Oxidative cyclo-rearrangement of helicenes into chiral nanographenes

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Nanographenes are emerging as a distinctive class of functional materials for electronic and optical devices. It is of remarkable significance to enrich the precise synthetic chemistry for these molecules. Herein, we develop a facile strategy to recompose helicenes into chiral nanographenes through a unique oxidative cyclo-rearrangement reaction. Helicenes with 7-9 ortho-fused aromatic rings are firstly oxidized and cyclized, and subsequently rearranged into nanographenes with an unsymmetrical helicoid shape through sequential 1,2-migrations. Such skeletal reconstruction is virtually driven by the gradual release of the strain of the highly distorted helicene skeleton. Importantly, the chirality of the helicene precursor can be integrally inherited by the resulting nanographene. Thus, a series of chiral nanographenes are prepared from a variety of carbohelicenes and heterohelicenes. Moreover, such cyclo-rearrangement reaction can be sequentially or simultaneously associated with conventional oxidative cyclization reactions to ulteriorly enrich the geometry diversity of nanographenes, aiming at innovative properties.
F
ing the impressive development of graphene mater-
ials, nanographenes with size limited in the nan-
ometer scale are currently emerging as prominent semicon-
ducting substances due to their open bandgap, which is
highly useful for electronic devices, energy storage, and
sensors. Conventional, nanographenes are prepared by frag-
mentation of relatively large-size carbon derivatives. Although
the fabrication procedures are normally simple and ready to scale
up, it is of enormous difficulty to make atomistically precise
products. To this end, “bottom-up” synthetic strategies are being
developed to construct nanographenes with accurate and well-
tunable molecular structures. Amongst, intramolecular cycliza-
tion of tailor-made dendritic oligophenylenes plays an indis-
pen
dential role as a result of its high conversion and broad
scope (Fig. 1a, left). This generally involves graphitization
through Scholl-type oxidative cyclization, photocyclization,
and HF zipping reactions. On the other hand, annulative π-
extension (APEX), alkyn benzannulation, and aryne cyclotrimerization
reactions, either by enlarging a polycyclic aromatic core or linking together aromatic fragments, are typical alternative pathways to complex nanographenes (Fig. 1a, right).

These advances have provided an access to a vast number of
nanographenes with relatively regular planar, curved, and helical
gometries. However, the synthesis of more sophisticated and distinct nanographenes remains a remarkable challenge as a consequence of the fact that most current reactions only allow the fusion of aromatic fragments into a larger system within a con-
stant geometry regime.

Helicenes are a type of chiral polycyclic aromatic molecules
constituted by ortho-fused benzenoid cycles. The distorted
sp2-carbon skeleton renders helicenes with relatively higher
chemical activities. Thus, helicenes undergo intramolecular
cyclization through Diels-Alder reaction into 3D bridge-ring
frameworks or deform into nearly planar structures through oxidative cyclization. Recent studies by scanning tunnel microscopy showed that the skeleton of helicene could transform on metal surfaces. This provides a unique portal to manipulate the aromatic skeletons and to construct nanographenes.

Herein, we aim to precisely harness the skeletal reconstruc-
tion of helicenes under a high-energy state generated by con-
trolled oxidation in solution (Fig. 1b). We report the formation of chiral nanographenes through enantio-persisting oxidative
cyclo-rearrangement of a variety of helicenes and study the
sketch transformation of the helicene precursors and the
properties of the resulting chiral nanographenes with the assistance of theoretical calculations. This is followed by the
extension of the aromatic structures through sequential or
simultaneous combination with conventional oxidative cycli-
ization reactions.

Results and discussion

Oxidative cyclo-rearrangement of carbohelicenes. It has been
reported previously that [5]helicene and [6]helicene derivatives
undergo Scholl cyclization upon oxidation and form planar or
negatively curved structures. Initially, we explored the oxidative reactions of primitive carbo[6]helicene 6H1 in the
presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)
and various acids (e.g., CF3COOH, H2SO4, CF3SO3H) (Fig. 2b
and Supplementary Table 1). However, all the attempts
ended with unreacted 6H1 or a mess of unidentifiable products,
indicating an uncontrollable oxidation process. Then, we shifted
our focus to carbo[8]helicene 8H1, a longer helicene with the two
ends fully overlapping with each other. Although the reactions
conducted under less acidic conditions (in the presence of
CF3COOH or CH3SO3H) led to similar undesired products, the
mixture containing triﬂic acid (CF3SO3H) predominantly
gave rise to a highly ﬂuorescent compound (O8H1, oxidized product
for 8H1) with a yield of 49% (Fig. 2b and Supplementary Table 1).
Mass spectrometry (Supplementary Fig. 1) indicated that
O8H1 possessed a C36H18 chemical formula with a loss of two
hydrogen atoms from the original precursor 8H1 (C36H20) and
1H NMR displayed a non-symmetric pattern other than the C2-
symmetric 8H1 (O8H1 revealed 18 1H signals, while 8H1 showed 10 1H signals due to the symmetry, Supplementary Figs. 2 and 28). X-ray diffraction of a single crystal further
conﬁrmed the formation of an unsymmetric chiral π-conjugated
system in which a benzo[ghi]perylen moiety was fused with a
[6]helicene skeleton (Fig. 2b). Further studies on the oxidation of
e nanopure 8H1 precursors showed that the helical chirality of
8H1 was integrally transferred to O8H1, where P-8H1 formed
exclusively-P-O8H1 and M-8H1 solely gave rise to M-O8H1
(Supplementary Fig. 96).

To gain more insights into this interesting oxidation reaction,
we introduced a variety of substituents on the helicene skeleton
and prepared 4-bromo, 4-fluoro, 4-triﬂuromethyl, 4-methyl and 5,6-diphenyl substituted carbo[8]
helicenes, namely, 8H1Br, 8H1F, 8H1C6F3, 8H1C6H3, and 8H12py
(Fig. 2c). After treated with DDQ and CF3SO3H, all these
precursors transformed into O8H1-like structures. 8H1F and
8H12py yielded a mixture of a structure (with the substituents
finally planted on the benzo[ghi]perylen side) and β structure
(substituents on the single-stranded helicoid side) with a ratio
of 9:1 and 3:1, respectively. On the other hand, 8H1C6F3
with a highly electron-withdrawing substituent formed a solely β
structure, while 8H1C6H3 and 8H12py with electron-donating
substituents only yielded a products.

Density functional theory (DFT) calculations on the possibly
involved intermediates and transition states indicated that the
above oxidation reaction may involve four major steps (Fig. 2d).
First, 8H1 undergoes an intramolecular oxidative cyclization
(between C1 and C20a) with the assistance of DDQ and CF3SO3H
and transforms into a cationic intermediate 8H1-IM1 with a
newly-formed hexagonal cycle in the center through either a
radical cation or an arenium cation pathway. Then, the
cationic 8H1-IM1 reforms into a spiro intermediate 8H1-IM2
through 1,2-migration to release the internal strain of the highly

Fig. 1 General synthetic strategies for nanographenes. a Traditional
cyclization and annulative expansion strategies. b Skeletal reconstruction
method developed in this work.
distorted structure. Subsequently, 8H-IM2 transforms into a helical cationic intermediate 8H-IM3 through a second 1,2-migration via a homoallylic transition state 8H-TS2. Notably, the migration might undergo through a homobenzylic pathway to afford a less crowded outward product but this is probably disfavored by relatively higher activation energy (Supplementary Fig. 104). Importantly, the helical chirality of 8H is integrally recorded by the spiro moiety in the first 1,2-migration and intactly recovered in the second 1,2-migration, thus keeping the memory of its chirality. Finally, deprotonation of cationic 8H-IM3 leads to the formation of a relatively stable neutral product O8H. It appears that the electron-withdrawing substituents destabilizes the initial cation and hence favor the formation of β structures, while the electron-donating substituents stabilized the cationic moiety and thus promote the formation of α structures.

**Fig. 2 Oxidative cyclo-rearrangement of carbo[8]helicenes.** a Cyclization of [5] and [6]helicene derivatives. b Oxidation of primitive 6H and 8H by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in various acidic conditions. The crystal structure of O8H is shown in thermal ellipsoid with a 30% probability. c Oxidative cyclo-rearrangement of substituted carbo[8]helicenes. d Proposed mechanism for the oxidative cyclo-rearrangement of 8H. Free energies are given in kcal mol\(^{-1}\) and the free energy of 8H is set as 0.
Further investigations showed that upon oxidation by DDQ in the presence of CF₃SO₃H, carbo[7]helicene 7H and carbo[9] helicene 9H also transformed into analogous structures, namely, O7H and O9H (Fig. 3a). Similarly, O9H efficiently inherited the absolute configuration of 9H (Supplementary Fig. 97). Notably, upon further treatment with DDQ and acid, O7H, O8H, and O9H subsequently transferred into more planar structures (Fig. 3a). O7H readily underwent a Scholl reaction to form a fully planar structure O07H (oxidized product of O7H, activation energy of the initial cyclization = +20.9 kcal mol⁻¹, Fig. 3b) like the [5]helicene derivatives. [6]helicene-like O8H experienced an unusual heptagonal cyclization via Scholl reaction24,30,31 and formed negatively curved O08H with twisted chirality (Fig. 5b)32,33. Calculations indicated that the formation of an irregular heptagon requires lower activation energy than an ordinary hexagon (+23.3 vs. +31.3 kcal mol⁻¹, Fig. 3b). Interestingly, [7]helicene-like O9H further transformed into a more π-extended structure O09H containing a coronene core and a [5] helicene moiety through a second oxidative cyclo-rearrangement under a weaker acidic condition (using CH₂Cl₂, 20 °C) and formed negatively curved O09H with twisted chirality (Fig. 5b)32,33. These molecules displayed blue to yellow emissions (Fig. 4e), and the enantiopure O8H and O9H products showed intense circularly polarized luminescence (CPL) with prominent dissymmetry factors g Scholl values36,37 of ±0.0055 and ±0.012, respectively (Fig. 4d).

Oxidative cyclo-rearrangement of heterohelicenes. Heteroatom-doping is an efficient and practical method to tailor the physical and chemical properties of polycyclic aromatic molecules38,39. To this end, we prepared sulfur-doped or/and nitrogen-doped methylthio[8]helicene 8Ha, aza[8]helicene 8Ha, and thioaza[8] helicene 8Hta. In a typical oxidative cyclo-rearrangement condition with one equivalent of DDQ, we observed that 8Hta transformed not only into an oxidized product 8Hta but also into a further oxidized product 8Hta (Fig. 5a). 8Hta showed an O8H-like structure with the thiophene cycle located at the single-stranded helicoid end, while 8Hta displayed a negatively curved feature caused by the heptagonal cycle. Due to the doping of sulfur, 8Hta revealed considerably bathochromic-shifted absorption and emission bands compared to O08H (Fig. 5b, c). 8Hta also transformed into the rearranged products 8Hta, and 8Hta respectively (Fig. 5d, e). It should be noted that protonation may occur to the nitrogen atoms, but obviously, this did not hinder the following oxidative cyclo-rearrangement, and the products can be neutralized by NaOH at the end. This protonation chemistry was further utilized to switch the chiroptical properties of enantiopure 8Hta (Supplementary Fig. 98, Fig. 5f, g), and remarkably the protonated product 8HtaH⁺ showed a

Fig. 3 Stepwise oxidations of 7H, 8H, and 9H. a Two-step oxidation of 7H. 8H, and 9H. b Possible cyclization processes following a radical cation mechanism and their activation energies (free energies of the corresponding transition states, TS, in kcal mol⁻¹). The free energies of the radical cation intermediates O7H⁺, O8H⁺, O9H⁺ are set as 0.
significantly bathochromic-shifted CPL compared to the neutral product O8H<sub>a</sub> (orange vs. green).

**Fabrication of more sophisticated nanographenes.** The oxidative cyclo-rearrangement reactions were ultimately associated with other reactions to fabricate more sophisticated nanographenes with distinctive geometries and properties. We first prepared an oligophenylene-like helicene derivative 6H<sub>DPT</sub> with a diphenyltriphenylene (DPT) group substituted on position 2 of 6H. Upon treatment with an excessive amount of DDQ in the presence of CF<sub>3</sub>SO<sub>3</sub>H, 6H<sub>DPT</sub> directly transformed to O6H<sub>DPT</sub> which showed a [6]helicene moiety fused to a slightly arched π-extended structure with a length of ca. 1.5 nm (Fig. 6a, b). This was probably generated by the formation of a [8]helicene moiety at first via Scholl cyclization followed by an oxidative cyclo-rearrangement at the more π-extended side. The highly extended π-system rendered O6H<sub>DPT</sub> with a strong absorption band around 490 nm and an intense greenish-yellow fluorescence around 510 nm (Fig. 6c). We also synthesized another bromo-substituted product O8H<sub>B</sub><sup>Br</sup> by treating 2-bromo[8]helicene (8H<sub>B</sub><sup>Br</sup>) with DDQ and CF<sub>3</sub>SO<sub>3</sub>H and subsequently fused it with a perylene diimide (PDI) moiety through boration and Suzuki coupling. Oxidative photocyclization of the resulting product O8H<sub>PDI</sub> finally afforded a dark brown product O8H<sub>PDI</sub> (Fig. 6d). Single-crystal analysis revealed that O8H<sub>PDI</sub> possessed a bilayer conjugated structure with the benzo[ghi]perylenyl and PDI moieties fused by a [8]helicene bridge (Fig. 6e). The two layers showed a typical AB stacking pattern with a short interlayer distance of 3.4 Å. The unsymmetrical bilayer structure presented a strong intramolecular charge transfer complexation with the HOMO located at the benzo[ghi]perylenyl layer and the LUMO at the PDI layer (Fig. 6g), leading to a broad absorption band from ca. 570 to 710 nm (Fig. 6f). Besides, the CO8H<sub>PDI</sub> molecules were found to be tightly piled up in the crystals with the PDI moiety of one molecule and the benzo[ghi]perylenyl fragment of the neighboring molecule.
packed in an AB stacking manner with a close distance of ca. 3.6 Å (Fig. 6e).

In summary, we have developed a distinctive oxidative cyclo-rearrangement method to reconstitute the skeleton of helicenes to precisely fabricate chiral nanographenes with unique topologies and absolute configurations integrally inherited from their helical precursors. The facile introduction of a variety of substituents at the periphery and heteroatoms in the aromatic core, along with the sequential oxidative cyclo-rearrangement reactions, have provided diverse access to a rich array of nanographenes. The flexible association with other conventional oxidative cyclization reactions has further allowed the designable fabrication of more sophisticated chiral nanographenes. Overall, this work demonstrates a unique route to activate and reform a highly distorted reservoir precursors together with controlled skeletal reconstruction reactions may open up an innovative pathway for future nanographene synthesis.

**Methods**

**Typical oxidative cyclo-rearrangement reaction.** 21.4 mg of 8H (0.05 mmol) and 13.6 mg of DDQ (0.06 mmol, 1.2 equiv.) were suspended in 20 mL of dried CH2Cl2 under argon at 20 °C, and 0.1 mL of CF3SO3H was added to the suspension dropwise with vigorous stirring. The mixture was stirred for 30 min and then quenched by 5 mL of saturated NaHCO3 aqueous solution. The mixture was extracted by CH2Cl2 and the organic layer was washed with water twice and dried over Na2SO4. The solvent was removed at reduced pressure and the residue was purified by silica column chromatography (heptane/CH2Cl2 = 10/1, v/v) to afford 8H as orange solid (10.5 mg, yield 49%).

**Theoretical calculations.** DFT calculations were carried out using Gaussian 09 program. Geometrical optimization calculations were carried out at the PBE0-D3/def2-SVP level without any symmetry assumptions unless otherwise stated. The Cartesian coordinates of the optimized geometries are provided in Supplementary Data 1. Harmonic vibration frequency calculations were performed at the same level for obtaining the thermodynamic energies and verifying the resulting geometries as local minima (with all the frequencies real) or saddle points (with only one imaginary frequency). The assignment of the saddle points was performed using the intrinsic reaction coordinate (IRC) calculations. Nucleus-independent chemical shifts (NICS) values were calculated at the GIAO-PBE0/def2-SVP level on the optimized structures. Time-dependent density functional theory (TD-DFT) calculations were performed at the PBE0-D3/def2-SVP level on the optimized geometries for the lowest 200 vertical singlet electronic excitations. No special shift or scaling was applied unless otherwise mentioned. Iso-surfaces of molecular orbitals (MOs) were drawn using the IQmol program with the isovalue set to 0.1. All calculations were performed under the SMD continuum solvent model for CH2Cl2.

**Data availability**

The authors declare that all the data supporting the findings of this study are available within the paper and Supplementary Information files, and also are available from the corresponding authors upon reasonable request. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 2049882 (9H), 2049080 (8HCTA), 2049081 (8FH1), 2049079 (7H), 2049136 (O7H), 2049140 (O8H).

**Fig. 5 Oxidative cyclo-rearrangement of hetero-atom-doped helicenes.** a Synthesis of sulfur-doped O8Hmt via oxidative cyclo-rearrangement of 8Hmt and further cyclization to O08Hmt. b UV-vis absorption and c fluorescence spectra of O08Hmt with comparison to O08H (in CH2Cl2, ε = 2.0 × 10⁻⁵ mol L⁻¹). d Synthesis of nitrogen-doped O8H via oxidative cyclo-rearrangement of 8H. e Synthesis of sulfur-doped and nitrogen-doped O8Hmt via oxidative cyclo-rearrangement of 8Hmt. f UV-vis absorption (bottom) and electronic circular dichroism (ECD) spectra (top) of 8H and O8Hmt (in CH2Cl2, ε = 2.0 × 10⁻⁵ mol L⁻¹). The inset photographs are recorded under irradiation at 365 nm. All calculated excitation energies and oscillator/rotatory strengths (velocity form) are displayed as sticks (the first 10 excitations).
Fig. 6 Synthesis of more sophisticated nanographenes. a Synthesis of O6H$_{\text{OPT}}$ through the association of oxidative cyclo-rearrangement with Scholl cyclization. b Crystal structure of O6H$_{\text{OPT}}$. c UV-vis absorption (red) and fluorescence (yellow) spectra of O6H$_{\text{OPT}}$ (in CH$_2$Cl$_2$, $c = 2.0 \times 10^{-5}$ mol L$^{-1}$). d Synthesis of O8H$_{\text{Br}}$ via oxidative cyclo-rearrangement and sequential formation of CO8H$_{\text{PDI}}$ via further fusion with a PDI moiety. e Stacking of CO8H$_{\text{PDI}}$ molecules in a crystal (alkyl side chains and hydrogen atoms are omitted for clarity). f UV-vis absorption spectrum of CO8H$_{\text{PDI}}$ (in CH$_2$Cl$_2$, $c = 2.0 \times 10^{-5}$ mol L$^{-1}$). Calculated excitation energies and oscillator strengths of CO8H$_{\text{PDI-CH3}}$ (the alkyl side chains are replaced with methyl groups for simplicity) are displayed as sticks (the first 10 excitations). g HOMO and LUMO of CO8H$_{\text{PDI-CH3}}$.

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Author contributions
C.S. and H.Q. conceived the project. C.S. and G.Z. designed the experiment and syn-
experiments and data analysis. C.S., N.Y., and G.Z. conducted the electrochemistry
experiments. C.S. and H.Q. wrote the manuscript with inputs from J.C. All the authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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