

## **Electronic supplementary information**

### **Off-off-on chiroptical property switching of a pyrene luminophore by stepwise helicate formation**

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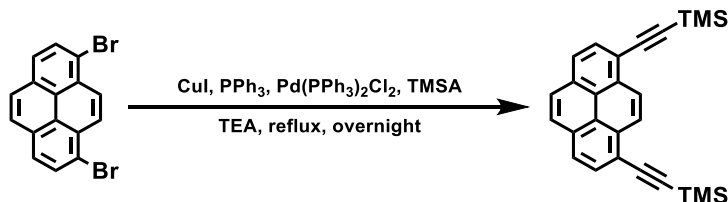
## Experimental Section

### Materials and Methods

All the chemical reagents were commercially available and used without purification. 1,8-dibromopyrene, (*R*)- and (*S*)-2-iodo-1-(2-methoxypropyl)-1*H*-imidazole were synthesized following procedures reported in literature.<sup>1,2</sup> <sup>1</sup>H NMR spectra were measured with JEOL JNM-ECZ400S (400 MHz) and JNM-ECA500 (500 MHz). Emission spectra were recorded by a JASCO FP-6500 fluorescence spectrophotometer. UV-Vis absorption and circular dichroism (CD) spectra were recorded by an Agilent Cary 8454 and JEOL J-725 spectrophotometer at ambient temperature, respectively. The emission lifetimes were recorded using FluoroCube (HORIBA, 3000U-YSP). ESI-MS spectra were measured with mass spectrometers (JEOL JMS-T100CS). The luminescence anisotropy factor ( $g_{\text{CPL}}$ ) was determined using the experimental setup designed based on a fluorescence spectrofluorometer (JASCO FP-6500) with a rotatable  $\lambda/4$  filter and a fixed linearly polarized plate.<sup>3</sup> TD-DFT calculation was conducted using Gaussian 09.

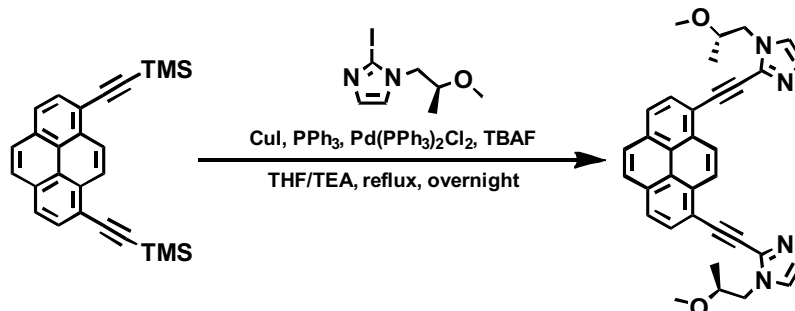
### Synthesis

#### 1,8-bis((trimethylsilyl)ethynyl)pyrene:



CuI (79 mg, 0.42 mmol) was placed in a flame dried 100 mL 2-necked flask, evacuated, and backfilled with Ar three times. To this flask, 1,8-dibromopyrene (3.0 g, 8.33 mmol), PPh<sub>3</sub> (109 mg, 0.42 mmol), and degassed triethylamine (30 mL) were added. Then, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (292 mg, 0.42 mmol) and trimethylsilylacetylene (3 mL, 21 mmol) were added and stirred at reflux for overnight. The reaction mixture was evaporated and dissolved in CHCl<sub>3</sub>. This solution was washed with saturated ammonium chloride solution and water, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The crude product was purified by silica gel column chromatography (CHCl<sub>3</sub>) to obtain 1,8-bis((trimethylsilyl)ethynyl)pyrene as yellow powder. This material contains *ca.* 30% of 1,6-bis((trimethylsilyl)ethynyl)pyrene (judged from <sup>1</sup>H NMR), we used it without further purification (2.3 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (s, 2H), 7.99–8.14 (m, 6H), 0.40 (s, 18H).

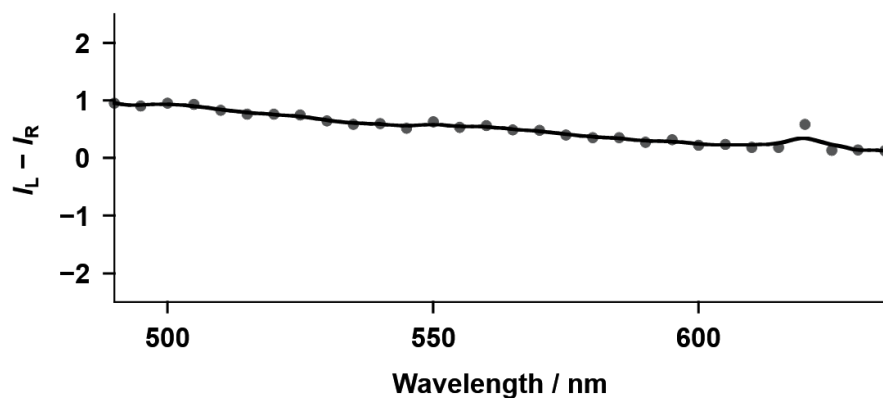
**1,8-bis((1-((*S*)-2-methoxypropyl)-1*H*-imidazol-2-yl)ethynyl)pyrene ( $L^S$ ):**



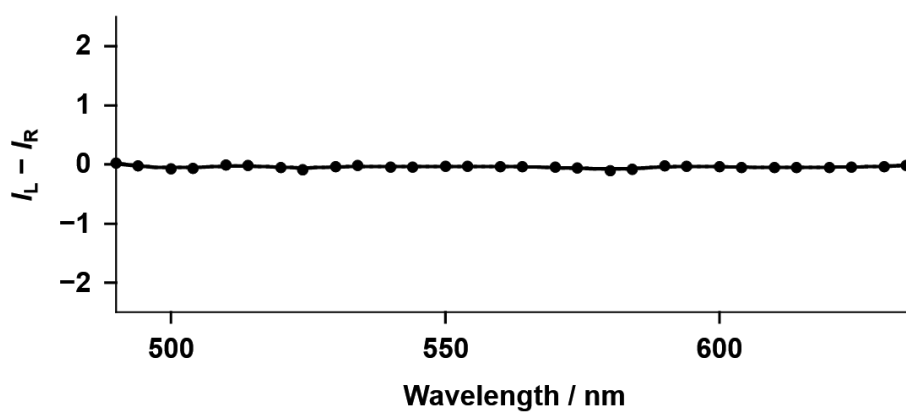
CuI (12 mg, 0.06 mmol) was placed in a flame dried 50 mL 2-necked flask, evacuated, and backfilled with Ar three times. To this flask, 1,8-bis((trimethylsilyl)ethynyl)pyrene (500 mg, 1.3 mmol), (*S*)-2-iodo-1-(2-methoxypropyl)-1*H*-imidazole (740 mg, 2.8 mmol), PPh<sub>3</sub> (17 mg, 0.06 mmol), and degassed dry THF (7 mL) and triethylamine (7 mL) were added. Then, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (44 mg, 0.06 mmol) and TBAF (1 M in THF, 3.2 mL, 3.2 mmol) were added and stirred at reflux for overnight. The reaction mixture was evaporated and dissolved in CHCl<sub>3</sub>. This solution was washed with saturated ammonium chloride solution and water, dried over Na<sub>2</sub>SO<sub>4</sub>, then evaporated. The crude product was purified by silica gel column chromatography (CHCl<sub>3</sub>/MeOH = 9/1) and GPC (CHCl<sub>3</sub>) to obtain 1,8-bis((1-((*S*)-2-methoxypropyl)-1*H*-imidazol-2-yl)ethynyl)pyrene ( $L^S$ ) as yellow powder (87 mg, 13%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.70 (s, 2H), 8.23 (d, *J* = 7.8 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.08 (s, 2H), 7.20 (s, 2H), 7.17 (s, 2H), 4.24–4.36 (m, 4H), 3.76–3.84 (m, 2H), 3.37 (s, 6H), 1.27 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 132.22, 131.80, 131.77, 130.28, 129.92, 128.33, 126.43, 125.42, 124.03, 121.97, 117.19, 91.71, 84.87, 76.22, 56.88, 52.01, 16.98.

1,8-bis((1-((*R*)-2-methoxypropyl)-1*H*-imidazol-2-yl)ethynyl)pyrene ( $L^R$ ) was also prepared by same procedure.

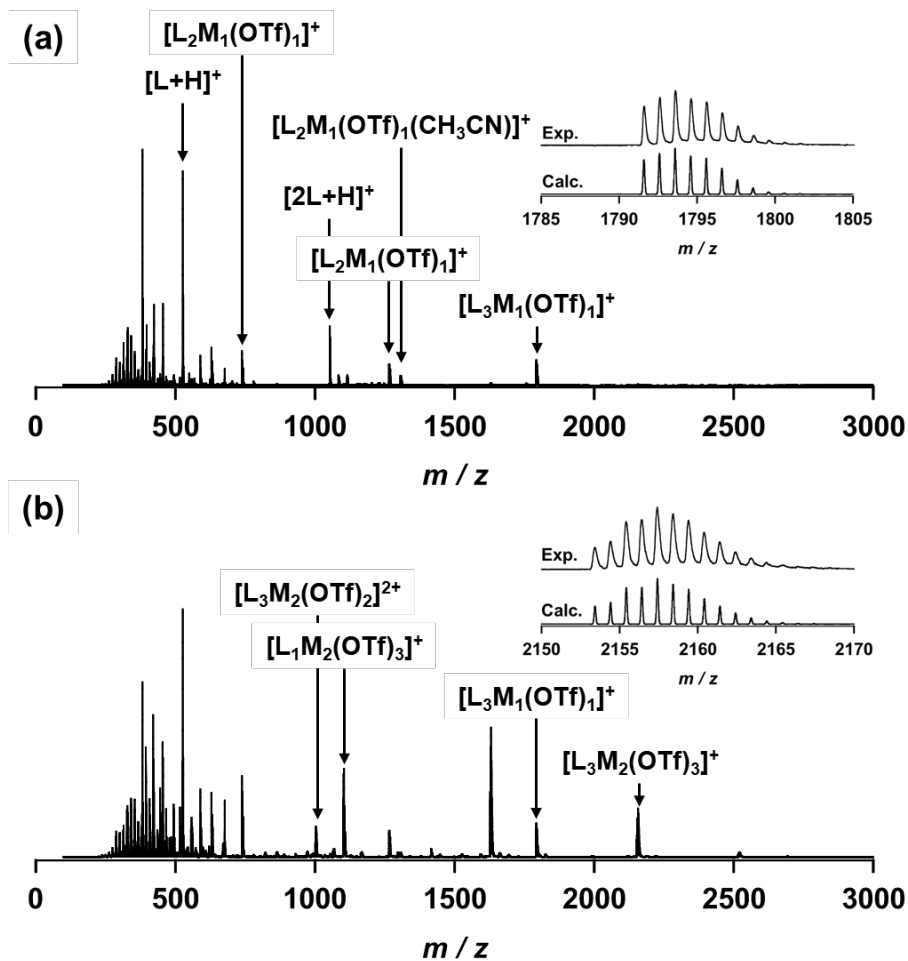
**Possibility of Micro/nanostructures:** We have examined the possibility of micro/nanostructures by concentration dependence of UV-Vis absorption spectrum of the assemblies, where the total concentrations of the components ( $L^S$  and Zn<sup>2+</sup>) are successively changed but the molar ratio is fixed at [Zn<sup>2+</sup>]/[ $L^S$ ]<sub>0</sub> = 0.33 or 1.0. If helical micro/nanostructures are formed in equilibrium in solution, the absorption spectral shape would be changed depending on the concentrations of the components. There is no appreciable absorption spectral shape change with a change in the total concentrations of the components (see ESI†, S8), indicating that helical micro/nanostructures could not be formed under our experimental conditions.



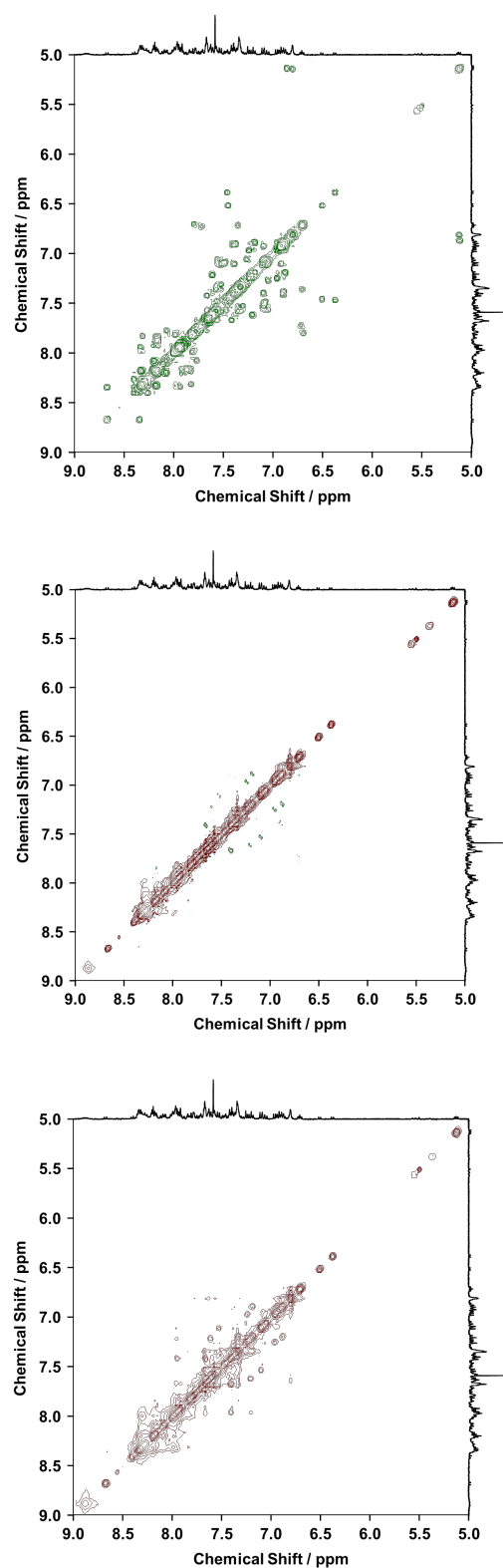
**Fig. S1** CPL spectrum of  $L^R$  ( $2.0 \times 10^{-5}$  M) in the presence of  $Zn^{2+}$  ( $6.6 \times 10^{-6}$  M) in acetonitrile. Excitation wavelength:  $\lambda_{ex} = 385$  nm.



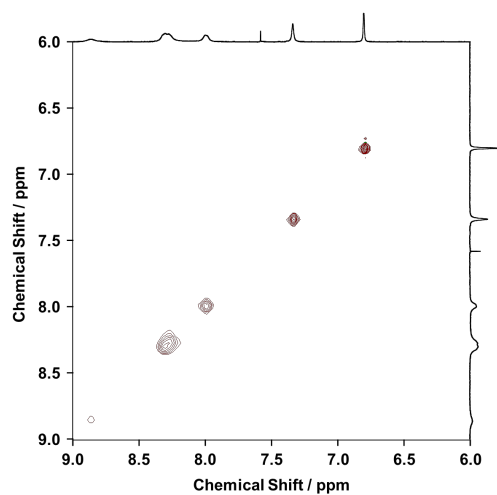
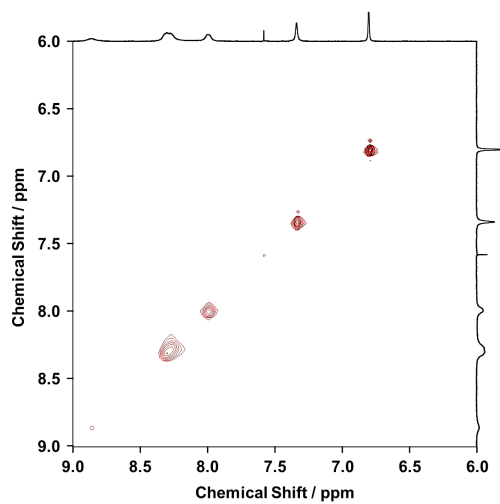
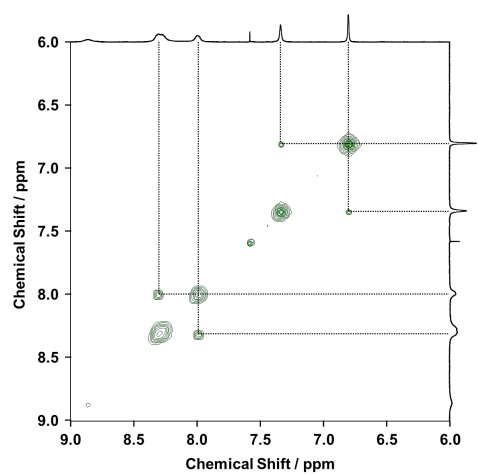
**Fig. S2** CPL spectrum of  $L^R$  in the absence of  $Zn^{2+}$  in acetonitrile. Excitation wavelength:  $\lambda_{ex} = 375$  nm.



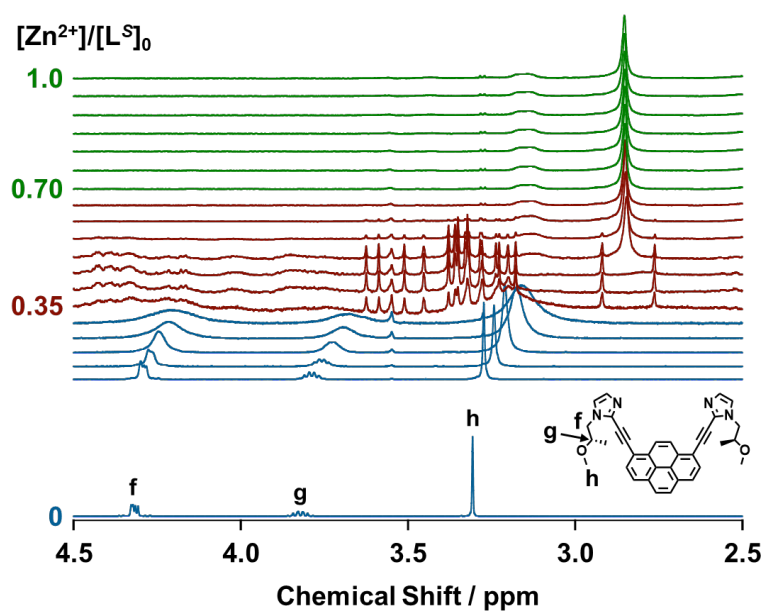
**Fig. S3** ESI MS (positive) of  $L^S$  in acetonitrile ( $1.0 \times 10^{-3}$  M) containing (a)  $3.5 \times 10^{-4}$  M and (b)  $7.0 \times 10^{-4}$  M of  $Zn(OSO_2CF_3)_2$ . Insets: Isotopically resolved signals at (a)  $m/z = 1791.58943$  ( $\{(L^S)_3(Zn)_1(OSO_2CF_3)_1\}^+$ ) and (b)  $m/z = 2153.42387$  ( $\{(L^S)_3(Zn)_2(OSO_2CF_3)_3\}^+$ ) with their calculated spectra.



**Fig. S4**  $^1H$ - $^1H$  COSY (top), ROESY (middle), and NOESY (bottom) NMR spectra of  $L^S$  ( $2.1 \times 10^{-3}$  M) in the presence of  $Zn^{2+}$  ( $1.0 \times 10^{-3}$  M) in  $CD_3CN$  at 298 K.



**Fig. S5**  $^1\text{H}$ - $^1\text{H}$  COSY (top), ROESY (middle), and NOESY (bottom) NMR spectra of  $\text{L}^{\text{S}}$  ( $2.1 \times 10^{-3}$  M) in the presence of  $\text{Zn}^{2+}$  ( $1.6 \times 10^{-3}$  M) in  $\text{CD}_3\text{CN}$  at 298 K.



**Fig. S6** Stacked  $^1\text{H}$  NMR spectra of  $\text{L}^{\text{S}}$  ( $2.0 \times 10^{-3}$  M) in the presence of  $\text{Zn}^{2+}$  ( $0$ – $6.0 \times 10^{-4}$  M (blue),  $7.0 \times 10^{-4}$ – $1.3 \times 10^{-3}$  M (red),  $1.4 \times 10^{-3}$ – $2.0 \times 10^{-3}$  M (green)) in  $\text{CD}_3\text{CN}$  at 298 K.



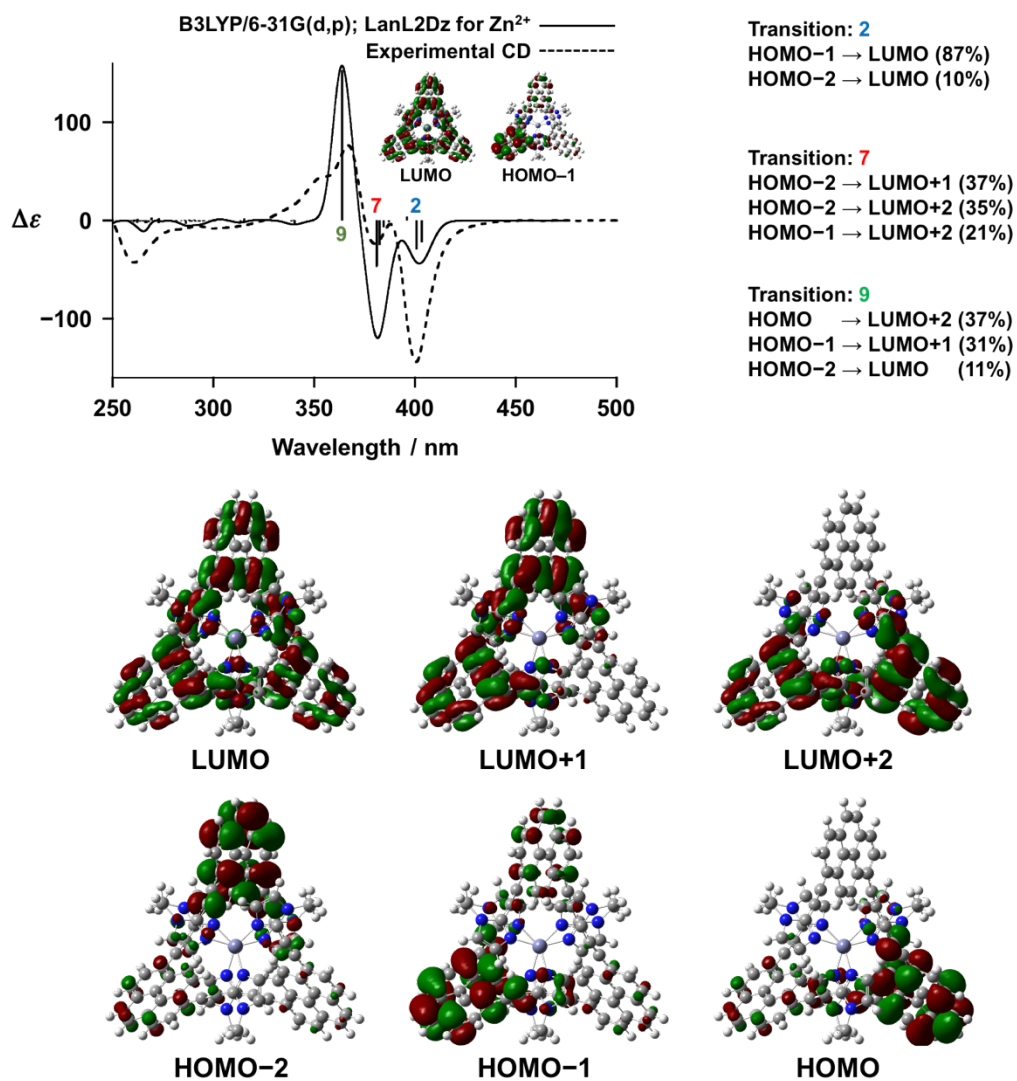
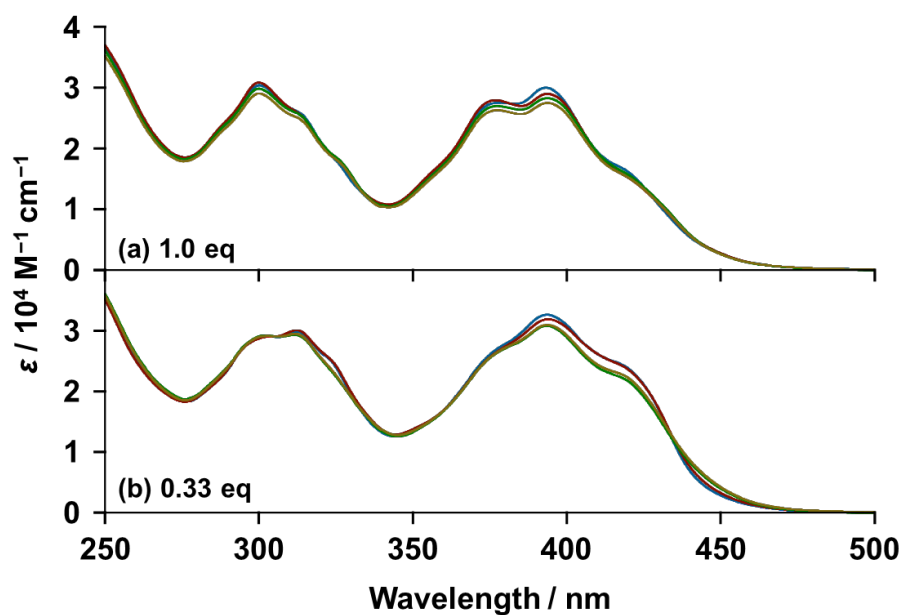


Fig. S7 Assignment of rotatory strength for  $P\text{-(L')}_3\text{(Zn}^{2+}\text{)}_2$ .



**Fig. S8** UV-Vis absorption spectra of  $L^S$  [ $3.5 \times 10^{-6} \text{ M}$  (blue),  $2.0 \times 10^{-5} \text{ M}$  (red),  $6.4 \times 10^{-5} \text{ M}$  (green),  $1.1 \times 10^{-4} \text{ M}$  (yellow)] in the presence of (a) 1.0 equiv. and (b) 0.33 equiv. of  $Zn^{2+}$  in acetonitrile.

## References

1. H. Bittermann, D. Siegemund, V. L. Malinovskii and R. Häner, *J. Am. Chem. Soc.*, 2008, **130**, 15285.
2. Y. Imai, Y. Nakano, T. Kawai and J. Yuasa, *Angew. Chem. Int. Ed.*, 2018, **57**, 8973.
3. Y. Okayasu and J. Yuasa, *Mol. Syst. Des. Eng.*, 2018, **3**, 66.