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Dynamic control of chirality and self-assembly of double-stranded helicates with light

Depeng Zhao, Thomas van Leeuwen, Jinling Cheng and Ben L. Feringa*

Helicity switching in biological and artificial systems is a fundamental process that allows for the dynamic control of structures and their functions. In contrast to chemical approaches to responsive behaviour in helicates, the use of light as an external stimulus offers unique opportunities to invert the chirality of helical structures in a non-invasive manner with high spatiotemporal precision. Here, we report that unidirectional rotary motors with connecting oligobipyridyl ligands, which can dynamically change their chirality upon irradiation, assemble into metal helicates that are responsive to light. The motor function controls the self-assembly process as well as the helical chirality, allowing switching between oligomers and double-stranded helicates with distinct handedness. The unidirectionality of the light-induced motion governs the sequence of programmable steps, enabling the highly regulated self-assembly of fully responsive helical structures. This discovery paves the way for the future development of new chirality-dependent photoresponsive systems including smart materials, enantioselective catalysts and light-driven molecular machines.

The helix structure, prominently present in nature's DNA^{1,2} and proteins³, has triggered the imagination of supramolecular scientists seeking to explore their unique three-dimensional architecture^{4,5}. Control of helical chirality is key to numerous artificial systems^{6,7}, ranging from oligonucleotides⁸ and peptidomimetics⁹ to foldamers^{10,11} and liquid crystals¹². It has proven to be essential in many self-assembly processes, for example to form fibres¹³, nanotubes¹⁴ and supramolecular polymers¹⁵. It also enables specific functions, as seen in metallo-helicates showing antibiotic activity¹⁶, the long-range relay of chiral information^{17–19}, foldamer receptors^{20–22} and DNA-based nanomechanical devices²³. As chiral information is embedded in the helical structure, switching the chirality allows dynamic control of functions. This is prominently seen in B-DNA to Z-DNA inversion in the cell²⁴ and in artificial responsive catalysts^{25,26}. Photochemical control of the twist sense of a dynamic single-stranded helical polyisocyanate and peptides has also been reported^{27–29}. Following the seminal work of Lehn and co-workers^{30,31} on the spontaneous self-assembly of metal double-stranded helicates^{32,33} from oligopyridine ligands, a number of elegant strategies for the control of dynamic helicates using chemical signals (metal binding, redox, pH and solvent) have evolved^{34–36}. Control of the handedness of the helicates was achieved by introducing chirality into the backbone of the ligands^{37,38} or via chiral templates³⁹. However, fully reversible handedness switching of double helicates remains highly challenging so far. In recognizing this, we proposed that light should allow non-invasive and dynamic control of multistage self-assembly processes of double helicates as well as control of their chirality, bringing these programmable supramolecular systems to the next level of sophistication. Fascinating prospects in the control of functions would arise from such a strategy (note that helical structures were recently used in chiral recognition^{17,22,40}, chiral memory⁴¹, transmission of chirality^{17,19,42} and chiral amplification⁴³). Here, we report molecular-motor-based double helicates in which, for the first time, the multistage assembly process and helicity can be driven by light in a fully reversible manner.

Results and discussion

Key to the design of these responsive systems is our first-generation unidirectional rotary motor⁴⁴ (Fig. 1a). A 360° unidirectional rotary

cycle of a single enantiomer of (*R,R*)-(*P,P*)-*trans*-1 involves four stages, in which one half of the molecule rotates with respect to the other half around a central double bond (axle of rotation). The rotary process features two photochemical isomerizations: step 1, stable (*P,P*)-*trans*-1 to less stable (*M,M*)-*cis*-1; step 3, stable (*P,P*)-*cis*-1 to less stable (*M,M*)-*trans*-1. Each of these energetically uphill photochemical conversions is followed by a thermodynamically downhill helix inversion: step 2, less stable (*M,M*)-*cis*-1 to stable (*P,P*)-*cis*-1; step 4, less stable (*M,M*)-*trans*-1 to stable (*P,P*)-*trans*-1. The chiral motor unit acts as a dynamic template to bind the two strands of oligobipyridine ligands (Fig. 1b). As the metal ion we chose Cu(I), because it is well known to form a tetrahedral coordination geometry³⁰. If the motor unit adopts a *trans* geometry, the two ligand strands will be remote from each other and we expect an oligomeric array (Fig. 1c).

Isomerization to the *cis* form will bring the two ligand strands in close proximity, allowing the formation of a double helicate upon copper binding, while the chirality (helical sense) is controlled by the configuration of the *cis* motor unit. Molecular modelling indicates that the less stable (*M,M*)-*cis*-L2 will induce a (*P'*)-double metal-helicate. We reasoned that this system represents a metastable helical structure and that subsequent thermal helix inversion of the less stable (*M,M*)-*cis*-L2 motor unit to the stable (*P,P*)-*cis*-L2 unit releases strain in the system. This comprises a thermodynamically favourable process that will consequently lead to concomitant reversal of the chirality of the double metal-helicate (Fig. 1c, from *P'* to *M'*). Finally, photochemical isomerization of the stable (*P,P*)-*cis*-motor unit in the monomeric double helicate will provide the (*P,P*)-*trans*-motor unit with dissociation of the double helicate by light and remoulding of the oligomeric complexes. The combined steps complete a full cycle of helix inversions and association–dissociation of the self-assembled double helical structure, driven by the input of light energy. In the present system (Fig. 1c) only three stages are studied, as the less stable (*M,M*)-*trans*-isomer, although observed as a transient species at lower temperatures, undergoes fast isomerization to stable (*P,P*)-*trans*-L2 (*vide infra*, see Supplementary Fig. 8).

Initial studies involved stable (*P,P*)-*trans*-L1 and stable (*P,P*)-*cis*-L1 in which two bipyridine ligands are connected via amide bond

Figure 1 | Schematic representation of the design and concept of the dynamic double-stranded helicates. a, Four-stage rotary cycle of molecular motor **1**. **b**, Procedure for synthesis of (R,R) -(P,P)-*trans*-**L1** and (R,R) -(P,P)-*trans*-**L2**. R indicates the configuration of the stereogenic centres. P (plus) and M (minus) indicate the helicities of the molecular motor core structure. P' and M' are used to define the chirality of right- and left-handed metal-helicate, respectively. As only the helicity changes, the indication of the central chirality R is omitted throughout. The helicity of the helicate (P' or M') is dictated by the helicity of the motor unit. **c**, Coordination oligomers of bipyridine-Cu(I) complex can be formed by treating the *trans*-molecular motor bearing oligobipyridines with Cu(I). These oligomers can split into monomers with P' -helicity due to the unidirectional rotation of the molecular motor from the stable (P,P) -*trans*-state to the less stable (M,M) -*cis*-state with light. The inversion of the chirality of the Cu-helicate from P' to M' is governed by a subsequent thermal helical inversion (from M,M to P,P) of the molecular motor core structure. Photoisomerization of stable (P,P) -*cis*-state to (M,M) -*cis*-state through the rotary cycle via the *trans*-oligomeric-state will invert the chirality of the Cu-helicate back from M' to P' (cycle shown for **L2**-Cu(I) complexes).

formation to the corresponding *trans* and *cis* isomers of enantiomerically pure bis-carboxylic-acid-functionalized motor **4** (Fig. 1b; see Supplementary Section 2 for details of synthesis, characterization and absolute configuration). The photochemical and thermal isomerization processes of **L1** were studied by UV-vis, circular dichroism (CD) and ^1H NMR spectroscopy (Fig. 2 and Supplementary Figs 3–5). Both stable (P,P) -*trans*-**L1** and stable (P,P) -*cis*-**L1**, upon irradiation at 312 nm, show clear isosbestic points in the UV-vis and CD spectra, pointing to selective photoisomerization processes. Analysis of the thermal isomerization data of the less stable (M,M) -*cis*-**L1** to stable (P,P) -*cis*-**L1** interconversion using the Eyring equation provided the standard Gibbs free energy of activation (referred to standard conditions throughout, 298 K and 1 atm) $\Delta^\ddagger G^\circ = 100.0 \text{ kJ mol}^{-1}$ and a half-life of (M,M) -*cis*-**L1** at

20 °C of 18.9 h (Supplementary Fig. 2). Similarly, following thermal isomerization from the less stable (M,M) -*trans*-**L1** to stable (P,P) -*trans*-**L1**, we obtained $\Delta^\ddagger G^\circ = 80.9 \text{ kJ mol}^{-1}$ and a half-life for (M,M) -*trans*-**L1** of 27 s at 20 °C and 2.2 min at 4 °C.

The binding of $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}$ (1.1 equiv.) to (P,P) -*trans*-**L1** results in the formation of oligomeric complexes, as seen in the ^1H NMR spectra (Fig. 2a,b). In contrast, binding of $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}$ (1.1 equiv.) to less stable (M,M) -*cis*-**L1**, obtained via irradiation at 312 nm of (P,P) -*trans*-**L1**, provided a well-defined mononuclear complex with distinct shifts for the protons of the motor and ligand units (see Fig. 2c,d for assignment). A similar well-defined mononuclear Cu(I) complex is obtained for stable (P,P) -*cis*-**L1** (prepared independently), although it is distinctly different from the related complex derived from less stable (M,M) -*cis*-**L1** (Fig. 2e,f). The copper-helicates

Figure 2 | ^1H NMR spectra of *(P,P)*-*trans*-**L1**, *(M,M)*-*cis*-**L1**, *(P,P)*-*cis*-**L1** and the corresponding Cu(I) complexes. **a**, ^1H NMR (400 MHz, CDCl_3) spectrum of compound *(P,P)*-*trans*-**L1**. **b**, ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) spectrum of *(P,P)*-*trans*-**L1**-Cu. **c**, ^1H NMR (400 MHz, CD_2Cl_2) spectrum of compound *(M,M)*-*cis*-**L1** upon irradiation of *(P,P)*-*trans*-**L1** (PSS: 90:10). **d**, ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) spectrum of *(M,M)*-*cis*-**L1**-Cu. **e**, ^1H NMR (400 MHz, CD_2Cl_2) spectrum of compound *(P,P)*-*cis*-**L1**. **f**, ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) spectrum of *(P,P)*-*cis*-**L1**-Cu. In all cases, addition of 1.1 equiv. of Cu (CH_3CN) $_4\text{OTf}$ to the ligand solution results in instant formation of the corresponding metal complex. Well-defined helicates are obtained for *(M,M)*-*cis*-**L1** and *(P,P)*-*cis*-**L1** while coordination oligomers are formed for *(P,P)*-*trans*-**L1**.

derived from both forms of *cis*-**L1** show strong CD absorptions between 300 and 400 nm, while comparing the CD spectra of *(M,M)*-*cis*-**L1**-Cu and *(P,P)*-*cis*-**L1**-Cu, an inverted helicity is observed (for the CD spectra of Cu-bound helicates of **L1** see Supplementary Fig. 15). Both *(P,P)*-*cis*-**L1**-Cu and *(M,M)*-*cis*-**L1**-Cu show increased CD absorption compared with free ligands *(P,P)*-*cis*-**L1** and *(M,M)*-*cis*-**L1** at 320–330 nm, corresponding to the ligand-centred $\pi-\pi^*$ transition of bipyridine and weak bands at ~ 450 nm with the same sign as the shorter wavelength signal coincident with a metal-to-ligand charge-transfer (MLCT) band.

Having established that **L1** showed the expected photochemical and thermal switching behaviour and that distinct helicates are formed upon Cu(I) binding to both *cis* isomers, we extended our studies to the oligomeric system **L2** with two bipyridine ligands at each strand (Fig. 1b; see Supplementary Section 2 for details of synthesis, characterization and absolute configuration). The photochemical and thermal isomerization processes of **L2** were studied by UV-vis, CD and ^1H NMR spectroscopy (Supplementary Figs 6 and 7). Again, both stable *(P,P)*-*trans*-**L2** and stable *(P,P)*-*cis*-**L2**, upon irradiation at 312 nm, show clear isosbestic points in UV-vis and CD spectra, pointing to selective photoisomerization processes and uncompromised motor functioning. The less stable *(M,M)*-*cis*-**L2** converts to stable *(P,P)*-*cis*-**L2** with $\Delta^\ddagger G^\circ = 100.3 \text{ kJ mol}^{-1}$ and a half-life of *(M,M)*-*cis*-**L2** of 22 h at 20 °C (Supplementary Fig. 8). Similarly, the thermal isomerization from less stable *(M,M)*-*trans*-**L2** to stable *(P,P)*-*trans*-**L2** shows $\Delta^\ddagger G^\circ = 80.6 \text{ kJ mol}^{-1}$ and a half-life for *(M,M)*-*trans*-**L2** of 24 s at 20 °C and 2.2 min at 4 °C.

Binding of Cu(I) (2.1 equiv.) to *(P,P)*-*trans*-**L2** again shows oligomer formation (Fig. 3a,b). Oligomeric Cu(I) complexes from *(P,P)*-*trans*-**L2** up to pentamers [**L2** $_5\text{Cu}_5(\text{OTf})_3$] $^{2+}$ were detected by cold-spray ionization mass spectrometry (ESI-MS, Supplementary Fig. 19). Two-dimensional ^1H -diffusion-ordered spectroscopy (DOSY) measurements on *(P,P)*-*trans*-**L2**-Cu $_2$ and *(P,P)*-*cis*-**L2**-Cu $_2$ showed diffusion coefficients D changing from 410 to 850 $\mu\text{m}^2 \text{ s}^{-1}$ (Supplementary Figs 25 and 27). This significant decrease by a factor of 1.5–2.0 is in the range observed for related oligomeric metal complexes^{45,46}, indicating the formation of larger oligomeric aggregates going from *cis*- to *trans*-Cu(I) complexes of **L2**. In contrast, well-defined bis-Cu(I) complexes of less stable *(M,M)*-*cis*-**L2** and stable *(P,P)*-*cis*-**L2** are formed, as is evident from ^1H NMR shifts and high-resolution mass spectrometry data (Fig. 3c–f and Supplementary Figs 49 and 50).

The CD spectra of *(M,M)*-*cis*-**L2**-Cu $_2$ and *(P,P)*-*cis*-**L2**-Cu $_2$ helicates also show a strong and distinctly inverted helicity (Fig. 4b). Specifically, on binding of Cu(I) to *(P,P)*-*cis*-**L2** or *(M,M)*-*cis*-**L2** to form *(P,P)*-*cis*-**L2**-Cu $_2$ and *(M,M)*-*cis*-**L2**-Cu $_2$, respectively, a strongly enhanced CD signal (compared to the CD spectra of the free ligands) with negative (*(P,P)*-*cis*-complex) and positive (*(M,M)*-*cis*-complex) CD absorption, is observed at approximately 320 nm, characteristic of the ligand-centred $\pi-\pi^*$ transition of bipyridine (Fig. 4b). Furthermore, weak CD bands (with the same sign as the shorter wavelength signal) are found at ~ 470 nm, coincident with an MLCT band in the UV-vis spectrum (Fig. 4a,b) for both *(P,P)*-*cis*-**L2**-Cu $_2$ and *(M,M)*-*cis*-**L2**-Cu $_2$. In accordance with

Figure 3 | ^1H NMR spectra of (P,P) -*trans*-L2, (M,M) -*cis*-L2, (P,P) -*cis*-L2 and the corresponding Cu(I) complexes. a, ^1H NMR (400 MHz, CD_2Cl_2) spectrum of compound (P,P) -*trans*-L2. b, ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) spectrum of (P,P) -*trans*-L2-Cu₂. c, ^1H NMR (400 MHz, CD_2Cl_2) spectrum of compound (M,M) -*cis*-L2 upon irradiation of (P,P) -*trans*-L2 (PSS: 88:12). d, ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) spectrum of (M,M) -*cis*-L2-Cu₂. e, ^1H NMR (400 MHz, CDCl_3) spectrum of compound (P,P) -*cis*-L2. f, ^1H NMR (400 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) spectrum of (P,P) -*cis*-L2-Cu₂. In all cases, addition of 2.1 equiv. of $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}$ to the ligand solution results in instant formation of the corresponding metal complex. Well-defined helicates are obtained for (M,M) -*cis*-L2 and (P,P) -*cis*-L2 while coordination oligomers are formed for (P,P) -*trans*-L2.

earlier structural studies on chiral oligopyridine-Cu(I)-double helicates^{47,48} and density functional theory (DFT) calculations of a model helicate (Supplementary Fig. 30), the considerably more intense CD absorption in Cu(I)-helicate (at 320 nm) compared to free ligand (Fig. 4b) is attributed to exciton coupling, while the sign of this CD band is directly related to the absolute configuration (positive absorption *P'*-helicity, negative absorption *M'*-helicity)^{37,39,47,49}. As a related enantiopure dinuclear Cu(I) complex⁵⁰ has been obtained by resolution of racemates and the rate of racemization at room temperature was determined to be slow, we assume that the interconversion between the diastereoisomers in our system (for example, *P'*-helical (P,P) -*cis*-L2-Cu₂ and *M'*-helical (P,P) -*cis*-L2-Cu₂) should also be slow on the NMR timescale. Based on this analogy and the fact that the helical structures are readily distinguished as they are diastereoisomers, the handedness excess can be estimated by NMR. NMR analysis (Fig. 3d,f and DOSY experiments in Supplementary Fig. 27) indicates a >90:10 preference for the (P,P) -*cis*-L2-Cu₂ and (M,M) -*cis*-L2-Cu₂ isomers based on integration of the major and minor diastereoisomers. Similar CD studies of (P,P) -*trans*-L2-Cu₂ showed the typical strong positive absorption at 320–330 nm (negative for free ligand (P,P) -*trans*-L2) and an MLCT CD band at 450 nm with the same sign, corresponding to a *P'*-double helicate structure (Fig. 4c). In contrast, the less stable (M,M) -*trans*-L2-Cu₂

showed a similar CD spectrum as the free ligand (M,M) -*trans*-L2, indicating that no chiral induction was achieved (Fig. 4d), although the Cu(I) complex was formed, according to the NMR and UV-vis analysis (Supplementary Figs 18, 23). Finally, the corresponding *n*-butyl bis-amide motor, lacking the oligobipyridine for Cu(I)-helicate formation, was prepared, and CD studies showed that the CD absorptions of motor and helicates are clearly distinct (Supplementary Fig. 28). The combined data clearly show well-defined double-stranded helicates for both *cis* forms and stable (P,P) -*trans*-L2-Cu₂, with a large preference for a specific handedness. Furthermore, these data indicate that double-stranded helicates with well-defined *P'* or *M'* helicity are formed with the *cis* isomers when shorter (L1) as well as more extended strands (L2) are connected to the chiral motor template.

Next, we examined the responsive behaviour of the Cu(I) complexes of L1 and L2 regarding the self-assembly process and inversion of the handedness of the helicates when triggered by light irradiation. The cycles start with the copper complexes of stable (P,P) -*trans*-L1 (L1-Cu) and stable (P,P) -*trans*-L2 (L2-Cu₂). Figure 5a,d shows the partial ^1H NMR spectra (in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$) of the oligomeric *trans* complexes (also Fig. 1c) and the spectral changes during photoisomerization (irradiation at 312 nm), indicating high selectivity (>90:10) in the conversion of

Figure 4 | Determination of the absolute configuration of L2-Cu₂. **a, b**, UV-vis (**a**) (CH₃CN, 1.0 × 10⁻⁵ M) and CD (**b**) spectra in CH₃CN of (P,P)-cis-L2-Cu₂ (black solid line), (M,M)-cis-L2-Cu₂ (red solid line), (P,P)-cis-L2 (black dashed line) and (M,M)-cis-L2 (red dashed line); UV-vis absorption in the visible light region is assigned to a metal-to-ligand charge-transfer (MLCT) band and the sign of the corresponding CD signal can be used to determine the absolute configuration of the dinuclear helicates (positive Cotton effect for *P'* helicity, negative for *M'* helicity). **c**, CD spectra of (P,P)-trans-L2 and (P,P)-trans-L2-Cu₂ (CH₃CN, 1.0 × 10⁻⁵ M). **d**, CD spectra of (M,M)-trans-L2 and (M,M)-trans-L2-Cu₂ (CH₃CN, 1.0 × 10⁻⁵ M, 233 K). **e, f**, Optimized structures of (M,M)-cis-L2-Cu₂ (**e**) and (P,P)-cis-L2-Cu₂ (**f**), obtained by DFT calculations at the B3LYP/6-31G(d,p) level for light atoms and LANL2DZ for copper atoms. Protons are omitted for clarity. An intramolecular hydrogen bond is observed between the amide groups (N-H...O) for both (M,M)-cis-L2-Cu₂ (bond length: 1.965 Å) and (P,P)-cis-L2-Cu₂ (bond length: 1.996 Å), which contributes to the stabilization of helical structures.

(P,P)-trans-L1-Cu to (M,M)-cis-L1-Cu and (P,P)-trans-L2-Cu₂ to (M,M)-cis-L2-Cu₂. Figure 5b,e shows the partial ¹H NMR spectra associated with the next steps, that is, the thermal isomerizations of less stable (M,M)-cis-L1-Cu to stable (P,P)-cis-L1-Cu and of less stable (M,M)-cis-L2-Cu₂ to stable (P,P)-cis-L2-Cu₂ upon warming to 65 and 70 °C, respectively. Again, highly selective conversions (>90:10) are observed, and the nature of the helicates is confirmed via the independently prepared Cu complexes of the isolated L1 and L2 isomers. The inversion of the CD absorption signals of the Cu(I)-helicate (300–350 nm, 400–600 nm) going

from (M,M)-cis-L2-Cu₂ to (P,P)-cis-L2-Cu₂ is in agreement with the change in handedness of the helicate during this isomerization step. The absolute configuration (*P'* or *M'*) of helicates (M,M)-cis-L2-Cu₂ and (P,P)-cis-L2-Cu₂ was deduced by the sign of the CD signal from both the ligand-centred band (320–330 nm) and the MLCT band (400–600 nm), where a positive Cotton effect indicates *P'* helicity and a negative Cotton effect indicates *M'* helicity^{37,39,47,49}. The thermal isomerizations of the less stable (M,M)-cis-Cu complexes to stable (P,P)-cis-Cu complexes were also investigated by following the ultraviolet absorption changes at 350 nm. On

Figure 5 | Programmed dynamic assembly processes of L1-Cu and L2-Cu₂ induced by light and heat. **a**, Partial ¹H NMR (400 MHz, CD₂Cl₂/CD₃CN); spectral changes of the photoisomerization step from (*P,P*)-*trans*-L1-Cu to (*M,M*)-*cis*-L1-Cu upon irradiation at 312 nm. **b**, Partial ¹H NMR (400 MHz, CD₂Cl₂/CD₃CN); spectral changes of the thermal isomerization step from (*M,M*)-*cis*-L1-Cu to (*P,P*)-*cis*-L1-Cu upon heating at 65 °C. **c**, Partial ¹H NMR (400 MHz, CD₂Cl₂/CD₃CN); spectral changes of the photoisomerization step from (*P,P*)-*cis*-L1-Cu to (*M,M*)-*cis*-L1-Cu via the *trans* state (marked by a dashed circle) upon irradiation at 312 nm. **d**, Partial ¹H NMR (400 MHz, CD₂Cl₂/CD₃CN); spectral changes of the photoisomerization step from (*P,P*)-*trans*-L2-Cu₂ to (*M,M*)-*cis*-L2-Cu₂ upon irradiation at 312 nm. **e**, Partial ¹H NMR (400 MHz, CD₂Cl₂/CD₃CN); spectral changes of the thermal isomerization step from (*M,M*)-*cis*-L2-Cu₂ to (*P,P*)-*cis*-L2-Cu₂ upon heating at 70 °C. **f**, Partial ¹H NMR (400 MHz, CD₂Cl₂/CD₃CN); spectral changes of the photoisomerization step from (*P,P*)-*cis*-L2-Cu₂ to (*M,M*)-*cis*-L2-Cu₂ via the *trans* state (marked by a dashed circle) upon irradiation at 312 nm. The full ¹H NMR spectra are shown in Supplementary Figs 9–14. See Figs 2 and 3 for proton labelling. The responsive behaviours of L1-Cu (**a–c**) and L2-Cu₂ (**d–f**) indicate that this programmed dynamic assembly systems proceeds smoothly with high conversions in each step, which include a dynamic assembled process from oligomers to monomers (**a,d**), thermal helix inversion of the helicate (**b,e**, *P'* → *M'*) and direct photo-induced helix inversion of the helicate via the *trans* state (**c,f**, *M'* → *P'*).

applying the Eyring equation, the standard Gibbs free energy of activation of (*M,M*)-*cis*-L1-Cu to (*P,P*)-*cis*-L1-Cu is $\Delta^\ddagger G^\circ = 110.0 \text{ kJ mol}^{-1}$. The half-life of (*M,M*)-*cis*-L1-Cu is 46 days at 20 °C. Similarly, the standard Gibbs free energy of activation for (*M,M*)-*cis*-L2-Cu₂ was determined to be $\Delta^\ddagger G^\circ = 114.6 \text{ kJ mol}^{-1}$, and the half-life of (*M,M*)-*cis*-L2-Cu₂ is 327 days at 20 °C.

Finally, we investigated whether a full cycle of assembly/disassembly and inversion of helicity following photochemical stimulus could be achieved with the two Cu(I)-helicates derived from L1 and L2. Starting with either stable (*P,P*)-*cis*-L1-Cu or (*P,P*)-*cis*-L2-Cu₂ on irradiation at 312 nm, a mixture of remaining stable *cis*-helicate, stable *trans*-oligomers and less stable *cis*-helicate was obtained after a short irradiation time (Fig. 5c,f). Prolonged irradiation results in nearly complete disappearance of stable *cis* isomers and stable *trans* isomers, and less stable *cis*-helicates (*M,M*)-*cis*-L1-Cu or (*M,M*)-*cis*-L2-Cu₂ are found (Fig. 5c,f). Subsequent thermal isomerization reconverts both systems to the stable *cis*-helicates (*P,P*)-*cis*-L1-Cu and (*P,P*)-*cis*-L2-Cu₂. Less stable (*M,M*)-*trans*-isomers are not observed in these experiments, due to the fact that rapid thermal isomerization to the (*P,P*)-stable *trans* isomers occurs within seconds under ambient conditions. It should be noted that the conversion of stable *cis* isomer into stable *trans* isomer is not a direct process, but proceeds through photoisomerization of stable *cis* isomers initially to the less stable *trans* isomers, which rapidly converted into stable *trans* isomers (as confirmed by independent NMR experiments). The formation of less stable *cis* isomers can be explained by the subsequent photoisomerization of the stable *trans* isomers under the irradiation conditions applied.

Conclusions. The combined experimental data show responsive supramolecular systems in which a stepwise change in self-assembly of metal complexes can be induced by a light-driven rotary motor scaffold. The precise mechanism of disassembly of the oligomers or unfolding of the metal-helicates following irradiation needs further investigations, but, most probably, partial unwrapping of the complex, assisted by acetonitrile as a small monodentate ligand for Cu(I), precedes the photoisomerization steps. The inversion of the chirality of the helicates, from metastable to stable helicates, is driven by the strong tendency of the motor to invert helicity when the isomerization from less stable (*M,M*)-*cis*-isomers to stable (*P,P*)-*cis*-isomers occurs. The sequence of events in this dynamic self-assembled system (from oligomers to monomers and a direction of helix inversion of *P'* → *M'* or *M'* → *P'*) is governed by the unidirectional rotary motion of the motor unit, which is an important feature to arrive at programmable responsive systems. The cycle of interconversion of assemblies and helicities shown here holds promise to design other dynamic systems driven out of equilibrium by light energy.

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Author contributions

D.Z. and B.L.F. conceived the project. D.Z. designed, synthesized and tested the compounds. T.v.L. synthesized L1. J.C. carried out the DFT modelling. B.L.F. guided the research. B.L.F. and D.Z. wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information and chemical compound information are available in the [online version of the paper](#). Reprints and permissions information is available online at [www.nature.com/reprints](#). Correspondence and requests for materials should be addressed to B.L.F.

Competing financial interests

The authors declare no competing financial interests.