = 15,884 M^{-1} cm^{-1}; **λ** 472 nm, ε = 9075 M^{-1} cm^{-1}. Elemental Analysis: $C_{17}H_7F_5N_2O_2$ (MW = 366.0 gmol^{-1}) requires: C, 55.75; H, 1.93; N, 7.65%. Found: C, 54.07; H,1.79; N, 7.93%; MS (MALDI-TOF, MeCN): *m/z* 367.260 (100%) [M+H]$^+$ (calcd for $C_{17}H_8F_5N_2O_2$ 367.050).

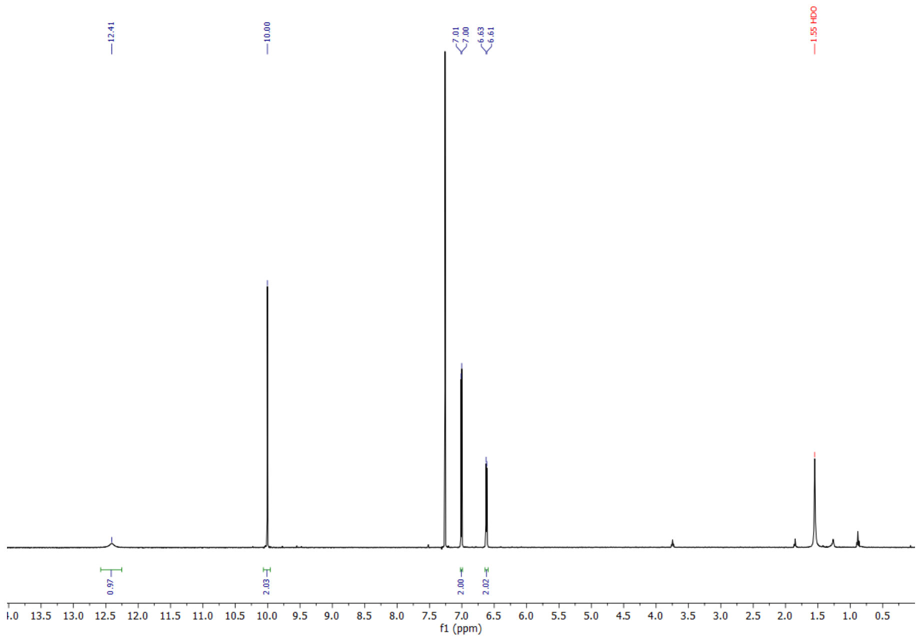


Figure S1 ^{1}H NMR spectrum of **4^{ox}** in CDCl$_3$.

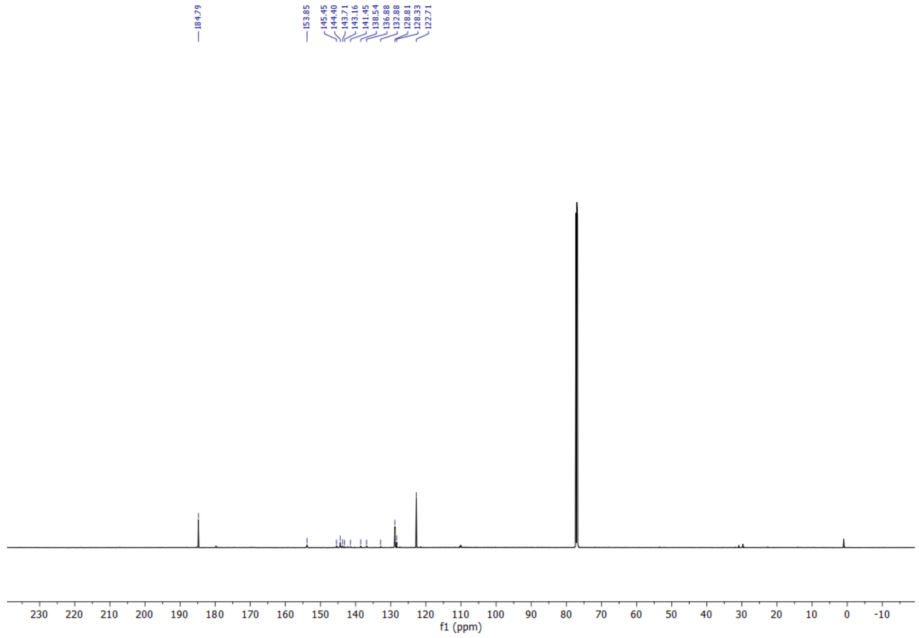


Figure S2 ^{13}C{^{1}H} NMR spectrum of **4^{ox}** in CDCl$_3$.

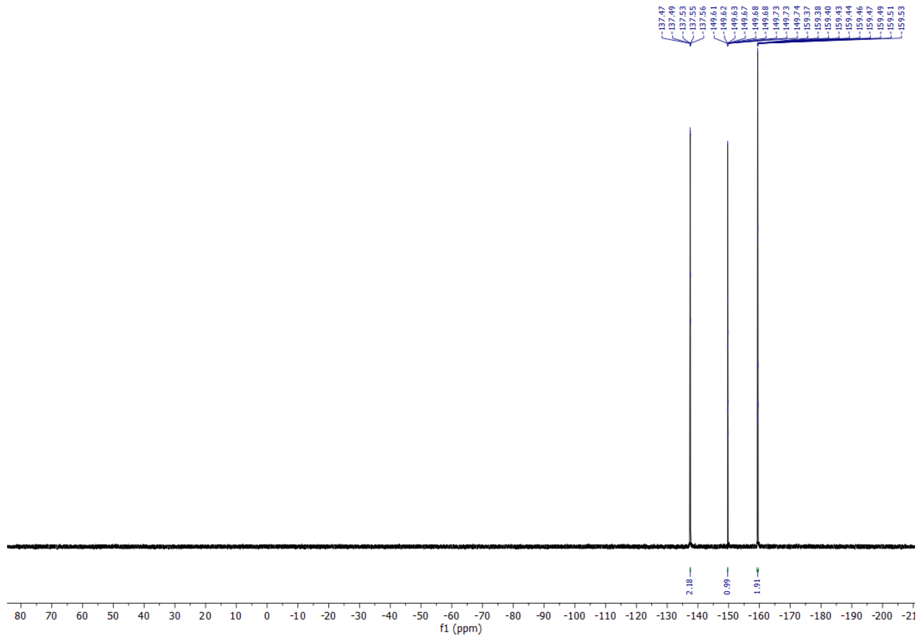


Figure S3 $^{19}F\{^{1}H\}$ NMR spectrum of **4^{ox}** in $CDCl_3$.

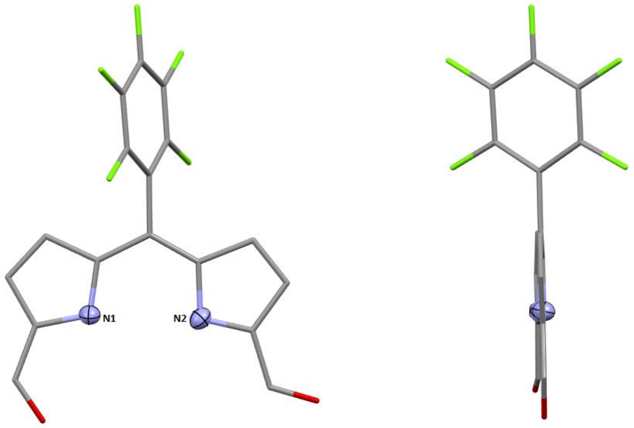
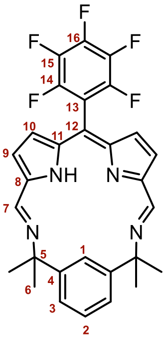


Figure S4 X-ray crystal structure of **4^{ox}**. For clarity, all hydrogen atoms are omitted (displacement ellipsoids are drawn at 50 % probability). Grey = C, blue = N, green = F, red = O.

2.2 Synthesis of H**L**



To a solution of 1,9-diformyl-5(pentafluorphenyl)dipyrromethane (1.92 g, 5.20 mmol, 1 eq) in MeCN (100 mL) was slowly added a solution of bis(*m*-aminoisopropyl)benzene (1 g, 5.20 mmol, 1 eq) in MeCN (50 mL)and stirred for 16 h. Greenish-red crystals of H**L** were formed which were isolated by filtration and dried under vacuum. Yield = 2.2 g (80 %). Crystals suitable for X-ray diffraction were grown during the synthesis. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 14.14 (1H, s, N*H*), 9.36 (1H, t, *J* = 1.9 Hz, C(1)*H*), 8.47 (2H, s, C(7)*H*), 7.36 (1H, dd, *J* = 8.6, 6.7 Hz, C(2)*H*), 7.29 (2H, m, C(3)*H*), 6.65 (2H, d, *J* = 4.3 Hz, C(9)*H*), 6.56 (2H, d, *J* = 4.2 Hz, C(10)*H*), 1.62 (12H, s, C(6)H_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ_C 154.32 (*C*(8)), 149.19 (C(4)), 147.37 (*C*(7)H), 144.76 (1F, d, $^1J_{CF}$ = 251.0 Hz, *C*(16)F), 142.32 (*C*(11)), 141.70 (d, $^1J_{CF}$ = 256.6 Hz, *C*(14)F), 137.52 (d, $^1J_{CF}$ = 254.1 Hz, *C*(15)F), 127.97 (*C*(10)H), 127.91 (*C*(9)H), 125.76 (*C*(1)H), 125.41 (*C*(12)), 122.53 (*C*(3)H), 119.98 (*C*(9)H), 62.21 (*C*(5)), 29.98 (*C*(6)H_3). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ_F **–**133.41 - **–**143.13 (2F, m, Ar^F *ortho*-F), **–**151.94 (1F, t, *J* = 21.0 Hz, Ar^F *para*-F), **–**158.66 to **–**168.98 (2F, m, Ar^F *meta*-F). FTIR (film) **ν**$_{max}$ 1576 cm^{-1} (C(7)=N). UV-vis (CH_2Cl_2): **λ**$_{max}$ 278 nm, ε = 29,301 M^{-1} cm^{-1}; **λ** 513.5 nm, ε = 22,132 M^{-1} cm^{-1}. Elemental analysis: $C_{29}H_{23}F_5N_4$ (MW = 522.2 gmol^{-1}) requires: C, 66.66; H, 4.44; N, 10.72 %. Found: C, 65.30; H, 4.54; N, 10.94 %. MS (MALDI-TOF, MeCN): *m/z* 524.533 (100 %) [M+H]$^+$ (calcd for $C_{29}H_{24}F_5N_4$ 523.192), 561.509 (31%) [M+K]$^+$ (calcd for $C_{29}H_{23}F_5N_4K$ 561.147), 545.527 (30 %) [M+Na]$^+$ (calcd for requires 545.174). mp: 230 °C (*dec* red to dark red/black).

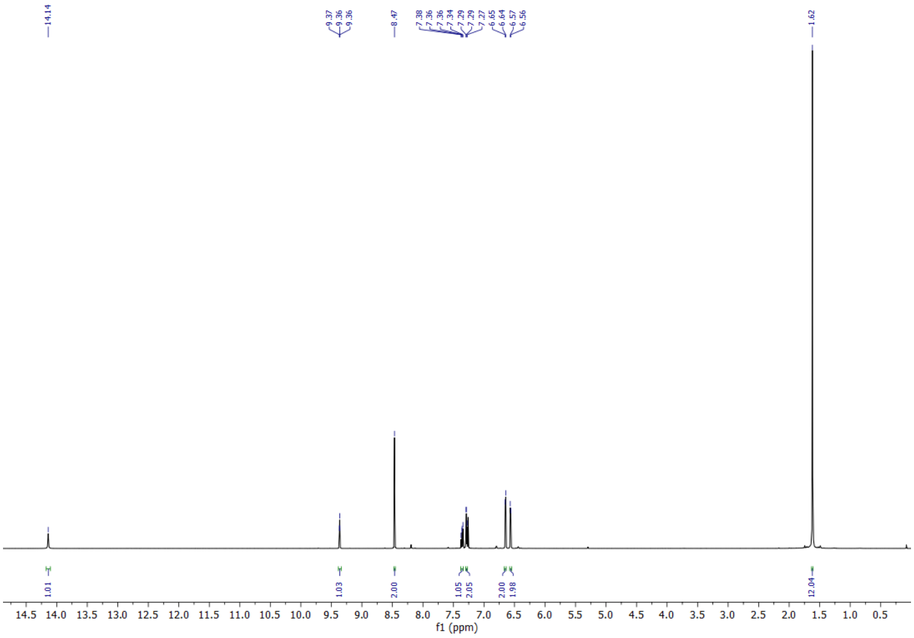


Figure S5 ^{1}H NMR spectrum of H**L** in $CDCl_3$.

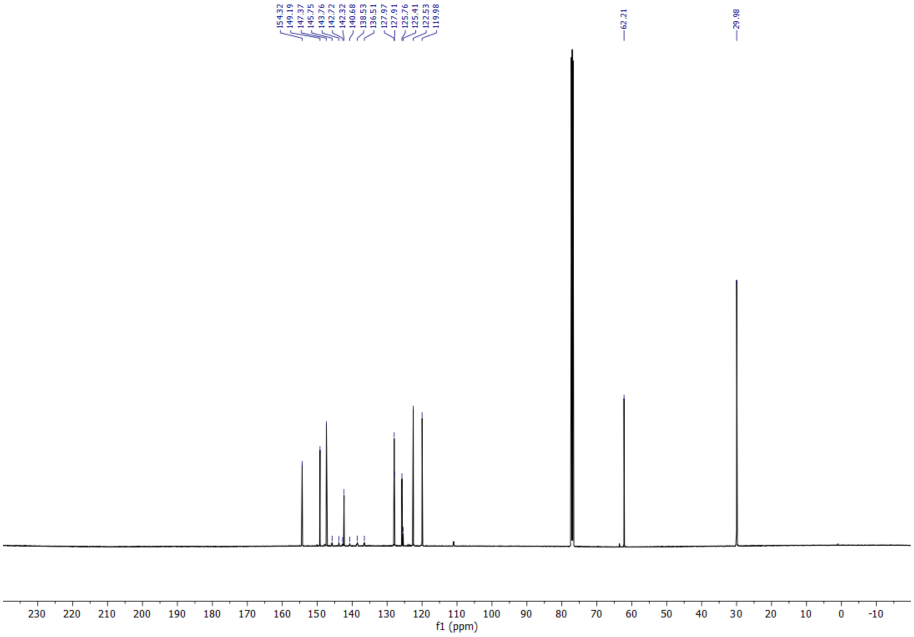


Figure S6 $^{13}C\{^1H\}$ NMR spectrum of H**L** in CDCl$_3$.

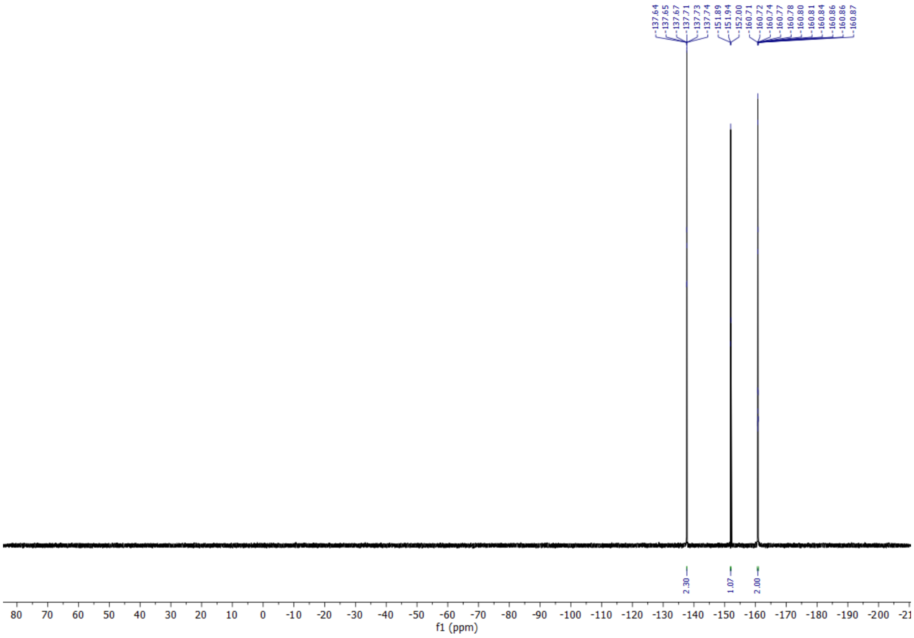


Figure S7 $^{19}F\{^1H\}$ NMR spectrum of H**L** in CDCl$_3$.

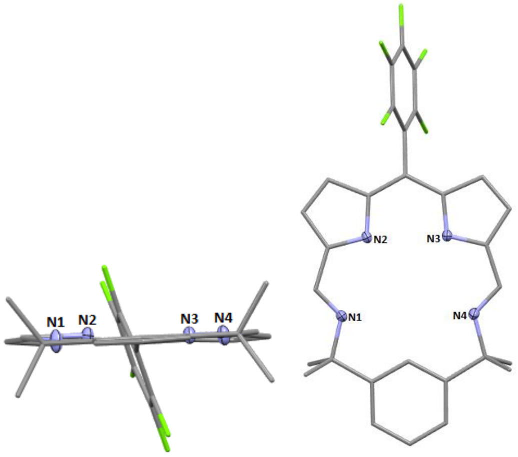
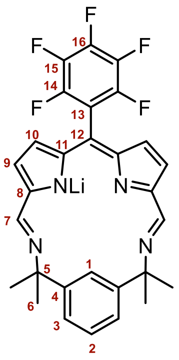


Figure S8 X-ray crystal structure of H**L**. For clarity, all hydrogen atoms and one MeCN solvent molecule have been omitted (displacement ellipsoids are drawn at 50 % probability). Grey = C, blue = N, green = F.

2.3 Synthesis of Li(**L**)



The synthesis was conducted under inert atmosphere using Schlenk techniques. A solution of $LiN(SiMe_3)_2$ (2.6 mmol, 430 mg, 1.1 eq) in toluene (25 mL) was slowly added to a solution of H**L** (1.22 g, 2.34 mmol, 1 eq) in dry toluene (200 mL) at 0 °C resulting in an immediate colour change from red to deep blue. The reaction mixture was allowed to slowly warm to rt and stirred for 16 h, after which the solvents were removed under vacuum, obtaining Li(**L**) as a purple solid which was dried at 50 °C. Crystals suitable for X-ray diffraction were grown via slow evaporation of a dilute but saturated *n*-hexane solution. Yield = 1.12 g (91 %). ^1H NMR (500 MHz, C_6D_6): δ_H 8.25 (1H, t, J = 2.1 Hz, C(1)*H*), 7.90 (1H, s, C(7)*H*), 7.17 (1H, d, J = 8.1 Hz, C(2)*H*), 7.08 (2H, dd, J = 7.7, 1.6 Hz, C(3)*H*), 6.69 (2H, d, J = 4.0 Hz, C(10)*H*), 6.55 (2H, d, J = 4.0 Hz, C(9)*H*), 1.33 (12H, s, C(6)H_3). $^7Li\{^1H\}$ NMR (194 MHz, C_6D_6): δ_{Li} 1.57 (1Li, S, Li). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ_C 157.02 (*C*(8)), 151.38 (*C*(7)H), 149.76 (*C*(4)), 144.85 (d, $^1J_{CF}$ = 258.1 Hz, Ar^F *C*(16)F), 143.93 (*C*(11)), 140.92 (d, $^1J_{CF}$ = 253.9 Hz, Ar^F *C*(14)F), 137.52 (*C*(13)), 137.24 (d, $^1J_{CF}$ = 252.6 Hz, Ar^F *C*(15)F), 129.58 (*C*(10)), 128.91 (*C*(1)H), 127.97 (*C*(12)), 127.27 (*C*(2)), 121.44 (*C*(3)H), 119.07 (*C*(9)H), 61.35 (*C*(5)), 28.27 (*C*(6)). $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6): δ_F –137.15 - –147.22 (2F, m, Ar^F *ortho*-F), –154.02 (1F, t, J = 21.5 Hz, Ar^F *para*-F), –162.00 (2F, dd, J = 21.7, 15.9 Hz, Ar^F *meta*-F). FTIR (film) $\boldsymbol{\nu}_{max}$ 1610 cm^{-1} (C(7)=N). UV-vis (THF): $\boldsymbol{\lambda}_{max}$ 303.5 nm, $\boldsymbol{\varepsilon}$ = 36,616 M^{-1} cm^{-1}; 595.5 nm, $\boldsymbol{\varepsilon}$ = 45,962 M^{-1} cm^{-1}. Elemental analysis: $C_{29}H_{22}F_5N_4Li$ (MW = 528.2 $gmol^{-1}$) requires: C, 65.91; H, 4.20; N, 10.60 %. Found: C, 64.97; H, 4.25; N, 10.30 % (no satisfactory analysis were measured with the low carbon value likely due to facile hydrolysis). MS (MALDI-TOF, THF): *m/z* 529.376 (100 %) $[M+H]^+$ (calcd for $C_{29}H_{23}F_5N_4Li$ 529.200); 535.387 (59 %) $[M+Li]^+$ (calcd for $C_{29}H_{22}F_5N_4Li_2$ 535.208); 545.353 (25 %) $[M-Li+H+Na]^+$ (calcd. for $C_{29}H_{23}F_5N_4Na$ requires 545.174); 551.371 (22 %) $[M+Na]^+$ (calcd for $C_{29}H_{22}F_5N_4LiNa$ 551.182); 561.335 (84 %) $[M-Li+H+K]^+$ (calcd for $C_{29}H_{23}F_5N_4K$ 561.147); 567.351 (31 %) $[M-Li+2Na]^+$ (calcd for $C_{29}H_{22}F_5N_4Na_2$ 567.155). HRMS (ESI^+) $C_{29}H_{23}F_5N_4Li$ $[M+H]^+$ requires 529.199742, found 529.199133 (-1.1 ppm, 100 %).

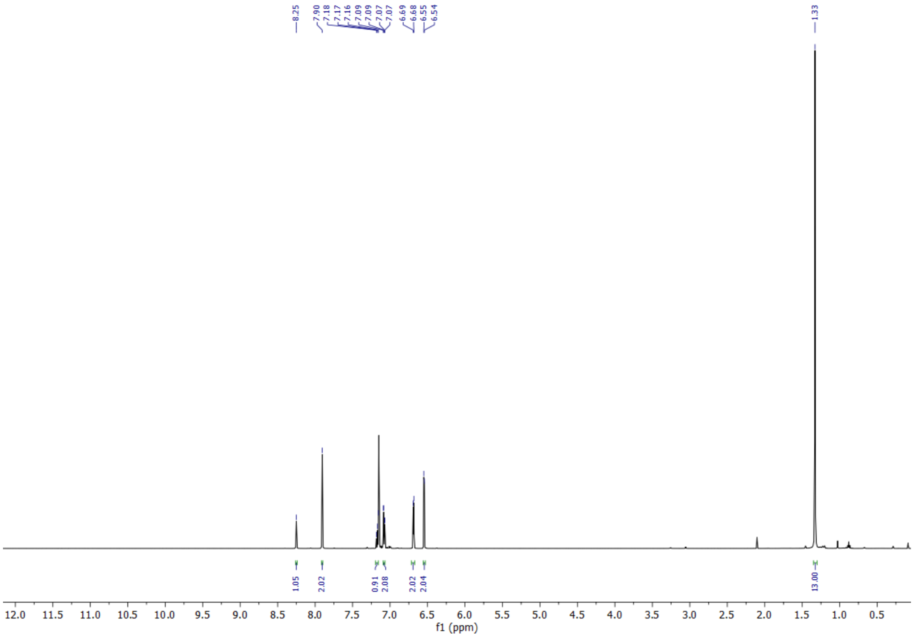


Figure S9 ^{1}H NMR spectrum of Li(**L**) in C_6D_6.

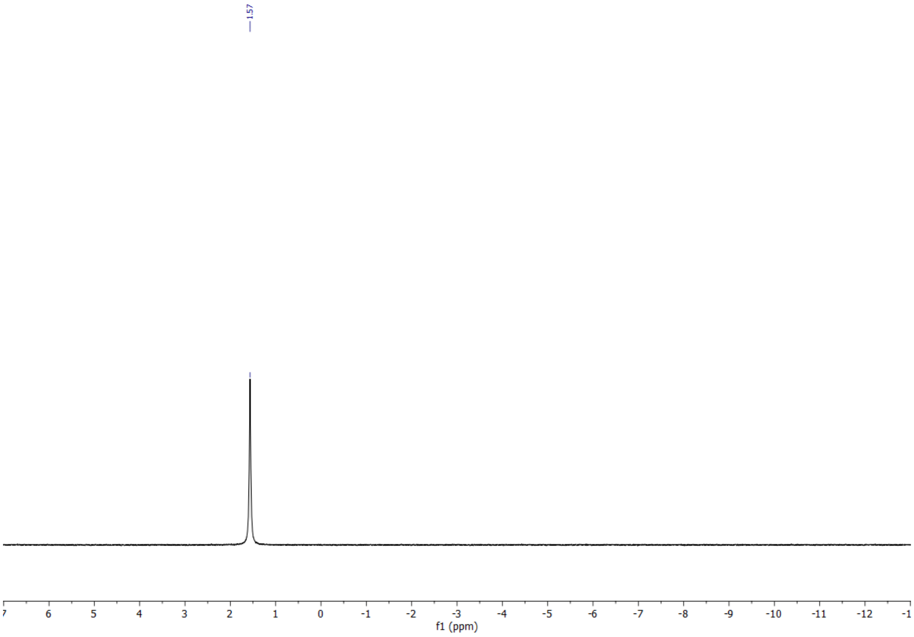


Figure S10 ^{7}Li NMR spectrum of Li(**L**) in C_6D_6.

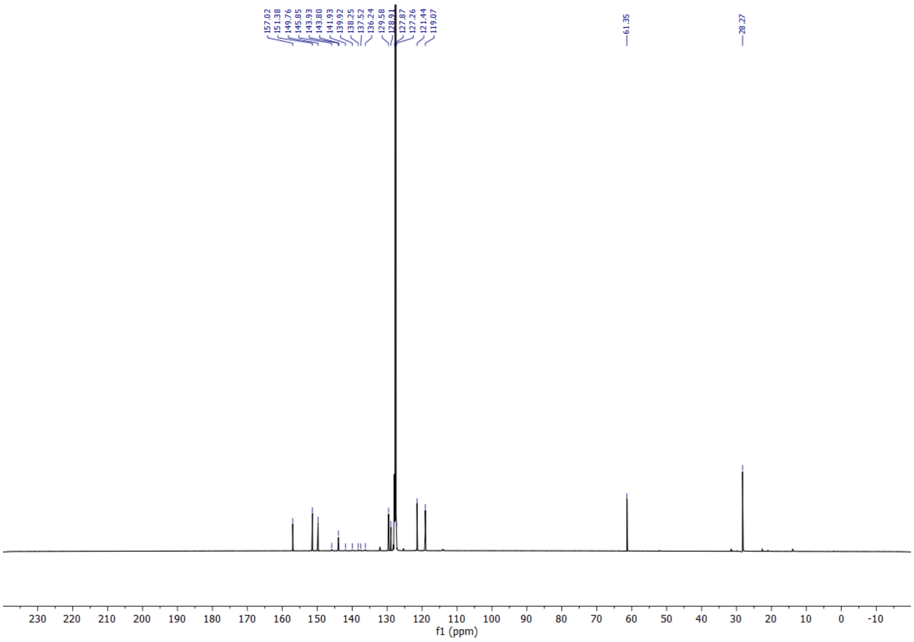


Figure S11 $^{13}C\{^1H\}$ NMR spectrum of Li(**L**) in C_6D_6.

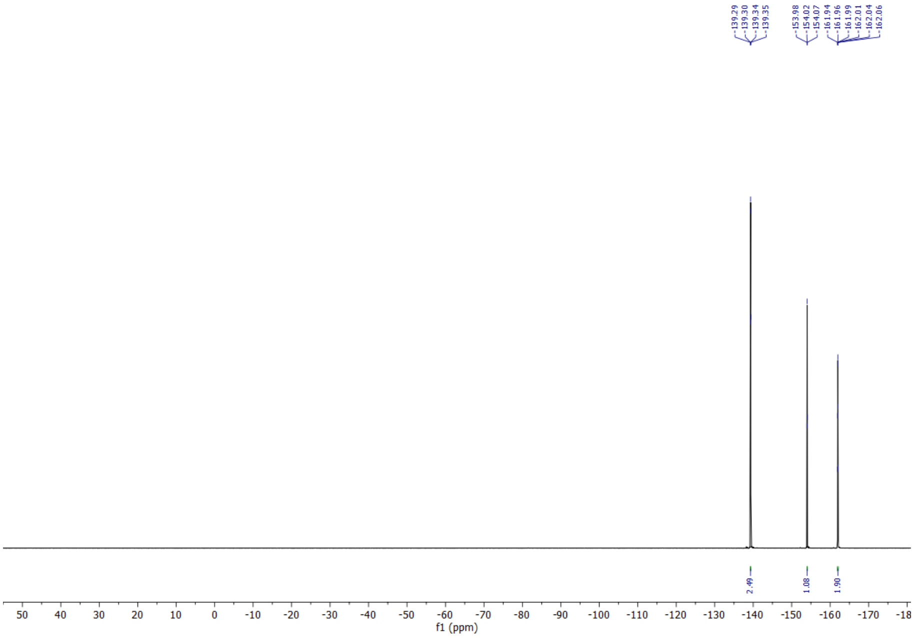


Figure S12 $^{19}F\{^1H\}$ NMR spectrum of Li(**L**) in C_6D_6.

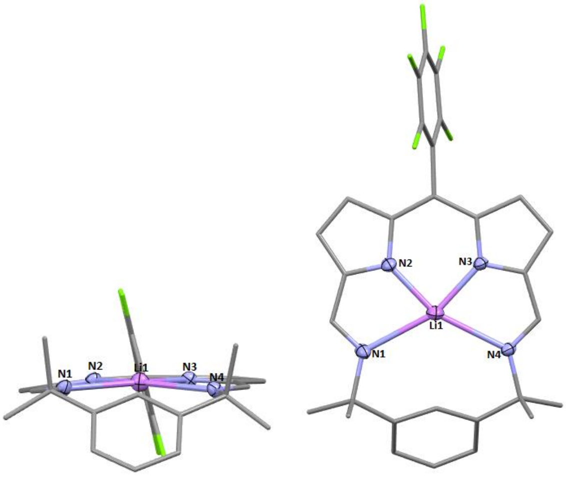


Figure S13 Solid-state structure of Li(**L**). For clarity, protons have been omitted (displacement ellipsoids at 50 %). Grey = C, blue = N, green = F, purple = Li.

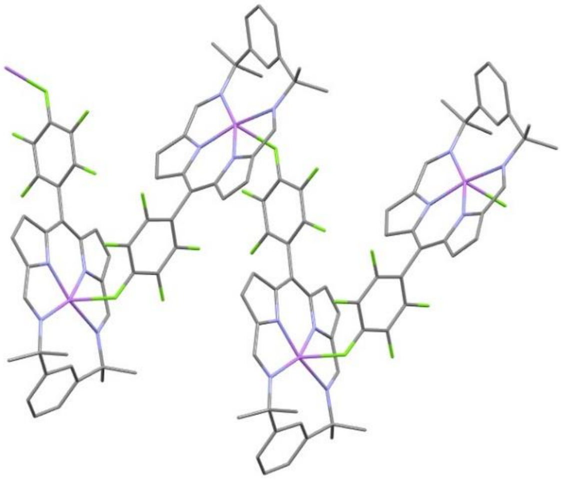
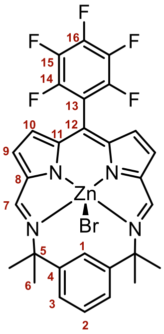


Figure S14 Extended solid-state structure of Li(**L**).

2.4 Synthesis of ZnBr(**L**)



The synthesis was conducted under inert atmosphere using Schlenk techniques. Solid $ZnBr_2$ (42.8 mg, 0.19 mmol, 1 eq) was added to a solution of Li**L** (100 mg, 0.19 mmol, 1 eq) in dry toluene (50 mL) resulting in a reddish blue solution that was stirred at rt for 16 h during which it turned pinkish blue. The reaction mixture was filtered, and the solvents were removed under vacuum, obtaining ZnBr(**L**) as a blue solid. Crystals suitable for X-ray diffraction were grown via slow evaporation of a dilute but saturated *n*-hexane solution. Yield = 89 mg, 70 %. ^{1}H NMR (500 MHz, C_6D_6): δ_H 9.62 (1H, t, *J* = 1.8 Hz, C(1)*H*), 7.76 (2H, s, C(7)*H*), 7.24 (1H, m, C(2)*H*), 7.13 (2H, dd, *J* = 7.7, 1.8 Hz, C(3)*H*), 6.48 (2H, d, *J* = 4.1 Hz, C(9)*H*), 6.26 (2H, d, *J* = 4.2 Hz, C(10)*H*), 1.80 (6H, s, C(6a)H_3), 1.34 (3H, s, C(6b)H_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ_C 154.45 (*C*(8)), 149.03 (*C*(7)H), 148.81 (*C*(4)), 144.55 (d, $^1J_{CF}$ = 251.8 Hz, Ar^F *C*(16)F), 142.50 (*C*(11)), 141.38 (d, $^1J_{CF}$ = 251.5 Hz, Ar^F *C*(14)F), 137.38 (d, $^1J_{CF}$ = 238.1 Hz, Ar^F *C*(15)F), 131.82 (*C*(9)), 131.40 (*C*(12)), 129.33 (*C*(1)H), 127.97 (*C*(2)H), 121.89 (*C*(3)H), 119.07 (*C*(10)H), 63.84 (*C*(5)), 30.90 (*C*(6a)H_3), 26.57 (*C*(6b)H_3). ^{19}F{^{1}H} NMR (376 MHz, C_6D_6): δ_F –136.70 (1F, d, *J* = 30.2 Hz, Ar^F *ortho*-F), –139.46 (1F, d, *J* = 25.6 Hz, Ar^F *ortho*-F), –151.95 (1F, t, *J* = 22.0 Hz, Ar^F *para*-F), –160.41 (1F, td, *J* = 23.3, 8.3 Hz, Ar^F *meta*-F), –161.44 (1F, td, *J* = 23.4, 8.5 Hz, Ar^F *meta*-F). FTIR (film): ν_{max} 1651 cm^{-1} (C(7)=N). UV-vis (THF): λ_{max} 300 nm, ε = 29,885 M^{-1} cm^{-1}; 601.5 nm, ε = 32,547 M^{-1} cm^{-1}. Elemental analysis: $C_{29}H_{22}F_5N_4ZnBr(C_7H_8)_{0.5}$ (MW = 710.06 gmol^{-1}) requires: C, 54.76; H, 3.68; N, 7.86 %. Found: C, 54.21; H, 3.45; N, 7.36 % (no satisfactory analyses were measured due to remaining salts). MS (MALDI-TOF, THF): *m/z* 585.329 (100 %) [M-Br]$^+$ (calcd for $C_{29}H_{22}F_5N_4Zn$ 585.105). HRMS (ESI$^+$) $C_{29}H_{23}F_5N_4ZnBr$ [M+H]$^+$ requires 667.029069, found 667.025720. (-5.0 ppm, 100 %); $(C_{29}H_{22}F_5N_4)_2Zn_2Br$ [M$_2$-Br]$^+$ requires 1253.103576, found 1253.125637 (17.0 ppm, 25 %, dimer formed in MS).

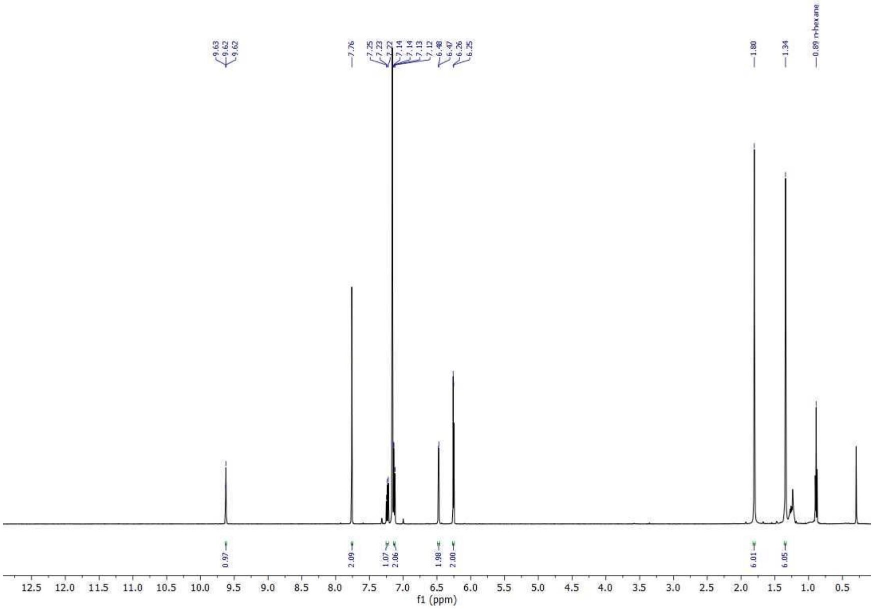


Figure S15 ^{1}H NMR spectrum of ZnBr(**L**) in C_6D_6.

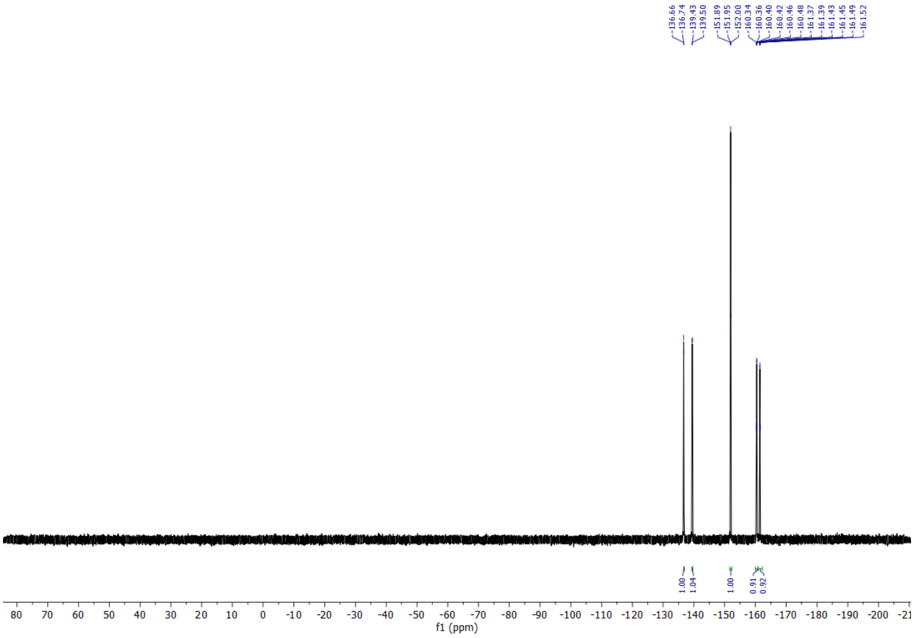


Figure S16 $^{19}F\{^{1}H\}$ NMR spectrum of ZnBr(**L**) in C_6D_6.

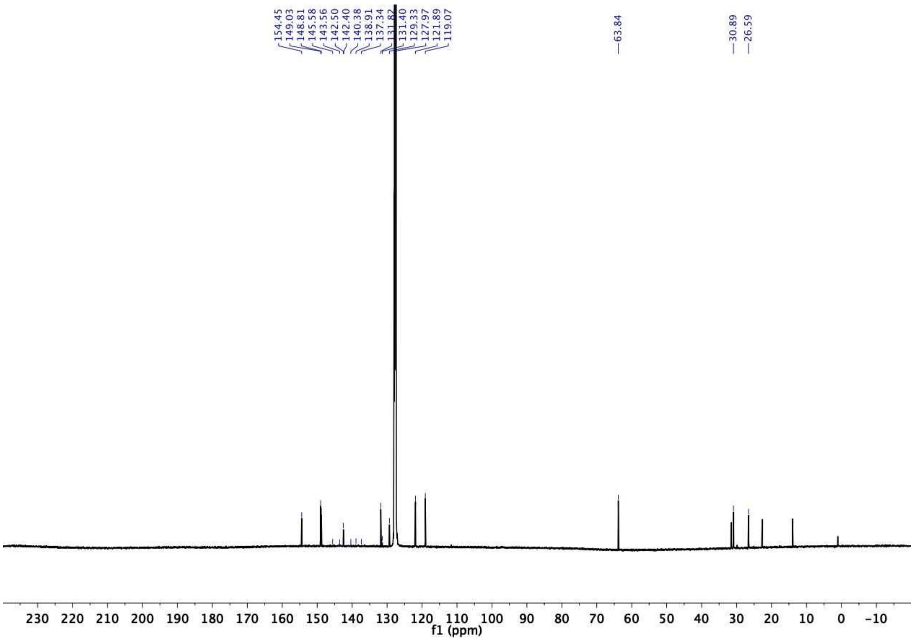


Figure S17 $^{13}C\{^{1}H\}$ NMR spectrum of ZnBr(**L**) in C_6D_6.

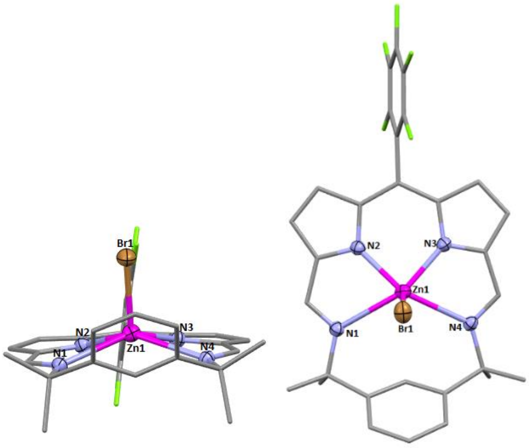
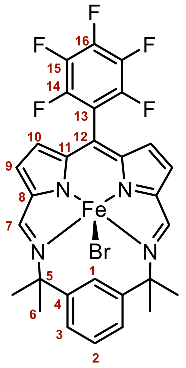


Figure S18 X-ray crystal structure of ZnBr(**L**). For clarity, all hydrogen atoms have been omitted (displacement ellipsoids are drawn at 50 % probability). Grey = C, blue = N, green = F, magenta = Zn, brown = Br.

2.5 Synthesis of FeBr(**L**)



The synthesis was conducted under inert atmosphere using Schlenk techniques. Solid $FeBr_2$ (41.3 mg, 0.19 mmol, 1 eq) was added to a solution of Li(**L**) (100 mg, 0.19 mmol, 1 eq) in dry THF (20 mL) and stirred for 16h during which the solution turned deeper blue. The solvent was removed under reduced pressure and the product was extracted in dry DCM. Diffraction-quality crystals were grown via slow evaporation of a dilute but saturated *n*-hexane solution. Yield = 25 mg, 20 %. FTIR (film): ν_{max} 1655 cm^{-1} (C(7)=N). UV-vis (THF): λ_{max} 310 nm, ε = 21,111 M^{-1} cm^{-1}; 614 nm, ε = 20,515 M^{-1} cm^{-1}. Elemental analysis: $C_{29}H_{22}F_5N_4FeBr$ (MW = 664.02 $gmol^{-1}$) requires: C, 53.00; H, 3.37; N, 8.52 %. Found: C, 50.33; H, 4.41; N, 6.93 % (no satisfactory analyses obtained after repeated efforts). MS (MALDI-TOF, THF): *m/z* 577.357 (100 %) $[M-Br]^+$ (calcd for $C_{29}H_{22}F_5N_4Fe$ 577.111). HRMS (ESI^+) $C_{29}H_{22}F_5N_4Fe$ $[M-Br]^+$ requires 577.110887, found 577.108631. (-3.9 ppm, 100 %); $C_{29}H_{22}F_5N_4FeBr$ $[M]^+$ requires 656.029375, found 656.026871 (-3.8 ppm, 27 %), $(C_{29}H_{23}F5N4)Fe_2Br$ $[M_2-Br]^+$ requires 1235.140353, found 1235.134305 (-4.9 ppm, 5 %, dimer formed in MS).

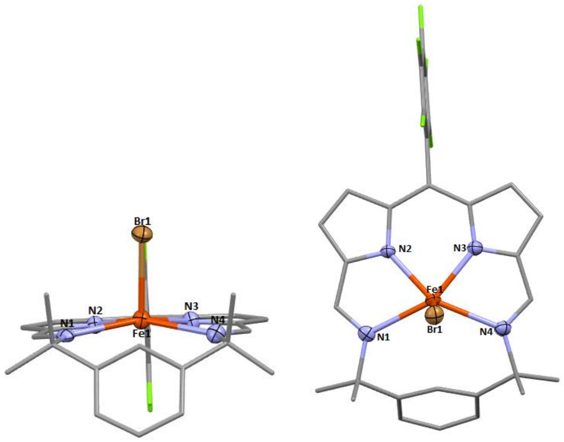


Figure S19 X-ray crystal structure of FeBr(**L**). For clarity, all hydrogen atoms and one CH_2Cl_2 solvent molecule have been omitted (displacement ellipsoids are drawn at 50 % probability). Grey = C, blue = N, green = F, orange = Fe, brown = Br.

3 X-ray Crystallographic Data

Table S1 Crystal data for **4**$^{\mathbf{ox}}$.

Crystal data	
Chemical formula	$C_{17}H_7F_5N_2O_2$
M_r	366.25
Crystal system, space group	Trigonal, *R*3
Temperature (K)	170
a, *c* (Å)	32.738 (2), 7.4920 (5)
V (Å^3)	6953.9 (11)
Z	18
Radiation type	Mo *K*α
μ (mm^{-1})	0.14
Crystal size (mm)	0.19 × 0.07 × 0.06
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.999, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39210, 2221, 1582
R_{int}	0.136
θ_{max} (°)	23.3
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.555
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.096, 1.04
No. of reflections	2221
No. of parameters	235
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.19
CCDC	2051272

Table S2 Crystal data for H**L**.

Crystal data	
Chemical formula	$C_{29}H_{23}F_5N_4 \cdot C_2H_3N$
M_r	563.57
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	10.0603 (2), 9.3452 (2), 14.9643 (3)
β (°)	103.994 (1)
V (Å^3)	1365.12 (5)
Z	2
Radiation type	Mo $K\alpha$
µ (mm^{-1})	0.11
Crystal size (mm)	0.36 × 0.3 × 0.08
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0550 before and 0.0515 after correction. The Ratio of minimum to maximum transmission is 0.9629. The λ/2 correction factor is Not present.
T_{min}, T_{max}	0.719, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	91541, 12936, 10665
R_{int}	0.048
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.827
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.103, 1.03
No. of reflections	12936
No. of parameters	382
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.28
Absolute structure	Flack x determined using 4286 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.13 (11)
CCDC	2051274

Table S3 Crystal data for Li(**L**).

Crystal data

Chemical formula	$C_{29}H_{22}F_5LiN_4$
M_r	528.44
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	10.0585 (6), 13.2365 (7), 22.1369 (12)
V (Å^3)	2947.3 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.69 × 0.54 × 0.31
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	99392, 6038, 5691
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.069, 1.04
No. of reflections	6038
No. of parameters	356
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.12, −0.17
Absolute structure	Flack x determined using 2403 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.10 (13)
CCDC	2051275

Table S4 Crystal data for ZnBr(**L**).

Crystal data	
Chemical formula	$C_{29}H_{22}BrF_5N_4Zn$
M_r	666.78
Crystal system, space group	Triclinic, *P*1
Temperature (K)	170
a, *b*, *c* (Å)	9.8072 (2), 11.5434 (3), 12.0315 (2)
α, β, γ (°)	86.721 (2), 86.179 (2), 84.625 (2)
V (Å^3)	1351.28 (5)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.45
Crystal size (mm)	0.44 × 0.10 × 0.10
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO* 1.171.40.54a (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.992, 0.997
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51141, 4931, 4347
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.078, 1.06
No. of reflections	4931
No. of parameters	365
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, −0.34
CCDC	2051273

Table S5 Crystal data for FeBr(**L**).

Crystal data	
Chemical formula	$C_{29}H_{22}BrF_5FeN_4·CH_2Cl_2$
M_r	742.19
Crystal system, space group	Triclinic, *P*1
Temperature (K)	170
a, *b*, *c* (Å)	9.6171 (6), 12.2102 (9), 13.8745 (10)
α, β, γ (°)	108.864 (6), 98.831 (6), 90.523 (5)
V (Å^3)	1520.44 (19)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.04
Crystal size (mm)	0.18 × 0.10 × 0.06
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO* 1.171.40.54a (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.996, 0.998
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	41369, 5570, 4175
R_{int}	0.124
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.090, 0.172, 1.18
No. of reflections	5570
No. of parameters	392
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.73
CCDC	2051276

4 Optimised DFT geometries

4.1 Compound **4**

Charge = 0 Multiplicity = 1

F	-0.70463	0.96457	-1.68792
F	-3.32204	1.17852	-2.25181
F	-1.76990	-1.48202	2.23117
F	-4.38585	-1.27091	1.63856
F	-5.18377	0.06599	-0.60131
O	3.31101	4.82682	-0.19670
N	2.26561	-1.87690	0.28246
H	2.69231	-1.74530	1.18974
N	1.65354	1.62729	-0.13749
O	4.66089	-3.31908	0.63599
C	0.32958	-0.36547	0.69700
C	1.12087	-1.30380	-0.18625
C	-1.58905	0.41280	-0.83727
C	-1.14187	-0.25858	0.29836
C	0.99601	0.98360	0.86752
C	-2.93647	0.53020	-1.15035
C	2.82630	-2.67985	-0.68507
C	2.14357	2.83719	0.31919
C	-3.88767	-0.03870	-0.31115
C	-2.12317	-0.82056	1.11497
C	-3.47928	-0.72018	0.82856
C	1.07013	1.78523	2.00357
H	0.65049	1.54182	2.96891
C	2.00555	-2.61430	-1.80320
H	2.16643	-3.13721	-2.73325
C	0.93570	-1.74694	-1.49291
H	0.11703	-1.47970	-2.14142
C	2.87700	3.74920	-0.54339
H	3.02188	3.38305	-1.58714
C	1.78484	2.94775	1.65841
H	2.03792	3.78172	2.29385
C	4.05640	-3.39837	-0.41776
H	4.41789	-4.03287	-1.25072
H	1.73067	1.28217	-1.08367
H	0.32134	-0.80900	1.69502

4.2 Compound **4**$^{\mathrm{ox}}$

Charge = 0 Multiplicity = 1

F	1.23832	-1.03810	-2.12251
F	3.92363	-1.12457	-2.10438
F	1.28490	0.99836	2.12205
F	3.97338	0.90356	2.13128
F	5.29983	-0.15655	0.01955
O	-4.48761	-3.96130	0.49267
N	-2.23825	1.55770	-0.16963
H	-2.91982	0.80899	-0.06204
N	-2.41046	-1.14808	0.12752
O	-4.82387	2.66366	-0.27615
C	-0.30478	0.04051	-0.00549
C	-0.89408	1.33868	-0.17263

C	1.88842	-0.55526	-1.06650
C	1.18271	-0.01728	0.00056
C	-1.01241	-1.11599	0.13782
C	3.27105	-0.60612	-1.07011
C	-2.48907	2.87371	-0.35714
C	-2.73462	-2.39778	0.29481
C	3.97517	-0.11087	0.01296
C	1.91451	0.47412	1.07296
C	3.29647	0.43158	1.09034
C	-0.50358	-2.46643	0.32911
H	0.53652	-2.74696	0.38677
C	-1.27319	3.53698	-0.48529
H	-1.14622	4.59624	-0.64368
C	-0.26949	2.57533	-0.37006
H	0.79400	2.74056	-0.42729
C	-4.15122	-2.81705	0.33796
H	-4.87915	-1.99402	0.21661
C	-1.58155	-3.27035	0.42719
H	-1.62262	-4.33772	0.57454
C	-3.85723	3.37563	-0.39991
H	-3.95324	4.46602	-0.55585

4.3 Compound HL

Charge = 0 Multiplicity = 1

F	3.59758	0.66382	2.25287
F	6.28499	0.66725	2.26807
F	7.65677	-0.02515	0.03490
F	6.32101	-0.72279	-2.21849
F	3.63657	-0.72928	-2.24623
N	0.04576	1.39115	-0.02919
H	-0.58383	0.58766	-0.03664
N	-0.01666	-1.27941	-0.02837
N	-2.64056	-2.21972	0.38422
N	-2.58157	2.20064	-0.17130
C	2.04520	-0.03050	-0.00445
C	1.37408	-1.22255	-0.02642
C	1.90733	-2.57300	-0.06281
H	2.95087	-2.84754	-0.05767
C	0.83687	-3.39839	-0.10037
H	0.83642	-4.47784	-0.13461
C	-0.33826	-2.54011	-0.06276
C	-1.74673	-2.97775	-0.07743
H	-1.93848	-3.96381	-0.51637
C	-4.06497	-2.54108	0.36862
C	-4.45646	-3.58431	-0.68471
H	-3.99219	-4.55148	-0.48000
H	-4.16120	-3.25692	-1.68361
H	-5.53463	-3.74078	-0.68804
C	-4.39683	-3.06143	1.77849
H	-3.87507	-4.00276	1.96673
H	-5.46959	-3.22993	1.88318
H	-4.08448	-2.33448	2.52830
C	-4.82385	-1.22198	0.13099
C	-6.21260	-1.20399	0.03930
H	-6.78575	-2.12054	0.11847

C	-6.88364	-0.00439	-0.14618
H	-7.96540	0.00059	-0.21436
C	-6.18350	1.18856	-0.24280
H	-6.73421	2.11127	-0.38626
C	-4.79383	1.19589	-0.15413
C	-4.13777	-0.01541	0.03289
H	-3.06529	-0.02142	0.11358
C	-4.00970	2.51575	-0.25197
C	-4.42367	3.44462	0.90000
H	-4.17622	2.98798	1.85950
H	-5.49770	3.63130	0.87896
H	-3.91590	4.40898	0.83089
C	-4.28663	3.18326	-1.60907
H	-3.95014	2.53695	-2.42083
H	-3.75947	4.13725	-1.68236
H	-5.35233	3.37275	-1.74130
C	-1.69076	3.09416	-0.11296
H	-1.88603	4.17268	-0.10717
C	-0.28961	2.69539	-0.05593
C	0.88668	3.44362	-0.04161
H	0.95049	4.52016	-0.05664
C	1.94984	2.53831	-0.01154
H	3.00110	2.77740	-0.00252
C	1.40343	1.24920	-0.00423
C	3.53369	-0.03413	0.00409
C	4.24535	0.32155	1.14152
C	5.62816	0.32750	1.16313
C	6.32983	-0.02680	0.02456
C	5.64665	-0.38380	-1.12377
C	4.26301	-0.38332	-1.12363

4.4 Compound Li(**L**)

Charge = -1 Multiplicity = 1

F	-3.62652	-1.49287	1.83115
F	-6.29953	-1.49018	1.81617
F	-7.65648	-0.00029	-0.00050
F	-6.29942	1.48999	-1.81675
F	-3.62641	1.49334	-1.83102
N	-0.03555	-1.36108	-0.00992
N	-0.03536	1.36128	0.01041
N	2.59660	2.27632	-0.11824
N	2.59633	-2.27635	0.11851
C	-2.02642	0.00025	0.00016
C	-1.36890	1.20902	0.26383
C	-1.88244	2.38046	0.92973
H	-2.89782	2.54207	1.26437
C	-0.80357	3.19958	1.12495
H	-0.79054	4.16237	1.61879
C	0.31610	2.51792	0.52495
C	1.72079	2.93076	0.51930
H	1.95942	3.80181	1.14693
C	4.01771	2.56625	-0.07657
C	4.34908	3.27250	-1.40421
H	3.83380	4.23531	-1.44902
H	4.00505	2.65984	-2.23766

H	5.42270	3.44294	-1.51025
C	4.45833	3.44831	1.10247
H	3.99713	4.43733	1.04802
H	5.53959	3.59048	1.09972
H	4.17950	2.98759	2.05240
C	4.76889	1.21714	-0.02878
C	6.16215	1.20082	-0.02958
H	6.72216	2.12915	-0.05741
C	6.85276	-0.00029	-0.00099
H	7.93779	-0.00037	-0.00134
C	6.16199	-1.20130	0.02807
H	6.72189	-2.12971	0.05560
C	4.76873	-1.21743	0.02814
C	4.08556	-0.00010	-0.00013
H	3.00358	-0.00002	0.00016
C	4.01740	-2.56643	0.07671
C	4.34893	-3.27197	1.40467
H	4.00495	-2.65888	2.23781
H	5.42257	-3.44229	1.51069
H	3.83369	-4.23476	1.45002
C	4.45767	-3.44921	-1.10191
H	4.17857	-2.98908	-2.05206
H	3.99646	-4.43819	-1.04671
H	5.53892	-3.59142	-1.09939
C	1.72035	-2.93088	-0.51871
H	1.95877	-3.80217	-1.14610
C	0.31572	-2.51782	-0.52436
C	-0.80406	-3.19936	-1.12431
H	-0.79120	-4.16221	-1.61802
C	-1.88278	-2.38002	-0.92924
H	-2.89816	-2.54146	-1.26396
C	-1.36905	-1.20859	-0.26345
C	-3.51501	0.00025	0.00008
C	-4.24338	-0.75708	0.91040
C	-5.62736	-0.76125	0.91973
C	-6.32153	-0.00010	-0.00030
C	-5.62730	0.76124	-0.92012
C	-4.24332	0.75743	-0.91040

4.5 Compound ZnBr(**L**)

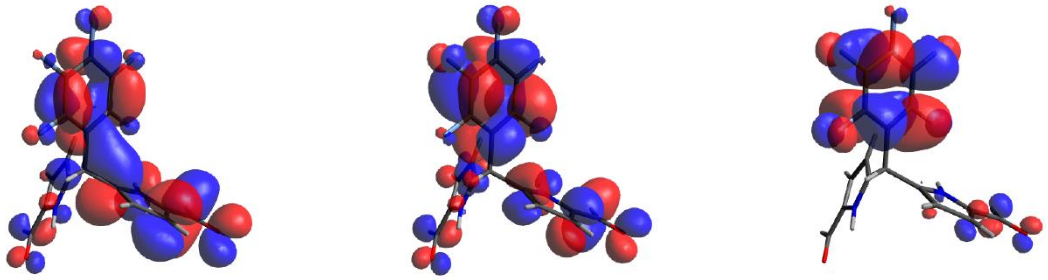
Charge = 0 Multiplicity = 1

Br	-2.00513	-0.17907	2.40814
Zn	-1.09475	-0.02377	0.23070
F	4.02480	0.76281	-2.31925
F	3.87472	-0.75362	2.15947
F	6.57472	-0.76010	2.24116
N	0.35558	-1.35244	-0.31831
F	8.00763	-0.00758	0.05196
N	0.34820	1.38321	-0.12276
N	-2.21240	-2.09911	-0.72459
F	6.72323	0.75238	-2.22590
N	-2.22361	2.18362	-0.37065
C	-1.32414	3.08755	-0.29299
H	-1.53543	4.15945	-0.32377
C	1.72550	-1.22492	-0.27083

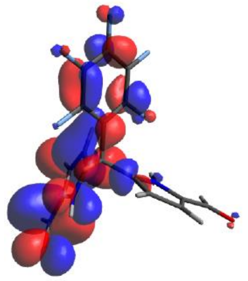
C	-4.45346	-1.18557	-0.57874
C	0.08127	-2.62451	-0.60863
C	-3.64452	-2.43273	-0.96731
C	-3.89844	0.06451	-0.83541
H	-2.96442	0.11310	-1.37699
C	-1.31072	-3.00168	-0.79988
H	-1.51973	-4.05193	-1.01841
C	0.06881	2.68562	-0.17090
C	3.86773	0.01038	-0.07951
C	2.37366	0.01380	-0.12094
C	-4.46014	1.25058	-0.37287
C	1.71935	1.25642	-0.07126
C	1.27806	-3.39065	-0.73649
H	1.34570	-4.44243	-0.97115
C	4.55314	-0.37964	1.07070
C	2.30142	2.57001	-0.05760
H	3.35511	2.79798	-0.01243
C	2.31522	-2.51108	-0.51842
H	3.37153	-2.72957	-0.55175
C	1.26096	3.46872	-0.12767
H	1.32292	4.54638	-0.15370
C	4.62888	0.38940	-1.18450
C	-3.65733	2.54993	-0.54010
C	-5.70358	1.18294	0.25786
H	-6.18731	2.07393	0.63607
C	-4.07211	-3.66699	-0.15376
H	-3.48088	-4.54197	-0.43043
H	-5.11569	-3.91775	-0.35102
H	-3.94920	-3.48569	0.91548
C	-3.82850	-2.70311	-2.47972
H	-3.47631	-1.85388	-3.06845
H	-4.88556	-2.86097	-2.70532
H	-3.27065	-3.59258	-2.78638
C	-5.69536	-1.23160	0.05690
H	-6.17293	-2.17592	0.28321
C	5.94196	-0.38735	1.12589
C	6.67502	-0.00250	0.00964
C	-3.85380	3.08737	-1.97774
H	-3.29979	4.01934	-2.12305
H	-4.91276	3.27973	-2.16437
H	-3.50399	2.35919	-2.71213
C	-4.07945	3.61542	0.48706
H	-3.94334	3.24332	1.50411
H	-5.12584	3.89280	0.34956
H	-3.49360	4.52861	0.36670
C	-6.32260	-0.05026	0.44415
H	-7.28443	-0.09512	0.94275
C	6.01788	0.38701	-1.15148

5 Calculated Molecular orbitals

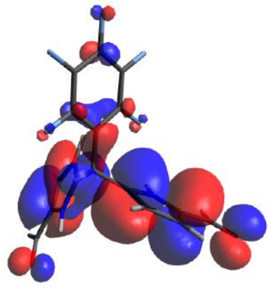
5.1 Compound **4**



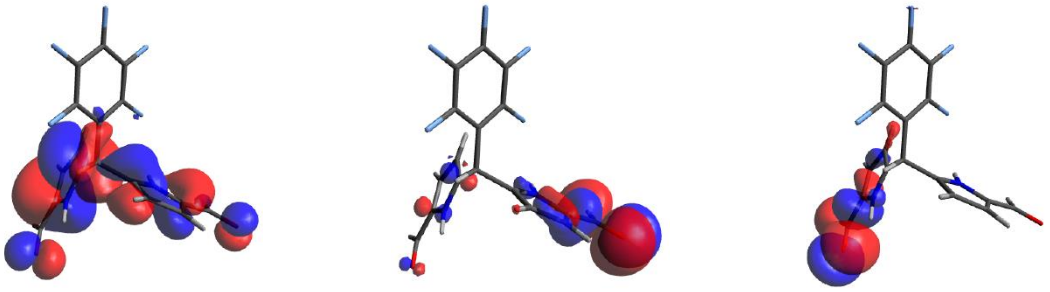
LUMO+1 **LUMO+2** **LUMO+3**



LUMO



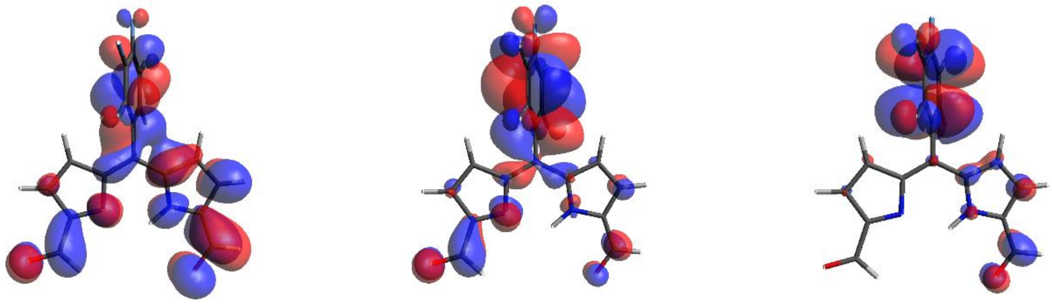
HOMO



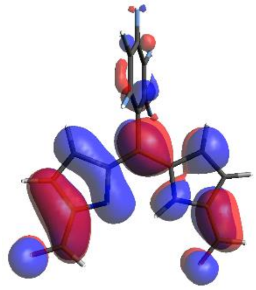
HOMO-1 **HOMO-2** **HOMO-3**

Figure S19 Molecular orbital diagram of **4**. ISO value of 0.02 au. Positive is blue; Negative is red.

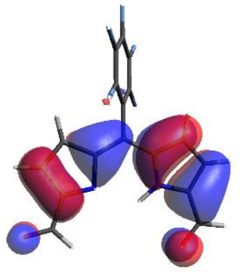
5.2 Compound **4**^{ox}



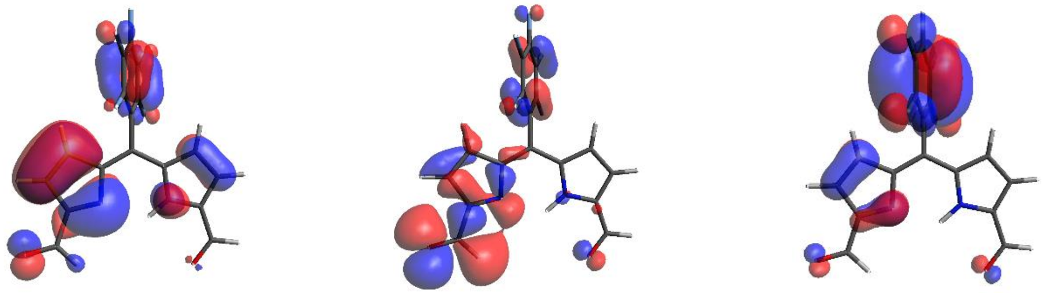
LUMO+1 **LUMO+2** **LUMO+3**



LUMO



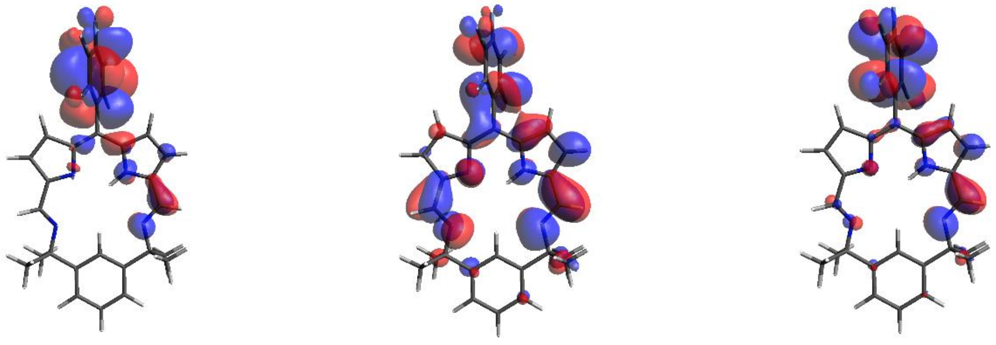
HOMO



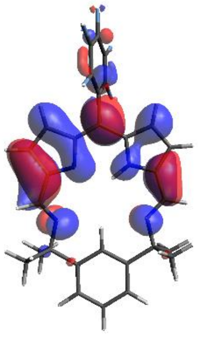
HOMO-1 **HOMO-2** **HOMO-3**

Figure S20 Molecular orbital diagram of **4**^{ox}. ISO value of 0.02 au. Positive is blue; Negative is red.

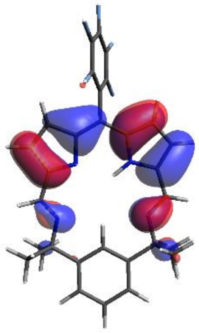
5.3 Compound H**L**



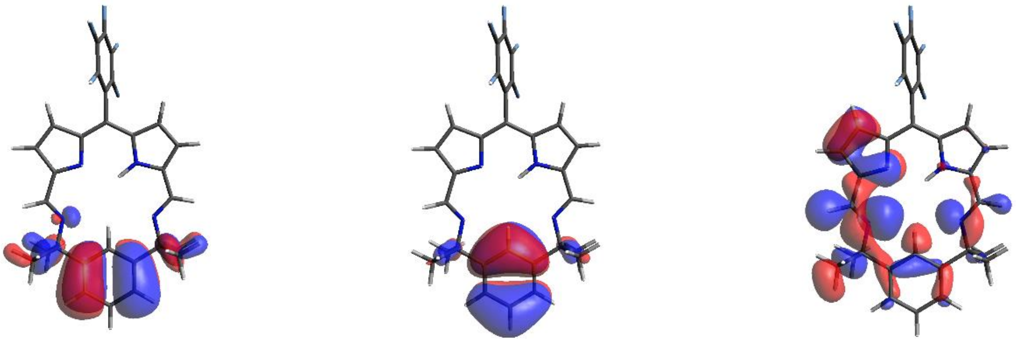
LUMO+1 **LUMO+2** **LUMO+3**



LUMO



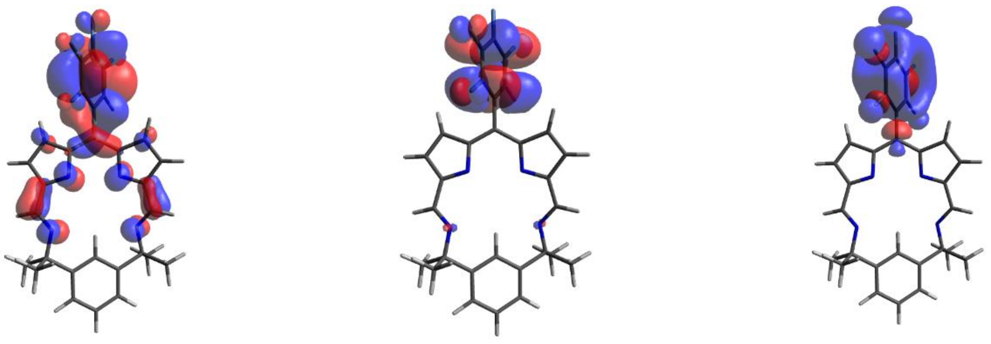
HOMO



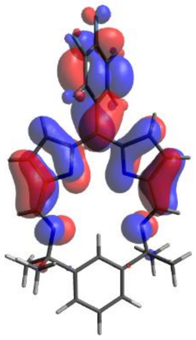
HOMO-1 **HOMO-2** **HOMO-3**

Figure S21 Molecular orbital diagram of H**L**. ISO value of 0.02 au. Positive is blue; Negative is red.

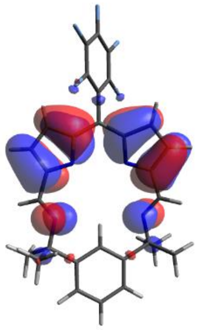
5.4 Compound Li(**L**)



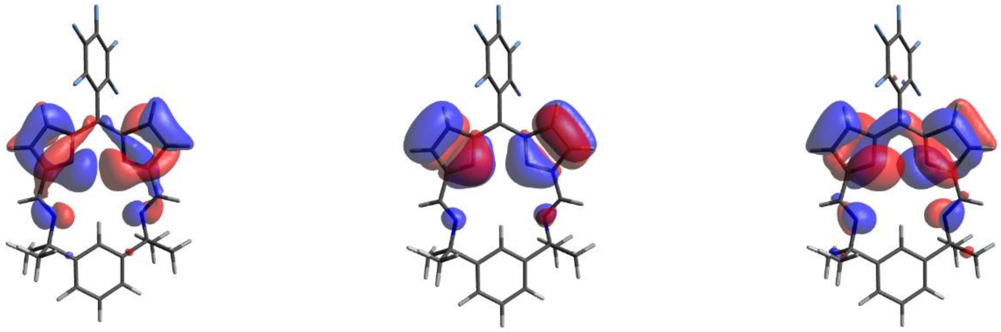
LUMO+1 **LUMO+2** **LUMO+3**



LUMO



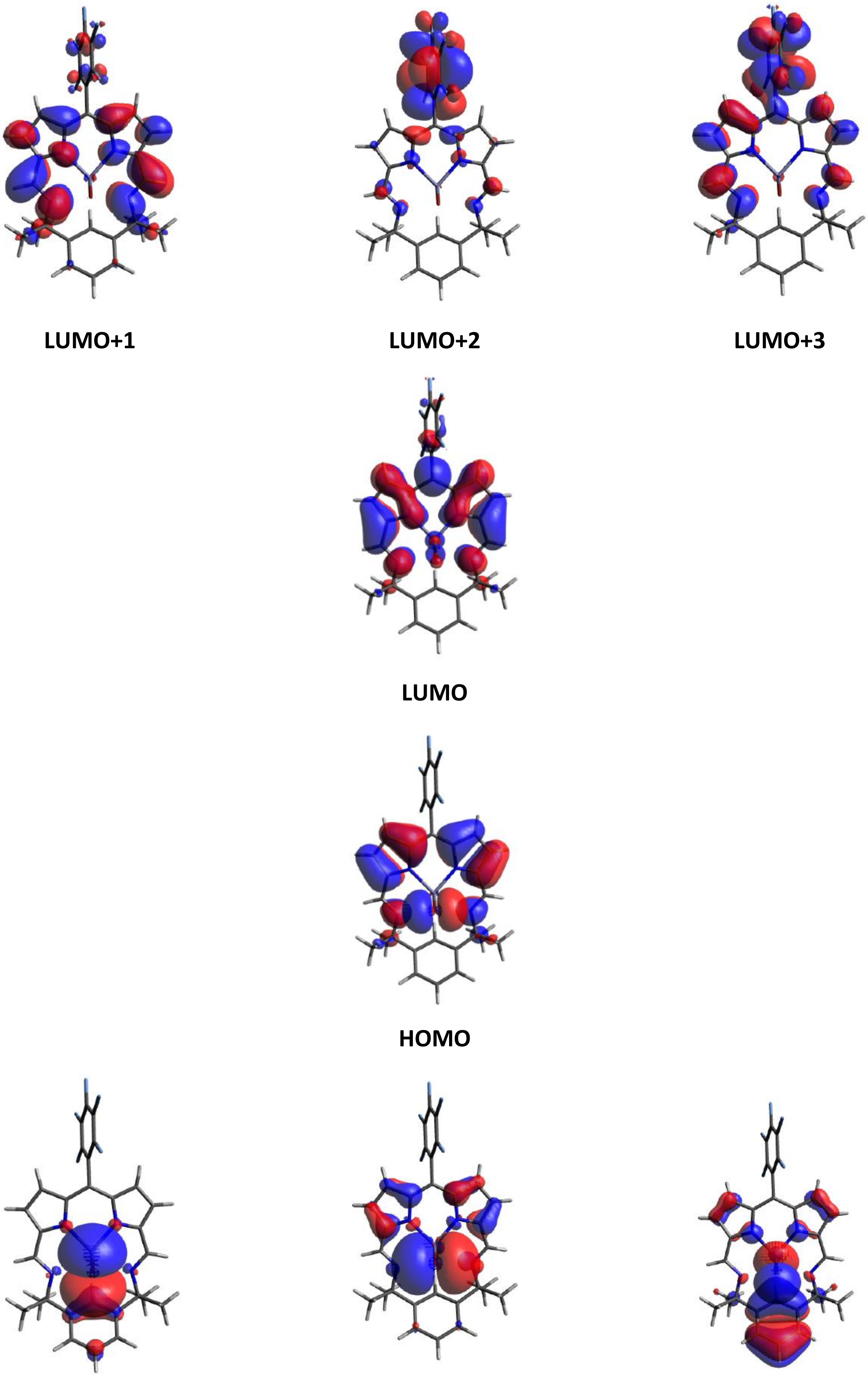
HOMO



HOMO-1 **HOMO-2** **HOMO-3**

Figure S22 Molecular orbital diagram of Li(**L**) (computed as **L**⁻). ISO value of 0.02 au. Positive is blue; Negative is red.

5.5 Compound ZnBr(**L**)



LUMO+1 **LUMO+2** **LUMO+3**

LUMO

HOMO

HOMO-1 **HOMO-2** **HOMO-3**

Figure S23 Molecular orbital diagram of ZnBr(**L**). ISO value of 0.02 au. Positive is blue; Negative is red.

6 Electronic Absorption Spectra

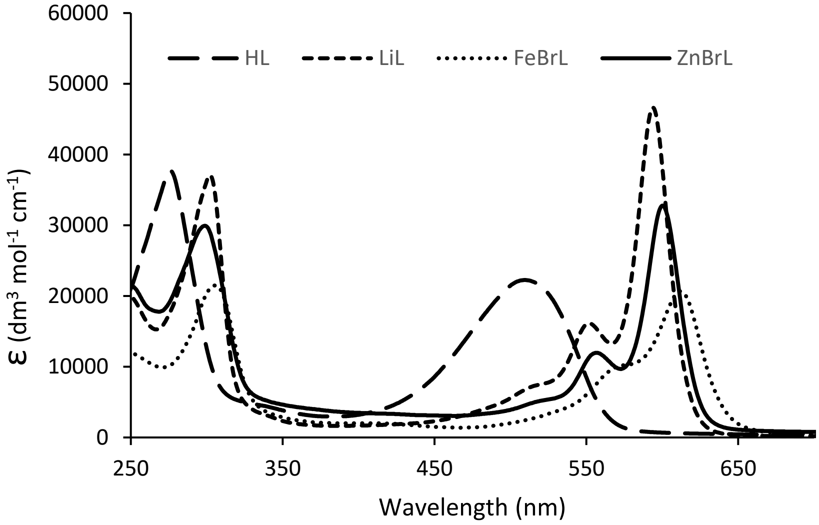


Figure S24 Experimental UV-vis of H**L**, Li(**L**), FeBr(**L**), and ZnBr(**L**) measured as a THF solution.

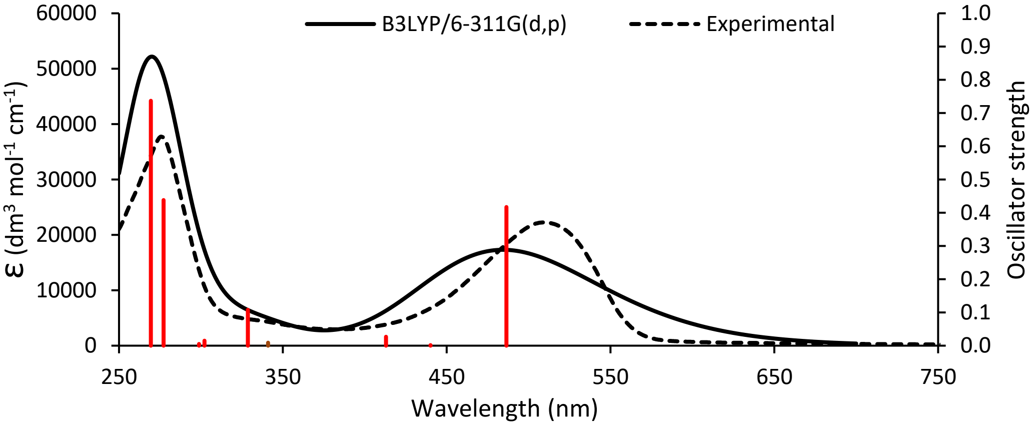


Figure S25 Experimental and simulated electronic absorption spectra of H**L**, measured as a THF solution. Individual calculated excitations are depicted in red.

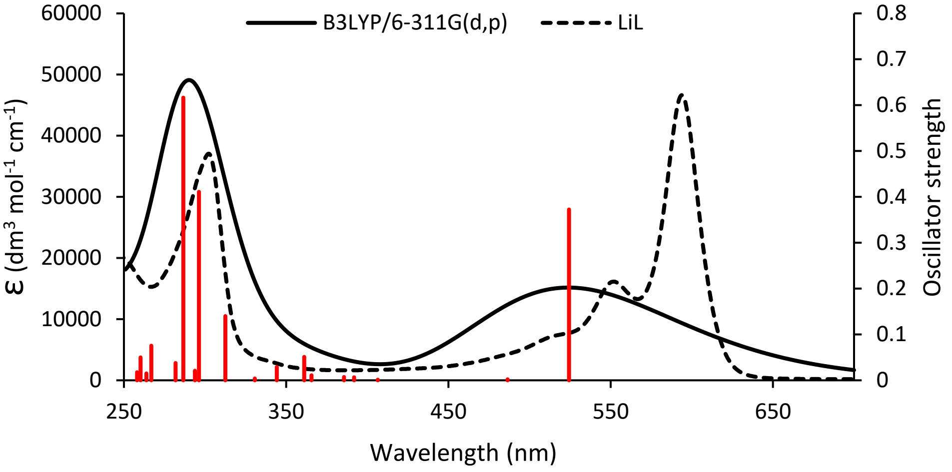


Figure S26 Experimental and simulated electronic absorption spectra of Li(**L**), measured as a THF solution. Individual calculated excitations are depicted in red.

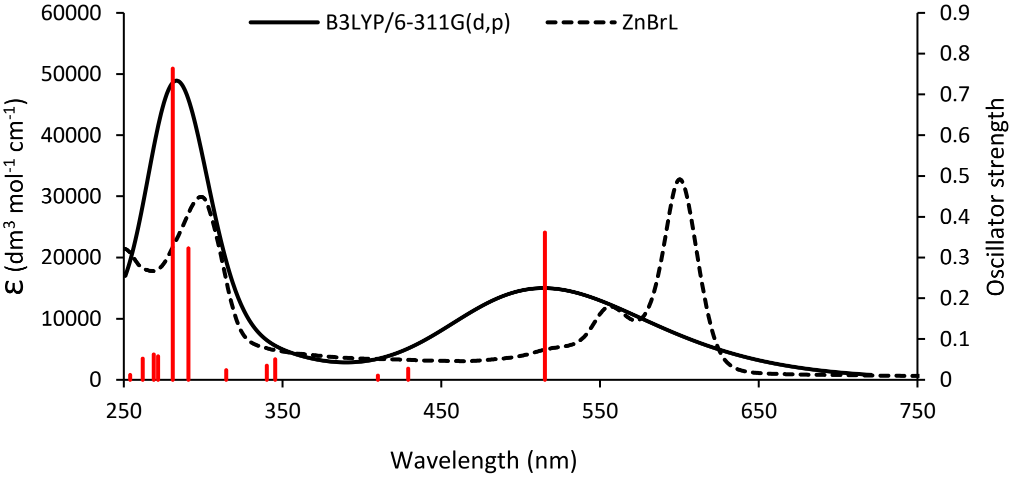


Figure S27 Experimental and simulated electronic absorption spectra of ZnBr(**L**), measured as a THF solution. Individual calculated excitations are depicted in red.

7 References

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