Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information

Metal ion clip: fine tuning aromatic stacking interactions in multistep formation of carbazole-bridged zinc(II) complexes

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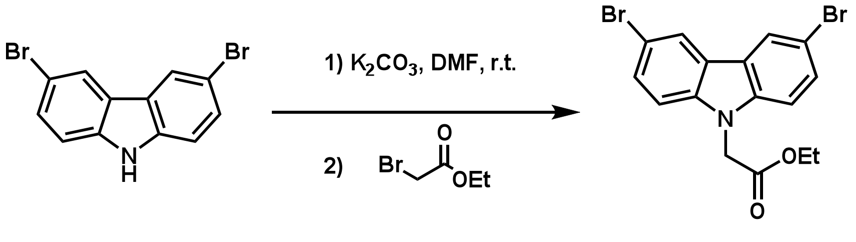
Experimental Section (S1)

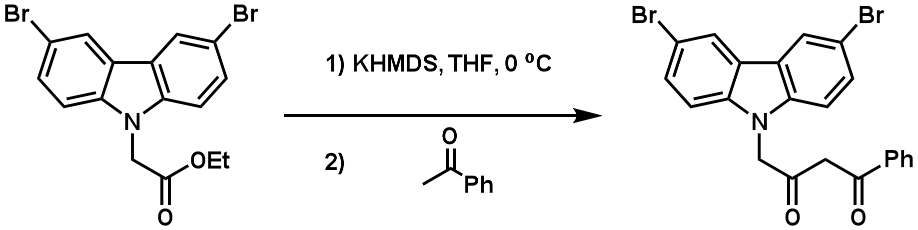
Synthesis

Ethyl 2-(3,6-dibromo-9*H*-carbazol-9-yl)acetate (1a):



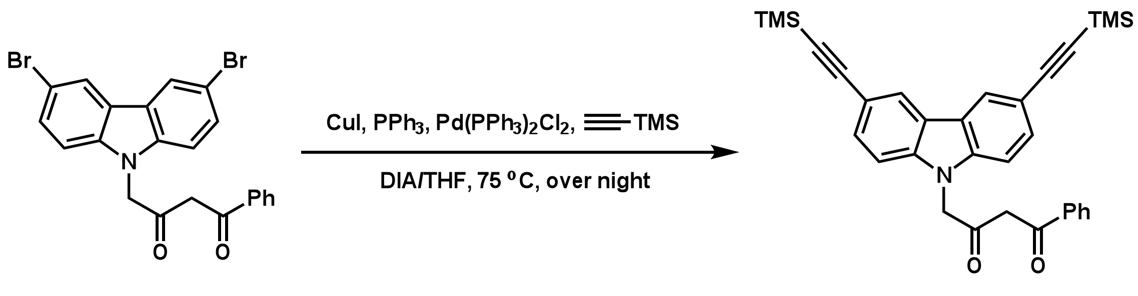
1a was prepared according to a procedure described previously.[1] Potassium carbonate (4.3 g, 31.1 mmol) and dry DMF (50 mL) were added to a 100 mL flask containing 3,6-dibromo-*9H*-carbazol (5.0 g, 15.4 mmol). The reaction mixture was stirred at 55 °C for 2 h. After this time, ethyl bromoacetate (3.8 mL, 33.7 mmol) was added to the flask and the reaction mixture was stirred at r.t. for 2 h and 55 °C for 1 h. Then, the mixture was poured into water and filtered. This compound was used for the next reaction without further purification. Yield: 6.2 g (97%)

4-(3,6-Dibromo-9*H*-carbazol-9-yl)-1-phenylbutane-1,3-dione (1b):



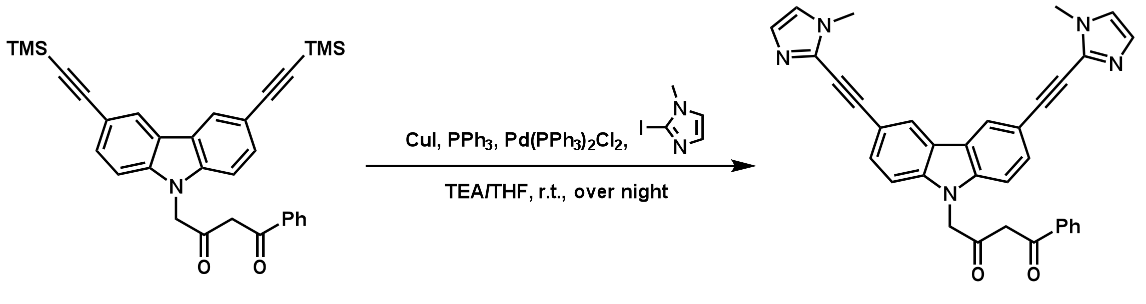
1b was also prepared according to a procedure described previously.[2] To a flame-dried 100 mL 2-necked flask containing hexamethyldisilazane potassium salt: KHMDS (21.9 mL of a 0.5 M solution in toluene, 10.95 mmol), acetophenone (1.3 mL, 10.95 mmol) in THF (12 mL) was added dropwise at 0 °C. Subsequently, the solution was stirred at r.t. for 1 h. After this time, compound **1a** (3 g, 7.30 mmol) in THF (12 mL) was added dropwise, and the resulting reaction mixture was stirred at r.t. for 12 h. Afterwards, the mixture was poured into water and acidified with diluted hydrochloric acid. The organic layer was extracted with chloroform, washed with water, and then dried with anhydrous sodium sulfate. The solvent was removed by reduced pressure. The crude product was purified by silica column chromatography (*n*-hexane/ethyl acetate = 10/3) to provide **1b** as a white powder (2.62 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, J = 1.8 Hz, 2H), 7.66–7.52 (m, 4H), 7.52–7.42 (m, 1H), 7.41–7.25 (m, 4H), 5.76 (s, 2H), 5.04 (s, 2H).

4-(3,6-Bis((trimethylsilyl)ethynyl)-9*H*-carbazol-9-yl)-1-phenylbutane-1,3-dione (1c):



To a flame-dried 2-neck flask, CuI (9 mg, 0.05 mmol), PPh_3 (12 mg, 0.05 mmol), **1b** (435 mg, 0.90 mmol), distilled diisopropylamine (4 mL), degassed THF (12 mL) and $Pd(PPh_3)_2Cl_2$ (31 mg, 0.05 mmol) were added. Then trimethylsilylacetylene (0.4 mL, 2.69 mmol) was added dropwise to the flask and the reaction mixture was stirred at 75 °C for overnight under Ar atmosphere. After filtered by celites, the filtrate was extracted with dichloromethane, washed with saturated aqueous ammonium chloride, water and dried over anhydrous sodium sulfate. The filtrate was concentrated and subjected to column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/3) to provide **1c** as a pale yellow powder (346 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, J = 1.6 Hz, 2H), 7.61 (dd, J = 8.5, 1.6 Hz, 2H), 7.57–7.50 (m, 2H), 7.50–7.41 (m, 1H), 7.38–7.27 (m, 4H), 5.67 (s, 2H), 5.07 (s, 2H), 0.29 (s, 18H).

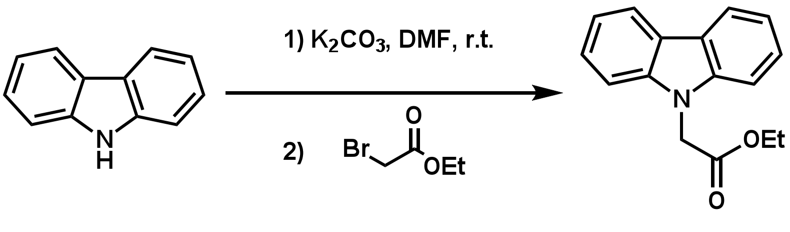
4-(3,6-Bis((1-methyl-1*H*-imidazol-2-yl)ethynyl)-9*H*-carbazol-9-yl)-1-phenylbutane-1,3-dione (L):



To a flame-dried 2-neck flask, CuI (9 mg, 0.05 mmol), PPh_3 (9 mg, 0.03 mmol), **1c** (346 mg, 0.67 mmol), 2-iode-1-methyl-1*H*-imidazole (346 mg, 1.66 mmol), distilled triethylamine (4 mL), degassed THF (12 mL) and $Pd(PPh_3)_2Cl_2$ (33 mg, 0.05 mmol) were added. Then tetra-*n*-butylammonium fluoride (1.7 mL of a 1.0 M solution in THF, 1.70 mmol) was added dropwise to the flask and the reaction mixture was stirred at r.t. for overnight under Ar atmosphere. After filtered by celites, the filtrate was extracted with dichloromethane, washed with saturated aqueous ammonium chloride, water and dried over anhydrous sodium sulfate.

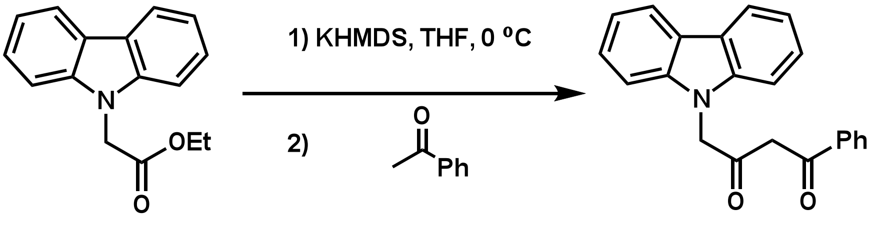
The filtrate was concentrated and subjected to column chromatography on silica gel (dichloromethane/methanol = 15/1). Then 4-(3,6-bis((1-methyl-1*H*-imidazol-2-yl)ethynyl)-9*H*-carbazol-9-yl)-1-phenylbutane-1,3-dione (**L**) was purified by GPC with chloroform to provide a pale yellow powder (71 mg, 20%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.33 (s, 2H), 7.71 (dd, J = 8.5, 1.1 Hz, 2H), 7.60 (dd, J = 8.9, 7.6 Hz, 2H), 7.52–7.41 (m, 1H), 7.42–7.30 (m, 4H), 7.11 (s, 2H), 6.96 (s, 2H), 5.83 (s, 2H), 5.11 (s, 2H), 3.84 (s, 6H). HRMS (EI) *m*/*z* calcd for $C_{34}H_{25}N_5O_2$ [M]$^+$ 535.2008, found 535.2009. ^{13}C NMR (100 MHz, CDCl$_3$): δ 191.67, 183.08, 140.88, 133.46, 132.94, 132.81, 130.42, 129.58, 128.69, 127.08, 124.50, 122.66, 121.32, 113.69, 109.16, 93.56, 93.23, 77.54, 49.05, 33.62.

4-(3,6-Bis((trimethylsilyl)ethynyl)-9*H*-carbazol-9-yl)-1-phenylbutane-1,3-dione (2a)



2a was prepared according to a procedure described previously.[1] To a 100 mL flask containing 9*H*-carbazol (3.0 g, 17.9 mmol) potassium carbonate (3.7 g, 26.9 mmol) and dry DMF (25 mL) were added. The reaction mixture was stirred at 55 °C for 2 h. After this time, ethyl bromoacetate (4.4 mL, 26.9 mmol) was added to the flask and the reaction mixture was stirred at r.t. for 2 h and 55 °C for 1 h. Then, the mixture was poured into water and filtered. This compound was used for the next reaction without further purification. Yield: 4.42 g (97%).

4-(9*H*-Carbazol-9-yl)-1-phenylbutane-1,3-dione (L')



To a flame-dried 50 mL 2-neck flask containing hexamethyldisilazane potassium salt: KHMDS (11.8 mL of a 0.5 M solution in toluene, 5.92 mmol), acetophenone (0.69 mL, 5.92 mmol) in THF (4 mL) was added dropwise at 0 °C. Subsequently, the solution was stirred at room temperature for 1 h. After this time, compound **2a** (1 g, 3.95 mmol) in THF (4 mL) was added dropwise, and the resulting reaction mixture was stirred at room temperature for 12 h.

Afterwards, the mixture was poured into water and acidified with diluted hydrochloric acid. The organic layer was extracted with chloroform, washed with water, and then dried with anhydrous sodium sulfate. The solvent was removed by reduced pressure. The crude product was purified by silica column chromatography (dichloromethane) and recrystallized in chloroform/methanol to provide 4-(9*H*-carbazol-9-yl)-1-phenylbutane-1,3-dione (**L'**) as a pale yellow crystal (520 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.11 (m, 2H), 7.59–7.52 (m, 2H), 7.52–7.25 (m, 9H), 5.80 (s, 2H), 5.08 (s, 2H). HRMS (EI) *m*/*z* calcd for $C_{22}H_{17}NO_2$ $[M]^+$ 327.1259, found 327.1267. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.79, 183.32, 140.48, 133.71, 132.63, 128.34, 127.02, 126.16, 123.18, 120.53, 119.82, 108.48, 93.17, 48.92.

Measurements. ^{1}H NMR spectra were measured with JEOL JMN-ECX-400P FT NMR SYSTEM (400 MHz). Emission spectra were recorded by a JASCO FP-6500 fluorescence spectrophotometer at various temperatures. UV-vis absorption spectra were recorded by a JASCO V-660 spectrophotometer at 298 K. The emission lifetimes were recorded using FluoroCube (HORIBA, 3000U-YSP). Mass spectra were measured with mass spectrometers (JEOL AccuTOF JMS-T100LC for ESI).

Monomer-dimer simulation. If we assume a monomer (M)-dimer (D) equilibrium (eqn (1)), the concentrations of monomer ([M]), dimer ([D]), and the population of dimer ($2[D]/[M]_0$) can be given by eqn (2)–(4), respectively, where ΔG^0 denotes the free energy change between the monomer and the dimer, and $[M]_0$ represents the initial concentration of the monomer. Simulation curves in Fig. S8 (see ESI† S8) were obtained with ΔG^0 = 1–10 kcal mol^{-1} and $[M]_0 = 1.0 \times 10^{-4}$ M by using eqn (4). The strength of aromatic stacking interactions in the multistep equilibrium could be difficult to determine accurately, because both monomer carbazole fluorescence and excimer emission is highly temperature dependent, where their emission intensities decrease with increasing the temperature (see ESI† S7).

$$\mathbf{2M} \xrightleftharpoons{\Delta G^0} \mathbf{D} \tag{1}$$

$$[M] = \frac{-1 + (1 + 8[M]_0 \exp(-\Delta G^0/RT))^{0.5}}{4\exp(-\Delta G^0/RT)} \tag{2}$$

$$[D] = [M]_0/2 - \frac{-1 + (1 + 8[M]_0 \exp(-\Delta G^0/RT))^{0.5}}{8\exp(-\Delta G^0/RT)} \tag{3}$$

$$2[D]/[M]_0 = 1 - \frac{-1 + (1 + 8[M]_0 \exp(-\Delta G^0/RT))^{0.5}}{4[M]_0\exp(-\Delta G^0/RT)} \tag{4}$$

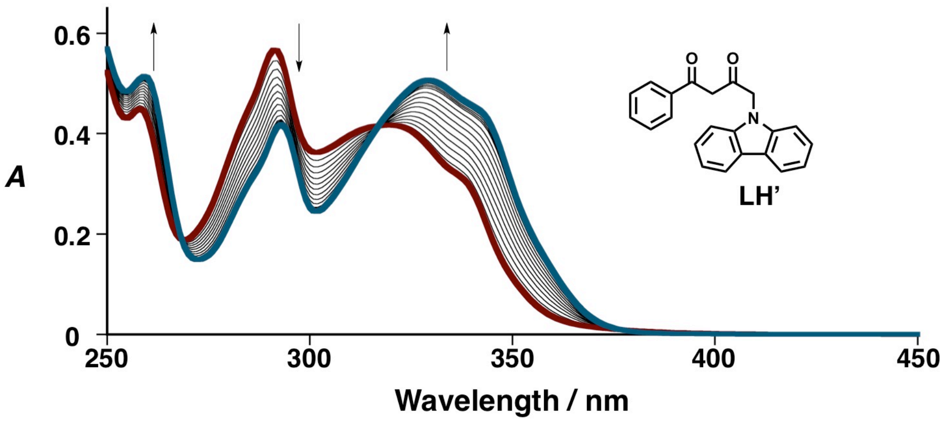


Fig. S2 UV-vis absorption spectra of LH' (2.0×10^{-5} M) in the presence of Zn^{2+} [0 M (red line)–3.4×10^{-5} M (blue line)] in methanol at 298 K. Inset shows the chemical structure of LH'.

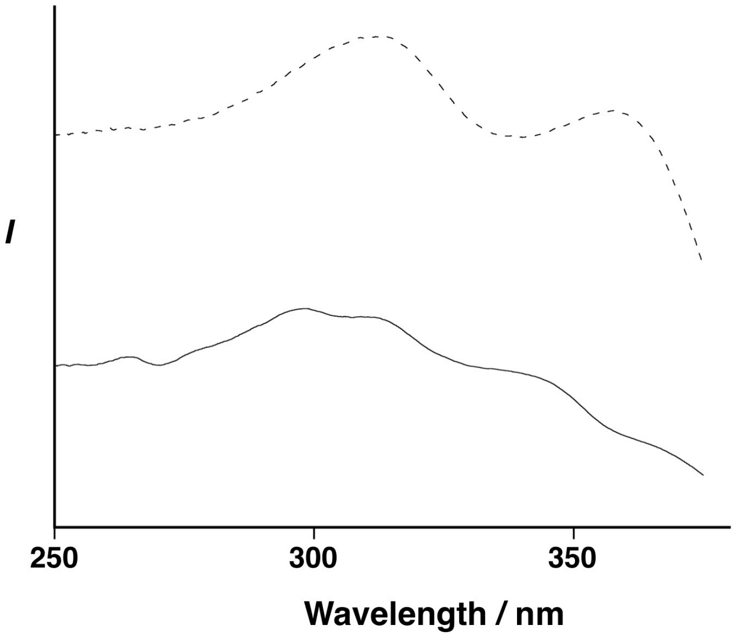


Fig. S3 Excitation spectra of LH (2.0×10^{-4} M) in the presence of Zn^{2+} (3.6×10^{-3} M) recorded at $\lambda = 392$ nm (solid line) and 450 nm (dashed line) in methanol at 298 K.

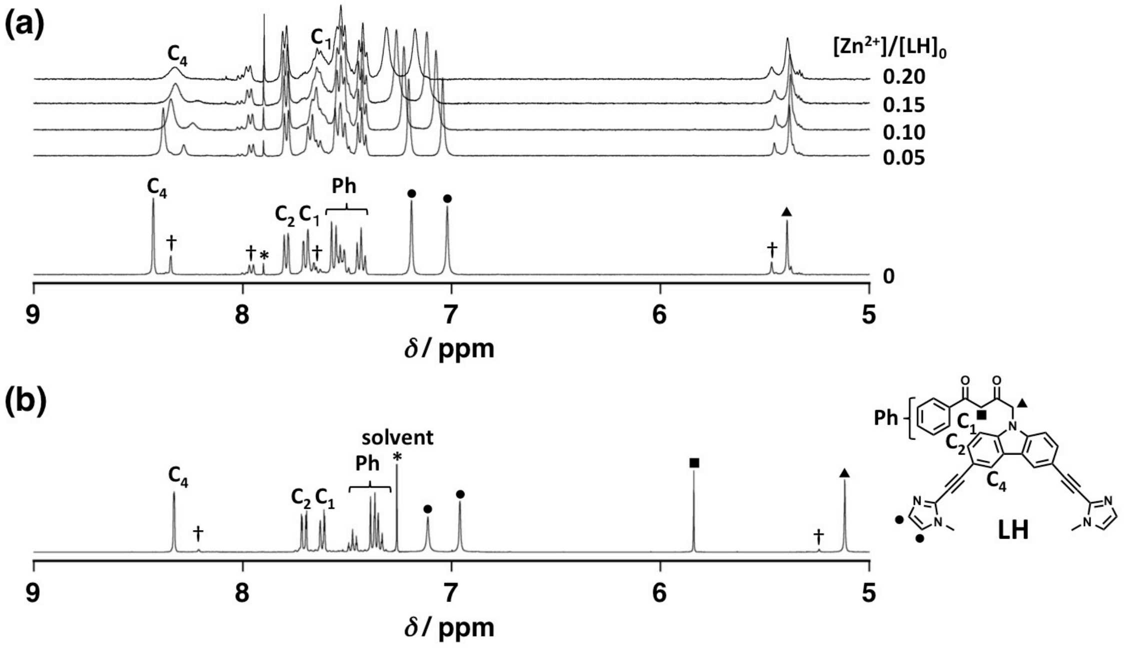


Fig. S4 (a) ^{1}H NMR spectra (400 MHz) of LH (2.0×10^{-2} M) in the presence of Zn^{2+} ($0–4.0 \times 10^{-3}$ M) in CD$_3$OD at 298 K. (b) ^{1}H NMR spectrum (400 MHz) of LH in CDCl$_3$. Symbols correspond to those in the chemical structure of LH. Small peaks (indicated by dagger) correspond to the enol isomer of LH.

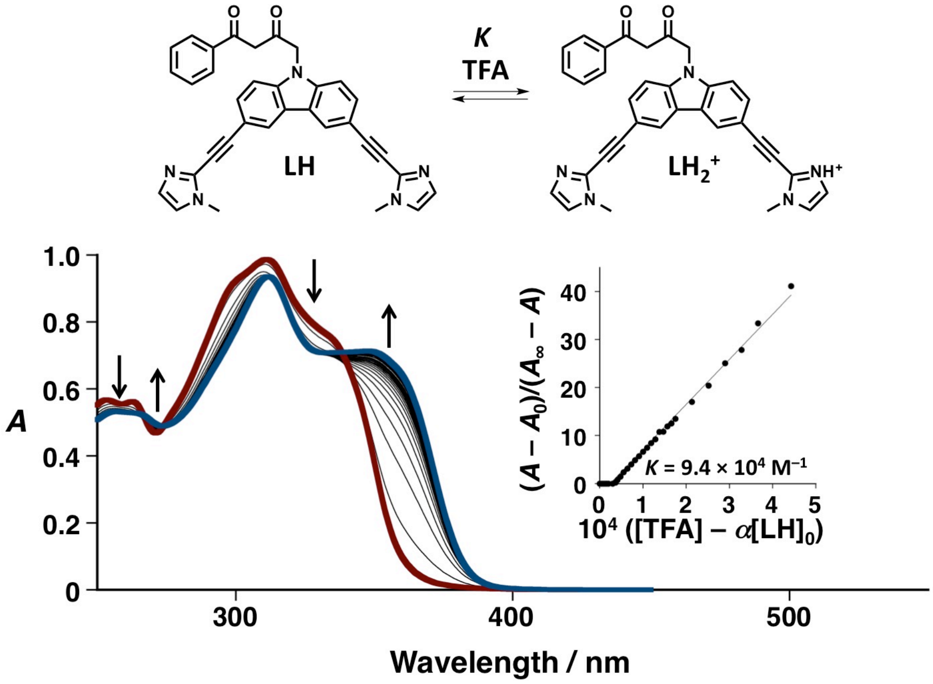


Fig. S5 UV-vis absorption spectra of LH ($[\mathrm{LH}]_0 = 2.0 \times 10^{-5}$ M) in the presence of trifluoromethanesulfonic acid [TFA: 0 M (red line)–1.3×10^{-3} M (blue line)] in methanol at 298 K. Inset: Plot of $(A - A_0)/(A_\infty - A)$ *vs*. [TFA] – $\alpha[\mathrm{LH}]_0$, where $\alpha = (A - A_0)/(A_\infty - A_0)$ at $\lambda = 375$ nm.

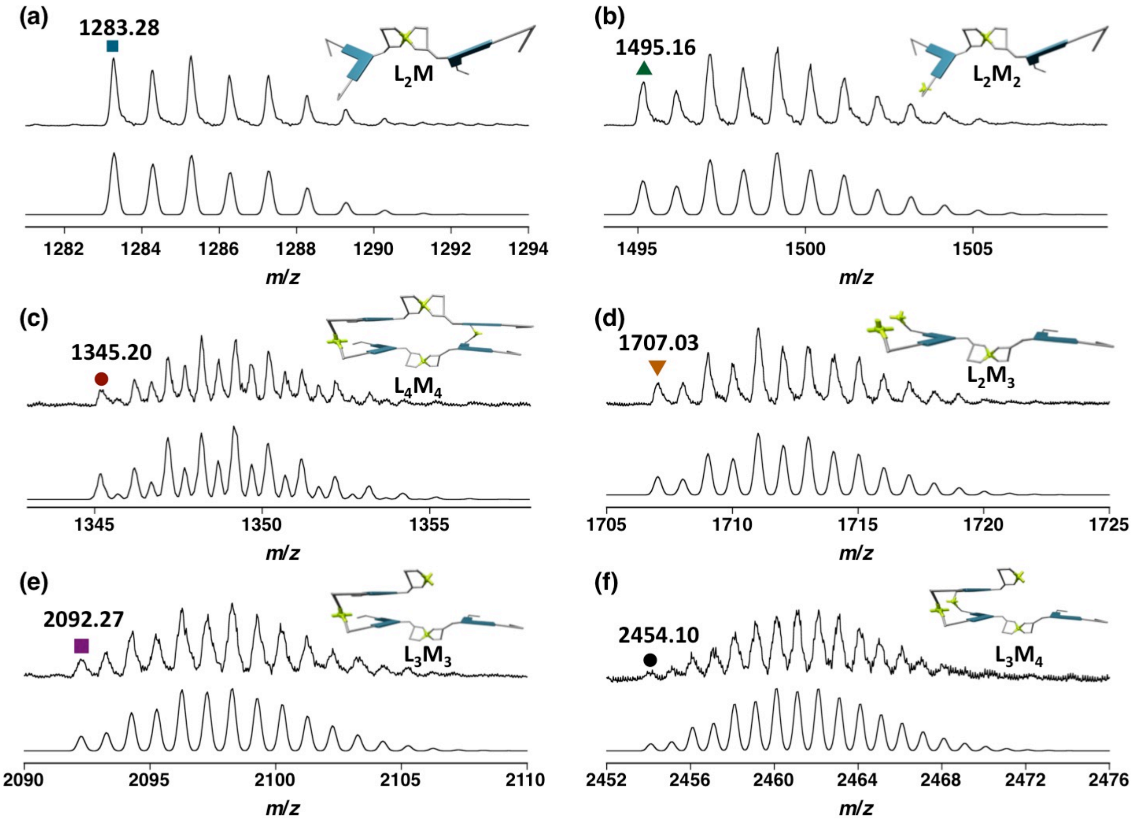


Fig. S6 Positive-ion ESI MS of a solution of LH (1.3×10^{-3} M) in methanol in the presence of $Zn(OSO_2CF_3)_2$ (1.3×10^{-3} M). Isotopically resolved signals at (a) *m*/*z* = 1283.28 and the calculated isotopic distributions for $\{[Zn(L)_2H_2](OSO_2CF_3)\}^+$, (b) *m*/*z* = 1495.16 and that for $\{[Zn_2(L)_2H](OSO_2CF_3)_2\}^+$, (c) *m*/*z* = 1345.2 and that for $\{[Zn_4(L)_4](OSO_2CF_3)_2\}^{2+}$ combined with $\{[Zn_2(L)_2](OSO_2CF_3)\}^+$ (1:1 ratio), (d) *m*/*z* = 1707.03 and that for $\{[Zn_3(L)_2](OSO_2CF_3)_3\}^+$, (e) *m*/*z* = 2092.27 and that for $\{[Zn_3(L)_3](OSO_2CF_3)_2\}^+$, and (f) *m*/*z* = 2454.10 and that for $\{[Zn_4(L)_3](OSO_2CF_3)_4\}^+$.

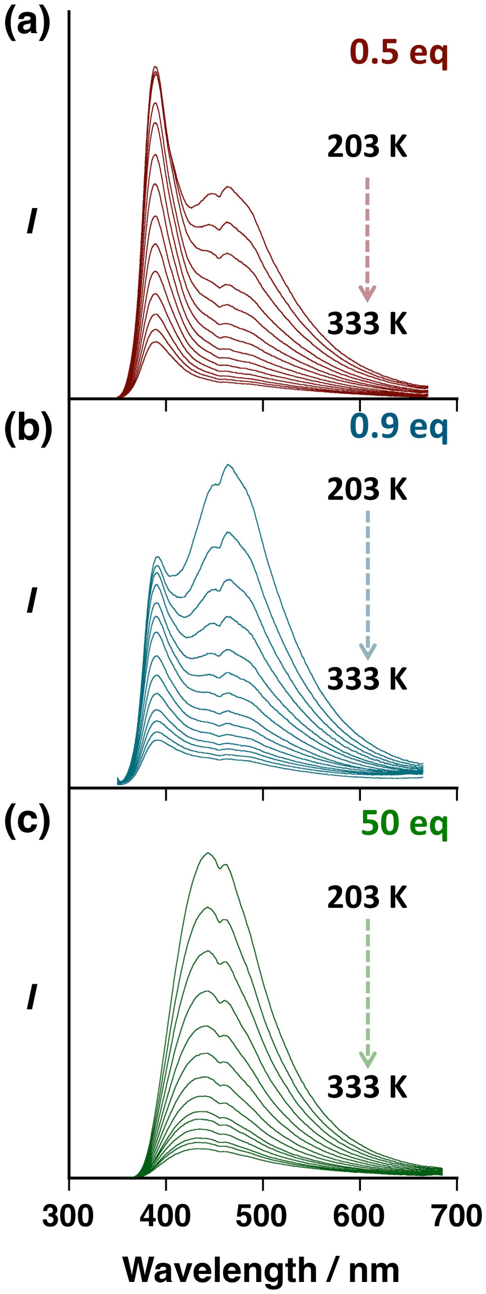


Fig. S7 Emission spectra of LH (2.0 × 10^{-4} M) in the presence of Zn^{2+} (a) (1.0 × 10^{-4} M), (b) (1.8 × 10^{-4} M), and (c) (1.0 × 10^{-2} M) in methanol at 203–333 K. Excitation wavelength: λ = 340 nm.

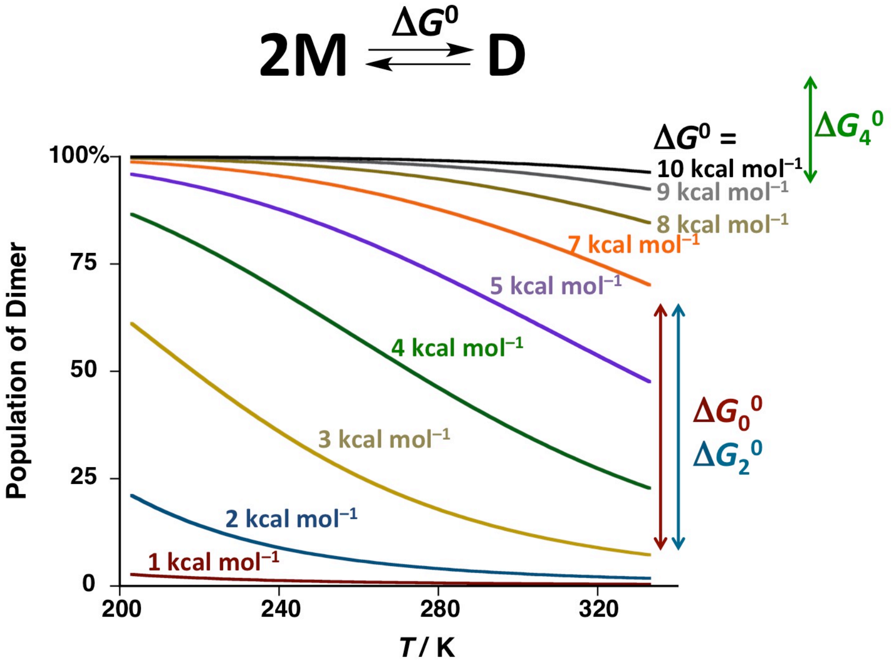


Fig. S8 Population of dimer (2[D]/[M]$_0$) *vs*. T. Simulation curves were obtained with ΔG^0 = 1–10 kcal mol^{-1} and [M]$_0$ = 1.0 × 10^{-4} M by using eqn (4). The ΔG^0 corresponds to ΔG_0^0, ΔG_2^0, and ΔG_4^0 in Fig. 4g.

References

(1) M. M. Conn, G. Deslongchamps, J. de Mendoza and J. Rebek Jr., *J. Am. Chem. Soc.*, 1993, **115**, 3548.

(2) N. Tian, A. Thiessen, R. Schiewek, O. J. Schmitz, D. Hertel, K. Meerholz and E. Holder, *J. Org. Chem.*, 2009, **74**, 2718.