View Article Online

Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Zhang, Y. Zhou, Y. Yao, Z. Cheng, T. Gao, H. Li and P. Yan, *J. Mater. Chem. C*, 2020, DOI: 10.1039/D0TC01044H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-c

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Jianpeng Zhang, Yanyan Zhou, Yuan Yao, Zhenyu Cheng, Ting Gao, Hongfeng Li* and Pengfei Yan

Optical and chiroptical photoswitches have found potential applications in advanced information technologies. Herein, a pair of chiral triple-stranded helicates $[Eu_2(o-L^{RR})_3](TOf)_6$ and $[Eu_2(o-L^{SS})_3](TOf)_6$, which have chirality, luminescence and light stimuli-responsive properties, have been designed and synthesized. The ligands $o-L^{RR/SS}$ are composed of a photochromic diarylethene moieties as spacer and two chiral 2,6-dipicolinic amides as coordination units. Through the comprehensive spectral characteristics in combination with semiempirical geometry optimization using Sparkle/RM1 model, it was confirmed that (R/S)-1-phenylethanamines decorated at the terminals of ligand successfully controlled the stereoselective self-assembly of the helicates. Upon alternating UV and visible light irradiation, the diarylethene experienced a reversible change between a colorless open-ring state and a pink closed-ring state. This photochromic process caused the variations of electronic structure and ligand conformation, and led to the presence of light-responsive optical (UV, PL) and chiroptical (ECD, CPL) switching properties. The helicate may therefore be considered as a completely reversible +/- ECD and on/off CPL switch. Furthermore, on the basis of these light-switchable optical properties, the INHIBIT and IMPLICATION logic gates were fabricated.

Introduction

Published on 13 April 2020. Downloaded on 4/15/2020 2:18:57 AM

Optical photoswitches have attracted much interest because of their promising applications in optical storage,¹ logic gate² and sensors.³ In recent years, following with the rapidly increasing demands for massive information storage and/or encryption, it might be a feasible strategy to extend the dimension of output signals, which can add extra storage density and increase the difficulty to decode data. Chiroptical photoswitches could demonstrate the changes of chiroptical signals besides the usual optical outputs upon alternating light irradiation.⁴ Circular dichroism (CD) and circularly polarized luminescence (CPL) spectroscopies can reflect the ground state and excited state chirality of molecules,⁵ which measure the differences of absorption and emission of left circularly polarized light versus right circularly polarized light, respectively. In comparison with the CD-based photoswitches,⁶ the examples exhibiting dynamic photoswitching of CPL are rare due to the relatively low luminescence dissymmetry factor (glum) of the most chiral luminophores,⁷ which increase the difficulties on the detection of CPL signals. The glum value represents the degree of preference of one type of circularly polarized light over the other, which is defined as $g_{lum} = 2(I_L - I_R) / (I_L + I_R)$, where $|g_{lum}| \le 2$, and I_L and I_R represent the left and right polarized emission intensities, respectively.

DOI:

C01044H

To facilitate the detection of CPL signal, the switches should have the high luminescence quantum yields (QYs) and/or large g_{lum} values. Generally, the high g_{lum} values could be obtained from the emission systems with electric dipole forbidden and/or magnetic dipole-allowed transitions.8 For most of the CPL materials comprising of organic fluorophores, such as those of small organic molecules,9 polymers10 and supramolecular assemblies,¹¹ their magnetic transition dipole moments (m) are much smaller than the electric transition dipole moments (μ), and thus, the g_{lum} values are typically within the range of 10^{-5} – 10^{-3} . In contrast, some of the f-f transitions in lanthanide ions are magnetic dipole-allowed transitions, which render the lanthanide CPL materials the larger glum values, typically in the range of 10- $^{2}-0.5$.¹² For instance, the Cs[Eu((+)-hfbc)₄] represents the highest reported glum value (1.38) of CPL materials in solution.13 As a consequence, the chiral lanthanide complexes might be the more valuable CPL photoswitch candidate due to their large g_{lum} values.

Diarylethenes (DAE) and their derivatives are known as the most widely used photo-responsive components in chiroptical switches besides the spiropyran and azobenzenes.^{14,15} However, the examples that could realize the reversible photoswitching of chiroptical signals in lanthanide assemblies are much more limited.¹⁶ As we known, there was only one example of a lanthanide assembly for simultaneously realizing CD and CPL photoswitching.^{16a}

In chiroptical switches, the introduction of chiral elements into the chromophore/luminophore or photochromic moieties is the general strategy for realizing the modulation of chiroptical

^a Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education; School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China. E-mail: lihongfeng@hlju.edu.cn; Yanpf@vip.sina.com.

^b †*Electronic Supplementary Information (ESI) available:* [¹H NMR, ¹³C NMR, ESI-TOF-MS, thermal stability, fatigue resistant property spectra, emission spectra and the methord for Φ_{o-c} and Φ_{c-o-}]. For ESI or other electronic format See DOI:10.1039/x0xx00000x

ARTICLE

signals.¹⁷ Helical structure is one of the most widespread and fascinating structures in nature, which is intrinsically chiral, possessing P or M helical senses. Although the reports are limited, a few chiral lanthanide dinuclear and multinuclear helical architectures have been developed by Gunnlaugsson,¹⁸ Law,¹⁹ Sun,²⁰ and us.²¹ As previously reported, the photoisomerization of diarylethene (DAE) units in helicate resulted in the dramatic changes of CD spectra in the visible region.^{16b} On the basis of above points, herein, we designed and synthesized a pair of chiral ditopic ligands o-L^{RR} and o-L^{SS},

which were composed of the photochromic vidiarylethene moieties as spacer and two chiral 2,604hpieo4ffffe04ffe04ff



Results and discussion

Published on 13 April 2020. Downloaded on 4/15/2020 2:18:57 AM

Synthesis and characterization of the ligands and complexes

The synthetic procedures for the enantiopure DAE-based bis(tridentate) ligands, o-L^{RR}/o-L^{SS} and their corresponding complexes are outlined in Scheme 1. The ligands are composed of three subunits, namely two coordinated 2,6-dipicolinic amides and one photochromic diarylethene. The former was prepared according to previously reported procedures,²² where the chirality was introduced through a condensation reaction between 7a and chiral (R/S)-1-phenylethanamine. The 3a was synthesized using the known methods.²³ Regarding the nitration of 3a, HNO₃/SnCl₄ was selected as nitration agent to substitute the general HNO₃/acetic anhydride partner, which effectively avoided the ring-opening of benzofurans. Finally, the two functional groups were connected via the amide-coupling reaction to give the final ligands. The ligands and some intermediates were characterized by 1H, 13C NMR spectroscopy and mass spectrometry (Figures S1-S11).

The Ln(III) triple-stranded helicates were obtained by reaction of the ligands (o- $L^{R/S}$) with the corresponding Ln(TOf)₃ (Ln = Eu, Y and Gd) in a 3:2 ratio in CH₃CN at room temperature for 1 h. The ¹H NMR characterizations suggest the formation of a single species in solution. The Eu(III) complexes show a single set of broadened but distinguishing signals (Figures S12 and S13). In comparison with the free ligands, most of the resonance peaks undergo high-field shifts. To more clearly confirm the formation of the single species and their diastereopurities in solution, the corresponding Y(III) complexes were isolated as substitute for ¹H NMR experiments. As shown Figure 1a, a single set of sharp resonance peaks are obtained, which displays about the same full-width half-maximum compared with the free ligand. Taking the Hⁱ as representative, only one sharp single peak is observed, which indicates the complex matching the C2 symmetric feature of the ligand and the time-averaged C3 symmetry of this triple-stranded helicate.

High-resolution electrospray ionization mass spectrometry (ESI-TOF-MS) analyses further confirm the formation of a triple-stranded helicate with a formula of $[Eu_2(o-L^{RR})_3](TOf)_6$ (Figure 1b and S14). The spectra show three cluster peaks with the correct isotopic distributions corresponding to the given charge state containing differing ratios of TOF counter anion ions. For example, the cluster of peaks with m/z at 878.6821, 1221.2135 and 1906.2639 could be assigned to $[[Eu_2(o-L^{RR})_3](TOf)_2]^{4+}$, $[[Eu_2(o-L^{RR})_3](TOf)_3]^{3+}$, and $[[Eu_2(o-L^{RR})_3](TOf)_4]^{2+}$ charge states (Figure 1b). The assignments are further verified by carefully comparing the

Published on 13 April 2020. Downloaded on 4/15/2020 2:18:57 AM

Journal Name

corresponding simulated isotopic patterns with high-resolution experimental data. The corresponding Y and Gd complexes also show the similar spectral patterns and the correct isotopic distributions (Figures S15–S18).



Fig. 1 Self-assembly of o-L^{RR} with Ln(TOf)₃. (a) ¹H NMR assignment of ligand and ¹H NMR (400 MHz) spectra of free ligand L^{RR} and the self–assembled Y complex [Y₂(**o**-L^{RR})₃](TOf)₆ in CD₃CN. (b) ESI-TOF-MS spectrum of [Eu₂(o-L^{RR})₃](TOf)₆ with inset showing the observed (Obs.) and simulated (Sim.) isotopic pattern of [[Eu₂(o-L^{RR})₃](TOf)₃]³⁺ cation peaks.

To obtain a better structural insight into this helical structure, a molecular mechanical modeling was built by using the MOPAC 2016 program implemented in the LUMPAC 3.0 software with a Sparkle/RM1 model.²⁴ It is known that the chiral terminal of ligand could effectively control the stereoselectivity during the assembly process. Herein, two possible conformations, *P* or *M* in one helicate were both considered in calculated process (Figure S19). In $[Eu_2(o-L^{RR})_3]^{6+}$, a *M* helical sense with the metal centers the $\Lambda\Lambda$ configuration give a lower system energy than that with a *P* configuration; conversely, a $\Delta\Delta$ configuration and a *P* helical sense is favored energetically in $[Eu_2(o-L^{SS})_3]^{6+}$. As shown in Figure 2, in one helicate, each Eu(III) ion is nine-coordinated by six O atoms and three N atoms from three ligands, giving rise to a tricapped trigonal prismatic geometry. The Eu–Eu distance is determined¹0¹0²⁰/07/4CA1014⁴/s noted that the DAE units in spacer all adopt the antiparallel conformations, which is the essential for realizing light cyclization reaction.



Fig. 2 Sparkle/RM1 ground state geometries of the $[Eu_2(o-L^{RR})_3](TOf)_6$ before (upper graph) and after (lower graph) irradiation with UV light.

Optical switch by UV–Vis and CD absorption

The optical and chiroptical photoswitching properties of the pair of helicates were firstly investigated by UV-Vis and CD spectra. Figure 3 shows the spectral changes of two ligands before and after UV irradiation. As shown in Figure 3a, the colorless o-LRR/o-LSS solution shows a broad band in range of 270-390 nm with the maximum absorbance at 303 nm before UV irradiation. Following UV light irradiation at 275 nm, the absorbance at 303 nm gradually decreases and a new band appeares at 508 nm (Figures S20 and S21), leading to an obvious color change of the solution from colorless to pink (Figure 3a, inset). This is the result of the photocyclization of the dithienylethene from open-ring to close-ring forms. Upon visible light irradiation at 526 nm for 3 min, the spectra reversibly returned to that of the original states (Figures S22 and S23), and these photochromic conversions could be repeated for several cycles without appreciable light fatigue (Figures S24 and S25). Moreover, the ligands also show excellent thermal stabilities in photostationary state (PSS). There are almost no changes of spectral shapes and intensities after heating for 2 h at 55 °C (Figures S26 and S27). On the basis of the plots of irradiation time dependence of absorption intensity at 508 nm and conversion ratios of photoisomerization (estimated by ¹H NMR in PSS, Figures S28 and S29), the photocyclization (Φ_{o-c}) and photocycloreversion (Φ_{c-o}) quantum yields were calculated to be 0.039, 9.7 \times 10⁻³ for L^{RR} and 0.044, 8.7 \times 10⁻³ for L^{SS}, respectively. To avoid the influence of high concentration of NMR testing solution on the accuracy of the conversion ratio of photoisomerization, the mole fraction of o-LRR/c-LRR were also

Published on 13 April 2020. Downloaded on 4/15/2020 2:18:57 AM

determined by high performance liquid chromatography (HPLC) method (Figure S42). The result shows that the photoconversion is 21.3%, which is consistence with the result calculated from the ¹H NMR test (21%).



Fig. 3 (a) UV-Vis absorption (lower curves) and CD spectra (upper curves) of the ligands (o-L^{RR}, blue dash line; L^{RR}-PSS, orange dash line and o-L^{SS}, blue solid line; L^{SS}-PSS, orange solid line) (1.0×10^{-5} M, CH₃CN, 293 K). (b) UV-Vis absorption (lower curves) and CD spectra (upper curves) of [Eu₂(L^{RR/SS})₃](TOf)₆ (3.3×10^{-6} M, CH₃CN, 293 K).

In comparison with the absorptions of free ligands, the helicates some differences in open-ring show and photostationary state (PSS). First, the absorption maximum of helicate is red-shifted by about 30 nm compared with the ligand (Figure 3b). We suggest that the red shift should originates from the electron-withdrawing effect of metal ion, which facilitates the intramolecular charge transfer transition, leading to the decrease of transition energy. Second, the helicate shows the lower absorbance than free ligand in visible light region after UV irradiation, which indicates that the ligand in complex should has the lower photocyclization quantum yield. Unfortunately, the ¹H NMR spectrum of [Y2(0-LRR/SS)3](TOf)6 did not offer the information to estimate the conversion ratio between o-LRR/SS and c-L^{RR/SS} forms, which only displayed a slight decrease of intensity and no new signals attributed to close-ring isomers or free ligands were found upon UV irradiation for 12 h (Figures S30 and S31). We infer that the protons in closed forms might have very similar magnetic environments, whose resonance signals are probably overlapped by those in open-ring isomers. However, the photoconversion ratio of close-ring isomers could be estimated by high performance liquid chromatography (HPLC) method (Figure S43). In PSS, a peak attributed to closering form was observed at retention time of 14.67 min, by which the conversion ratio of photoisomerization was calculated to be 2% and the photocyclization (Φ_{0-c}) and photocycloreversion (Φ_{c-c}) _o) quantum yields were calculated to be 7.6×10^{-3} and 0.057. The

The antiparallel conformations have two kinds of helical senses, P and M. Since the chiral centers localize in terminal of the ligands, such chirality cannot be effectively transferred to the chromophore and/or cause the diastereomer excess between P and M conformations. As a result, the CD signals of both ligands are rather weak in their open-ring and close-ring states (Figure 3a). However, this point chirality could be effectively transferred to the chromophores as helical chirality after self-assembly with Ln(III) ions. As shown in Figure 3b, the open-ring helicates show the mirror-image and strong CD signals in the corresponding UV region. Moreover, two pairs of positive exciton couplets with Cotton effect at 260, 276 nm and 312, 364 nm are observed in [Eu₂(o-L^{RR})₃](TOf)₆, while the mirror-imaged CD signals exhibit in [Eu₂(o-L^{SS})₃](TOf)₆. Generally, the pattern of exciton couplet correlates with the absolute configuration of the metal center,²⁵ wherein a positive exciton couplet correlating to a Λ configuration; on the contrary, correlating to a Δ configuration. On the basis of this empirical rule, the Eu(III) ions are suggested to adopt $\Lambda\Lambda$ configurations in $[Eu_2(\mathbf{0}-\mathbf{L}^{RR})_3](TOf)_6$. This result is consistent with the optimized molecular structures by molecular mechanical modeling.

Under exposure to UV light, the spectra of the helicates display strong CD signals with bisignated exciton couplets in visible region. This result implies that the chirality of (R/S)-1phenylethanamine has been successfully transferred into closering DAE units, wherein the helical chirality is formed. In comparison with open-ring form, the CD signals show the decrease of intensities and slight red-shift in UV region. Upon alternative irradiation with UV and visible light, the chiroptical switching by CD signals are realized.

Optical switch by PL and CPL

To investigate the photomodulate luminescence properties of [Eu₂(o-L^{RR/SS})₃](TOf)₆, the emission from center Eu(III) ions was determined by excited at $\lambda = 400$ nm (Figures S40, with a low intensity at this wavelength). In open-ring state, the helicates show four characteristic emission bands of Eu(III) ion at 594, 615, 650, and 695 nm, corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J = 1-4) transitions (Figure 4). After reaching closed photostationary state (PSS), the emission intensities decrease to 24% of its initial value. This is the result of the photocyclization of the dithienylethene unit, which deactivate the ⁵D₀ excited state of Eu(III) ions. In photochromic fluorescent switches, the luminescent quenching generally depends on Förster resonance energy transfer (FRET) mechanism.²⁶ The absorption of closering helicate covers the visible spectral region of 430-680 nm (Figure 3b), thus it seems that the FRET quenching mechanism is reasonable. However, in lanthanide systems, the Dexter electron exchange between the ligand triplet state and excited state of Ln(III) as sensitization mechanism should not be excluded.²⁷ Thus, the triplet state energy level (T, ${}^{3}\pi\pi^{*}$) of ligand

in open-ring and PSS are estimated by the phosphorescence spectra of $[Gd_2(L^{SS})_3](TOf)_6$ (Figure S41). The $[Gd_2(\mathbf{0}-\mathbf{1})_{12}](TOf)_6$ L^{SS})₃](TOf)₆ shows a characteristic phosphorescence band of lanthanide complex with three vibrational progressions. From the highest energy band, the open-ring To energy level was calculated to be 21 231 cm⁻¹ (471 nm, higher than ⁵D₀ energy level, 17 500 cm⁻¹), which implied that an effective energy transfer from ligand to metal center could occur and turn on the emission of Eu(III) ion. However, in close-ring PSS state, $[Gd_2(L^{SS})_3](TOf)_6$ show a new band at 613 nm besides a hypsochromic shift high energy band at 434 nm. This lower energy band could be attributed to the close-ring ligand phosphorescence. By this band, the close-ring T_c was estimated to be 16 313 cm⁻¹, which is lower than the ${}^{5}D_{0}$ energy level, which indicates that the sensitization to Eu(III) ion would be invalid. In our opinion, the FRET and Dexter energy transfer mechanisms might coexist in the photomodulate luminescent process.



Fig. 4 Total luminescence (lower curve, right axis) and CPL spectra (upper curves, left axis) of the helicates in open-ring $[Eu_2(o-L^{RR/SD})_3](TOf)_6$ and PSS states.

The photomodulate luminescence properties are also reflected in the spectral variations of CPL. In CPL spectra, the mirror-image CPL signals corresponding to above four characteristic transitions of Eu(III) ion are observed before and after UV irradiation. Among these bands, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions display the larger emission intensities than the other bands, which are consistent with those observed in PL spectra. In PSS, in view of the decrease of total emission intensities, the ΔI also show the significant decreases in CPL intensities. On the other hand, the luminescence dissymmetry factor, glum is the essential parameter for estimating the degree of CPL, where $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, $(-2 \le g_{lum} \le 2)$. The higher g_{lum} indicates the more intense polarized emission relative to total emission, and the easier to be detected. Generally, the chiral luminophores with large magnetic dipole transition often exhibit the large g_{lum} . Herein, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is magnetic dipole transition, which shows the largest |g_{lum}| values of 0.1 and 0.04 in open-ring and PSS states, respectively. The corresponding $|g_{lum}|$ values for other transitions are listed in Table 1. Under irradiation of visible light, the CPL intensities and g_{lum} values can be recovered, which indicate the chiroptical switches by CPL are obtained.

ournal of Materials Chemistry C Accepted Manus

Table 1. g_{lum} values for ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ of Eu^{3+} ion. View Article Online

		$g_{lum} {}^5D_0 \rightarrow {}^7F$	D0TC01044H	
Complexes	J = 1	J = 2	J = 3	J = 4
	(589 nm)	(613 nm)	(651 nm)	(694 nm)
$Eu_2(o-\mathbf{L}^{RR})_3(TOf)_6$	-0.100	0.050	-0.056	0.030
$Eu_2(o-L^{SS})_3(TOf)_6$	0.101	-0.051	0.055	-0.030
$Eu_2(c-\mathbf{L}^{RR})_3(TOf)_6$	-0.040	0.027	-0.025	0.025
$Eu_2(c-\mathbf{L}^{SS})_3(TOf)_6$	0.040	-0.028	0.025	-0.024

Application in logic circuit

It is clear from the above results that the optical (UV, PL) chiroptical (CD, CPL) signals could be effectively modulated by UV and visible light stimuli. As a result, the helicates can be used as the molecular logic gate (MLG) when the UV and visible light are selected as input and the intensity variations of absorption (UV and CD) and emission (PL and CPL) as output. To construct the logic switch, the following conditions are defined: the openring form of helicate is used as an initial state of MLG, UV light $(\lambda = 365 \text{ nm})$ is employed as input (In 1) and visible light ($\lambda =$ 526 nm) as input (In 2), and the logical inputs 0 and 1 are assigned to the absence and presence of stimulus, respectively. Regarding to the output, the absorption at $\lambda = 500$ nm in UV and CD spectra and the emission at $\lambda = 615$ nm in PL and CPL spectra are considered as the detectable signals, and named as O_{CD}, O_{UV}, O_{PL} and O_{CPL}, respectively. O_{UV} and O_{CD} are defined as 1, when the absorbances $\lambda = 500$ nm are large than zero, otherwise O_{UV} and O_{CD} are 0. As shown in Figure 5, on the basis of these definitions, two INHIBIT logic gates were successfully fabricated by UV and CD signals. It implies only when In1 = 1and In2 = 0, the output signal (O_{UV} and O_{CD}) are 1. In PL and CPL, O_{PL} and O_{CPL} are defined as 1, when the emission intensities at $\lambda = 615$ nm are large than 50% of the maxima values, otherwise they are 0. Thus, the IMPLICATION logic gates were fabricated by determining the variations of luminescent intensities. In a word, two kinds of logic gates based on optical and chiroptical switching properties were successfully fabricated.



Fig. 5 The truth table and symbolic representation of the logic circuit triggered by *In1* (irradiation with 365 nm light) and *In2* (irradiation with526 nm light); the open $[Eu_2(o-L^{RR})_3]$ isomer as the initial state. The output is defined as O_{CD} (positive CD signal at 500 nm), O_{CPL} (CPL signal at 615 nm), O_{UV} (UV-Vis absorbance at 500 nm), O_{PL} (PL signal at 615 nm).

Conclusions

In summary, a pair of chiral triple-stranded helicates [Eu2(o-L^{RR})₃](TOf)₆ and [Eu₂(o-L^{SS})₃](TOf)₆ that have light-responsive optical and chiroptical switching properties were successfully designed and synthesized. The helicate integrates the molecular chirality, helical chirality, light stimuli-response, and lanthanide luminescence in one architecture. Upon alternatively UV and visible light irradiation, the helicate realized a reversible change between a colorless open-ring state and a pink closed-ring state. In close-ring photostationary state, the new absorption bands in UV and CD spectra were observed in the visible light region, meanwhile the emissions of Eu(III) ions were partly quenched, leading to the decrease of intensities of PL and CPL. Notably, the luminescence dissymmetry factor, glum was found to have a decrease from 0.1 to 0.04 (by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition). which indicated that the photochromic transformation causing conformation variation of helical structure. After irradiation with visible light, the spectra reversibly returned to those of the original states. Thus, the helicate could be considered as a completely reversible optical and chiroptical switch. Finally, on the basis of above photoswitching properties, two INHIBIT and IMPLICATION logic gates were described.

Experimental

Published on 13 April 2020. Downloaded on 4/15/2020 2:18:57 AM

Materials and instruments

All commercially available reagents and chemicals involved in this experiment were purchased from commercial companies and were used without further purification if not otherwise stated. The ¹H NMR and ¹³C NMR spectra are recorded on a Bruker Avance III 400 MHz spectrometer. HPLC analysis were recorded on a SHIMASZU LC 20AT HPLC instrument with InertSustain C18 column (Acetonitrile; flow rate: 1.0 mL/min). Elemental analyses were carried out by using an Elementar Vario EL cube analyzer. Electrospray time-of-flight (ESI-TOF) and Electron ionization (EI) mass spectra were measured on Bruker maXis mass spectrometers and Agilent 5975N, respectively. CD and CPL spectra were performed on an Olis DM245 spectrofluorimeter. UV-Vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Emission and excitation spectra were recorded using an Edinburgh FLS 1000 fluorescence spectrophotometer. Luminescence lifetimes were measured by using a single-photon-counting spectrometer from Edinburgh Instrument (FLS 1000) with a microsecond pulse lamp as the excitation sources. The data were analyzed by software supplied by Edinburgh Instruments. The values reported were the average of three independent determinations for each sample.

Computational Details

The ground state geometries of $[Eu_2(L^{RR})_3](TOf)_6$ and $[Eu_2(L^{SS})_3](TOf)_6$ were optimized by calculations using LUMPAC with a Sparkle/RM1 model implemented in the MOPAC 2016 software. The keywords used in the calculation reported here were RM1, PRECISE, BFGS, GNORM = 0.25,

GEO-OK, SCFCRT = 1.D-10 (to increase the SCF_vconvergence criterion) and XYZ (for Cartesian coordinates) 0.1039/D0TC01044H

Synthetic procedures

2-Methylbenzofuran (1a). To a solution of benzofuran (1.2 g, 10 mmol) in THF (20 mL), *n*-BuLi (5.2 mL, 13.0 mmol, 2.5 M in hexane,) was added at -78 °C and kept stirring for 2 hours. After the solution become a pale suspension, CH₃I (2.5 mL, 40 mmol) was added and stirred for 8 h at room temperature. The solution was then quenched with water and extracted three times with CH₂Cl₂ and dried over anhydrous MgSO₄. Purification by flash chromatography (pentane) afforded 2-methylbenzofuran (**1a**) as a colourless liquid in 85 % yield (1.2 g). ¹H NMR (400 MHz, CDCl₃) δ = 7.51 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5Hz, 1H), 7.22 (m, *J* = 7.5, 6.6 Hz, 2H), 6.40 (s, 1H), 2.49 (s, 3H). EI-MS m/z = 132.16 M⁺.

3-Bromo-2-methylbenzofuran (2a). To a solution of **1a** (1.5 g, 10.3 mmol) in THF (100 mL), N-bromosullirimide (2.0 g, 11.4 mmol) was added at 0 °C, then stirred for 24 h at room temperature. The reaction mixture was poured into sodium thiosulfate solution and extracted with ethyl acetate. The product was purified by column chromatography (petroleum ether as the eluent) and give 1.2 g of **2a** as a light yellow liquid in 48% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.49 (s, 3H), 7.25–7.34 (m, 3H), 7.40–7.47 (m, 1H). EI-MS m/z = 212.06 M⁺.

1,2-Bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (**3a).** To a solution of **2a** (1.2 g, 5.7 mmol) in THF (40 mL), n-BuLi (4.0 mL, 6.4 mmol, 1.6 M in hexane,) was added at -78 °C. After stirring for 30 min, the octafluorocyclopentene (0.6 g, 2.8 mmol) was added slowly to the reaction mixture at -78 °C, then stirred for 12 h. The reaction mixture was poured into concentrated sodium chloride solution and extracted with ethyl acetate. The organic phase was dried over anhydrous MgSO₄ and evaporated in vacuo. The crude product was purified by column chromatography (petroleum ether as the eluent) to give 0.6 g of **3a** as colorless crystals in 42% yield. ¹H NMR (200 MHz) δ 2.07 (s, 3H), 2.16 (s, 3H), 7.14-7.30 (m, 4H), 7.36–7.48 (m, 2H), 7.59–7.77 (m, 2H). EI-MS m/z = 436.35 M⁺.

1,2-bis(2-methyl-6-nitro-1-benzofuran-3-yl)perfluorocyclopentene (4a). To a dried CH₂Cl₂ (5 mL) cooled to 0 °C, the fuming nitrate (0.2 mL) and SnCl₄ (0.6 mL, 3.0 mmol) was slowly added and stirred for 15 min. Then it was added slowly to a solution of **3a** (0.1 g, 0.2 mol) in CH₂Cl₂ at 0 °C. The reaction was monitored via TLC. After the reaction completion, the reaction mixture was poured into the water (40 mL) and neutralized to pH = 7. The mixture was then extracted with ethyl acetate (3 × 30 mL) and dried over MgSO₄. The product was purified by column chromatography (hexane/ethyl acetate, v/v, 5/1) and give 0.1 g of **4a** as a yellow solid in 83% yield. ¹H NMR (400 MHz, Chloroform-d) δ 8.32–8.37 (d, *J* = 2.0 Hz, 2H), 8.10– 8.21 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.50–7.57 (d, *J* = 8.7 Hz, 2H), 2.23 (s, 6H). ESI-TOF-MS *m/z* = 549.0772 [M + Na]⁺.

1,2-bis(2-methyl-6-amino-1-benzofuran-3-yl)perfluoroc-

yclopentene (5a). To a solution of 4a (0.2 g, 0.4 mmol) in EtOH, NiCl₂·6H₂O (0.21 g, 0.9 mmol) was added at 0 °C and kept stirring for 15 min. Then NaBH₄ (0.2 mg, 5.6 mmol) was added slowly and stirred for 2 h at room temperature. The reaction mixture was poured into the dichloromethane (20 mL). The Published on 13 April 2020. Downloaded on 4/15/2020 2:18:57 AM.

ARTICLE

Journal Name

mixture then was washed with brine and dried over Na₂SO₄. The product was purified by column chromatography (CH₂Cl₂/acetone, v/v, 10/1), and give 180 mg of **5a** as a gray solid in 56% yield. ¹H NMR (400 MHz, CD₃CN) δ 7.07–7.13 (d, J = 8.4 Hz, 2H), 6.67-6.72 (d, J = 2.0 Hz, 2H), 6.50–6.57 (dd, J = 8.4, 2.1 Hz, 2H), 4.29 (s, 4H), 2.08 (s, 6H). ESI-TOF-MS m/z = 467.1380 [M + H]⁺.

Dimethyl Pyridine-2,6-dicarboxylate (6a). To a solution of dipicolinic acid (5.0 g, 30.0 mmol) in MeOH (100 mL), concentrated H₂SO₄ (2.5 mL) was added dropwise. Then, the mixture was heated to reflux for 24 h. The reaction was monitored via TLC. After the reaction completion, the solvent was removed and gave 5.9 g of 6a as a white solid in 99% yield. No further purification was needed. ¹H NMR (400 MHz, DMSO d_6): δ 8.26–8.13 (m, 3H), 3.90 (s, 6H). EI-MS m/z = 195.19 M⁺. 6-(Methoxycarbonyl)picolinic Acid (7a). To a solution of 6a (1.9 g, 9.9 mmol) in MeOH (75 mL), the KOH pellets (557 mg, 9.9 mmol) was added at 0 °C and kept stirring for 4 h. The reaction was monitored via TLC. After the reaction completion, the MeOH was removed by evaporation in vacuo. The white salt was washed with EtOAc $(3 \times 30 \text{ mL})$ then dissolved in water (25 mL), and the solution was acidified to pH = 2. The solution was extracted with chloroform $(3 \times 25 \text{ mL})$, then dried over MgSO₄. The organic layer was evaporated and give 1.5 g of 7a as a white powder in 81% yield ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.23–8.14 (m, 3H), 3.90 (s, 3H). ESI-MS $m/z = 180.09 [M - H]^{-}$.

Methyl (R/S)-6-((1-phenylethyl)carbamoyl)picolinate (8a) and (R/S)-6-(2-phenylpropylcarbamoyl)-picolinic acid (9a). To a solution of 7a (0.4 g, 2.2 mmol), 1-ethyl-3-(3dimethylaminopropyl)carbodiimide (EDC, 0.5 g, 2.6 mmol, 1.2 equiv), and hydroxybenzotriazole (HOBT, 0.4 g, 2.6 mmol, 1.2 equiv) in dry DMF (10 mL), then stirred for 30 min at room temperature. The (R/S)-1-methylphenethylamine (0.3 g, 2.6 mmol, 1.2 equiv) was then added to the reaction mixture and reacted overnight at room temperature. DMF was evaporated under vacuum, and the resulted solid was taken up in EtOAc (10 mL) and extracted with copious amounts of saturated NaHCO₃ (10 mL \times 3). The organic layer was evaporated under vacuum and purified by EtOAc and hexane column chromatography. Hydrolysis was then performed by stirring the product in a solution of 1 M NaOH (8 mL) and THF (2 mL) at room temperature. Once the hydrolysis was complete by TLC, the solution was acidified with 4 M HCl to pH 4 and the precipitate was collected via vacuum filtration and give 3.9 g of 9a as white solid in 46% yield. ¹H NMR (400 MHz, DMSO- d_6 , δ): 13.13 (s, 1H), 9.42–9.48 (d, J = 8.5 Hz, 1H), 8.21–8.29 (dq, J = 8.0, 1.7 Hz, 2H), 8.16–8.24 (m, 1H), 7.37–7.43 (d, J = 7.2 Hz, 2H), 7.29– 7.37 (dd, J = 8.5, 6.7 Hz, 2H), 7.19–7.28 (m, 1H), 5.24 (p, J = 7.2 Hz, 1H), 1.52–1.59 (d, J = 7.0 Hz, 3H) ESI-MS m/z = 270.30 M^+ .

Ligand L^{RR} and L^{SS}. A solution containing **9a** (0.272g, 1.0 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC, 0.05 g, 0.26 mmol), and hydroxybenzotriazole (HOBT, 0.035 g, 0.26 mmol, 1.2 equiv) in dry DMF (10 mL) was firstly stirred for 30 min at room temperature. Then **5a** (0.1 g, 0.21 mmol, 1 equiv), was added to above reaction mixture and react overnight at room temperature. DMF was evaporated under vacuum, and

the reaction was taken up in EtOAc (10 mL) and extracted with copious amounts of saturated NaHCO₃ (10 mL^{0.4}3)?/Phe or gamme layer was evaporated under vacuum and purified by column chromatography (hexane/ethyl acetate, v/v, 1/3), and give 0.13g of $L^{RR/SS}$ as a light pink solid in 64.5% yield. ¹H NMR (400 MHz, Acetonitrile-*d*3) δ 10.13 (s, 2H), 8.65–8.72 (d, J = 8.3 Hz, 2H), 8.31–8.37 (dd, *J* = 7.7, 1.2 Hz, 2H), 8.25–8.31 (dd, *J* = 7.8, 1.2 Hz, 2H), 8.05–8.14 (m, 6H), 7.34–7.42 (m, 6H), 7.23–7.31 (dd, *J* = 8.3, 6.9 Hz, 6H), 7.14–7.23 (m, 2H), 5.27 (p, *J* = 7.2 Hz, 2H), 2.18 (s, 6H), 1.56 (d, *J* = 7.1 Hz, 6H). ESI-TOF-MS *m/z* = 993.3150 [M + Na]⁺.

Synthesis [Ln₂(o-L)₃](TOf)₆. To a solution of the (o-L) (0.1 mg, 0.1 mmol) in CH₃CN (10 mL) was added dropwise a solution of Ln(TOf)₃ (Ln = Eu, Y, Gd; 0.067 mmol) in 10 mL CH₃CN at room temperature. After stirring for 2 h, the resulting solution was dropped slowly into dry diethyl ether and washed with CHCl₃ (3×10 mL), then dried under vacuum to give the desired products.

$$\begin{split} & [\mathbf{Eu}_2(\mathbf{0}-\mathbf{L^{RR}})_3](\mathbf{TOf})_6. \quad \text{Yield: } 82\% \quad \text{Anal. calc. for} \\ & \mathrm{C}_{165}\mathrm{H}_{120}\mathrm{Eu}_2\mathrm{F}_{36}\mathrm{N}_{18}\mathrm{O}_{36}\mathrm{S}_6 \ (4111.0955): \ \mathrm{C}, \ 48.21; \ \mathrm{H}, \ 2.94; \ \mathrm{N}, \ 6.13. \\ & \mathrm{Found: } \mathrm{C}, \ 48.16; \ \mathrm{H}, \ 2.97; \ \mathrm{N}, \ 6.19. \ \mathrm{ESI-TOF-MS:} \ m/z = \\ & 1221.2135 \ [[\mathrm{Eu}_2(\mathbf{0}-\mathbf{L^{RR}})_3](\mathrm{TOf})_3]^{3+}. \end{split}$$

 $[Eu_{2}(o-L^{SS})_{3}](TOf)_{6}.$ Yield: 79% Anal. calc. for C₁₆₅H₁₂₀Eu₂F₃₆N₁₈O₃₆S₆ (4111.10): C, 48.21; H, 2.94; N, 6.13; O, 14.01. Found: C, 48.24; H, 3.02; N, 6.11. ESI-TOF-MS: *m/z* = 1221.2243 [[Eu₂(o-L^{SS})₃](TOf)₃]³⁺.

 $[Gd_2(o-L^{RR})_3](TOf)_6$. Yield: 81% Anal. calc. for $C_{165}H_{120}Gd_2F_{36}N_{18}O_{36}S_6$ (4121.6675): C, 48.08; H, 2.93; N, 6.12. Found: C, 47.98; H, 2.96; N, 6.16. ESI-TOF-MS: m/z = 1225.5792 [[Gd₂(o-L^{RR})₃](TOf)₃]³⁺.

 $[Gd_2(o-L^{SS})_3]$ (TOf)₆. Yield: 86% Anal. calc. for $C_{165}H_{120}Gd_2F_{36}N_{18}O_{36}S_6$ (4121.6675): C, 48.08; H, 2.93; N, 6.12. Found: C, 48.02; H, 2.98; N, 6.19. ESI-TOF-MS: m/z = 1225.2454 [[Gd₂(o-L^{SS})₃](TOf)₃]³⁺.

 $[Y_2(0-L^{RR})_3]$ (TOf)₆. Yield: 76% Anal. calc. for $C_{165}H_{120}Y_2F_{36}N_{18}O_{36}S_6$ (3984.9792): C, 49.73; H, 3.04; N, 6.33. Found: C, 49.75; H, 3.12; N, 6.37. ESI-TOF-MS: $m/z = 1179.1815 [[Y_2(0-L^{RR})_3](TOf)_3]^{3+}$.

 $[Y_2(0-L^{SS})_3](TOf)_6$. Yield: 78% Anal. calc. for $C_{165}H_{120}Y_2F_{36}N_{18}O_{36}S_6$ (3984.9792): C, 49.73; H, 3.04; N, 6.33. Found: C, 49.64; H, 3.18; N, 6.25. ESI-TOF-MS: $m/z = 1179.1823 [[Y_2(0-L^{SS})_3](TOf)_3]^{3+}$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Nos. 51773054 & 51872077). We also thank the Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, P. R. China for supporting this work.

ARTICLE

References

- (a) N. P. M. Huck, W. F. Jager, B. de Lange and B. L. Feringa, *Science*, 1996, 273, 1686-1688. (b) B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev.*, 2000, 100, 1789–1816.
- (a) C. Liu, D. Yang, Q. Jin, L. Zhang and M. Liu, *Adv. Mater.*, 2016, 28, 1644-1649; (b) K. Szaciłowski, *Chem. Rev.*, 2008, 108, 3481-3548.
- M. Liu, L. Zhang and T. Wang, Chem. Rev., 2015, 115, 7304-7397.
- (a) Z. Li, G. Wang, Y. Ye, B. Li, H. Li and B. Chen, Angew. Chem. Int. Ed., 2019, 58, 18025–18031; (b) M. Estrader, J. S. Uber, L. A. Barrios, J. Garcia, P. Lloyd-Williams, O. Roubeau, S. J. Teat and G. Aromí, Angew. Chem. Int. Ed., 2017, 56, 15622– 15627; (c) H. Wu, Y. Chen and Y. Liu, Adv. Mater., 2017, 29, 1605271; (d) T. van Leeuwen, W. Danowski, S. F. Pizzolato, P. Štacko, S. J. Wezenberg and B. L. Feringa, Chem. – Eur. J., 2018, 24, 81–84.
- (a) J. P. Riehl and F. S. Richardson, Chem. Rev., 1986, 86, 1-16;
 (b) H. G. Brmtain, Chirality, 1996, 8, 357-373;
 (c) F. Zinna and L. Di Bari, Chirality, 2015, 27, 1-13;
 (d) G. Muller, and J. P. Riehl, in Comprehensive Chiroptical Spectrometry: Instrumentation, Methodologies, and Theoretical Simulations, Wiley, 2012, pp. 65-90.
- (a) C. Jurissek, F. Berger, F. Eisenreich, M. Kathan and S. Hecht, *Angew. Chem. Int. Ed.*, 2019, **58**, 1945–1949; (b) R.-J. Li, J. J. Holstein, W. G. Hiller, J. Andréasson and G. H. Clever, *J. Am. Chem. Soc.*, 2019, **141**, 2097–2103; (c) W. Li, X. Li, Y. Xie, Y. Wu, M. Li, X.-Y. Wu, W.-H. Zhu and H. Tian, *Sci. Rep.*, 2015, **5**, 9186; (d) H. K. Bisoyi and Q. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 2994-3010; (e) S. Saha and J. F. Stoddart, *Chem. Soc. Rev.*, 2007, **36**, 77-92; (f) B. L. Feringa, *J. Org. Chem.*, 2010, **38**, 6635-6652.
- (a) L. Ji, Q. He, D. Niu, J. Tan, G. Ouyang and M. Liu, *Chem. Commun.*, 2019, **55**, 11747–11750; (b) H. Jiang, Y. Jiang, J. Han, L. Zhang and M. Liu, *Angew. Chem. Int. Ed.*, 2019, **58**, 785–790; (c) J. Qiao, S. Lin, J. Li, J. Tian and J. Guo, *Chem. Commun.*, 2019, **55**, 14590–14593; (d) Y. Hashimoto, T. Nakashima, J. Kuno, M. Yamada and T. Kawai, *ChemNanoMat*, 2018, **4**, 815–820; (e) Y. Hashimoto, T. Nakashima, D. Shimizu and T. Kawai, *Chem. Commun.*, 2016, **52**, 5171–5174; (f) H. Hayasaka, T. Miyashita, K. Tamura and K. Akagi, *Adv. Funct. Mater.*, 2010, **20**, 1243–1250.
- (a) G. Muller, Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials (Ed.: A. de Bettencourt-Dias), Wiley, Hoboken, 2014; (b) F. S. Richardson and J. P. Riehl, Chem. Rev., 1977, 77, 773–792; (c) E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz and S. de la Moya, Chem. – Eur. J., 2015, 21, 13488–13500.
- (a) Z.-B. Sun, J.-K. Liu, D.-F. Yuan, Z.-H. Zhao, X.-Z. Zhu, D.-H. Liu, Q. Peng and C.-H. Zhao, *Angew. Chem. Int. Ed.*, 2019, 58, 4840–4846; (b) C. M. Cruz, S. Castro-Fernández, E. Maçôas, J. M. Cuerva and A. G. Campaña, *Angew. Chem. Int. Ed.*, 2018, 57, 14782–14786; (c) S. Feuillastre, M. Pauton, L. Gao, A. Desmarchelier, A. J. Riives, D. Prim, D. Tondelier, B. Geffroy, G. Muller, G. Clavier and G. Pieters, *J. Am. Chem. Soc.*, 2016, 138, 3990–3993.
- (a) S. Lee, K. Y. Kim, S. H. Jung, J. H. Lee, M. Yamada, R. Sethy, T. Kawai and J. H. Jung, *Angew. Chem. Int. Ed.*, 2019, **58**, 18878–18882; (b) B. A. San Jose, J. Yan and K. Akagi, *Angew. Chem. Int. Ed.*, 2014, **53**, 10641–10644; (c) B. A. San Jose, S. Matsushita and K. Akagi, *J. Am. Chem. Soc.*, 2012, **134**, 19795– 19807.
- (a) N. Hellou, M. Srebro-Hooper, L. Favereau, F. Zinna, E. Caytan, L. Toupet, V. Dorcet, M. Jean, N. Vanthuyne, J. A. G.

Williams, L. Di Bari, J. Autschbach and J. Crassous Angewe Chem. Int. Ed., 2017, **56**, 8236–8239; (b) D: Hang J. Hang Statuce Z. Qu, T. Jiao, M. Liu and P. Duan, Chem. Commun., 2018, **54**, 5630–5633; (c) P. Reiné, A. M. Ortuño, S. Resa, L. Álvarez de Cienfuegos, V. Blanco, M. J. Ruedas–Rama, G. Mazzeo, S. Abbate, A. Lucotti, M. Tommasini, S. Guisán-Ceinos, M. Ribagorda, A. G. Campaña, A. Mota, G. Longhi, D. Miguel and J. M. Cuerva, Chem. Commun., 2018, **54**, 13985–13988; (d) R. Aoki, R. Toyoda, J. F. Kögel, R. Sakamoto, J. Kumar, Y. Kitagawa, K. Harano, T. Kawai and H. Nishihara, J. Am. Chem. Soc., 2017, **139**, 16024–16027.

- (a) R. Carr, N. H. Evans and D. Parker, Chem. Soc. Rev., 2012, 12 41, 7673-7686; (b) J. Gregoliński, P. Starynowicz, K. T. Hua, J. L. Lunkley, G. Muller and J. Lisowski, J. Am. Chem. Soc., 2008, 130, 17761-17773; (c) Y. Hasegawa, Y. Miura, Y. Kitagawa, S. Wada, T. Nakanishi, K. Fushimi, T. Seki, H. Ito, T. Iwasa, T. Taketsugu, M. Gon, K. Tanaka, Y. Chujo, S. Hattori, M. Karasawa and K. Ishii, Chem. Commun., 2018, 54, 10695-10697; (d) T. Wu and P. Bouř, Chem. Commun., 2018, 54, 1790-1792; (e) E. Kreidt, L. Arrico, F. Zinna, L. Di Bari and M. Seitz, Chem. - Eur. J., 2018, 24, 13556-13564; (f) F. Zinna and L. Di Bari, Chirality, 2015, 27, 1-13; (g) L. Armelao, D. B. Dell'Amico, L. Bellucci, G. Bottaro, L. Di Bari, L. Labella, F. Marchetti, S. Samaritani and F. Zinna, Inorg. Chem., 2017, 56, 7010-7018; (h) M. Leonzio, A. Melchior, G. Faura, M. Tolazzi, F. Zinna, L. Di Bari and F. Piccinelli, Inorg. Chem., 2017, 56, 4413-4422.
- J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki and G. Muller, J. Am. Chem. Soc., 2008, 130, 13814–13815.
- (a) Z.-Y. Li, J.-W. Dai, M. Damjanović, T. Shiga, J.-H. Wang, J. Zhao, H. Oshio, M. Yamashita and X.-H. Bu, *Angew. Chem. Int. Ed.*, 2019, **58**, 4339–4344; (b) T. Toyama, K. Higashiguchi, T. Nakamura, H. Yamaguchi, E. Kusaka and K. Matsuda, *J. Phys. Chem. Lett.*, 2016, **7**, 2113–2118; (c) C. Sarter, M. Heimes and A. Jäschke, *Beilstein J. Org. Chem.*, 2016, **12**, 1103–1110; (d) M. Herder, B. M. Schmidt, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 2738–2747; (e) T. Buckup, C. Sarter, H.-R. Volpp, A. Jäschke and M. Motzkus, *J. Phys. Chem. Lett.*, 2015, **6**, 4717–4721; (f) H. K. Bisoyi and Q. Li, *Chem. Rev.*, 2016, **116**, 15089-15166.
- (a) A. Vlasceanu, M. Koerstz, A. B. Skov, K. V. Mikkelsen and M. B. Nielsen, *Angew. Chem. Int. Ed.*, 2018, **57**, 6069–6072; (b) D. J. van Dijken, P. Kovaříček, S. P. Ihrig and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 14982–14991; (c) A. Gopal, M. Hifsudheen, S. Furumi, M. Takeuchi and A. Ajayaghosh, *Angew. Chem. Int. Ed.*, 2012, **51**, 10505–10509; (d) A. Julià-López, D. Ruiz-Molina, J. Hernando and C. Roscini, *ACS Appl. Mater. Inter.*, 2019, **11**, 11884–11892; (e) A. S. Terpstra, W. Y. Hamad and M. J. MacLachlan, *Adv. Funct. Mater.*, 2017, **27**, 1703346; (f) L. Kortekaas and W. R. Browne, *Chem. Soc. Rev.*, 2019, **48**, 3406-3424.
- (a) Y. Hashimoto, T. Nakashima, M. Yamada, J. Yuasa, G. Rapenne and T. Kawai, *J. Phys. Chem. Lett.*, 2018, 9, 2151–2157;
 (b) L.-X. Cai, L.-L. Yan, S.-C. Li, L.-P. Zhou and Q.-F. Sun, *Dalton Trans.*, 2018, 47, 14204–14210.
- (a) W. Miao, S. Wang and M. Liu, *Adv. Funct. Mater.*, 2017, 27, 1701368; (b) C. Shen, X. He, L. Toupet, L. Norel, S. Rigaut and J. Crassous, *Organometallics*, 2017, 37, 697–705; (c) Y. Cai, Z. Guo, J. Chen, W. Li, L. Zhong, Y. Gao, L. Jiang, L. Chi, H. Tian and W.-H. Zhu, *J. Am. Chem. Soc.*, 2016, 138, 2219–2224; (d) B. A. San Jose, T. Ashibe, N. Tada, S. Yorozuya and K. Akagi, *Adv. Funct. Mater.*, 2014, 24, 6166–6171; (e) M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, 114, 12174–12277; (f) T. Yamaguchi, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1997, 119, 6066–6071.
- (a) O. Kotova, S. Comby, K. Pandurangan, F. Stomeo, J. E. O'Brien, M. Feeney, R. D. Peacock, C. P. McCoy and T.

Journal of Materials Chemistry C Accepted Manuscript

DOI: 10.1039/D0TC01044H

Gunnlaugsson, Dalton Trans., 2018, 47, 12308-12317; (b) F. Stomeo, C. Lincheneau, J. P. Leonard, J. E. O'Brien, R. D. Peacock, C. P. McCoy and T. Gunnlaugsson, J. Am. Chem. Soc., 2009, 131, 9636-9637.

- 19 (a) C.-T. Yeung, W. T. K. Chan, S.-C. Yan, K.-L. Yu, K.-H. Yim, W.-T. Wong and G.-L. Law, Chem. Commun., 2015, 51, 592-595; (b) C.-T. Yeung, K.-H. Yim, H.-Y. Wong, R. Pal, W.-S. Lo, S.-C. Yan, M. Y.-M. Wong, D. Yufit, D. E. Smiles, L. J. McCormick, S. J. Teat, D. K. Shuh, W.-T. Wong and G.-L. Law, Nat. Commun., 2017, 8, 1128.
- 20 (a) X.-Z. Li, L.-P. Zhou, L.-L. Yan, D.-Q. Yuan, C.-S. Lin and Q.-F. Sun, J. Am. Chem. Soc., 2017, 139, 8237-8244; (b) L.-L. Yan, C.-H. Tan, G.-L. Zhang, L.-P. Zhou, J.-C. Bünzli and Q.-F. Sun, J. Am. Chem. Soc., 2015, 137, 8550-8555.
- Y. Zhou, H. Li, T. Zhu, T. Gao and P. Yan, J. Am. Chem. Soc., 21 2019, 141, 19634-19643.
- 22. A. Y. Chen, P. W. Thomas, A. C. Stewart, A. Bergstrom, Z. Cheng, C. Miller, C. R. Bethel, S. H. Marshall, C. V. Credille, C. L. Riley, R. C. Page, R. A. Bonomo, M. W. Crowder, D. L. Tierney, W. Fast and S. M. Cohen, J. Med. Chem., 2017, 60, 7267-7283.
- 23. (a) S. Vásquez-Céspedes, K. M. Chepiga, N. Möller, A. H. Schäfer and F. Glorius, ACS Catal., 2016, 6, 5954-5961; (b) R. Wang, S. Pu, G. Liu, S. Cui and H. Li, Tetrahedron Lett., 2013, 54, 5307-5310; (c) T. Yamaguchi and M. Irie, J. Org. Chem., 2005, 70, 10323-10328.
- 24. J. D. L. Dutra, T. D. Bispo and R. O. Freire, J. Comput. Chem., 2004, 35, 772-775.
- 25. S. G. Telfer, T. M. McLean and M. R. Waterland, Dalton Trans., 2011, 40, 3097-3108.
- 26. (a) T. Förster, Naturwissenschaften, 1946, 33, 166-175; (b) Y. Qin, L.-J. Chen, Y. Zhang, Y.-X. Hu, W.-L. Jiang, G.-Q. Yin, H. Tan, X. Li, L. Xu and H.-B. Yang, Chem. Commun., 2019, 55, 11119-11122.
- 27. (a) M. W. Mara, D. S. Tatum, A.-M. March, G. Doumy, E. G. Moore and K. N. Raymond, J. Am. Chem. Soc., 2019, 141, 11071-11081; (b) D. L. J. Dexter, J. Chem. Phys., 1953, 21, 836-850.

View Article Online

Journal of Materials Chemistry C Accepted Manuscript

View Article Online DOI: 10.1039/D0TC01044H

A light triggered optical and chiroptical switch based on a homochiral

Eu₂L₃ Helicate

Jianpeng Zhang, Yanyan Zhou, Yuan Yao, Zhenyu Cheng, Ting Gao, Hongfeng Li* and Pengfei Yan



A pair of homochiral triple-stranded helicates $[Eu_2(o-L^{RR})_3](TOf)_6$ and $[Eu_2(o-L^{SS})_3](TOf)_6$ show light-responsive optical (UV, PL) and chiroptical (ECD, CPL) switching properties upon alternating UV and visible light irradiation.