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In situ control of polymer helicity with a non-covalently bound photoresponsive molecular motor dopant

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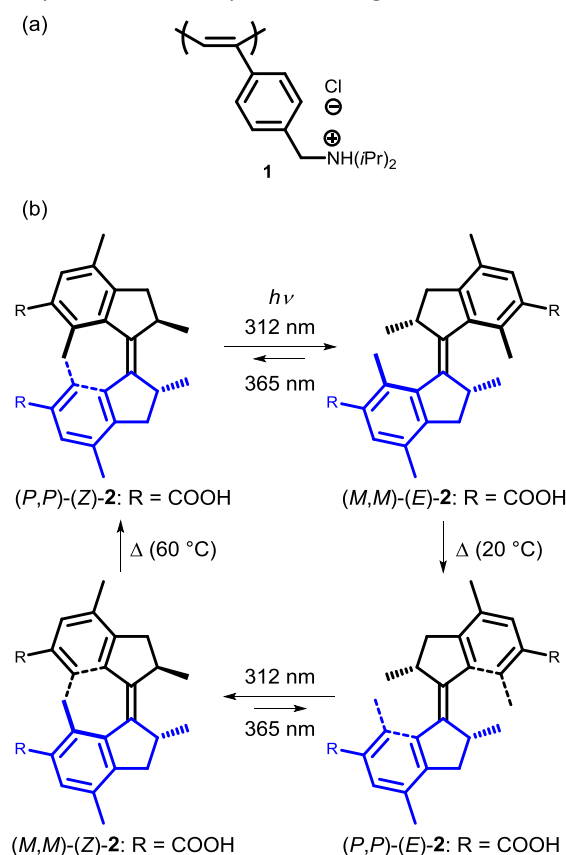
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In the application of light-driven molecular motors, the transfer of chirality is paramount. Considering the enormous potential of dynamic helical polymers, new ways are explored to transfer chirality from molecular motors to helical polymers in a non-covalent approach. The findings described herein will advance the development of novel functional and responsive polymeric systems.

The ability of molecular switches and motors to change geometry, dipole moment, extent of conjugation and hydrophobicity, among other properties allow for the dynamic control of material properties and biological functions.¹ In our research, we focus on the development and application of light-driven molecular rotary motors. Typically, these light-driven motors are based on chiral overcrowded alkenes which can undergo a series of photochemical and thermal isomerization steps to achieve unidirectional 360° rotation around the central bond (Scheme 1).² While the isomerization of commonly used photoswitches (e.g. azobenzenes and diarylethenes) bring about a change in geometry, molecular motors additionally exhibit an inversion of helical chirality. This unique feature has been used, for example, in photoswitchable catalysis³ and the dynamic inversion of stereoselective anion binding.⁴ For optimal functioning of molecular motor-based systems, the efficient transfer of chirality from the motor part to the unit performing the desired task is crucial. In this respect, transfer of chiral information by supramolecular means has proven to be a promising approach.⁵ The doping of liquid crystals with molecular motors resulted in amplification of the dynamic chirality, which in turn could be harnessed rotate of microscale objects.⁶

Dynamic helical polymers,⁷ i.e. chiral polymers with a relatively

low helical inversion barrier, have been applied for making gels,⁸ tunable column material,⁹ polymeric catalysts¹⁰ and for the detection of very small ee's.¹¹ Control over the polymer helicity by external stimuli could be used to manipulate material properties but examples of such control are limited. For polyisocyanates, inversion of helical chirality has been accomplished with light as a trigger using covalently bound azobenzenes,¹² bicyclic ketones¹³ or molecular motors.¹⁴ Inspired by the great potential of dynamic helical polymers, elegantly demonstrated by Yashima, Suginome and others we

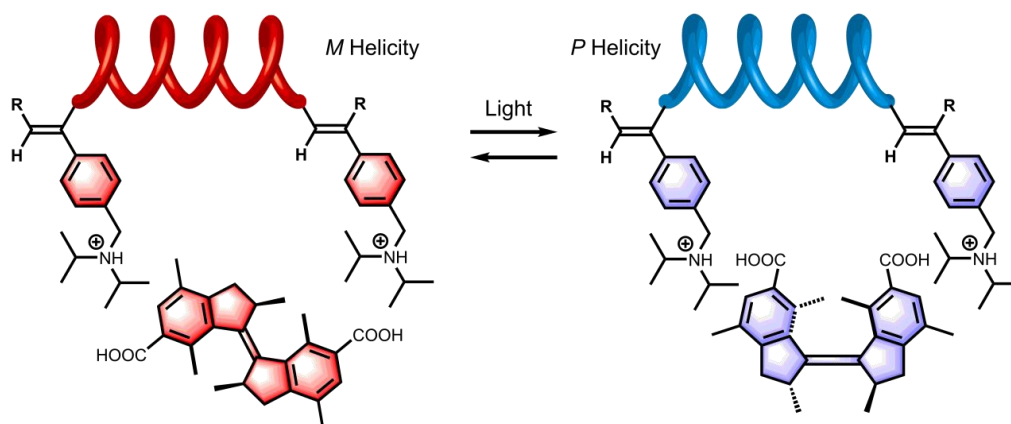


Scheme 1: a) Water-soluble dynamic helical polymer developed by Yashima et al.¹⁵ b) Photochemical and thermal isomerization of a molecular motor.

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Scheme 2: Proposed control over the helicity of the polymer using a photoresponsive molecular motor as dopant.

pursued alternative ways to transfer the chirality of molecular motors to dynamic helical polymers with the ultimate goal to achieve dynamic control of polymer function. Although the covalent functionalization of dynamic helical polymers with photoswitches has been successful towards developing photoresponsive dynamic helical polymers, strategies that are based on less synthetic effort and which feature a higher degree of reversibility, can offer attractive alternatives. We envisioned that the non-covalent interactions of molecular motors with dynamic helical polymers could offer a highly versatile and viable approach, as it allows for facile screening of various photoswitchable dopants, which can be detached by a chemical stimulus. The non-covalent binding of photoresponsive dopants to dynamic helical polymers has to the best of our knowledge, not been explored yet. Here we provide the first example using a chiral overcrowded alkene as the dopant.

The water soluble polymer developed by Yashima and co-workers, a polyphenylacetylene with ammonium side groups (**1**) offers a good starting point for its ability to bind hydrophobic molecules (e.g. BINOL).¹⁵ In our design of a photoresponsive dopant, it was reasoned that, next to the hydrophobic interactions, ionic interactions could add to the binding strength. For this reason, it was opted to investigate the interaction of dicarboxylic acid functionalized motor **2** with polymer **1** (Scheme 1). For the synthesis of **1** the procedure developed by Yashima and co-workers was followed.¹⁵ The synthesis of (*R,R*)-**2** was performed according to a procedure previously reported by our group.^{3b}

As is known for this particular kind of overcrowded alkenes, (*R,R*)-**2** has four different diastereoisomers, i.e. (*P,P*)-(*E*)-**2**, (*M,M*)-(*E*)-**2**, (*P,P*)-(*Z*)-**2** and (*M,M*)-(*Z*)-**2**, which can be interconverted into each other using light and heat as stimuli (Scheme 1). At room temperature only three states of **2** are

accessible due to the small half-life ($t_{1/2} < 1$ min) of (*M,M*)-(*E*)-**2** (Scheme 2). Hence, irradiation of either (*P,P*)-(*Z*)-**2** or (*P,P*)-(*E*)-**2** at 312 nm gives the same photostationary state (PSS) mixture of (*P,P*)-(*E*)-**2** and (*M,M*)-(*Z*)-**2** (35:65), as was demonstrated by circular dichroism (CD) and ¹H-NMR spectroscopy (Figure S1-S3). In case of (*P,P*)-(*Z*)-**2**, first (*M,M*)-(*E*)-**2** is formed upon irradiation at 312 nm but this isomer has a very short half-life at rt. Irradiation of (*M,M*)-(*Z*)-**2** at 365 nm leads to the reverse isomerization to afford (*P,P*)-(*E*)-**2**. Alternatively, (*M,M*)-(*Z*)-**2** can undergo a thermal helix inversion (THI) to (*P,P*)-(*Z*)-**2**. The reaction rate of this process was determined by UV/Vis spectroscopy at five temperatures between 50 °C and 70 °C in H₂O. The Gibbs free energy of this process was determined by Eyring plot analysis and was found to be 100 kJ/mol corresponding to a half-life of approximately 21 h at 20 °C (Figure S4).

Next, the chirality transfer of **2** to **1** was studied. The doping was accomplished by the slow evaporation of a solution of (*P,P*)-(*Z*)-**2** or (*P,P*)-(*E*)-**2** in Et₂O layered on top of a solution of **1** in double distilled H₂O (1 mg/mL). Filtration gave a clear solution which was analysed by CD spectroscopy. The obtained CD spectra were comparable to those of **1** doped with either BINOL or chiral carboxylic acids (Figure 1).^{15,16} This observation confirms that **2** interacts with **1** and is able to induce a preferred helicity in the polymer backbone. Interestingly, the CD spectrum of **1** doped with (*P,P*)-(*E*)-**2** is the mirror image (cf. opposite helicity) of the CD spectrum of **1** doped with (*P,P*)-(*Z*)-**2**, even though the *E* and *Z* isomers have the same absolute configuration at their stereogenic centres and same helical chirality in their core. Considering the structural differences between (*P,P*)-(*E*)-**2** and (*P,P*)-(*Z*)-**2**, most notably the distance between the carboxylic acid groups, it is proposed that their binding modes are distinct, leading to a different preferred polymer handedness. By varying the amount of dopant added,

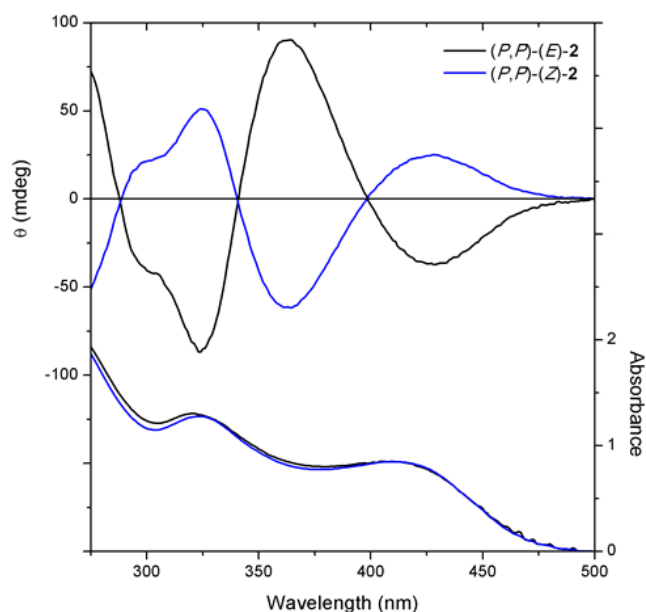


Figure 1: CD and UV/vis absorption spectrum of **1** in H₂O (1 mg/mL) doped with *(P,P)*-(*Z*)-**2** and *(P,P)*-(*E*)-**2**.

it was found for both *(P,P)*-(*E*)-**2** and *(P,P)*-(*Z*)-**2** that the CD signal of **1** did not increase further when more than 0.04 mg of dopant was used per 1 mg of polymer. In other words, the polymer was saturated at a ratio of about 0.025:1 (dopant:monomer unit), which represents an efficient transfer of chirality from the dopant to the polymer. This result is also in accordance with the findings of Yashima et al, showing an efficient transfer of chirality from BINOL to **1** in H₂O.¹⁵

The effect of pH and salt addition was investigated in order to get more insight in the specific mode of binding of **2** to **1**. The concentration of NaCl was increased from 0 M to 1 M, which led to a decrease in the amplitude of the CD signal of more than a factor of 2, while the UV/Vis spectrum remained unchanged (Figure S5-S6). It is expected that the addition of NaCl results in a decrease in the strength of the ionic interactions between the ammonium groups of **1** and the carboxylate groups of **2**. Decreasing the pH to 1, at which the carboxylate groups are in their neutral carboxylic acid form, resulted in the disappearance of the CD signal. The signal reappeared when the pH of the same sample was increased back to 7, albeit of lower intensity (Figure S9). Furthermore, in a control experiment it was found that the corresponding methyl ester of **2** did not induce any CD signal. From these observations, it can be concluded that the ionic interactions between the carboxylate and ammonium moieties are crucial for the transfer of chirality from **2** to **1**.

After establishing that **2** binds to **1**, it was investigated whether **2** could still be photoisomerized while associated to the polymer and how this would influence the helical conformation. Irradiation at 312 nm of a sample of **1** doped with *(P,P)*-(*Z*)-**2** resulted in an inversion of the CD signal and hence, the inversion of the handedness of the polymer (Figure 3 and S7).¹⁷ Irradiation of *(P,P)*-(*Z*)-**2** at room temperature gives a PSS mixture of *(M,M)*-(*Z*)-**2** and *(P,P)*-(*E*)-**2**. As indicated above, *(P,P)*-(*E*)-**2** induces the opposite helicity in **1**, compared

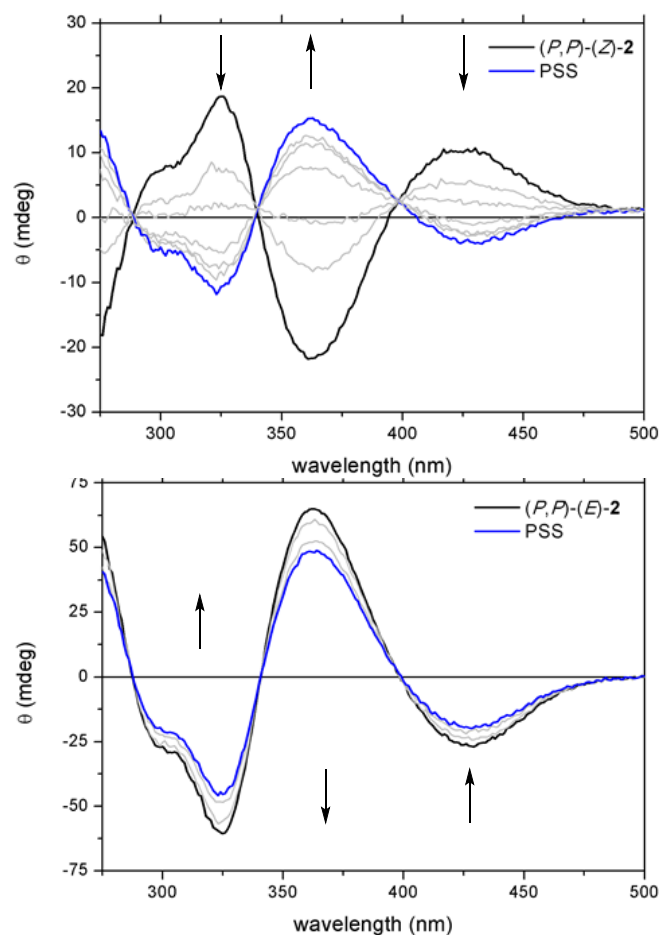
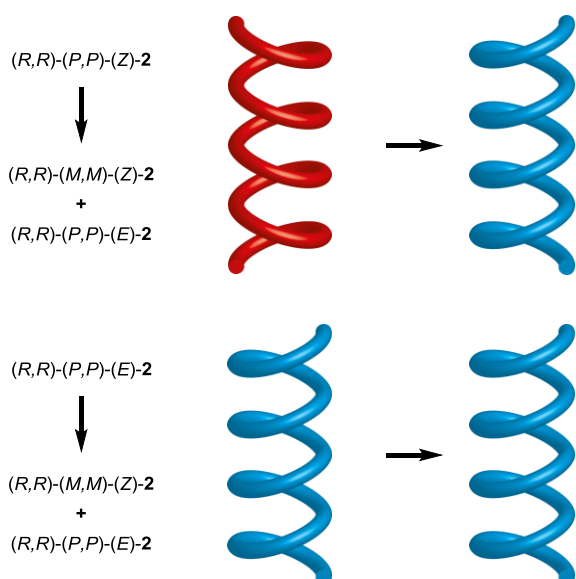


Figure 2: (Top) Changes in CD absorption spectrum of **1** in H₂O (1 M NaCl) doped with *(P,P)*-(*Z*)-**2** upon irradiation at 312 nm. (Bottom) Changes in CD absorption spectrum of **1** in H₂O (1 M NaCl) doped with *(P,P)*-(*E*)-**2** upon irradiation at 312 nm.

to *(P,P)*-(*Z*)-**2**. It is proposed that *(M,M)*-(*Z*)-**2**, as it is a pseudo-enantiomer of *(P,P)*-(*Z*)-**2**, also induces the opposite helicity, (compared to *(P,P)*-(*Z*)-**2**).¹⁸ Interestingly, it was found that the addition of NaCl (1 M) decreases the irradiation time required to reach the PSS. This observation indicates that the dopant first needs to dissociate in order to photoisomerize after which it can associate again and induces the opposite helicity.

In sharp contrast, when a sample of **1** doped with *(P,P)*-(*E*)-**2** was irradiated, no inversion of the CD signal was observed, only a decrease in intensity in the CD spectrum (Figure 2 and S8). This is expected as the irradiation of *(P,P)*-(*E*)-**2** at room temperature give rise to a PSS mixture of *(M,M)*-(*Z*)-**2** and *(P,P)*-(*E*)-**2**, which as reasoned above, would both induce the same helicity in **1**. The decrease in CD signal could be attributed to a somewhat lower inducing effect of *(M,M)*-(*Z*)-**2** compared to *(P,P)*-(*E*)-**2**.¹⁹ The photoisomerization of *(P,P)*-(*E*)-**2** to PSS would therefore result in a small decrease, but not in an inversion of the CD signal of **1**.

These combined results show that the photoswitchable chirality of a dopant can be transferred to dynamic helical polymers via non-covalent interactions. Moreover, the helicity could be inverted *in situ* using light as stimulus. These results pave the way for the development of functional supramolecular assemblies using the combined strength of



Scheme 3: Changes in helical chirality of **1** upon switching of the photoresponsive chiral dopant **2**. (*P,P*)-(Z)-**2** and (*P,P*)-(E)-**2** induce an opposite helicity in **1**. Upon irradiation different behavior is observed. In the case of **1** doped with (*P,P*)-(Z)-**2** an inversion of helicity is achieved, while in the case of **1** doped with (*P,P*)-(E)-**2** no inversion is observed.

functional dynamic helical polymers, and the photoaddressable chirality of overcrowded chiral alkenes. Further research focuses on the development of dynamic helical polymers which functions, such as their templating abilities or its catalytic properties can be controlled via non-covalently bound molecular motors.

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- When an irradiated sample was left over several hours, it was found that both the CD as UV absorptivity decreased, indicative of degradation of **1** due to the exposure to UV light.
- This cannot be unequivocally determined, as (*M,M*)-(Z)-**2** cannot be isolated.
- This is consistent with the fact that (*P,P*)-(E)-**2** is more efficient in the chirality transfer to **1** compared to (*P,P*)-(Z)-**2**.