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Unidirectional rotary motion in achiral molecular motors

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1. Introduction

1.1. Artificial molecular motors

- Mimicking the dynamic and mechanical functions of complex biological motor systems.
  (*e.g.* ATP-synthase rotary motor, muscle linear motor *etc.*)

- The basic requirements for any successful design of a rotary molecular motor:
  - **(i) rotary motion**
  - **(ii) energy consumption**
  - **(iii) unidirectional rotation**

  (i), (ii) → Achieved by a combination of photochemical *E-Z* isomerization (PEZ) and thermal helical inversion (THI). (*Figure* 1)[1,2]
- The key of molecular design to performing mechanical tasks:

"How to control over the unidirectionality of rotary motion?"

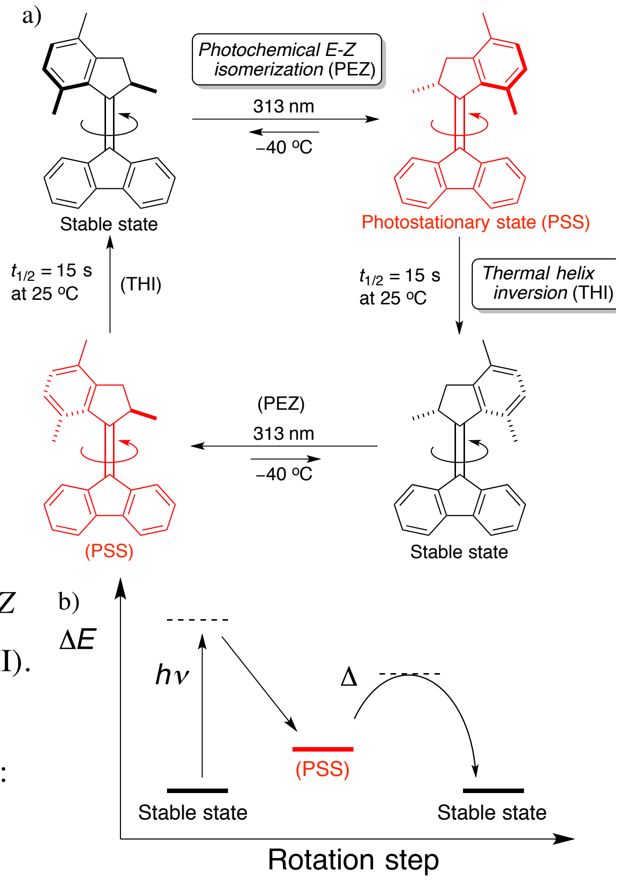

***Fig.* 1** The mechanism of rotary motion of molecular motor **1** through PEZ and THI.[1,2]

1.2. Conventional light-driven molecular motors

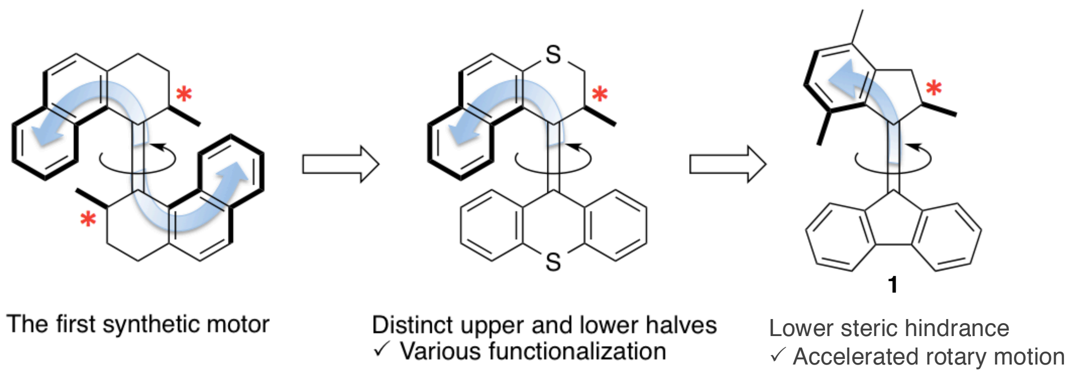

***Fig.* 2** The transition of light-driven molecular motors.[1,3]

- **The point chirality of the motors** transferred to helical chirality has been an essential feature to induce unidirectional rotation.

➡ ***"Is chirality really necessary for autonomous directional rotary motion?"***

"Can unidirectional rotary function be achieved with an achiral molecule?"

1.3. This work

- Investigation of achiral molecular motors in the presence of a pseudo-asymmetric carbon atom.

2. Theoretical design of the achiral molecular motors

- Loss of chirality but maintaining a pseudo-asymmetric carbon (C2 in *Figure* 3) by merging two enantiomers of a motor **1**.

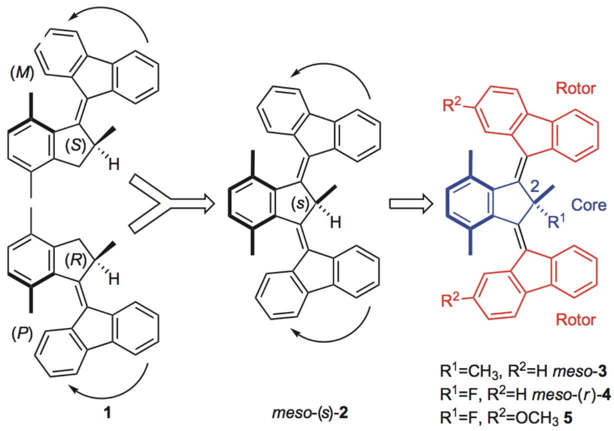

***Fig.* 3** The Design of an achiral molecular motors.

- Attaching two different-sized substituents on a pseudo-asymmetric carbon to provide a difference in energy between two possible meso isomers.

➡ The meso isomer having lower energy is formed preferentially, which enables unidirectional rotation. (In case of **4**, *meso*-(*r*)-**4** is preferred.)

➡ *meso*-**3** would not demonstrate unidirectional rotation.

➡ At least, **Some chiral information in the form of pseudo-assymmetry** is necessary to achieve unidirectional rotation.

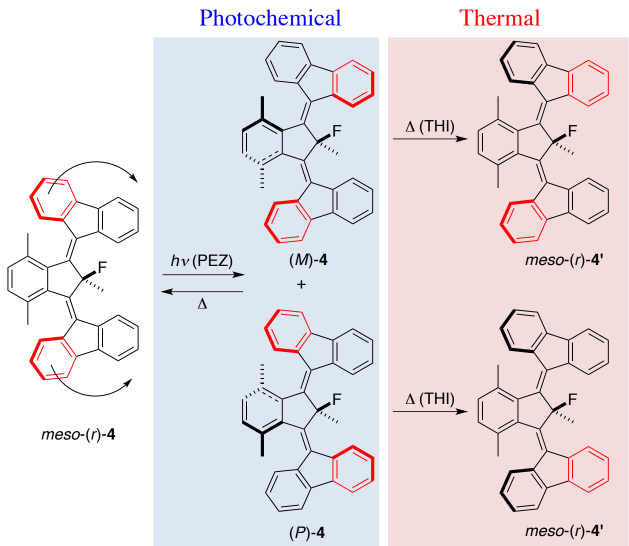

***Fig.* 4** Rotational behaviour of **4**.

(*meso*-(*r*)-**4** = *meso*-(*r*)-**4'**)

- Making the rotors asymmetry in order to identify a single PEZ-THI sequence and prove the unidirectionality in the rotary motion (motor **5**).

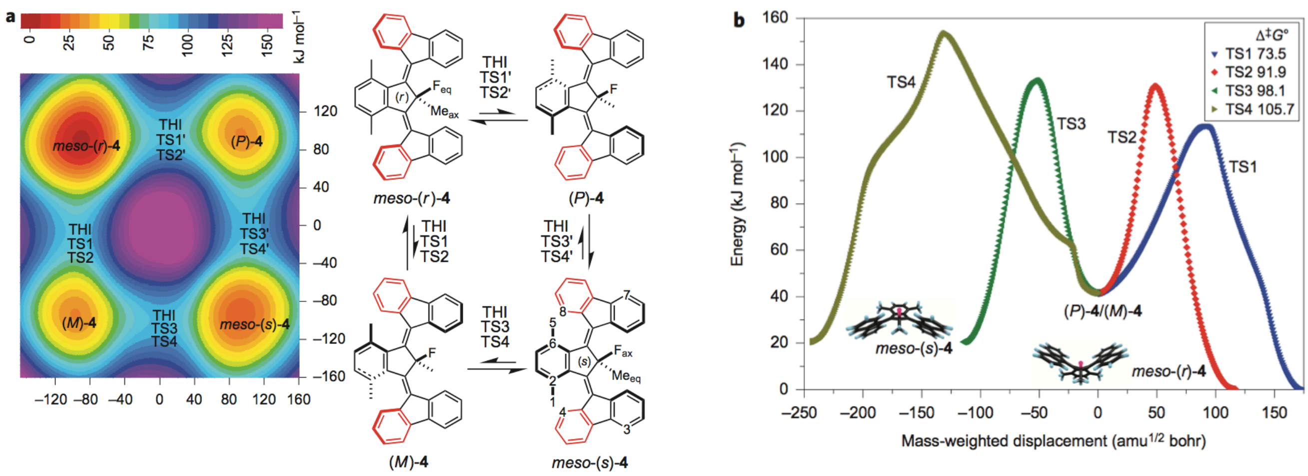

***Fig.* 5** Calculated thermal behavior of **4**. **a**, Potential energy surface (PES) of the ground state of 4 (PM6; x axis: 1-2-3-4 dihedral angle (in degrees); y axis: 5-6-7-8 dihedral angle (in degrees)). **b**, Intrinstic reaction coordinates were calcurated for all THIs (DFT B3LYP/6-31G(d,p)).

3. Result and discussion

3.1. Demonstration of unidirectional rotation: motor 4

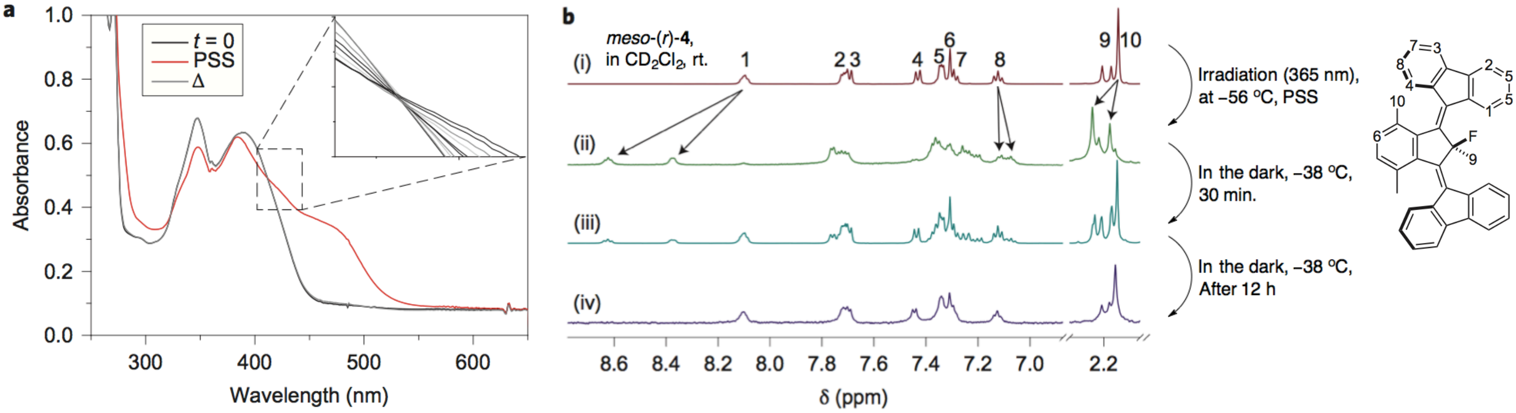

Fig. 6 Photochemical and thermal isomerization processes of **4**. **a**, UV-Vis absorption spectrum of **4** (t = 0: in CH_2Cl_2, at rt.; irradiation (365 nm) to PSS at –80 °C, then warming to rt.) **b**, ^{1}H-NMR spectra of meso-(r)-4 with proton assignment (in CD_2Cl_2).

- Irradiation (365 nm) was accompanied by…

  (i) a bathochromic shift in UV-Vis spectrum (*Figure* 6a)

  (ii) The loss of equivalence between two rotors in ^{1}H-NMR spectra (*Figure* 6b, H1 and H8).

➡ An increase in alkene strain and the loss of C_S symmetry because of isomerization to (*P*)-**4**/(*M*)-**4**.
(*meso*-(*r*)-**4**:(*P*)-**4**/(*M*)-**4** = 7.5:92.5 in PSS; estimated from ^{1}H-NMR, *Figure* 6b(ii))

- An isosbestic point in the same wavelength (412 nm) and full reversal to the original spectrum were observed during both photochemical and thermal process (*Figure* 6a).

➡ The absence of formation of *meso*-(*s*)-**4**.

- Increasing the temperature after reaching PSS, *meso*-(*r*)-**4’** was observed (*Figure* 6a, *Figure* 6b (iv))

➡ The unidirectional rotation of **4** (*Figure* 3) is strongly suggested **(unproven)**.

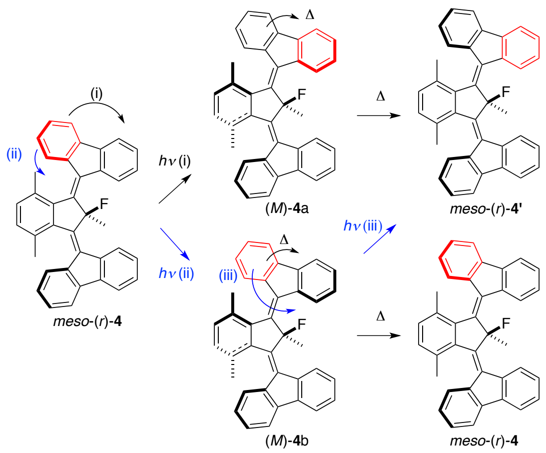

Fig. 7 The possible routes of rotation.

3.2. The proof of the unidirectionality of rotation

- Three possible routes of rotation (*Figure* 7):

  (i) *meso*-(*r*)-**4** → photoisomerization(i) → (*M*)-**4**a → THI → *meso*-(*r*)-**4’**

  (ii) *meso*-(*r*)-**4** → photoisomerization(ii) → (*M*)-**4**b → THI → *meso*-(*r*)-**4**

  (iii) *meso*-(*r*)-**4** → photoisomerization(ii) → (*M*)-**4**b → photoisomerization(iii) → *meso*-(*r*)-**4’**

- In PSS, (*P*)-**4**/(*M*)-**4** is a major isomer. (*meso*-(*r*)-**4**:(*P*)-**4**/(*M*)-**4** = 7.5:92.5)

➡ Photoisomerization stops at (*P*)-**4**/(*M*)-**4** and another photo-isomerization to *meso*-(*r*)-**4'** does not proceed. (Route (iii) is denied.)

- In case of **5**, (*r*,*Z*,*Z*)-**5** and (*r*,*E*,*E*)-**5** were produced through a sequence of PEZ and THI (*Figure* 8).

➡ If the rotation proceeds through route (ii), only (*R*,(*Z*,*M*),(*E*,*P*))-**5** (corresponding to *meso*-(*r*)-**4** in *Figure* 7) would be observed. (Route (ii) is denied.)

➡ Rotation proceeds through route (i) (**The unidirectionality of rotation is proved.**)

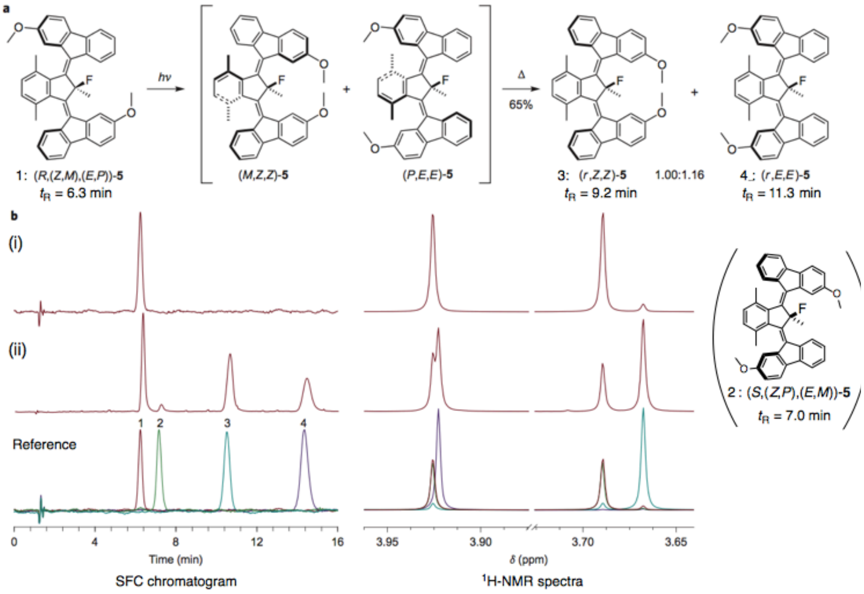

***Fig.* 8** Unidirectional rotation of (*R*,(*Z*,*M*),(*E*,*P*)-**5**. **a**, a PEZ-THI sequence of (*R*,(*Z*,*M*),(*E*,*P*))-**5**. **b**, SFC chromatogram and ^{1}H-NMR spectra. (i): isolated (*R*,(*Z*,*M*),(*E*,*P*))-**5**; (ii): mixture after irradiation (365 nm, 3 h, −100 °C, in CH_2Cl_2), directly followed by thermal isomerization(in the dark, 1 h, rt); Reference: superimposition of all isolated isomers of **5**.

- The products of each PEZ-THI sequence will keep rotating unidirectionally following the absorption of another photon.

➡ Achiral motor undergoes sequential rotation upon irradiation with UV light at room temperature.

4. Conclusion

- Unidirectional rotary motion is achieved in achiral molecular motors possessing C_s symmetry.
- Molecular chirality (permanent point chirality) is not required for unidirectional rotation.
- Some chiral information such as **a pseudo-asymmetric carbon atom with two substituents of distinct size** is necessary in the structure of an achiral molecular motor to achieve unidirectional rotary motion.

5. Reference

1. Pollard, M. M.; Meetuma, A.; Feringa, B. L.; *Org. Biomol. Chem.* **2008**, *6*, 507–512.
2. Leigh, D. A.; Zerbetto, F.; Kay, E. R.; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191.
3. Koumura, N.; Geertsema, E. M.; van Gelder, M. B.; Meetuma, A.; Feringa, B. L.; *J. Am. Chem. Soc.* **2002**, *124*, 5037–5051.