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)-1H-imidazole were synthesized following procedures reported in literature.\(^1\)\(^2\) \(^\text{\textsuperscript{1}}\)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 \((\text{g}_{\text{CPL}})\) 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.\(^3\) TD-DFT calculation was conducted using Gaussian 09.

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

Cul (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\(_3\) (109 mg, 0.42 mmol), and degassed triethylamine (30 mL) were added. Then, Pd(PPh\(_3\))\(_2\)Cl\(_2\) (292 mg, 0.42 mmol) and trimethylsilylethynyl (3 mL, 21 mmol) were added and stirred at reflux for overnight. The reaction mixture was evaporated and dissolved in CHCl\(_3\). This solution was washed with saturated ammonium chloride solution and water, dried over Na\(_2\)SO\(_4\), and evaporated. The crude product was purified by silica gel column chromatography (CHCl\(_3\)) to obtain 1,8-bis((trimethylsilyl)ethynyl)pyrene as yellow powder. This material contains \textit{ca}. 30% of 1,6-bis((trimethylsilyl)ethynyl)pyrene (judged from \(^\text{\textsuperscript{1}}\)H NMR), we used it without further purification (2.3 g, 70%). \(^\text{\textsuperscript{1}}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.64 (s, 2H), 7.99–8.14 (m, 6H), 0.40 (s, 18H).
1,8-bis((1-((S)-2-methoxypropyl)-1H-imidazol-2-yl)ethynyl)pyrene (L^S): 

Cul (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)-1H-imidazole (740 mg, 2.8 mmol), PPh₃ (17 mg, 0.06 mmol), and degassed dry THF (7 mL) and triethylamine (7 mL) were added. Then, Pd(PPh₃)₂Cl₂ (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 CHCl₃. This solution was washed with saturated ammonium chloride solution and water, dried over Na₂SO₄, then evaporated. The crude product was purified by silica gel column chromatography (CHCl₃/MeOH = 9/1) and GPC (CHCl₃) to obtain 1,8-bis((1-((S)-2-methoxypropyl)-1H-imidazol-2-yl)ethynyl)pyrene (L^S) as yellow powder (87 mg, 13%).

**1H NMR (500 MHz, CDCl₃)** 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).

**13C NMR (100 MHz, CDCl₃)** 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)-1H-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 Zn²⁺) are successively changed but the molar ratio is fixed at [Zn²⁺]/[L^S]₀ = 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\textsuperscript{R} (2.0 × 10\textsuperscript{-5} M) in the presence of Zn\textsuperscript{2+} (6.6 × 10\textsuperscript{-6} M) in acetonitrile. Excitation wavelength: \(\lambda_{\text{ex}} = 385\) nm.

Fig. S2 CPL spectrum of L\textsuperscript{R} in the absence of Zn\textsuperscript{2+} in acetonitrile. Excitation wavelength: \(\lambda_{\text{ex}} = 375\) nm.
Fig. S3 ESI MS (positive) of L₅ in acetonitrile (1.0 × 10⁻³ M) containing (a) 3.5 × 10⁻⁴ M and (b) 7.0 × 10⁻⁴ M of Zn(OSO₂CF₃)₂. Insets: Isotopically resolved signals at (a) m/z = 1791.58943 ([L₅]₃(Zn)₁(OSO₂CF₃)₁⁺) and (b) m/z = 2153.42387 ([L₅]₃(Zn)₂(OSO₂CF₃)₃⁺) with their calculated spectra.
Fig. S4 $^1$H-$^1$H COSY (top), ROESY (middle), and NOESY (bottom) NMR spectra of $L^5$ (2.1 × 10$^{-3}$ M) in the presence of Zn$^{2+}$ (1.0 × 10$^{-3}$ M) in CD$_3$CN at 298 K.
Fig. S5 $^1$H-$^1$H COSY (top), ROESY (middle), and NOESY (bottom) NMR spectra of L$^5$ (2.1 × 10$^{-3}$ M) in the presence of Zn$^{2+}$ (1.6 × 10$^{-3}$ M) in CD$_3$CN at 298 K.
Fig. S6 Stacked $^1$H NMR spectra of $L^S$ ($2.0 \times 10^{-3}$ 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 CD$_3$CN at 298 K.
Fig. S7 Assignment of rotatory strength for \( P-(L')_3(Zn^{2+})_2 \).
**Fig. S8** UV-Vis absorption spectra of $L^5 [3.5 \times 10^{-6} \text{ M (blue), } 2.0 \times 10^{-5} \text{ M (red), } 6.4 \times 10^{-5} \text{ M (green), } 1.1 \times 10^{-4} \text{ M (yellow)}]$ in the presence of (a) 1.0 equiv. and (b) 0.33 equiv. of Zn$^{2+}$ in acetonitrile.

**References**