

UC Berkeley

UC Berkeley Previously Published Works

Title

Dynamically Chiral Expanded Helicenes

Permalink

<https://escholarship.org/uc/item/0mk6p6qs>

Journal

Journal of the American Chemical Society, 147(49)

ISSN

0002-7863

Authors

Rothenberger, August J

Park, Inji

Kiel, Gavin R

et al.

Publication Date

2025-12-10

DOI

10.1021/jacs.5c19964

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Dynamically Chiral Expanded Helicenes

August J. Rothenberger, Inji Park, Gavin R. Kiel, and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

ABSTRACT: Expanded helicenes are a class of chiral nanographenes with a screw-shaped skeleton and a larger diameter than their classical ortho-fused counterparts. The flexibility of this internal cavity results in helicenes that are often difficult to isolate as single enantiomers. Expanded helicenes are therefore an intriguing target for exploration of dynamic chirality, a phenomenon resulting from introduction of chiral auxiliaries to control structure in a racemic system. This contribution describes installation of chiral amine substituents into the cavity of a diformyl expanded [11]-helicene by mild, efficient, and reversible imine condensations. The resulting helicenes display strong molar circular dichroism up to $|\Delta\epsilon| = 300 \text{ M}^{-1}\text{cm}^{-1}$ and absorption dissymmetry factors of $|g_{\text{abs}}| = 0.010$. The magnitude of circular dichroism can be varied by using different chiral amine substituents, which is correlated to the diastereomeric ratios of the helicenes. This is the first instance of dynamic chirality being used to observe a chiroptic response in expanded helicenes and is a significant synthetic improvement over methods which require conventional enantiomer resolution.

Introduction

Chiral polycyclic aromatic hydrocarbons (PAHs) represent an intriguing space within the field of soft organic materials. The prototypical chiral PAH is a classical helicene, with ortho-fused conjugated rings forming a screw-shaped skeleton with (*M*)- and (*P*)-enantiomers of opposite handedness.^{1–3} The extended conjugated π -system within a chiral molecule results in a variety of useful properties, the preeminent of which is the absorption and emission of polarized light, particularly for visible wavelengths.^{4,5} Helicenes find uses in various fields, including optoelectronics,⁶ asymmetric catalysis,⁷ and chiroptical devices such as photonic transistors,⁸ and switches,⁹ and spin filters.^{10–12}

In 2017, this research group introduced expanded helicenes as a broad new class of helicenes, possessing a wider diameter than classical helicenes due to the combination of linear fusion elements along with the traditional angular fusion of classical helicenes (Figure 1a).¹³ The resulting structures display unprecedented supramolecular properties due to their increased flexibility,^{14–17} often at the expense of rapid racemization of enantiomers. Expanded [11]-helicenes have very low enantiomerization barriers, typically $\Delta G^\ddagger \approx 10 \text{ kcal/mol}$, as the arms of the helicene

have little steric hinderance prohibiting them from moving past one another.¹⁵ One feature of the larger helical diameter is the potential for installation of substituents in the helicene cavity, a strategy which has successfully raised the barrier to enantiomerization in examples such as Toyota's anthracenyl helicenes¹⁸ and Alcarazo's "in-fjord" substituted helicenes (Figure 1b).¹⁹ However, the prevailing method for synthesis of expanded helicene enantiomers that are resistant to racemization has been to increase the number of aromatic rings in the backbone, generating carbohelicenes with as many as 35 rings.^{17,20–23} While these methods have generated helicenes with remarkable dissymmetry factors, they often require many steps, have low overall yields, and require separation of enantiomers by chiral high-performance liquid chromatography, a slow and scale-limiting process.

An alternative approach for the incorporation of a chiroptical response, without traditional enantiomer purification, involves the introduction of dynamic chirality. Axial chirality can be induced into racemic helical systems by addition of a chiral auxiliary that leads to a difference in energy between the helicene's (*M*)- and (*P*)-group states.^{24–26} This strategy has been used with success in Nuckolls' synthesis of dynamically

chiral perylene diimide-based twistacenes.^{27–29} Notably, the circular dichroism response of the twistacenes could be inverted by appending a substituent with the opposite chirality. Expanded helicenes, with large internal cavities combined with their significant flexibility, also represent a promising platform for installation of chiral auxiliaries.

This contribution describes a diformyl-substituted, expanded [11]-helicene that readily undergoes in-cavity derivatizations. Reactions of the formyl groups with chiral aryl amines are rapid, mild, and high yielding. The resulting helicenes display remarkable chiroptical properties considering their relatively short length, with molar circular dichroic absorption values of $|\Delta\epsilon| = 300 \text{ M}^{-1}\text{cm}^{-1}$

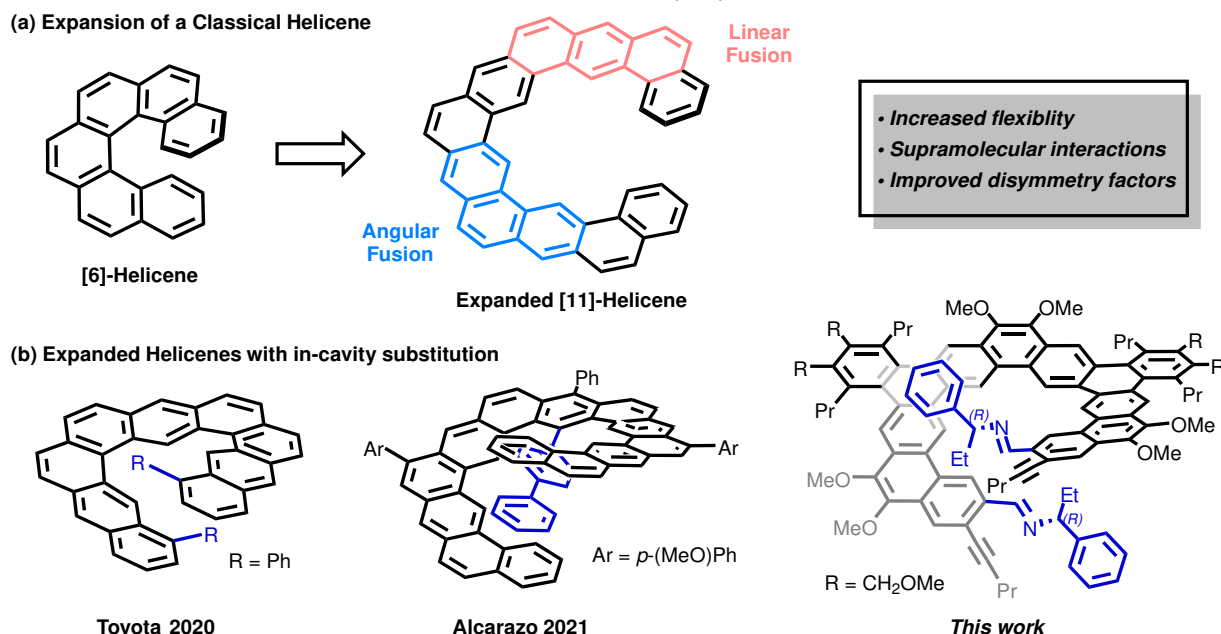


Figure 1. (a) Classical [6]-helicene compared to expanded [11]-helicene; (b) Expanded helicenes with in-cavity substitutions highlighted in blue

and absorption dissymmetry factors up to $|g_{\text{abs}}| = 0.010$. These are the first ECD spectra recorded for expanded [11]-helicenes, as substitution with achiral bulky groups has not proven successful for isolation of enantiomers. Additionally, the magnitude of circular dichroism can be influenced by the appended, chiral substituent. The new helicenes were cast as thin films that retain their chiroptical properties, presenting opportunities for device fabrication.

Results and Discussion

An in-cavity dibrominated expanded [11]-helicene was prepared in a manner similar to that for the nonfunctionalized variant (Scheme 1). Precursor 2,7-dibromo-9,10-dimethoxy-3,5-dipentynyl-phenanthrene **1** was dilithiated and then treated with iodine to generate phenanthrene **2**. Compound **1** was then monolithiated and treated with ZnCl_2 before being utilized in a Negishi coupling with **2** to generate **3**. An iridium catalyzed, diyne selective [2+2+2] cycloaddition³⁰ with 1,4-dimethoxybut-2-yne was then used to give **4** in good yields on a gram scale.

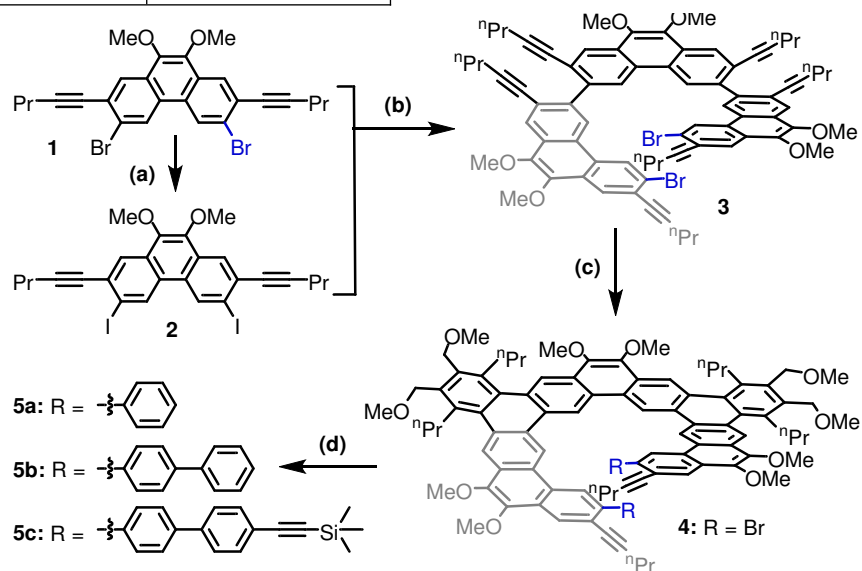
An initial goal for stabilization of enantiomers, starting from helicene **4**, involved installation of bulky groups on the helicene arms to raise the barrier for enantiomerization. A Negishi coupling with $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ as catalyst was used to install phenyl (**5a**), 1,1'-biphenyl (**5b**), and 4'-(trimethylsilylethynyl)-1,1'-biphenyl (**5c**) groups in the cavity of the helicene with decreasing yields as the substituent increased in size. Larger groups such as pyrenyl or *p*-quaterphenylene could not be coupled onto the [11]-helicene in yields sufficient for purification attempts. The $\Delta G^\ddagger$ values for racemization of helicenes **5a-c** in toluene-*d*₈ were measured by variable temperature ¹H NMR spectroscopy, as described in previous studies,^{15,31} using the methylene protons on the MeOCH_2 - substituents for determination of the coalescence temperature. Further information regarding the experimental setup and calculations is included in the SI (page S49). The measured barriers, summarized in Table 1 and compared to that for **4**, indicate that none of these helicenes are stable to racemization at room temperature. It would appear that steric pressure from the helicene end groups may to some degree facilitate enantiomerization by

forcing the helicene “arms” apart in the transition state.³²

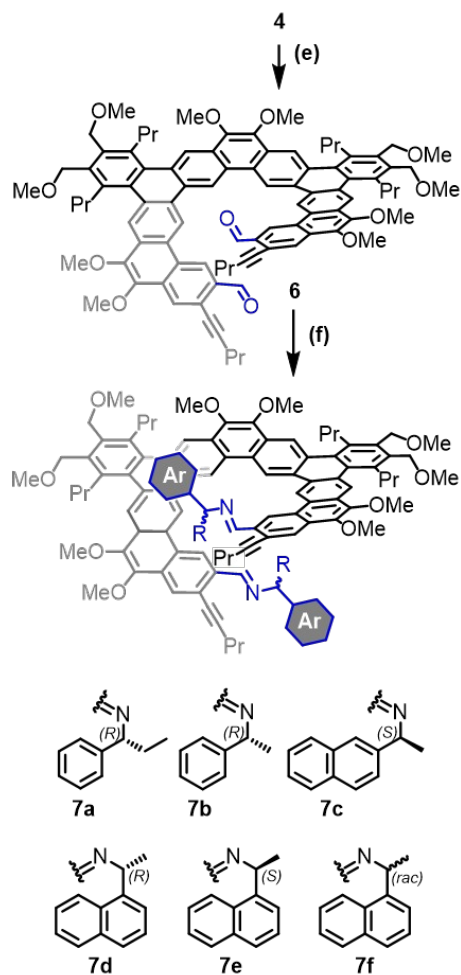
Table 1. Comparison of Helicene Enantiomerization Barriers

Helicene	$\Delta G^\ddagger_{(T_c)}$ (kcal/mol) by VT ^1H NMR	Coalescence Temperature, T_c (K)
----------	---	--

4	< 11.9	< 243
5a	15.7 ± 0.3	318
5b	18.4 ± 0.3	368
5c	> 18.8	> 373



Scheme 1. Synthesis of in-cavity substituted expanded [11]-helicenes. Reagents and conditions: (a) 2.2 equiv. $^n\text{BuLi}$, 2.5 equiv. I_2 , THF, -78 to 23 °C, 4 h, 74%. (b) 2.6 equiv. **1**, 2.4 equiv. $^n\text{BuLi}$, 2.9 equiv. ZnCl_2 , then 1.0 equiv. **2**, 0.1 equiv. $\text{Pd}(\text{PPh}_3)_4$, THF, -78 to 23 °C, 6 h, 64%. (c) 5.0 equiv. 1,4-dimethoxy-2-butyne, 0.1 equiv. $[\text{Ir}(\text{COD})\text{Cl}]_2$, 0.2 equiv. diphenylphosphinoethylene, toluene, 90 °C, 2 h, 77%. (d) 4.0 equiv. aryl zinc chloride solution, 0.1 equiv. $\text{Pd}(\text{P}^t\text{Bu}_3)_2$, THF, 60 °C, 18 h, 86-69%.



Scheme 2. Substitution of expanded [11]-helicenes with chiral amines. Reagents and conditions: (e) 2.5 equiv. n BuLi, 10 equiv. DMF, water, THF, -78 to 23 $^{\circ}$ C, 2 h, 82%. (f) 2.2 equiv. amine, THF, 90-95%.

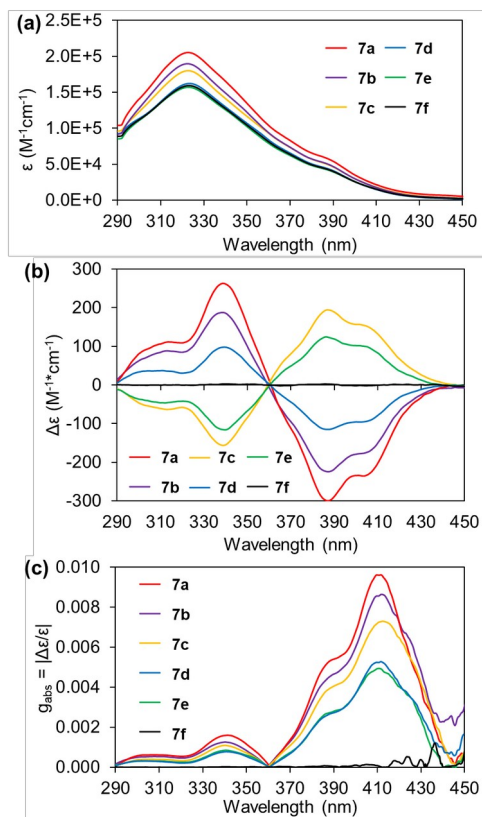


Figure 2. Photophysical spectra for helicenes **7a-f** in chlorobenzene. (a) absorption; (b) ECD; (c) absorption dissymmetry factor

The rapid enantiomerization of [11]-helicenes with in-cavity substituents indicated that non-covalent locking strategies are of limited use for such flexible helicene cores. However, this observation led to consideration of

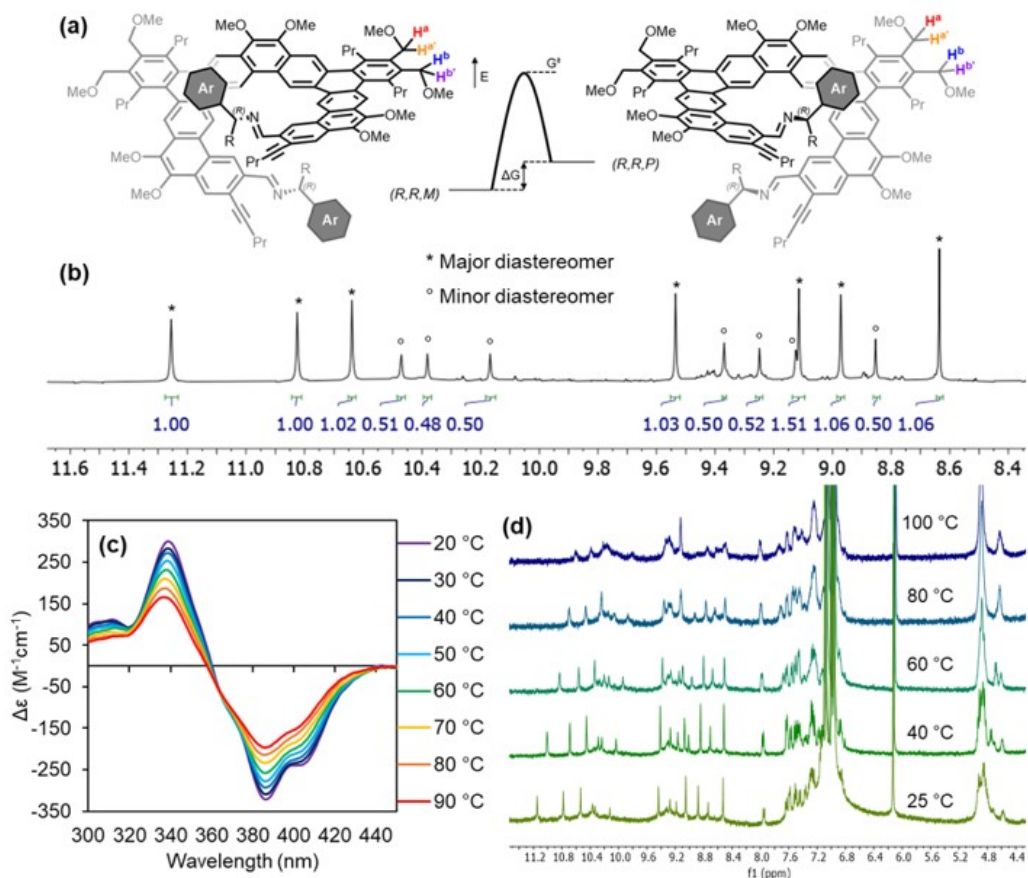


Figure 3. (a) Demonstration of enantiomerization barrier and non-degenerate group states for general diastereomers of **7**; (b) Diastereomers of **7d** visible by ^1H NMR (500 MHz, benzene- d_6); (c) attenuation of ECD spectra for **7a**; (d) variable temperature ^1H NMR (500 MHz, toluene- d_8) for **7d** demonstrating diastereomer coalescence.

[11]-helicenes as promising platforms for dynamic chirality. First, a diformyl helicene **6** was synthesized from **4** by the Bouveault reaction (Scheme 2). Then, a series of chiral arylamines were attached to the helicene by mild, rapid imine condensation reactions to generate **7a-f**. The isolated yields of these reactions were nearly quantitative after stirring for 30 minutes in THF at room temperature, and purification consisted of simply washing the product with methanol to remove unreacted amine. These reactions are reversible, and treatment of the imine species **7a-f** with a mild acid such as saturated NH_4Cl resulted in regeneration of helicene **6** (see SI Page S63).

These expanded [11]-helicene products display a chiroptical response that is apparent in electronic circular dichroism (ECD) spectra. The helicenes display a positive Cotton effect for those substituted with an (*R*)-amine-**7a**, **7b**, **7d**-and a negative Cotton effect for those with (*S*)-amines, **7c** and **7e**, (Figure 2b). Racemic sample **7f** did not display such a response. The magnitude of molar circular dichroism ($\Delta\epsilon$) for **7a-e** ranges from $100 \text{ M}^{-1}\text{cm}^{-1}$ to as high as $300 \text{ M}^{-1}\text{cm}^{-1}$ at 388 nm in chlorobenzene. The

maximum molar absorptivity of **7a-f** is more unified, $1.59 \times 10^5 < \epsilon < 2.05 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ at 323 nm in the same solvent conditions (Figure 2a). The absorption dissymmetry factors $|g_{\text{abs}}|$ were subsequently calculated to be as high as 0.010 at their peak of 412 nm (Figure 2c). There exists a solvent dependence for ECD response, whereby the helicenes showcase the highest $\Delta\epsilon$ in benzene, chlorobenzene, carbon tetrachloride, and dichloromethane. While aromatic solvents generally gave the best results, there does not appear to be a distinct trend between solvent dielectric or dipole moment and $\Delta\epsilon$ magnitude (see SI page S22).

Helicenes **7a-f** displayed similar photoluminescence properties with two emission peaks at 450 and 475 nm. The peak excitation wavelength was 330 nm for emission at 450 nm. The average fluorescence lifetime was 9.62 ns with an average quantum yield of 3.2%. Further details regarding photoluminescence study are provided in the SI (page S20). Circularly polarized luminescence (CPL) spectra acquisition was attempted but very weak signal was observed, even at long acquisition times. An emission intensity experiment showed an

89% loss in intensity for a 5×10^{-6} M sample after excitation for 14 hours (Figure S7). This photobleaching effect has complicated further study of CPL. Increasing the sample concentration has provided slightly more defined spectra which suggests a CPL response (Figure S8), but further experimentation is ongoing in this area.

According to the principles of dynamic chirality, helicenes **7a-f** exist in solution as diastereomers which can rapidly interconvert. With an (*R*)-amine, the diastereomers are (*R,R,M*) and (*R,R,P*) and have non-degenerate ground state energies, such that one diastereomer will be present in a larger amount (Figure 3a). The diastereomeric pairs are visible in the ^1H NMR spectra, most notably for naphth-1-yl amines in **7d** and **7e** (Figure 3c). In general, the diastereomeric ratio for the helicenes positively correlates with the magnitude of their ECD response (See SI page S60). Installation of a racemic amine leads to observation of two new diastereomers, (*R,S,M*) and (*R,S,P*). Upon heating a sample of **7d** in toluene- d_8 , the ^1H NMR resonances for the diastereomers coalesce, indicating more rapid enantiomerization at the increased temperature (Figure 3d). Additionally, the magnitude of the ECD response was attenuated by heating, as shown in Figure 3c for **7a**, demonstrating that rapid enantiomerization lowers the chiral response.

The mild conditions used to generate the imine helicenes have important implications for potential applications in devices. The helicenes are very amenable to processing and fabrication, since they are readily spun- or drop-cast onto glass slides from solution, with retention of their ECD response (Figure 4a). The ECD responses for thin films are red-shifted with respect to those in solution, possibly due to helicene J-aggregation in the solid-state. Additionally, the imine condensation reaction is rapid enough to be observed by in-situ ECD. Figure 4b shows two separate ECD spectra of (*R*)-phenylpropylamine and **6**, neither of which exhibits circular dichroism between 360 to 440 nm. After addition of 50 μL of (*R*)-phenylpropylamine to a cuvette containing a solution of **6**, CD spectra were acquired at regular intervals, demonstrating the production of helicene product **7a** as the CD magnitude increases at 380 nm. Thus, this system acts as a simple detector, showing ECD response to detect the presence of the chiral amine in solution

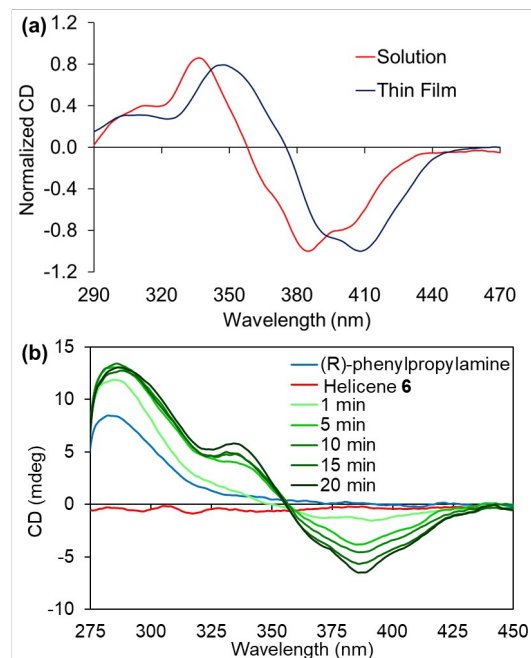


Figure 4. (a) Solid state ECD spectrum compared to solution state for **7b**; (b) In-situ ECD spectra demonstrating the generation of **7a** over time

Conclusion

The incorporation of dynamic chirality offers a scalable solution to the otherwise difficult resolution of expanded helicene enantiomers. The method developed for installation of chiral amines onto formylated expanded [11]-helicenes by imine condensation is a simple and effective way to induce a chiroptical response in a single and scalable step from a racemic precursor. The helicene ECD response can be tuned by the choice of chiral amines and the reaction is reversible, allowing for recovery of starting material if needed. Additionally, the ease of casting thin films which retain chiroptical properties indicates the potential for dynamic chirality to be useful for the high-throughput fabrication of devices.

ASSOCIATED CONTENT

Supporting Information. All data are available in the main text or the supplementary materials.

AUTHOR INFORMATION

Corresponding Author

*T. Don Tilley - Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States; orcid.org/0000-0002-6671-9099; Email: tdtalley@berkeley.edu

Authors

August J. Rothenberger - Department of Chemistry, University of California, Berkeley, Berkeley, California

94720, United States; orcid.org/0000-0002-6787-0727

Inji Park - Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States; <https://orcid.org/0009-0002-4639-938X>

Gavin R. Kiel – Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States; <https://orcid.org/0000-0001-6449-8547>

Author Contributions

The manuscript was written through contributions of all authors

Funding Sources

National Science Foundation grant CHE-2506019; Office of Science, Office of Basic Energy Sciences, United States

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was funded by the National Science Foundation under Grant No. CHE-2103696. The LBNL Catalysis Laboratory, led by Dr. Cooper Citek, provided photophysical instrumentation. The authors thank Dr. Hasan Celik, Dr. Raynald Giovine, and Pines Magnetic Resonance Center's Core NMR Facility (PMRC Core) for spectroscopic assistance. The instruments used in this work were supported by the PMRC Core. The authors would also like to acknowledge Nathalie Co and Harrison Bergman for thoughtful discussions during the assembly of this manuscript.

REFERENCES

- (1) Shen, Y.; Chen, C.-F. Helicenes: Synthesis and Applications. *Chem. Rev.* **2012**, *112* (3), 1463–1535. <https://doi.org/10.1021/cr200087r>.
- (2) Gingras, M. One Hundred Years of Helicene Chemistry. Part 1: Non-Stereoselective Syntheses of Carbohelicenes. *Chem. Soc. Rev.* **2013**, *42* (3), 968–1006. <https://doi.org/10.1039/C2CS35154D>.
- (3) Peng, L.-J.; Wang, X.-Y.; Li, Z.-A.; Gong, H.-Y. All Carbon Helicenes and π -Extended Helicene Derivatives. *Asian J. Org. Chem.* **2023**, *12* (12), e202300543. <https://doi.org/10.1002/ajoc.202300543>.
- (4) Nakai, Y.; Mori, T.; Inoue, Y. Theoretical and Experimental Studies on Circular Dichroism of Carbo[n]Helicenes. *J. Phys. Chem. A* **2012**, *116* (27), 7372–7385. <https://doi.org/10.1021/jp304576g>.
- (5) Gingras, M. One Hundred Years of Helicene Chemistry. Part 3: Applications and Properties of Carbohelicenes. *Chem. Soc. Rev.* **2013**, *42* (3), 1051–1095. <https://doi.org/10.1039/C2CS35134J>.
- (6) Xiao, X.; Pedersen, S. K.; Aranda, D.; Yang, J.; Wiscons, R. A.; Pittelkow, M.; Steigerwald, M. L.; Santoro, F.; Schuster, N. J.; Nuckolls, C. Chirality Amplified: Long, Discrete Helicene Nanoribbons. *J. Am. Chem. Soc.* **2020**. <https://doi.org/10.1021/jacs.0c11260>.
- (7) Sakamoto, D.; Gay Sánchez, I.; Rybáček, J.; Vacek, J.; Bednářová, L.; Pazderková, M.; Pohl, R.; Čísařová, I.; Stará, I. G.; Starý, I. Cycloiridated Helicenes as Chiral Catalysts in the Asymmetric Transfer Hydrogenation of Imines. *ACS Catal.* **2022**, *12* (17), 10793–10800. <https://doi.org/10.1021/acscatal.2c01816>.
- (8) Yang, Y.; da Costa, R. C.; Fuchter, M. J.; Campbell, A. J. Circularly Polarized Light Detection by a Chiral Organic Semiconductor Transistor. *Nat. Photonics* **2013**, *7* (8), 634–638. <https://doi.org/10.1038/nphoton.2013.176>.
- (9) Isla, H.; Crassous, J. Helicene-Based Chiroptical Switches. *Comptes Rendus Chim.* **2016**, *19* (1), 39–49. <https://doi.org/10.1016/j.crci.2015.06.014>.
- (10) Kettner, M.; Maslyuk, V. V.; Nürenberg, D.; Seibel, J.; Gutierrez, R.; Cuniberti, G.; Ernst, K.-H.; Zacharias, H. Chirality-Dependent Electron Spin Filtering by Molecular Monolayers of Helicenes. *J. Phys. Chem. Lett.* **2018**, *9* (8), 2025–2030. <https://doi.org/10.1021/acs.jpclett.8b00208>.
- (11) Kiran, V.; Mathew, S. P.; Cohen, S. R.; Hernández Delgado, I.; Lacour, J.; Naaman, R. Helicenes—A New Class of Organic Spin Filter. *Adv. Mater.* **2016**, *28* (10), 1957–1962. <https://doi.org/10.1002/adma.201504725>.
- (12) Kulkarni, C.; Mondal, A. K.; Das, T. K.; Grinbom, G.; Tassinari, F.; Mabesoone, M. F. J.; Meijer, E. W.; Naaman, R. Highly Efficient and Tunable Filtering of Electrons' Spin by Supramolecular Chirality of Nanofiber-Based Materials. *Adv. Mater.* **2020**, *32* (7), 1904965. <https://doi.org/10.1002/adma.201904965>.
- (13) Kiel, G. R.; Patel, S. C.; Smith, P. W.; Levine, D. S.; Tilley, T. D. Expanded Helicenes: A General Synthetic Strategy and Remarkable Supramolecular and Solid-State Behavior. *J. Am. Chem. Soc.* **2017**, *139* (51), 18456–18459. <https://doi.org/10.1021/jacs.7b10902>.
- (14) Nakakuki, Y.; Hirose, T.; Matsuda, K. Synthesis of a Helical Analogue of Kekulene: A Flexible π -Expanded Helicene with Large Helical Diameter Acting as a Soft Molecular Spring. *J. Am. Chem. Soc.* **2018**, *140* (45), 15461–15469. <https://doi.org/10.1021/jacs.8b09825>.
- (15) Kiel, G. R.; Bay, K. L.; Samkian, A. E.; Schuster, N. J.; Lin, J. B.; Handford, R. C.; Nuckolls, C.; Houk, K. N.; Tilley, T. D. Expanded Helicenes as Synthons for Chiral Macrocyclic Nanocarbons. *J. Am. Chem. Soc.* **2020**, *142* (25), 11084–11091. <https://doi.org/10.1021/jacs.0c03177>.
- (16) Samkian, A. E.; Kiel, G. R.; Jones, C. G.; Bergman, H. M.; Oktawiec, J.; Nelson, H. M.; Tilley, T. D. Elucidation of Diverse Solid-State Packing in a Family of Electron-Deficient Expanded Helicenes via Microcrystal Electron Diffraction (MicroED). *Angew. Chem. Int. Ed.* **2021**, *60* (5), 2493–2499. <https://doi.org/10.1002/anie.202012213>.
- (17) Fujise, K.; Tsurumaki, E.; Wakamatsu, K.; Toyota, S. Construction of Helical Structures with Multiple Fused Anthracenes: Structures and Properties of Long Expanded Helicenes. *Chem. – Eur. J.* **2021**, *27* (14), 4548–4552. <https://doi.org/10.1002/chem.202004720>.

- (18) Fujise, K.; Tsurumaki, E.; Fukuhara, G.; Hara, N.; Imai, Y.; Toyota, S. Multiple Fused Anthracenes as Helical Polycyclic Aromatic Hydrocarbon Motif for Chiroptical Performance Enhancement. *Chem. – Asian J.* **2020**, *15* (16), 2456–2461. <https://doi.org/10.1002/asia.202000394>.
- (19) Suárez-Pantiga, S.; Redero, P.; Aniban, X.; Simon, M.; Golz, C.; Mata, R. A.; Alcarazo, M. In-Fjord Substitution in Expanded Helicenes: Effects of the Insert on the Inversion Barrier and Helical Pitch. *Chem. – Eur. J.* **2021**, *27* (53), 13358–13366. <https://doi.org/10.1002/chem.202102585>.
- (20) Kiel, G. R.; Bergman, H. M.; Samkian, A. E.; Schuster, N. J.; Handford, R. C.; Rothenberger, A. J.; Gomez-Bombarelli, R.; Nuckolls, C.; Tilley, T. D. Expanded [23]-Helicene with Exceptional Chiroptical Properties via an Iterative Ring-Fusion Strategy. *J. Am. Chem. Soc.* **2022**. <https://doi.org/10.1021/jacs.2c09555>.
- (21) Toya, M.; Omine, T.; Ishiwari, F.; Saeki, A.; Ito, H.; Itami, K. Expanded [2,1]*n*Carbohelicenes with 15- and 17-Benzene Rings. *J. Am. Chem. Soc.* **2023**, *145* (21), 11553–11565. <https://doi.org/10.1021/jacs.3c00109>.
- (22) Huo, G.-F.; Fukunaga, T. M.; Hou, X.; Han, Y.; Fan, W.; Wu, S.; Isobe, H.; Wu, J. Facile Synthesis and Chiral Resolution of Expanded Helicenes with up to 35 Cata-Fused Benzene Rings. *Angew. Chem. Int. Ed.* **2023**, *62* (18), e202218090. <https://doi.org/10.1002/anie.202218090>.
- (23) Zheng, W.; Ikai, T.; Oki, K.; Yashima, E. Consecutively Fused Single-, Double-, and Triple-Expanded Helicenes. *Nat. Sci.* **2022**, *2* (2), e20210047. <https://doi.org/10.1002/ntls.20210047>.
- (24) Wu, J.-H.; Fang, S.; Zheng, X.; He, J.; Ma, Y.; Su, Z.; Wang, T. Organocatalytic Dynamic Kinetic Resolution Enabled Asymmetric Synthesis of Phosphorus-Containing Chiral Helicenes. *Angew. Chem. Int. Ed.* **2023**, *62* (49), e202309515. <https://doi.org/10.1002/anie.202309515>.
- (25) Weiss, C.; Sharapa, D. I.; Hirsch, A. Coronohelicenes with Dynamic Chirality. *Chem. – Eur. J.* **2020**, *26* (62), 14100–14108. <https://doi.org/10.1002/chem.202001703>.
- (26) Xiao, X.; Cheng, Q.; Bao, S. T.; Jin, Z.; Sun, S.; Jiang, H.; Steigerwald, M. L.; Nuckolls, C. Single-Handed Helicene Nanoribbons via Transfer of Chiral Information. *J. Am. Chem. Soc.* **2022**, *144* (44), 20214–20220. <https://doi.org/10.1021/jacs.2c09288>.
- (27) Bao, S. T.; Jiang, H.; Schaack, C.; Louie, S.; Steigerwald, M. L.; Nuckolls, C.; Jin, Z. Remote Control of Dynamic Twistacene Chirality. *J. Am. Chem. Soc.* **2022**. <https://doi.org/10.1021/jacs.2c08323>.
- (28) Bao, S. T.; Louie, S.; Jiang, H.; Jiang, Q.; Sun, S.; Steigerwald, M. L.; Nuckolls, C.; Jin, Z. Near-Infrared, Organic Chiroptic Switch with High Dissymmetry Factors. *J. Am. Chem. Soc.* **2024**, *146* (1), 51–56. <https://doi.org/10.1021/jacs.3c10578>.
- (29) Jiang, H.; Čavlović, D.; Jiang, Q.; Ng, F.; Bao, S. T.; Telford, E. J.; Steigerwald, M. L.; Roy, X.; Nuckolls, C.; McNeill, J. M. Spin Filtering with Surface-Active Helicene- and Twistacene-Based Perylene Diimides. *J. Am. Chem. Soc.* **2025**. <https://doi.org/10.1021/jacs.5c02723>.
- (30) Kiel, G. R.; M. Bergman, H.; Don Tilley, T. Site-Selective [2 + 2 + *n*] Cycloadditions for Rapid, Scalable Access to Alkynylated Polycyclic Aromatic Hydrocarbons. *Chem. Sci.* **2020**, *11* (11), 3028–3035. <https://doi.org/10.1039/C9SC06102A>.
- (31) Rickhaus, M.; Jundt, L.; Mayor, M. Determining Inversion Barriers in Atrop- Isomers – A Tutorial for Organic Chemists. *Chim. Int. J. Chem.* **2016**, *70* (3), 192–202. <https://doi.org/10.2533/chimia.2016.192>.
- (32) Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. Total Syntheses of Angular [7]-, [8]-, and [9]Phenylene by Triple Cobalt-Catalyzed Cycloisomerization: Remarkably Flexible Heliphenes. *Angew. Chem. Int. Ed.* **2002**, *41* (17), 3227–3230. [https://doi.org/10.1002/1521-3773\(20020902\)41:17<3227::AID-ANIE3227>3.0.CO;2-T](https://doi.org/10.1002/1521-3773(20020902)41:17<3227::AID-ANIE3227>3.0.CO;2-T)

