Supporting Information

Metal-directed synthesis of quadruple-stranded helical Eu(III) molecule switch: a significant improvement on photocyclization quantum yield

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1. Experimental Section.

1.1 General: All reagents were obtained from commercial suppliers and were used without further purification. $LnCl_3 \cdot 6H_2O$ was prepared according to the literature by dissolving 99.99% oxide in a slight excess of hydrochloric acid. The solution was evaporated and the precipitate was collected from water.

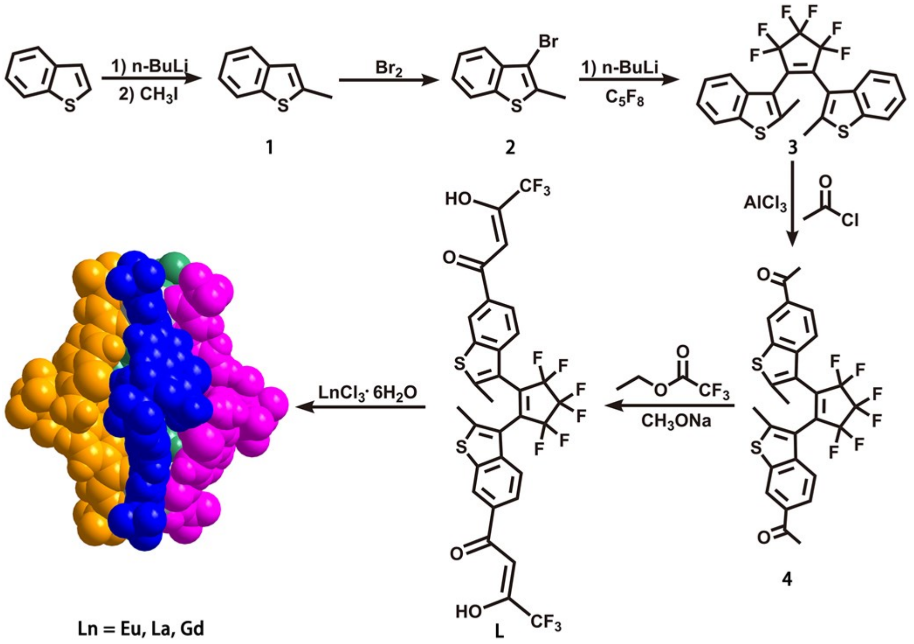
1.2 Spectroscopic Measurements: The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded with a Bruker Avance III 400 MHz spectrometer and the chemical shifts are referenced internally to tetramethylsilane (TMS) or solvents in parts per million (ppm). ^1H NMR spectra assignments are reported as follows (s = singlet, d = doublet, t = triplet, m = multiplet, coupling constant(s) in Hz; integration). Elemental analyses were performed on an Elementar Vario EL cube analyser. Electrospray time-of-flight (ESI-TOF) mass spectra were measured on a Bruker maXis mass spectrometer. UV−vis spectra were recorded on a PerkinElmer Lambda 25 spectrometer. The excitation, emission spectra, and luminescence lifetimes were performed on an Edinburgh FLS 980 fluorescence spectrophotometer. The lifetime fitting curves were analyzed by software provided by Edinburgh Instruments. The quantum yields of the Eu(III) center emissions were determined by an absolute method using an integrating sphere equipped on an Edinburgh FLS 980 fluorescence spectrophotometer. The values of QYs are the average of three independent measurements per sample. The absolute quantum yield was calculated by the following formula:

$$\Phi = \frac{\int L_{\text{emisson}}}{\int E_{\text{reference}} - \int E_{\text{sample}}}$$

where L_{emission} is the emission curve of the sample, collected by integrating the sphere, E_{sample} is the curve of incident light, and $E_{\text{reference}}$ is the curve of the light used for excitation with only the reference in the sphere. The accuracy of the method is within 10%.

1.3 Synthesis and Characterization.

The compound 1–4 were synthesized according to the procedures previously reported. [1,2]



Scheme S1 Synthetic routes of **L** and the corresponding complexes $(HNEt_3)_2[Ln_2\mathbf{L}_4]$

2-methylbenzo[*b*]thiophene (1)

Benzo[b]thiophene (5.70 g, 42.47 mmol) was dissolved in 100 mL anhydrous tetrahydrofuran (THF) and cooled to −78 °C. 37.50 mL of n-butyllithium (1.6 M, 60.00 mmol) was slowly added to the solution. The resulting mixture was warmed to room temperature, and iodomethane (3.50 mL, 54.25 mmol) was added dropwise to the mixture. After stirring for 1 h, methanol and water were added to the mixture. Organic products were extracted with ethyl acetate and dried with Na_2SO_4. After Na_2SO_4 was filtered off, the solvent was removed by evaporation. The crude product was purified by column chromatography on a silica gel using petroleum ether as an eluent to give a white crystal in 90.48% yield (5.70 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.57 (s, 3H, CH_3), 6.96 (s, 1H, ArH), 7.20–7.36 (m, 2H, ArH), 7.63 (d, 1H, ArH), 7.74 (d, 1H, ArH).

3-bromo-2-methylbenzo[*b*]thiophene (2)

Bromine (1.70 mL, 33.18 mmol) was slowly added to 80 mL chloroform solution containing **1** (5.00 g, 33.73 mmol) at 0 °C. After stirring for 2 h at 0 °C, aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$ was added to the mixture. The resulting mixture was extracted with ethyl acetate and washed several times with an aqueous solution of sodium thiosulfate. After removal of residual water with Na_2SO_4, the solvent was removed by evaporation. The crude product was purified by column chromatography on a silica gel using petroleum ether as an eluent to give a white crystal in 92.69% yield (7.10 g). ^1H NMR (400 MHz, $CDCl_3$, ppm): 2.54 (s, 3H, CH_3), 7.24–7.53 (m, 2H, ArH), 7.68–7.72 (m, 2H, Ar).

1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (3)

2 (5.00 g, 22.01 mmol) was dissolved in anhydrous THF (75 mL), and 17 mL of n-butyllithium (1.6 M, 27.20 mmol) was added dropwise to the solution at −78 °C under nitrogen. The mixture was stirred for 1 h, and 1.5 mL of octafluorocyclopentene (11.18 mmol) was slowly added at −78 °C. After stirring for 30 min, the cooling bath was removed. The resulting mixture was warmed to room temperature and stirred over night. Then methanol and water was added to the solution. The resulting solution was extracted with ethyl acetate and dried with Na_2SO_4. After Na_2SO_4 was filtered off, the solvent was removed by evaporation. The crude product was purified by column chromatography on a silica gel (petroleum ether) and then recrystallized from hexane to give **3** in 46.96% yield (2.20 g). 3 consists of two conformational isomers (parallel (p) and antiparallel (ap)). ^1H NMR (400 MHz, $CDCl_3$, ppm): 2.19 (s, 3H, ap-CH_3), 2.47 (s, 3H, p-CH_3), 7.14–7.38 (m, 8H, −Ar).

1,2-bis(6-acetyl-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (4)

3 (1.00 g, 2.13 mmol) were dissolved in 20 mL nitrobenzene, and acetyl chloride (0.87 g, 11.08 mmol) was added to the solution and stirred for 30 min. $AlCl_3$ (1.50 g, 11.25 mmol) was slowly added to the solution at room temperature, and then hydrochloric acid (1.0 M) was added to the reaction mixture. The resulting solution was extracted twice with ethyl acetate and dried with Na_2SO_4. After filtration of Na_2SO_4 and removal of solvent, 4 was isolated by column chromatography (ethyl acetate/petroleum ether = 1/4) to obtained white solid in 45.76% yield (0.54 g). ^1H NMR (400 MHz, $CDCl_3$, ppm): 2.19 (s, 3H, ap-CH_3), 2.49 (s, 3H, p-CH_3), 2.52 (s, 3H, ap-CH_3), 2.58 (s, 3H, p-CH_3), 7.45–8.25 (m, 6H, ArH).

1,2-bis(6-(4,4,4-trifluoro-1,3-dioxobutyl)-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (L)

A mixture of sodium methoxide (0.40 g, 7.24 mmol) and ethyl trifluoroacetate (2.56 g, 18.10 mmol) in 30 mL DME (ethylene glycol dimethyl ether) was stirred for 10 min, followed by the addition of 4 (1.00 g, 1.81 mmol). Then, it was further stirred at room temperature for

24 h. The resulting solution was quenched with water and acidified to pH = 2−3 using hydrochloric acid (1.0 M solution). The resulting orange precipitate was filtered and dried in vacuum. Recrystallization from ethyl acetate and n-hexane to gave yellow crystals in 68.15% yield (0.92 g). L consists of two conformational isomers (parallel (p) and antiparallel (ap)). ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ v/v = 1:1, ppm): 2.41 (s, 3H, ap-CH_3), 2.61 (s, 3H; p-CH_3), 6.79 (s, H; p-CH), 6.87 (s, H; ap-CH), 7.77–7.81 (d, 2H, Ar-H), 7.86–7.90 (d, H, ap-Ar-H), 8.02–8.07 (d, H, ap-Ar-H), 8.44 (s, H, ap-Ar-H), 8.53 (s, H, p-Ar-H). ^{13}C NMR (100 MHz, 1 : 1 $CD_3OD/CDCl_3$, ppm): 197.92, 184.95, 148.70, 148.45, 142.08, 141.95, 138.66, 138.59, 138.31, 133.24, 129.06, 124.65, 124.50, 123.84, 123.61, 123.47, 122.62, 122.42, 122.15, 121.88, 121.64, 119.04, 118.58, 116.00, 115.77, 15.20. ESI-MS *m/z* = 743.0273 $[M - H]^-$.

$(HNEt_3)_2[Ln_2L_4]$ [Ln = Eu, Gd, La]

L (0.20 g, 0.27 mmol) and triethylamine (0.06 g, 0.59 mmol) were dissolved in 10 mL methanol. $LnCl_3{\cdot}6H_2O$ (0.13 mmol) of methanol (10 mL) were added dropwisely to the above solution and stirred for 24 h. The precipitate formed after the addition of water was filtered, and washed successively with H_2O (2.0 × 10 mL), then dried under vacuum to give the desired products.

$(HNEt_3)_2[Eu_2L_4]$. Yield: 81.3%. Anal. calcd. for $C_{124}H_{56}O_{16}F_{48}S_8Eu_2$: C 46.96, H 2.55, N 0.81. Found: C 46.86, H 2.69, N 0.90. ESI-MS *m/z* = 1638.0864 $[Eu_2L_4]^{2-}$.

$(HNEt_3)_2[Gd_2L_4]$. Yield: 84.2%. Anal. calcd. for $C_{124}H_{56}O_{16}F_{48}S_8Gd_2$: C 46.82, H 2.54, N 0.80. Found: C 46.74, H 2.65, N 0.91. ESI-MS *m/z* = 1642.3687 $[Gd_2L_4]^{2-}$.

$(HNEt_3)_2[La_2L_4]$. Yield: 83.7%. Anal. calcd. for $C_{124}H_{56}O_{16}F_{48}S_8La_2$: C 47.31, H 2.57, N 0.81. Found: C 47.18, H 2.68, N 0.93. ESI-MS *m/z* = 1624.0252 $[La_2L_4]^{2-}$.

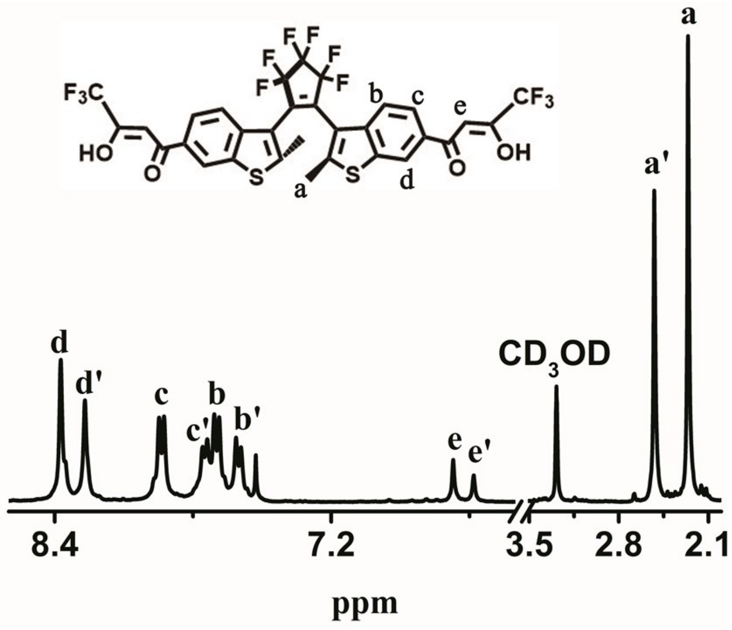


Figure S1. 400 MHz ^{1}H NMR spectrum of **L** in $CD_3OD/CDCl_3$ (v/v = 1:1).

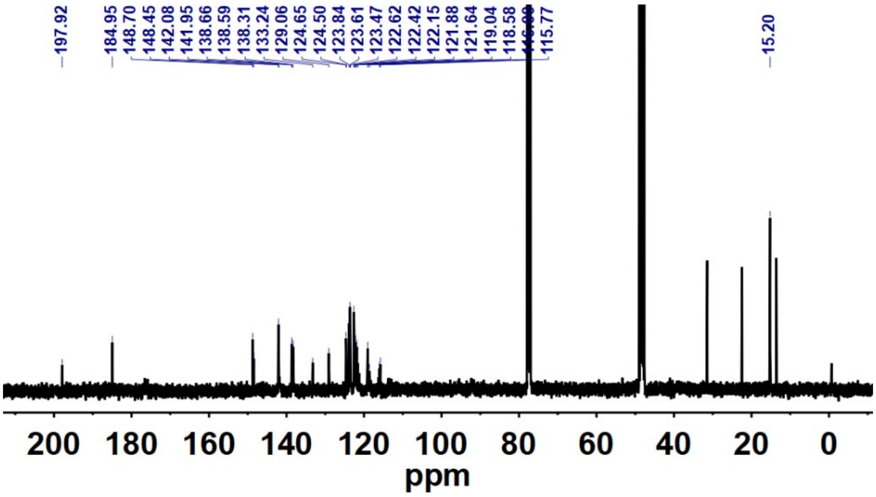


Figure S2. 100 MHz ^{13}C NMR spectrum of **L** in $CD_3OD/CDCl_3$ (v/v = 1:1).

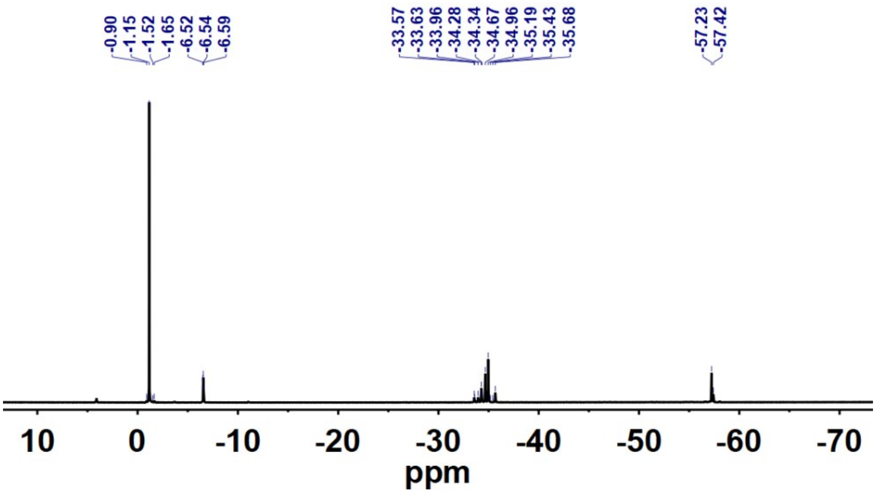


Figure S3. ^{19}F NMR spectrum of **L** in $CD_3OD/CDCl_3$ (v/v = 1:1).

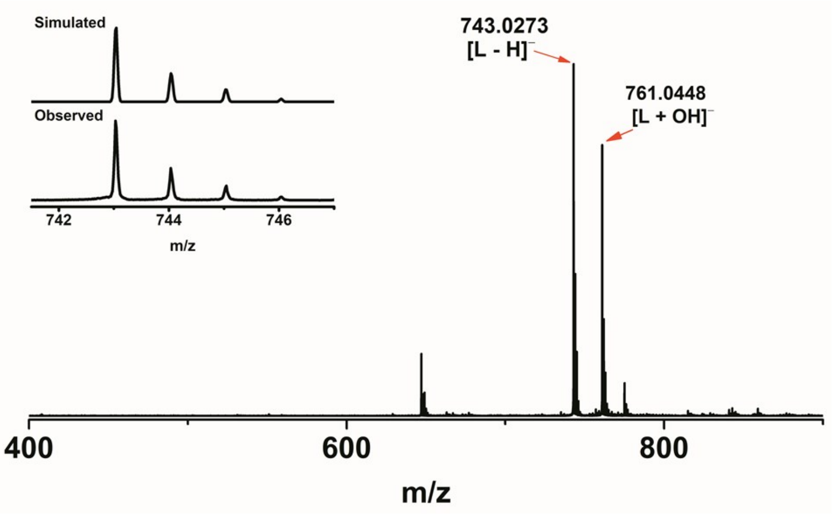


Figure S4. ESI-TOF mass spectrum of **L**.

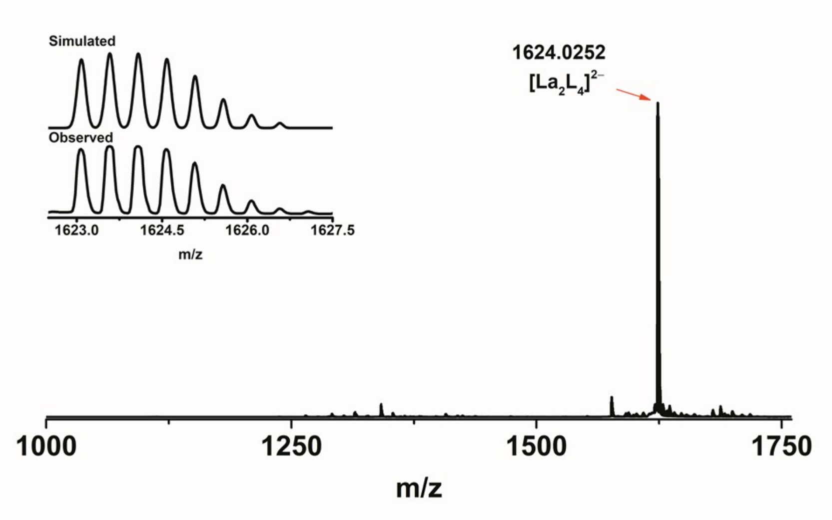


Figure S5. ESI-TOF mass spectrum of $[\mathrm{La}_2\mathbf{L}_4]^{2-}$.

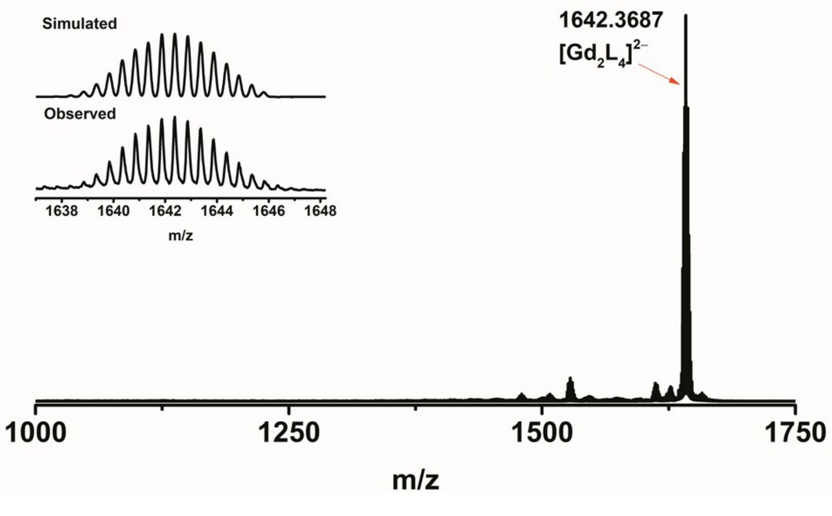


Figure S6. ESI-TOF mass spectrum of $[\mathrm{Gd}_2\mathbf{L}_4]^{2-}$.

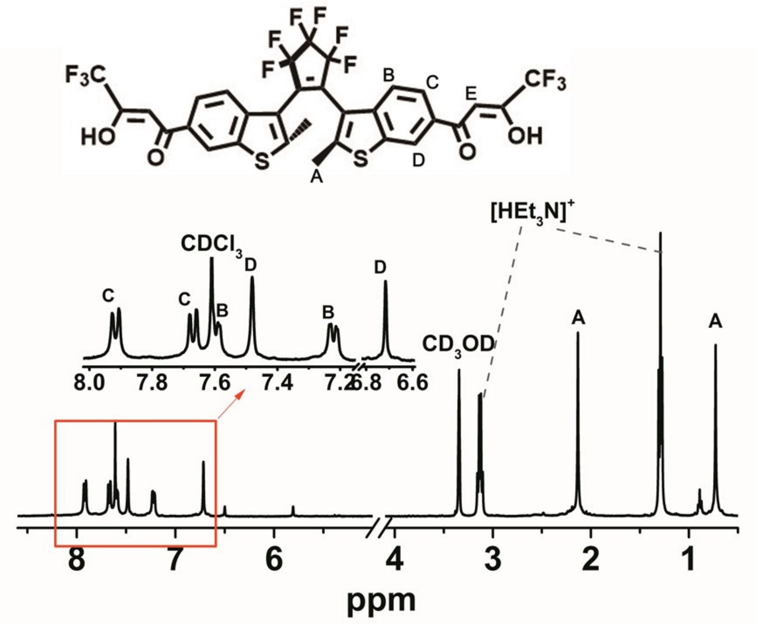


Figure S7. 400 MHz ^{1}H NMR spectrum of $(HNEt_3)_2[La_2\mathbf{L}_4]$ in $CD_3OD/CDCl_3$ (v/v = 1:1).

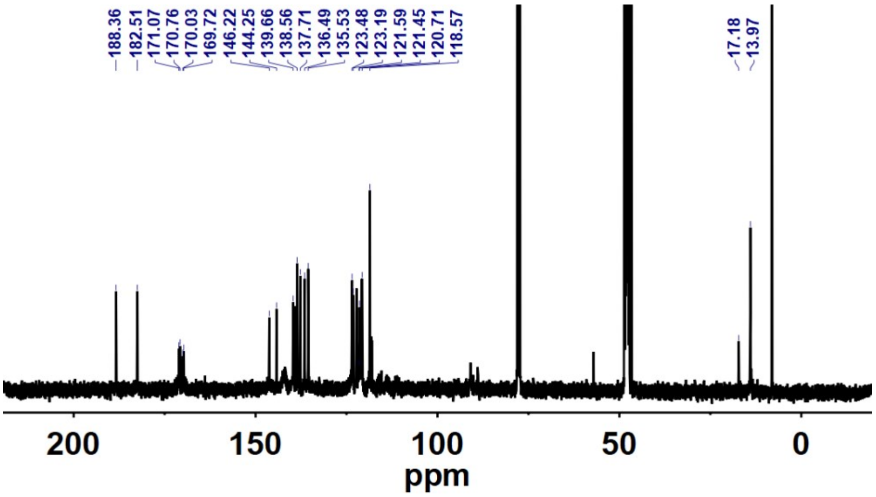


Figure S8. 100 MHz ^{13}C NMR spectrum of $(HNEt_3)_2[La_2\mathbf{L}_4]$ in $CD_3OD/CDCl_3$ (v/v = 1:1).

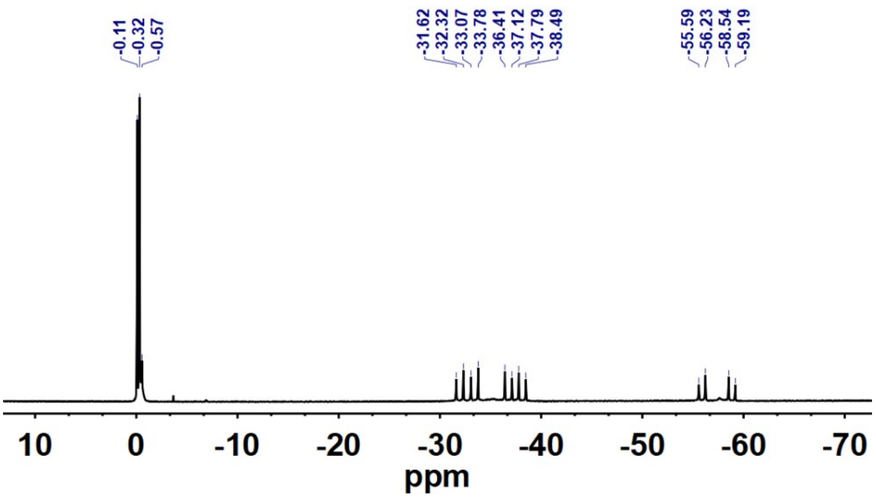


Figure. S9. ^{19}F NMR spectrum of $(HNEt_3)_2[La_2L_4]$ in $CD_3OD/CDCl_3$ (v/v = 1:1).

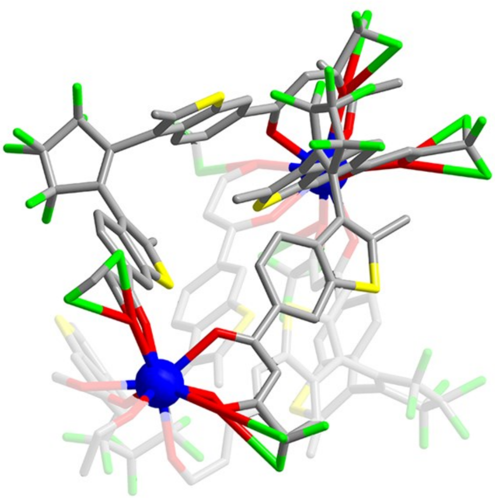


Figure S10. Crystallographic structures of $(HNEt_3)_2[La_2\mathbf{L}_4]$.

2. The cyclization and cycloreversion properties studies of ligand and complexes

2.1 The cyclization and cycloreversion quantum yields calculation.

The quantum yields of photoisomerization reactions were measured following the reported method (supplementary eq 1–7). The kinetics of re-equilibration from an arbitrary initial photostationary state (A_0) to a new phostationary state (A_{pss}) dictated by exposure to light of a given wavelength, is monoexponential (Fig. 3 and supplementary eq 1). The rate constant of equilibration (κ_{eq}) is given by the sum of the two apparent first-order rate constants defining the overall transition and the equilibrium constant (K_{pss}) by their ratio. κ_{ex} is the rate constants for absorption at excitation wavelength. σ_{ex} (cm^2 $molecule^{-1}$) is the absorption cross-section at excitation wavelength λ_{irr} (nm). ψ_{ex} (photons $s^{-1}cm^{-2}$) is the photon flux. I ($W\ cm^{-2}$) is the intensity of irradiation light, it is 1.45 mW/cm^2 for 365 nm and 2.22 mW/cm^2 for 526 nm. N_a is the Avogadro's constant. α_{pss} is the fractional population of closed form in PSS under 365-nm irradiation and calculated from ^1H NMR (Fig. S13 and S14). $c_{c\text{-}pss}$ is the concentration for close-ring forms molecule and c is initial concentration for open-ring forms molecule. The concentration for L, and Eu_2L_4 in $CH_3OH/CHCl_3$ are 1.0×10^{-5} M and 2.5×10^{-6} M respectively.

$$A(t) = A_{pss} + (A_0 - A_{pss})\, e^{-\kappa_{eq} t} \quad (1)$$

$$\kappa_{eq} = \kappa_{o\rightarrow c} + \kappa_{c\rightarrow o} \quad (2)$$

$$K_{pss} = [\text{Open form}]/[\text{closed form}] = \kappa_{o\rightarrow c}/\kappa_{c\rightarrow o} \quad (3)$$

$$a_{pss} = K_{pss}/(1 + K_{pss}) = \kappa_{o\rightarrow c}/\kappa_{eq} \quad (4)$$

$$\kappa_{ex} = \sigma_{ex}\, \psi_{ex},\ \sigma_{ex} = (10^3 \ln 10/Na)\, \varepsilon_{irr},\ \psi_{ex} = 5 \times 10^{15} \lambda_{irr}\, I \ (5)$$

$$\Phi_{o\rightarrow c} = \kappa_{o\rightarrow c}/\kappa_{ex,o} \ (6)$$

$$\Phi_{c\rightarrow o} = \kappa_{c\rightarrow o}/\kappa_{ex,c} \ (7)$$

$$c_{c\text{-}pss} = (\alpha_{pss}\, n)/v = \alpha_{pss}\, c \ (8)$$

$$\varepsilon_{526} = A_{526}/(c_{c\text{-}pss}\, b) \ (9)$$

Table S1 | Molar extinction coefficients and photoconversion yields of L and La_2L_4 in $CH_3OH/CHCl_3$ (v/v = 1:1) under 365 nm UV irradiation

Compounds	**ε_λ (L mol^{-1} cm^{-1})**		**$\alpha_{pss.\ 365\ nm}$**
	Open form (365 nm)	**Closed form (526 nm)**	
L	17843	15256	20%
La_2L_4	68372	56158	40%

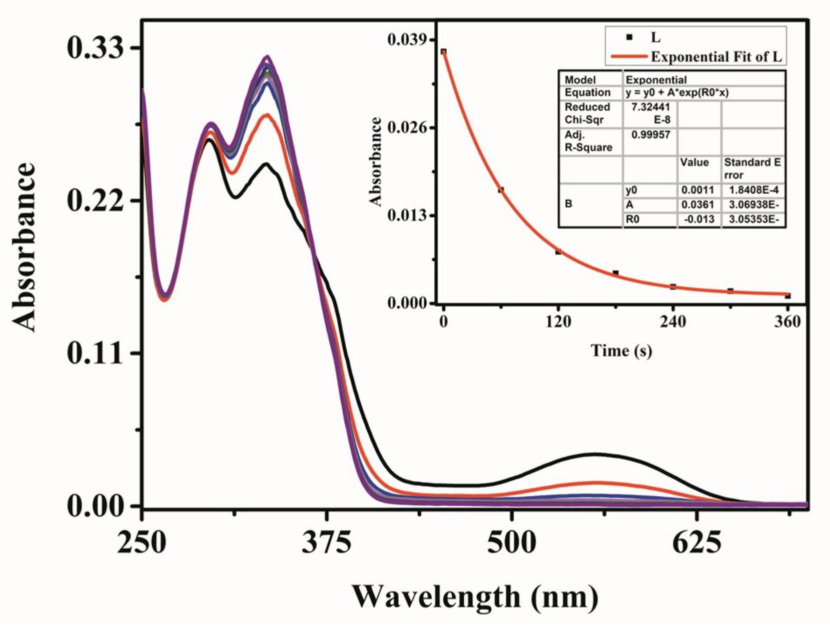


Figure S11. Electronic absorption spectra changes of *c*-**L** in the solution of $CH_3OH/CHCl_3$ (v/v = 1:1) upon irradiation with 526 nm light.

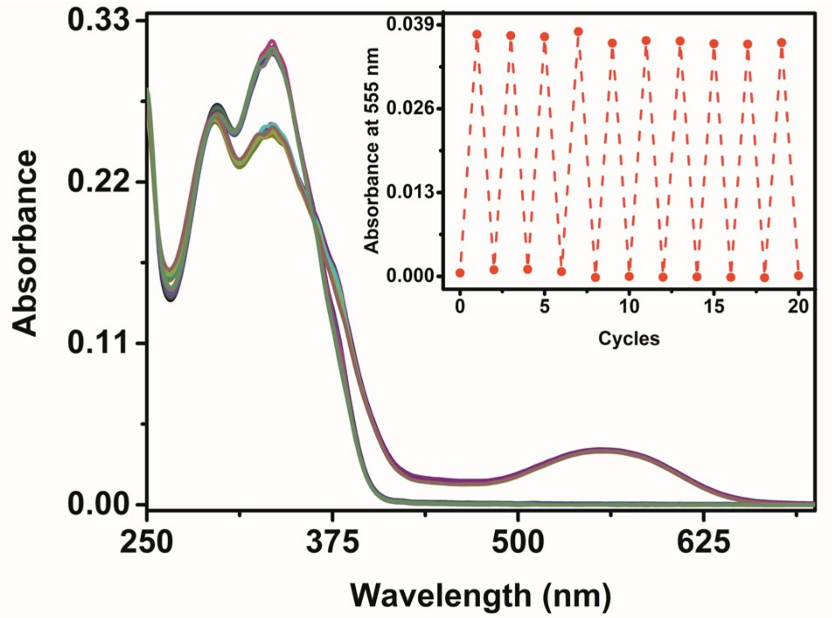


Figure S12. UV−vis spectral changes of **L** (1.0×10^{-5} M) in $CH_3OH/CHCl_3$ (v/v = 1:1) upon alternating UV (365 nm, 3 min) and visible light (> 420 nm, 1 min.) irradiations. Inset: the absorbance changes at 555 nm upon repeated alternating UV−vis irradiations.

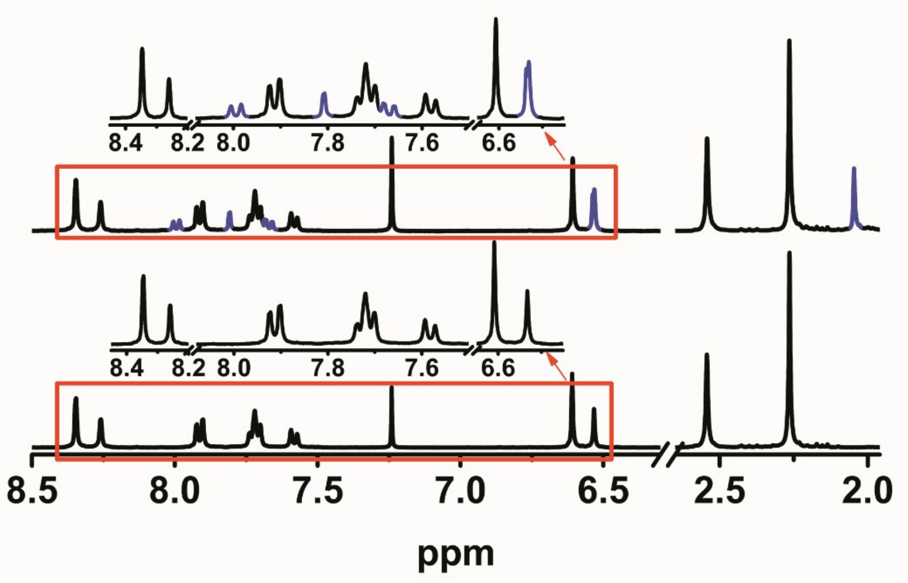


Figure S13. ^{1}H NMR spectral changes observed for **L** upon irradiation with UV light (365 nm, top) and subsequent irradiation with visible light (> 420 nm) in $CD_3OD/CDCl_3$ (v/v = 1:1) at 298 K (bottom).

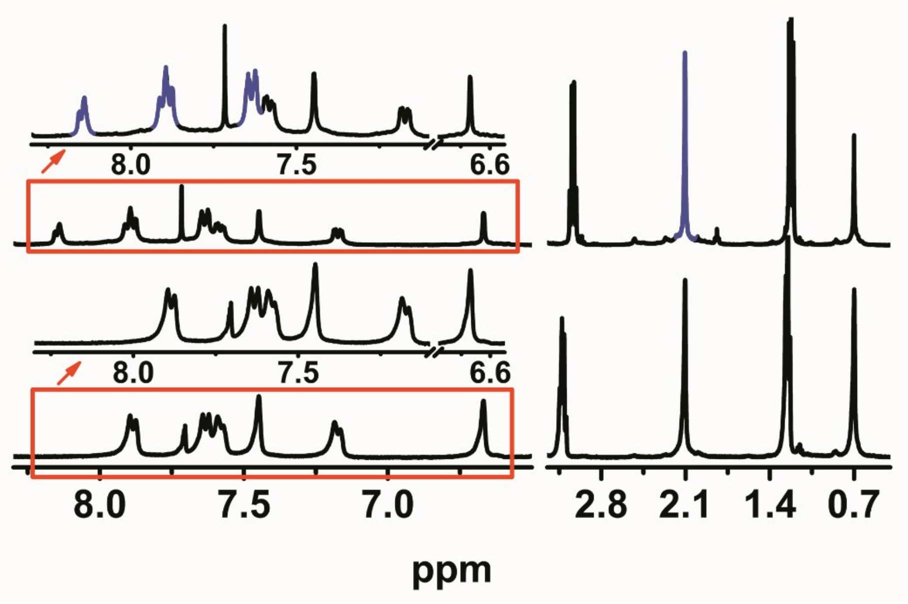


Figure S14. ^{1}H NMR spectral changes observed for $(HNEt_3)_2[La_2\mathbf{L}_4]$ upon irradiation with UV light (365 nm, top) and subsequent irradiation with visible light (> 420 nm) in $CD_3OD/CDCl_3$ (v/v = 1:1) at 298 K (bottom).

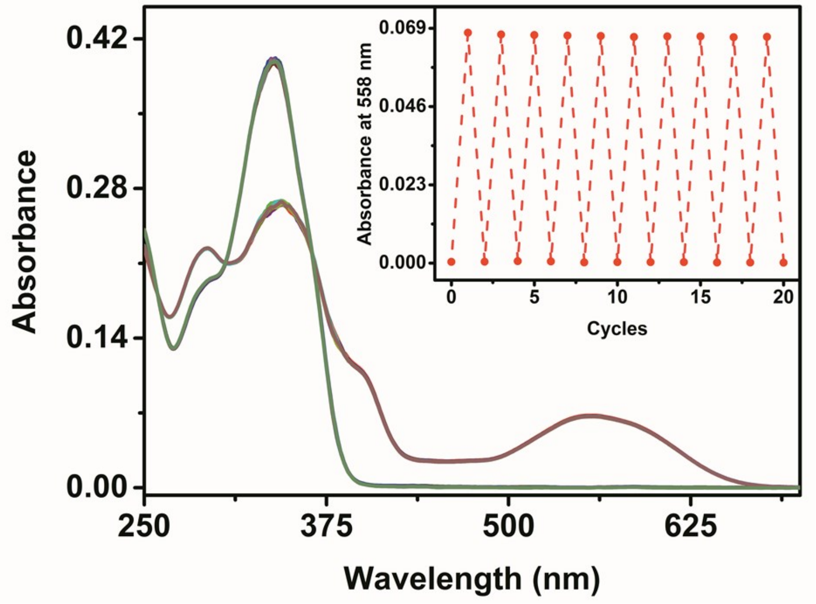


Figure S15. UV−vis spectral changes of assembly $(HNEt_3)_2[Eu_2\mathbf{L}_4]$ (2.5×10^{-6} M) in $CH_3OH/CHCl_3$ (v/v = 1:1) upon alternating UV (365 nm, 3 min) and visible light (> 420 nm, 1 min) irradiations. Inset: the absorbance changes at 558 nm upon repeated alternating UV−vis irradiations.

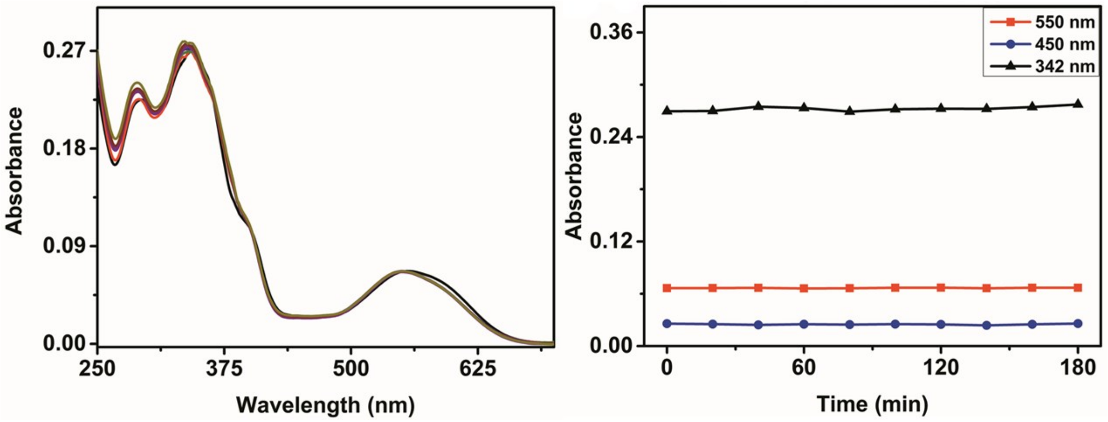


Figure S16. UV−vis spectra of a mixture of *c*-$Eu_2\mathbf{L}_4$ (obtained by UV irradiation of *o*-$Eu_2\mathbf{L}_4$ in $CH_3OH/CHCl_3$ (v/v = 1:1) heated for 3 h at 55 °C (left). Absorbance changes of the *o*-$Eu_2\mathbf{L}_4$/ *c*-$Eu_2\mathbf{L}_4$ mixture monitored at 550, 450, and 342 nm (right).

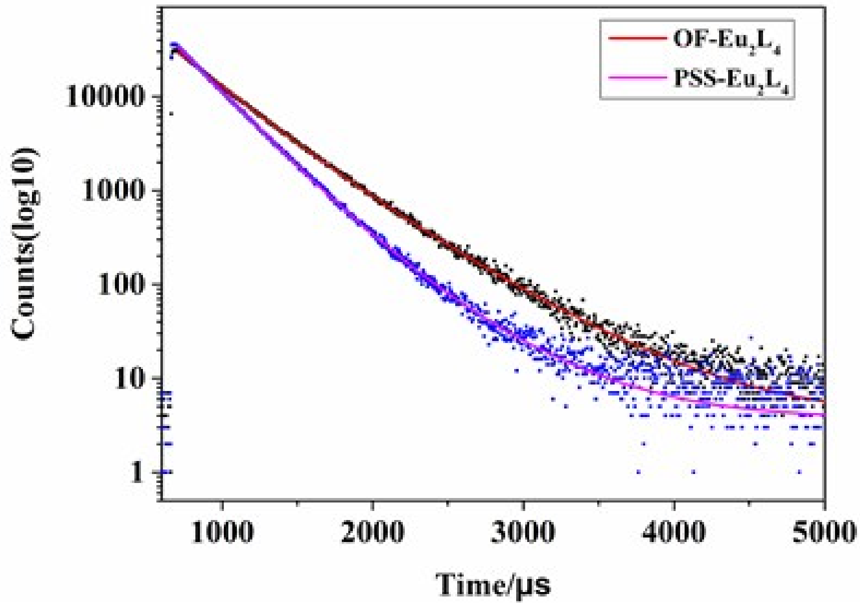


Figure S17. Luminescence decay curves of *o*-$Eu_2\mathbf{L}_4$ and *c*-$Eu_2\mathbf{L}_4$ in $CH_3OH/CHCl_3$ (v/v = 1:1) monitored at 612 nm.

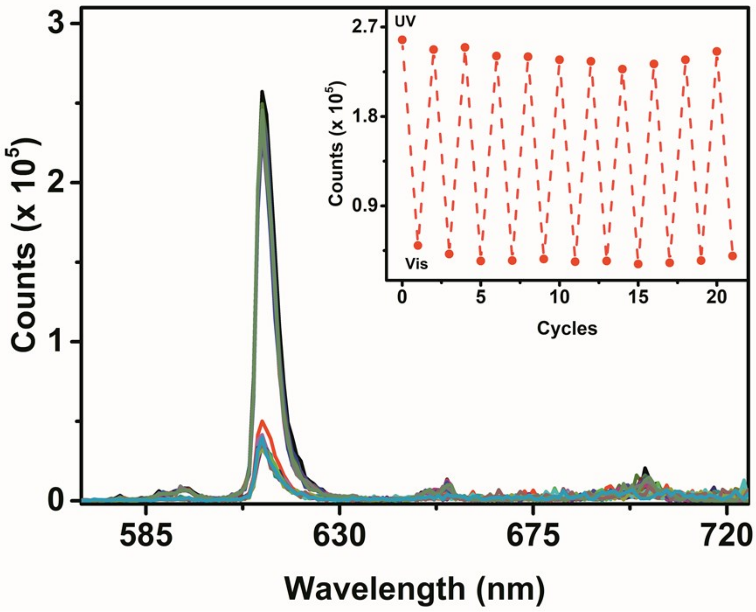


Figure S18. Fluorescence spectra changes of assembly $(HNEt_3)_2[Eu_2\mathbf{L}_4]$ (2.5×10^{-6} M) in $CH_3OH/CHCl_3$ (v/v = 1:1) upon alternating UV (365 nm, 3 min) and visible light (> 420 nm, 2 min) irradiations. Inset: the intensity changes at 612 nm upon repeated alternating UV−vis irradiations.

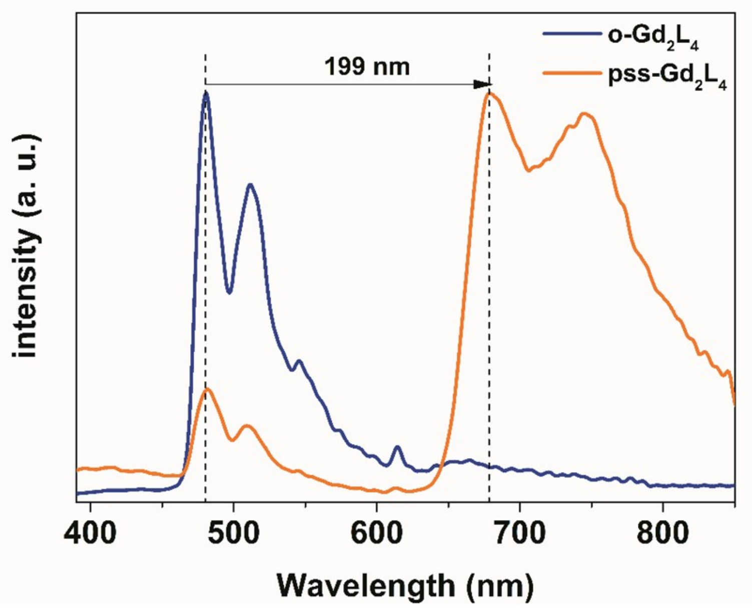
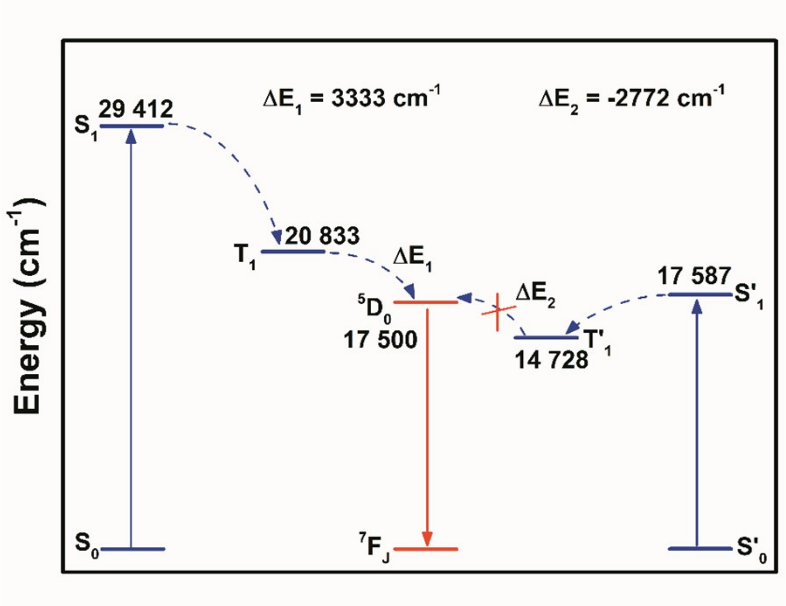


Figure S19. Phosphorescence spectra of *o*-$Gd_2\mathbf{L}_4$ and *c*-$Gd_2\mathbf{L}_4$ in $CH_3OH/CHCl_3$ (v/v = 1:1).



Scheme S2. Schematic energy transfer process for *o*-$Eu_2\mathbf{L}_4$ and *c*-$Eu_2\mathbf{L}_4$.

References

[1] H.-A. Wagenknecht, R. Hofsäß and D. Rombach, *Synlett*, 2017, **28**, 1422−1426.

[2] J. Mamiya, A. Kuriyama, N. Yokota, M. Yamada and T. Ikeda, *Chemi. Eur. J.*, 2015, **21**, 3174−3177.