Doubly linked chiral phenanthrene oligomers for homogeneously π-extended helicenes with large effective conjugation length

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Helically twisted conductive nanocarbon materials are applicable to optoelectronic and electromagnetic molecular devices working on the nanometer scale. Herein, we report the synthesis of per-peri-perbenzo[5]- and [9]helicenes in addition to previously reported π-extended [7]helicene. The homogeneously π-extended helicenes can be regarded as helically fused oligo-phenanthrenes. The HOMO–LUMO gap decreased significantly from 2.14 to 1.15 eV with increasing helical length, suggesting the large effective conjugation length (ECL) of the π-extended helical framework. The large ECL of π-extended helicenes is attributed to the large orbital interactions between the phenanthrene subunits at the 9- and 10-positions, which form a polyene-like electronic structure. Based on the experimental results and DFT calculations, the ultrafast decay dynamics on the sub-picosecond timescale were attributed to the low-lying conical intersection.
Helical structures are chiral structural motifs that are found universally in nature, and scientists have been curious about their functions derived from the unique asymmetric structures\(^1\). Helically twisted polycyclic aromatic hydrocarbons (HPAHs), represented by helicenes\(^3\), are one of the major targets in synthetic chemistry with potential applications in asymmetric catalysis\(^8\), optoelectronics\(^9\), and nonlinear optical materials\(^5\). The unique properties derived from helical molecular structures, such as selective response to circularly polarized lights\(^9\), chirality-induced spin selectivity\(^8\), and mechanical structural changes that behave as molecular springs\(^10\), have been extensively investigated from both experimental and theoretical perspectives. The availability of HPAHs with high electric conductivity will open up further potential applications; for example, helical graphenes are theoretically considered as promising candidates for efficient nanometer-sized molecular solenoids\(^1\).

Since carbo[n]helicene (C\(_{2n}H\(_n\)) was synthesized by Newman and Lednicer in 1954\(^1\), many synthetic chemists have been engaged in the synthesis of various HPAHs. The longest carbo[n]helicene, i.e., carbo[14]helicene (C\(_{62}H\(_{30}\)), was synthesized by Murase and Fujita in 2015\(^13\). π-Expanded helicenes with large helical diameters have been reported by Vollhardt (C\(_{42}H\(_{18}\)) in 2002\(^13\), Tilley (C\(_{60}H\(_{30}\)) in 2017\(^16\), and our group (C\(_{72}H\(_{42}\)) in 2018\(^10\). The recent success in the synthesis of π-extended HPAHs with large helical widths represents a remarkable development in organic chemistry, Morin reported in 2017 a pioneering work on doubly linked triphenylene polymers, which are regarded as helically coiled graphene nanoribbons\(^17\). Helical bilayer nanographene (C\(_{30}F\(_{30}(\text{Bu})\(_{2}\)) was successfully synthesized by Martin in 2018\(^18\).

Campaña reported in the same year a hexa-peri-hexabenzocoronene-based π-extended [7]helicene (C\(_{114}F\(_{30}(\text{CO})\(_3(\text{Bu})\(_{2}\)) that is a undecabenzo[7]superhelicene derivative with two carbonyl group embedded at the ends\(^19\). Wang reported the synthesis of undecabenzo[7]superhelicene (C\(_{114}H\(_{30}(\text{Bu})\(_{2}\)) without carbonyl group in 2021\(^20\). Although various π-extended HPAHs have been synthesized, the HPAHs reported so far share a common feature that the absorption edge (\(\lambda_{\text{edge}}\)) does not exceed 650 nm (1.91 eV) despite their relatively large molecular structures, suggesting that increasing the effective conjugation length (ECL) of HPAHs with distorted molecular structures is a challenging issue.

Considering the transport of charge carriers along a covalently bonded organic π-conjugated system, large interactions between the π-electrons of adjacent units are the key to good carrier conductivity. In this context, π-conjugated molecules with large ECLs are potentially applicable to conductive materials in the nanometer scale, which are called molecular wires\(^21,22\). Several promising molecular structures have been developed as molecular wires, including doubly linked naphthalene oligomers, or rylenes, by Müllen and Wu (\(\lambda_{\text{edge}}\sim2500\) nm)\(^23,24\), triply linked porphyrin tapes by Osuka (\(\lambda_{\text{edge}}\sim2500\) nm)\(^25,26\), polyynes by Lambert and Tykowski (\(\lambda_{\text{edge}}\sim700\) nm)\(^27-29\), and carbon-bridged oligo(p-phenyleinylene) by Tsuji and Nakamura (\(\lambda_{\text{edge}}\sim550\) nm)\(^30,31\). The large ECLs observed in the molecular wires are likely attributed to a strong electronic coupling between adjacent repeating units; the energy gap between the HOMO and LUMO is greatly reduced when there are large in-phase (bonding) and out-of-phase (anti-bonding) interactions in each of the LUMOs and HOMOs, respectively (Fig. 1a). Thus, the concepts and examples of molecular wires with linear and planar structures have been developed; however, chiral molecular wires with helical structures are hardly developed at the moment.

In this work, we report that a class of doubly linked helical phenanthrene oligomers has a significant increase in ECL with increasing molecular length, which is a promising candidate for the helically twisted chiral molecular wires (Fig. 1b). Given that phenanthrene has the largest orbital coefficients at the 9- and 10-positions (i.e., the convex armchair edge with a significant C=C double bond character, the so-called K-region\(^32\)), we conceived that the strongest electronic coupling can be obtained when the K-region of phenanthrene are covalently connected together, which gives the helical phenanthrene oligomers. The 1-to-1’ ‘10-to-10’ doubly linked helical phenanthrene oligomers thus designed have a significantly smaller HOMO–LUMO gap than the linear structural isomer in which the K-region is differently connected to the 1 or 8 positions of phenanthrene (see section 2.1 of Supplementary Information for details). The systematic synthesis of the doubly linked phenanthrene-based π-extended HPAHs with the different molecular length—i.e., tetra-peri-tetrazeno[5]helicene (1, C\(_{10}H_{32}(\text{CH}_2)_3\)), hexa-peri-hexabenzo[7]helicene (2, C\(_{18}H_{42}\));\(^33\), and octa-peri-octabenzo[9]helicene (3, C\(_{26}H_{52}\))—enabled us to investigate the electronic and photophysical properties of the helically twisted nanographene molecules with remarkably large ECLs. It is noted that 3, with only 62 π-electrons, has a low-energy absorption edge that reaches the near-infrared region (\(\lambda_{\text{edge}}\sim1020\) nm).

**Results and discussion**

**Synthesis of the π-extended HPAHs.** The synthesis of the π-extended [7]helicene 2 has been previously reported by our group\(^33\). The key synthetic strategy of the homogeneously π-extended HPAH was first to form a partially saturated ring-stabilized [7]helicene—i.e., hexa-peri-hexa(1,3-propylene)—[7]helicene (5)—by a photochemical reaction followed by a dehydrogenative aromatization reaction (Fig. 2a), which is an efficient approach to create π-conjugated molecules with highly strained helical geometry. In applying the same strategy to the π-extended [9]helicene 3, 2,3,4-trihydro-5,10-(1,3-propylene)anthracene-1-one (7) was designed as a π-extended terminal subunit (Fig. 2b). Compound 7 was synthesized from 1-formyl-2-methoxynaphtharene under nine reaction steps in ca. 25% total yield (see section 1 of Supplementary Information for details). A 2-fold McMurry coupling reaction of dodecahydridobenzof[ghi]perylen-1,14-dione (6)\(^33\) with excess amount of 7 afforded a 3,6-bis(β-(naphthalene-2-yl)vinyl)phenanthrene derivative 8 in 53% yield. Subsequently, photocyclodehydrogenation of 8 in the presence of iodine and propylene oxide followed by dehydrogenative aromatization using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provided the target compound 3 in 6% yield in the two steps.

[5]Helicene is known to undergo an annulation reaction upon photoradiation, which produces a planar PAH, i.e., benzol[ghi]perylen\(^34\). To prevent undesired overannulation during photochemical reaction steps, we intentionally introduced methyl groups at the inner position of the π-extended [5]helicene 1 (Fig. 2c)\(^35\). To this end, compound 10, that is the 8-methyl derivative of 7, was prepared from 1-formyl-4-methylnaphthalene through nine steps in ca. 8% total yield (see section 1 of Supplementary Information for details). Dimerization of 10 by a McMurry coupling reaction afforded 11 in 95% yield, and subsequent photocyclodehydrogenation of 11 gave 1,14-dimethyl-tetra-peri-tetra(1,3-propylene)[5]helicene (12) in 41% yield. No overannulation was detected during the photochemical reaction of 11. The dehydrogenative aromatization of 12 successfully proceeded, affording a mixture of 1 together with its unexpected closed-ring isomer 1c in 25% yield. Interestingly, 1 and 1c showed a reversible photoisomerization behavior; 1 isomerized to 1c upon irradiation with violet light at 400 nm, and 1c isomerized back to 1 upon irradiation with UV light at 337 nm (see section 2.2 of Supplementary Information for details). The two isomers 1 and 1c were separated by high-performance liquid chromatography (HPLC) under dark conditions, and no thermal isomerization between 1 and 1c was observed at room temperature.
The structures of 1 and 3 were fully characterized by $^1$H NMR, $^{13}$C NMR, HMQC/HEMBC measurements, and high-resolution mass spectrometry (see section 3 of Supplementary Information for details). π-Extended helicenes 1–3 were stable under ambient conditions in solution and in the solid state for more than one month.

Bond length and aromaticities of the π-extended HPAHs. Our group has previously reported the single crystal structure of 2. In this work, single crystals of 1 and 3 suitable for X-ray analysis were obtained by a slow vapor diffusion of methanol into a concentrated solution of 1 in chloroform and a slow evaporation of toluene solution of 3, respectively (Fig. 2). The C–C bond lengths along the inner helical rims were 1.47–1.48 Å for the even-numbered rings (i.e., rings B, D, and so on), which are significantly longer than the values for the odd-numbered rings (i.e., 1.39–1.40 Å for rings A, C, E, and so on) (Fig. 3a). The large bond length alternation was commonly found in the inner helical rims of 1–3, suggesting a polyene-like electronic structure inside their helical skeleton. According to the nucleus independent chemical shifts (NICS) calculations of 1–3, the even-numbered rings have small NICS(1) values (i.e., $-0.31$ to $1.93$ ppm for the rings B, D, and so on), suggesting the non-aromatic characters of the six-membered rings that doubly link the phenanthrene sub-units (Fig. 3b). Furthermore, moderate NICS(1) values were found on the middle rings of the phenanthrene subunits (i.e., $-6.24$ to $-4.61$ ppm for the rings C and so on), while negatively large NICS(1) values on the terminal and outer rings (i.e., $-9.83$ to $-7.22$ ppm for the rings A, K, L, and so on). The NICS values of 1–3 suggested a characteristic electronic structure that can be explained as a phenanthrene oligomers terminally capped with the naphthalene-1,8-diyl subunits, which is consistent with the bond lengths determined by the X-ray crystallography and the anisotropy of current-induced density calculations (see section 2.4 of Supplementary Information for details). The observed electronic structure is also reasonably explained by the Clar's sextet theory; the number of the Clar's sextet circles is maximized when they are located at the outer rings. As a result, the sp$^2$ carbon atoms at the 9- and 10-positions of phenanthrene subunits (i.e., the K-region) form a polyene-like structure along the inner helical rims with all-(Z) configuration (Fig. 3c).

UV-vis-NIR absorption and CD spectra. Figure 4a shows the UV-vis-NIR absorption spectra of π-extended helicenes 1–3 in toluene. Compounds 1–3 showed the lowest-energy absorption bands at 500–1020 nm ($\lambda_{max}$ = 1900 M$^{-1}$ cm$^{-1}$ at 529 nm for 1, 4700 M$^{-1}$ cm$^{-1}$ at 675 nm for 2, and 2500 M$^{-1}$ cm$^{-1}$ at 814 nm for 3). With increasing helical length, the absorption maxima of the π-extended HPAHs were prominently red-shifted, which is in marked contrast to the unsubstituted carbon[n]
helicenes; the long-wavelength absorption edges of carbo[n]helicenes appear below 500 nm, even for the longest derivative, i.e., [16]helicene (C₆₆H₃₆)⁷,¹³. To the best of our knowledge, the absorption edge of 3 (λₑₓ = 1020 nm) is the longest wavelength among the helical HPAHs in the neutral closed-shell electronic state reported so far²⁴,³², suggesting that the π-extended HPAHs 1–3 is a characteristic chemical structure that shows the large ECL while having a helically distorted chiral geometry.

According to the time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-311G(2d,p) level of theory, the characteristic lowest-energy absorption bands were attributed to the HOMO → LUMO transitions (λₑₓ,calc = 552, 752, and 899 nm for 1, 2, and 3, respectively). The HOMO and LUMO of 1–3 are delocalized throughout the helical molecular framework, and relatively large orbital coefficients were found at the inner helical rim with increasing helical length (Fig. 4c). The elongation of ECLs was quantitatively investigated by plotting the lowest singlet excitation energies (i.e., for the S₀ → S₁ transition) of carbo[n]helicenes, rylene, and the π-extended HPAHs against the reciprocal of the numbers of π-electrons (1/Nₑl) (Fig. 4b). The excitation energies of carbo[n]helicenes approached about 2.5 eV with increasing helical length, suggesting no significant elongation of ECL in the conventional helicenes. Interestingly, the excitation energies of the π-extended HPAHs approached about 1.0 eV, and the decrease in excitation energies was comparable to that of rylene, indicating that the doubly linked phenanthrene oligomers are expected to exhibit properties as the helical molecular wires.

Electrochemical measurements revealed the redox activities of the π-extended HPAHs 1–3, reflecting their small HOMO–LUMO gap. The π-extended [5]helicene 1 showed an oxidation potential at 0.34 V and reduction potential at −2.01 V vs. Fc/Fc⁺ in dry
and negative CD signals, respectively. The dissymmetry factor of doubly linked phenanthrene oligomers. Benzenoid rings are highlighted in blue and the polyene-like electronic structure found in the inner helical rim is calculated at the GIAO-B3LYP/6-311G(2d,p) level of theory. NICS(1) values are shown in parentheses. The NICS(1) value was calculated at a vertical distance of 1 Å from the centroid of each benzene ring, in the front direction from the paper. c Resonance structures of the π-extended HPAHs based on the doubly linked phenanthrene oligomers. Benzenoid rings are highlighted in blue and the polyene-like electronic structure found in the inner helical rim is highlighted in red.

Fig. 3 Bond length and local aromaticity. a Representative bond lengths of 1 (left), 2 (middle), and 3 (right) in angstrom determined by X-ray crystallography. The ring structures highlighted in gray represent phenanthrene and naphthalene substructures. b NICS(0) values of (P)-1, 2, and 3 calculated at the GIAO-B3LYP/6-311G(2d,p) level of theory. NICS(1) values are shown in parentheses. The NICS(1) value was calculated at a vertical distance of 1 Å from the centroid of each benzene ring, in the front direction from the paper. c Resonance structures of the π-extended HPAHs based on the doubly linked phenanthrene oligomers. Benzenoid rings are highlighted in blue and the polyene-like electronic structure found in the inner helical rim is highlighted in red.

THF, which leads to an electrochemical HOMO–LUMO gap (ΔE\text{el}) of 2.35 eV. The π-extended [7] and [9] helicenes 2 and 3 showed oxidation potentials at 0.09 and −0.10 V and reduction potentials at −1.71 and −1.63 eV, respectively, and the ΔE\text{el} values were estimated as 1.80 and 1.53 eV for 2 and 3 (Table 1). According to the DFT calculations, their HOMO–LUMO gaps (ΔE\text{DFT}) were determined to be 2.55, 2.04, and 1.83 eV for 1, 2, and 3, respectively (Table 1), which is in good agreement with experimentally determined ΔE\text{opt} as well as ΔE\text{opt} determined by the absorption edges (λ\text{edge}).

Enantiomers of π-extended helicenes were successfully separated by chiral HPLC (see section 2.7 of Supplementary Information for details) and their circular dichroism (CD) spectra were recorded in toluene (Fig. 4a). Based on the comparison of the sign of CD spectra with the result of TD-DFT calculations, the chiralities of π-extended helicenes were determined as follows: the (P)- and (M)-isomers of 1–3 commonly show the first positive and negative CD signals, respectively. The dissymmetry factor of absorption (i.e., \(g_{\text{CD}}\) defined as \(g_{\text{CD}} = Δε/ε\)) was found to improve significantly with increasing helical length; the \(g_{\text{CD}}\) values were 0.0020 (at 529 nm), 0.016 (at 680 nm), and 0.030 (at 809 nm) for 1, 2, and 3, respectively, and the \(g_{\text{CD}}\) value of 3 was more than 10 times that of 1. It is noted that the CD signal observed in the near-infrared region (i.e., 780–1020 nm) is rare, and the large \(g_{\text{CD}}\) value on the order of \(10^{-2}\) is relatively high compared to the recently reported values for organic molecules.

The thermal stability of the isolated enantiomers is an important aspect when considering the applications as chiral molecular wires. No racemization of 2 and 3 between the (P)– and (M)-isomers was detected in toluene at 90 °C for 7 h (see section 2.8 of Supplementary Information for details). Unfortunately, the racemization process of 1 was hard to investigate due to photoisomerization caused by the probe light during CD measurements. Based on DFT calculations at the B3LYP/6-311G(2d,p) level, the activation barriers of helical inversion (ΔG\text{‡}) were calculated to be 169.3, 187.3, and 180.8 kJ mol\(^{-1}\) for 1, 2, and 3, respectively, indicating their long half-lives of enantiomers longer than one hundred years at 298 K. The high configurational stability of π-extended helicenes is comparable to that of carbo[n]helicenes: i.e., ΔG\text{‡} = 184.9, 174.5, and 182.0 kJ mol\(^{-1}\) experimentally determined for 1,14-dimethylated [5]helicene derivative, [7]helicene, and [9]helicene, respectively.

Ultrafast dynamics in the excited state. In the previous work, we reported that the π-extended [7]helicene 2 showed an ultrafast de-excitation dynamics from the S\(_2\) to S\(_0\) states, with the lifetime of only τ\(_{S_2}\) = 1.2 ps, which is 4 orders of magnitude shorter than
Orbital correlation diagram of helicenes (black square), π-extended helicenes (red circle), and rylene (blue triangle) calculated at the TD-RB3LYP/6-311G(2d,p) level of theory.

Table 1 Summary of the optoelectronic properties of 1, 2, and 3.

| Compd. | optical a | electrochemical b | theoretical c |
|--------|-----------|-------------------|---------------|
|        | λedge/nm  | ΔEopt/eV | Eox/V | Ered/V | ΔEel/eV | ΔEcorr/eV |
| 1      | 580       | 2.14     | 0.34  | -2.01  | 2.35    | 2.55     |
| 2      | 800       | 1.55     | 0.09  | -1.71  | 1.80    | 2.04     |
| 3      | 1020      | 1.22     | -0.10 | -1.63  | 1.53    | 1.53     |

aλedge absorption edge determined at 10% of maximum absorption; ΔEopt optical energy gap determined by λedge, Eox the first oxidation potential; Ered the first reduction potential.

bΔEel electrochemical energy gap determined by Eox and Ered, the HOMO-LUMO gap determined by DFT calculations.

cBased on absorption spectra measured in toluene.

that the remarkably short S1-state lifetime on the order of picoseconds is a characteristic property of the π-extended HPAHs 1-3, which is observed regardless of the helical length (Fig. 5a). Based on the analyses of time profiles (see section 2.9 of Supplementary Information for details), the S1-state lifetimes for 1 and 3 were determined as τS1 = 0.76 and 0.38 ps, respectively, and the time constants of the vibrational cooling in the ground state were τv = 8.5 and 4.9 ps for 1 and 3, respectively. The determined time constants for 1 and 3 are comparable to those reported for 2 (i.e., τS1 = 1.2 ps and τv = 9.7 ps)33. The non-radiative decay rate for the S1 → S0 transition (knr) was determined as knr = 1.3 × 1012, 8.3 × 1011, and 2.6 × 1012 s⁻¹ for 1, 2, and 3, respectively, which are 4 orders of magnitude faster than those of unsubstituted carbohelicenes, i.e., knr = 3.7 × 10⁷, 7.0 × 10⁷, and 1.0 × 10⁸ s⁻¹ for [5], [7], and [9]helicenes, respectively42. It is noted that recently reported π-extended helicenes, which do not have the polycene-like electronic structure along the inner helical rim, exhibit emission properties with the knr values on the order of 10⁷ to 10⁸ s⁻¹ (see Table S8 in Supplementary Information for details).

The ultrafast excited state dynamics of 1-3 suggests that the electronic excited states are likely de-activated via a conical
intersection (CI)\textsuperscript{43,44} that is located near the vertically excited Franck–Condon (FC) state. To investigate the photophysical cause of the ultrafast dynamics of the \(\pi\)-extended HPAHs, the minimum energy CI (MECI) structures in the S\(_1\) state were calculated using the spin-flip TD-DFT method\textsuperscript{45,46}. The relative energy of the MECI against FC (\(\Delta E_{\text{MECI}} - \Delta E_{\text{FC}}\)) were found to be negative for the \(\pi\)-extended HPAHs (i.e., \(\Delta E_{\text{MECI}} - \Delta E_{\text{FC}} = -0.63\), \(-0.17\), and \(-0.06\) eV for \(1\), \(2\), and \(3\), respectively), which is in marked contrast to the positive \(\Delta E_{\text{MECI}} - \Delta E_{\text{FC}}\) values for the conventional carbon helicenes (i.e., \(\Delta E_{\text{MECI}} - \Delta E_{\text{FC}} = +0.63\), \(+0.50\), and \(+0.85\) eV for \([5]\), \([7]\), and \([9]\) helicene, respectively). The negative \(\Delta E_{\text{MECI}} - \Delta E_{\text{FC}}\) values of \(1\)–\(3\) suggest that the energy of the MECI structures are lower than those of FC, where the excited state of the \(\pi\)-extended HPAHs can be deactivated via MECI immediately after photoexcitation (Fig.\textsuperscript{5}b). Figure \textsuperscript{5}c shows the structural change from the FC to MECI states of the \(\pi\)-extended \([7]\) helicene \(2\) optimized using SF-\(\omega\)B97XD/6-31G(d) level of theory.

is noted that the nonradiative deactivation dynamics of \(2\) and \(3\) are comparable to that of \(1\) showing photochemical cyclization to \(1\textsuperscript{c}\)\textsuperscript{47,48}, and the structural change from the FC to MECI structures is reminiscent of the electrocyclic reaction of \(1,3,5\)-hexatriene\textsuperscript{49}. Thus, the ultrafast decay dynamics of \(\pi\)-extended HPAHs \(1\)–\(3\) can be explained by their low-lying MECIs compared to the FC states that are likely derived from the polyene-like electronic structure found in the inner helical rim of the doubly linked chiral phenanthrene oligomers.

In summary, we have synthesized \(\pi\)-extended \([5]\)- and \([9]\)helicenes in addition to previously reported \(\pi\)-extended \([7]\)helicene, and have proved that the combination of photochemical reaction followed by aromatization reactions is an effective strategy for the synthesis of the helically twisted \(\pi\)-extended HPAHs. The extraordinarily large ECL observed for the \(\pi\)-extended helicenes indicates that phenanthrene (the number of benzene rings, \(n\textsuperscript{ring} = 3\)), which has an angularly annulated PAH framework, is an essential repeating unit in the creation of a helical molecular wire, in contrast to naphthalene (\(n\textsuperscript{ring} = 2\)) that forms a linear molecular wire. The large ECL and ultrafast excited state dynamics of the \(\pi\)-extended HPAHs \(1\)–\(3\) can be attributed to
the significant contribution of the polyene-like structure consisting of the K-region of the phenanthrene repeating units. The established molecular design of the chiral π-conjugated framework leads to the creation of helically twisted molecular wires. The development of helical molecular wires with sufficient length is of potential interest, as graphene nanoribbons with sufficient length have been experimentally achieved by on-surface synthesis. The creation of other π-extended HPAsHs with different spatial distributions of frontier orbitals, e.g., HPAHs having a large ECL length have been experimentally achieved by on-surface synthesis.

The helically twisted nanocarbon materials are currently ongoing distributions of frontier orbitals, e.g., HPAHs having a large ECL length have been experimentally achieved by on-surface synthesis. Further researches on magnetic and spintronic devices based on the helically twisted nanocarbon materials are currently ongoing in our group.

Methods

Synthesis of 1,14-bis(1,2,3,9,10,11-hexahydrobenzo[b]anthracene-8-ylidene)-2,3,4,5,6,7,8,9,10,11-decahydrobenzo[5,6][1,4]benzodioxine.[b]benzene-1-one (4).

A solution of TICl4 (7.9 mg, 42 mmol) in dry THF (8.5 mL) was added to Na2S2O3 (conc. ca. 10 mL). The reaction product was extracted with CH2Cl2 (ca. 150 mL) and washed with water. The organic layer was dried over MgSO4, filtered, and then was concentrated in vacuo. The crude product was very complicated probably due to the mixture of trans/isomers, which hampered further assignment (Supplementary Figure 53). Note that the production of 8 was confirmed by LR-MALDI-TOF mass spectrometry. LRMS–MALDI–TOF (m/z): [M + H]+ calculated for C62H31N3O7S, 802; found, 802.

Synthesis of 1,14-bis(1,2,3,9,10,11-hexahydrobenzo[b]anthracene-8-ylidene)-3,5,6,7,8,9,10,11,12-decahydrobenzo[5,6][1,4]benzodioxine.[b]benzene-1-one (3).

A solution of TiCl4 (4.5 × 102 mg, 1.9 mmol) in dry THF (50 mL) was degassed by N2 bubbling at 80 °C for 5 min. After the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 150 mg, 0.66 mmol), the resulting solution was stirred at 80 °C for 2 min under nitrogen atmosphere. Then the solution was cooled and immediately quenched by the addition of eq. Na2S2O3 (conc. ca. 10 mL). The reaction product was extracted with toluene (ca. 100 mL) and the combined organic layer was concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/CH2Cl2 = 90/10 to 85/15) and GPC to give a mixture of 1 and the closed-ring isomer 1c (10 mg, 0.022 mmol, 25%) as a deep red solid. A pure form of 1c was obtained by HPLC (HPLC column, Mitygyl Si 60 250 mm-46 mmf, 5 μm; eluent: hexane/CH2Cl2, 95/5; flow rate, 1.0 mL/min; detection wavelength, 500 nm; Rt = 10.0 and 11.6 min for 1c and 1, respectively). HRMS–APCI–Orbitrap (m/z): [M + H]+ calculated for C63H47N3O9S, 657.3794 found, 657.3797.

Synthesis of 1,14-bis(1,2,3,9,10,11-hexahydrobenzo[b]anthracene-8-ylidene)-4. A round-bottom quartz stirred and irradiated with a super-high-pressure mercury lamp (500 W) through a sharpen-cut filter (UV-29) for 75 min. The resulting solution was stirred with Na2S2O3 powder, filtered, and then was concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/CH2Cl2 = 90/10 to 85/15) and GPC to give a mixture of 1 and a yellow solid. 1H NMR (600 MHz, CDCl3, δ): 0.76 (s, 6H), 0.69–0.67 (m, 4H), 2.20–2.31 (m, 4H), 3.07–3.31 (m, 16H), 6.82 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 6.0 Hz, 2H). 13C NMR (151 MHz, CDCl3, δ): 22.1, 23.1, 23.4, 27.2, 27.8, 36.3, 121.4, 124.4, 126.7, 127.0, 127.8, 128.8, 129.1, 129.2, 131.3, 132.0, 132.5. HRMS–APCI–Orbitrap (m/z): [M + H]+ calculated for C63H47N3O9S, 467.2733; found, 467.2727.

X-ray crystallography.

Single crystals of compound 1, 1c, and 3 were prepared by a slow vapor diffusion of methanol into a concentrated solution of 1 or 1c in chloroform and a slow evaporation of toluene solution of 3 at room temperature. X-ray crystallographic analyses for 1c and 3 was performed on a Rigaku Saturn724+ CCD diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection and cell refinement were performed using CrystalClear-SM Expert 2.1 b46 software (Rigaku, 2016). X-ray crystallographic analysis for 1 was performed on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å). The data collection and cell refinement were performed using APEX3 software (v2016.9-0, Bruker AXS, 2016). The structure of 1 observed based on the diffraction data was refined as a two-component twin using Olex2 software. The all structures were solved by direct methods (SHELXT) and refined by a full-matrix least-squares techniques against F2 (SHELXL). The all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Data availability

All data supporting the findings of this study are included in this article and its Supplementary Information. The X-ray crystallographic data have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2118093 (1), CCDC 2211809 (1c), and CCDC 2117834 (3). Copies of the data are available free of charge via https://www.ccdc.cam.ac.uk/structures/.

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References

1. Yashima, E. et al. Wupramolecular helical systems: helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions. Chem. Rev. 116, 13752–13990 (2016).
2. Shen, Y. & Chen, D.-F. Helicenes: synthesis and applications. Chem. Rev. 112, 1463–1533 (2012).
3. Yavari, K. et al. Helicenes with embedded phosphole units in enantioselective gold catalysis. Angew. Chem., Int. Ed. 53, 861–865 (2014).
4. Yang, Y., da Costa, R., Fuchter, M. J. & Campbell, A. J. Circularly polarized light detection by a chiral organic semiconductor transistor. Nat. Photonics 7, 634–638 (2013).
5. Gingras, M. One hundred years of helicene chemistry. part 3: applications and properties of carbohelicenes. Chem. Soc. Rev. 42, 1051–1095 (2013).

6. Kobayashi, H. et al. Tuning transition electric and magnetic dipole moments: [7] helicenes showing intense circularly polarized luminescence. J. Phys. Chem. Lett. 12, 686–695 (2021).

7. Nakai, Y., Mori, T. & Inoue, Y. Theoretical and experimental studies on circular dichroism of carbon[n]helicenes. J. Phys. Chem. A 116, 7372–7385 (2012).

8. Kato, M. et al. Chirality-dependent electron spin filtering by molecular monolayers of helicene. J. Phys. Chem. Lett. 9, 2025–2030 (2018).

9. Matxain, J. M. et al. Chirality induced spin selectivity of photoexcited electrons in carbon-sulfur [n]helicenes. ChemPhotoChem 3, 770–777 (2019).

10. Nakaduki, Y. et al. Hexa-...
