Synthesis, Structures, and Properties of π-Extended Double Helicene: A Combination of Planar and Nonplanar π-Systems

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S *Supporting Information*

ABSTRACT: The synthesis, structures, and properties of a π-extended double helicene **1** are described. This double helicene **1** was synthesized by a four-fold oxidative C−H biphenylation of naphthalene followed by the Scholl reaction or via five steps including the Suzuki−Miyaura cross-coupling reaction and the Scholl reaction. Due to the two helical substructures, **1** has three isomers, i.e., two enantiomers in a twisted form [(*P*,*P*) and (*M*,*M*)] and one diastereoisomer in a meso form. X-ray crystallographic analysis of the twisted isomers (*twisted*-**1**) revealed a tightly offset packing pattern of (*P*,*P*)- and (*M*,*M*)-twisted isomers, affording a three-dimensional lamellar stacking structure. A high isomerization barrier (43.5 kcal mol^{-1}) and the relative thermal stability of *twisted*-**1** isomer over *meso*-**1** by 0.9 kcal mol^{-1} were estimated by DFT calculations. The three isomers were successfully separated by chiral HPLC and characterized by circular dichroism spectroscopy as well as by TD-DFT studies. Electronic state variation resulting from the molecular geometry difference between the two diastereoisomers (*twisted*-**1** and *meso*-**1**) was observed by UV−vis absorption and fluorescence spectra.

A New π-Extended Double Helicene
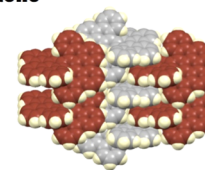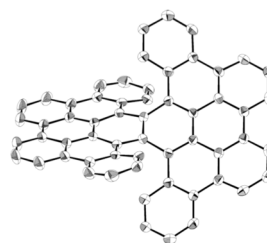
- *Three separable isomers [(P,P), (M,M), (P,M)] derived from two [6]helicene substructures*
- *High isomerization barrier*
- *Contorted 3D lamellar stacking in crystal*

■ INTRODUCTION

Controlling the molecular packing of aromatic compounds in crystalline state is an essential issue for functional materials.[1] From this perspective, planar and nonplanar aromatic compounds mutually show contrasting properties. Planar aromatic systems such as acenes, phenacenes, and rylenes tend to exhibit strong π−π stacking since the planar π-surfaces overlap with each other.[2] However, the molecular packing of polycyclic aromatic hydrocarbons (PAHs) is difficult to control precisely and is limited to either the herringbone (CH−π dominant) or lamellar (π−π dominant) structures.[2] Nonplanar aromatic systems such as [*n*]circulenes (*n* ≠ 6)[3] and helicenes[4] possess curved or twisted π-surfaces. While nonplanar molecules show a variety of fascinating molecular packing with respect to planar molecules, the curved π-electron system often disturbs π−π stacking, which is indispensable for self-assembling or semiconducting materials utilizing the inter-molecular electronic interaction.[5] To achieve the π−π overlap, [*n*]circulenes (*n* ≠ 6) are required to stack in a one-dimension manner to fit their curvatures completely. As for conventional helicenes, only partial π−π stacking is usually observed. Hence, it is important to uncover unconventional molecular packing that maintain π−π stacking, in order to discover the unexplored functionalities of nonplanar aromatic systems in their crystalline state. Herein, we report the synthesis, structures, and photophysical properties of π-extended double helicene **1** (C$_{58}$H$_{28}$) bearing concatenated two planar tribenzo[*b,n,pqr*]-perylene substructures with fully conjugated double [6]helicene

substructures, a combination of planar and nonplanar π-systems (Figure 1). Studying π-extended double helicene **1** is considered to be a good starting point to explore a new area that merges the aspects of planar and nonplanar aromatic systems.

Helicenes are helically shaped molecules defined as *ortho*-fused polycyclic aromatic compounds in which all rings are angularly arranged.[4] The helical structures of helicenes are a consequence of the repulsive steric interaction between terminal aromatic rings, resulting in chirality despite the absence of asymmetric carbons and chiral centers. In comparison with planar PAHs, the helical structure of helicene results in chiroptical properties, nonplanarity, a large optical rotation, dynamic behavior, and perturbations to the π-system.[1a,4,6] These characteristics of helicene have been exploited in the fields of asymmetric catalysis, molecular machines, molecular recognition, and liquid crystals in various ways.[1a,4,6] In addition to simple helical π-conjugated systems, helicenes with multihelicity and/or extended π-system have gained considerable attention in recent years (Figure 2).[7−10] Multihelicity provides plural electronic states and molecular dynamics, and π-extension often causes a dramatic change of electronic structure. Both of them also define three-dimensional molecular shape and molecular packing in crystalline state. These characteristics of multihelical and/or extended π-systems
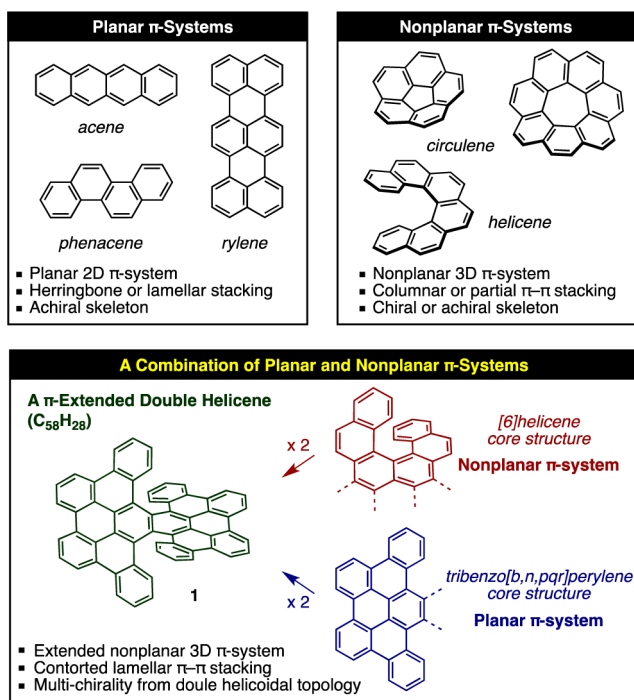
Figure 1. Planar and nonplanar π-systems and a new π-extended double helicene **1**.
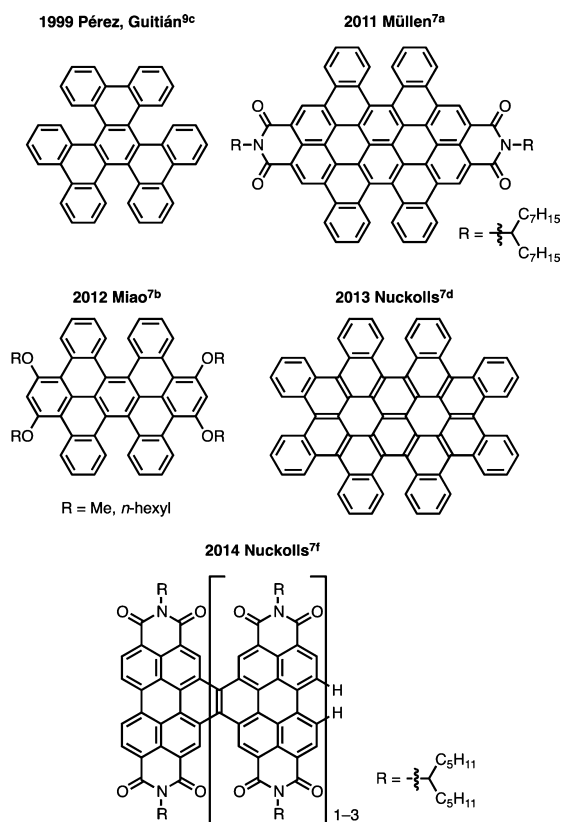

Figure 2. Representative examples of extended multihelical π-systems.

expand the applicability of helicenes toward crystal engineering, supramolecular organization, and chiroptical sensing.

Besides the interesting properties as noted above, molecular entities of nonplanar π-systems also attract many chemists due to their characteristic reactivity, redox activity, photophysical properties, and high solubility compared with planar ones.[3,4,6−11] To add these attractive properties in planar π-systems, proper incorporation of heteroatom and functionalization are often employed. Alternatively, introduction of curved π-systems can be a useful strategy for tuning molecular properties. Therefore, studying π-extended double helicene **1** would be a good starting point to explore not only a new area that merges the aspects of planar and nonplanar π-systems but also a fundamental science of nonplanar aromatic compounds with extended multihelical π-system.

■ RESULTS AND DISCUSSION

Synthesis of Double Helicene 1. We developed two synthetic routes for double helicene **1** using (1) a step-economical C−H activation[12] or (2) Suzuki−Miyaura coupling reactions (Scheme 1). We began by applying our Pd(II)/o-chloranil catalytic method[13] to allow the rapid installation of biphenyl units onto naphthalene by C−H arylation. Thus, naphthalene was treated with tris(o-biphenylyl)boroxine in the presence of Pd(OAc)$_2$ and o-chloranil to afford a complex mixture containing regioisomers of four-fold biphenylated naphthalene **2**. The formation of **2** was confirmed by mass

Scheme 1. Synthesis of Double Helicene 1[a]
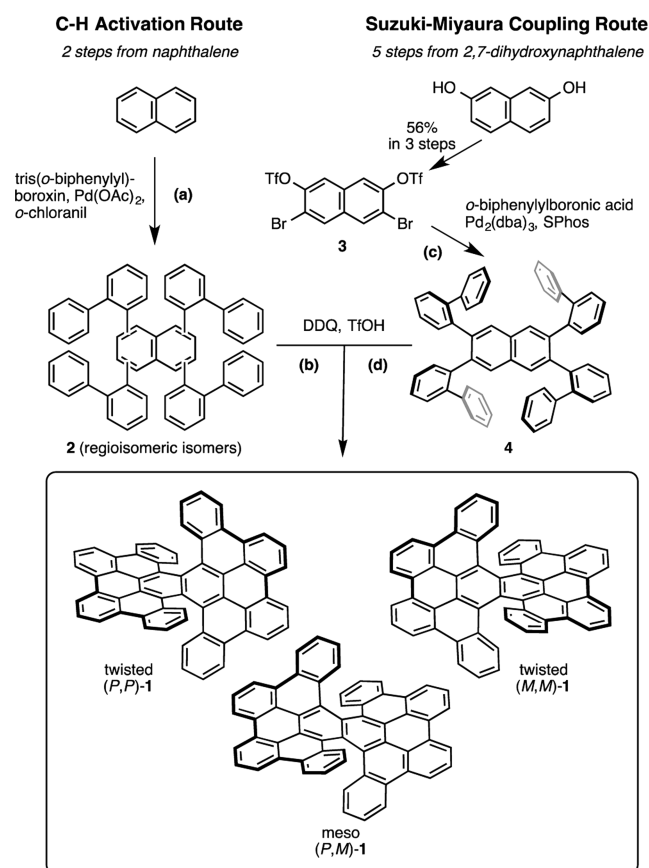
[a]Reagents and conditions: (a) tris(o-biphenylyl)boroxine (1.5 equiv), Pd(OAc)$_2$ (1 equiv), o-chloranil (4 equiv), 1,2-dichloroethane, 80 °C, 3 h; (b) DDQ (3.5 equiv), 1,2-dichloroethane/TfOH (100:1), 0 °C, 30 min (1% yield in two steps); (c) o-biphenylylboronic acid (8 equiv), Pd$_2$(dba)$_3$·CHCl$_3$ (10 mol %), SPhos (20 mol %), Cs$_2$CO$_3$ (8 equiv), toluene/H$_2$O (3:1), 80 °C, 3 d (84% yield); (d) DDQ (7 equiv), 1,2-dichloroethane/TfOH (100:1), 0 °C, 1 h (64% yield). The ratio of *twisted*-**1**/*meso*-**1** was determined to be 43:57 by ^{1}H NMR.

spectroscopy. Although the exact structures and isomer ratio of **2** could not be determined, treatment of the mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 1,2-dichloroethane/trifluoromethanesulfonic acid (TfOH) successfully promoted the Scholl reaction (cyclodehydrogenation) to afford double helicene **1**.[14,15] Unfortunately, the yield was too low to be practical (1% yield in two steps from naphthalene).

Thus, to obtain sufficient amounts of **1**, we switched to a classical Suzuki−Miyaura coupling route. Commercially available 2,7-dihydroxynaphthalene was converted to **3** by using the reported bromination-triflation procedure (56% yield in three steps).[16] Next, a four-fold Suzuki−Miyaura coupling reaction of **3** with *o*-biphenylylboronic acid in the presence of Pd$_2$(dba)$_3$, 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos), and Cs$_2$CO$_3$ provided 2,3,6,7-tetrabiphenylylnaphthalene (**4**) in 84% yield. The final Scholl reaction of **4** with DDQ (7 equiv) in 1,2-dichloroethane/TfOH at 0 °C afforded **1** as a red solid in 64% yield.[14,15,17] Double helicene **1** is expected to exist as three isomers: the twisted (*P*,*P*)- and (*M*,*M*)-enantiomers and the (*P*,*M*)-isomer as the meso form. ^{1}H NMR spectra of the isomeric mixture of **1** indicated the existence of two different species, which we assigned as *twisted*-**1** and *meso*-**1** (in a 43:57 ratio).

Structure and Packing Mode of *twisted*-1. The "two-blade propeller" structure of *twisted*-**1** was unambiguously confirmed by X-ray crystallography using a racemic single crystal, recrystallized from a CS$_2$ solution of an isomeric mixture of **1** via slow addition of *n*-hexane vapor at room temperature (Figure 3a). The X-ray crystal structure of racemic *twisted*-**1** confirms an extended doubly twisted π-system. The dihedral angle of the two blades reached to 40.28°, which is much larger than that observed in the optimized structures calculated by various methods (22−29°).[18] This difference is likely to be attributed to the strong intermolecular interaction in the crystal packing structure. This is supported by the fact that the (*P*,*P*)- and (*M*,*M*)-isomers of crystal **1** tightly arrange themselves in an offset stacking array so that no solvent molecules were present inside the crystal (Figure 3b−d). Although planar π-conjugated molecules tend to adopt herringbone or lamellar packing structures,[2] it is difficult to categorize the crystal packing of *twisted*-**1** in these typical patterns, as **1** displays a contorted three-dimensional lamellar packing structure.[1b,e] Homochiral molecular layers of each isomer lying on the *ac* plane (Figure 3d) alternately laminate along the *b*-axis (Figure 3b,c), in which unilateral blades in a homochiral layer fill the gaps of the adjacent enantio-homochiral layer. Inside the homochiral layer, slipped π−π stacking is observed along the *c*-axis. In addition, heterochiral stacking exhibits π−π stacking over different homochiral layers. Consequently, in contrast to one- or two-dimensional stacking of planar π-system, the crystal of *twisted*-**1** has three-dimensional electronic interactions exhibiting the unconventional molecular packing by exploiting the virtues of "planarity" and "nonplanarity".

Isomerization, Separation, and Circular Dichroism of the Isomers of 1. To uncover the thermal stability and dynamic behavior of *twisted*-**1** and *meso*-**1**, we conducted DFT calculations at the B3LYP/6-31G(d) level (Figure 4a). From these calculations, it was estimated that *twisted*-**1** is thermodynamically more stable than *meso*-**1** by 0.9 kcal mol^{-1}. The *twisted*-to-*meso* interconversion process was found to proceed through the transition state with face-to-face oriented terminal aromatic rings of [6]helicene.[19] The
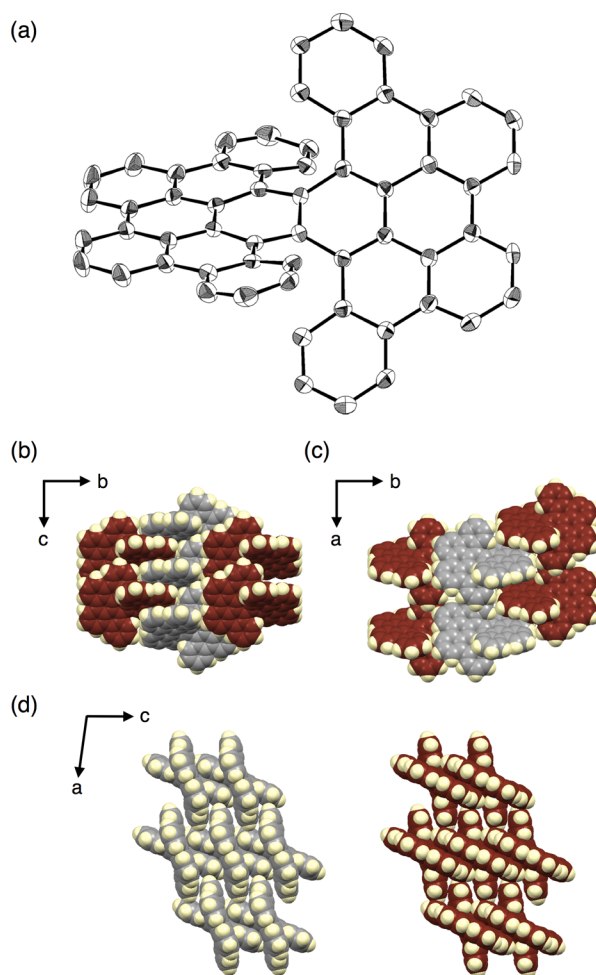

Figure 3. (a) ORTEP drawing of (*P*,*P*)-**1** with 50% probability. (b−d) Packing structure as a space-filing model ((*P*,*P*)-**1** is colored in red and (*M*,*M*)-**1** is colored in gray; shown in (d) is a view of the two homochiral molecular layers from the same direction along the *b*-axis). See Figure S3 for distances between the intermolecular mean planes of the π-systems based on least-squares planes.

calculated isomerization barrier (43.5 kcal mol^{-1}) was considerably higher than that of [6]helicene (37.3 kcal mol^{-1}, Figure 4b) and comparable with that of [7]helicene (41.7 kcal mol^{-1}).[20,21]

The very high isomerization barriers between the isomers prompted us to separate these isomers. After extensive investigation, we found that the three isomers could be separated by a chiral HPLC (column, CHIRALPAK IF; eluent, *n*-hexane/chloroform = 3:7) (Figure 5). While the poor solubility of a mixture of **1** to general organic solvents (e.g., chloroform, 0.15 g/L; carbon disulfide, 0.60 g/L; *n*-hexane, insoluble) hampered separation of quantitative amount of each isomer upon HPLC separation, enantiopure *twisted*-**1** showed increased solubility to organic solvents compared with racemic sample. Note that enantiopure *twisted*-**1** is soluble to *n*-hexane even though there is no applicable value on solubility. Judging from the good agreement of the circular dichroism spectra with the simulated spectra by TD-DFT calculations (B3LYP/6-31G(d)), the three peaks in the chiral HPLC were suggested to be (*P*,*P*)-**1** (first peak), (*M*,*M*)-**1** (second peak), and (*P*,*M*)-**1** (third peak). Unlike the large optical rotation of (*P*)-[6]helicene ([α]$^{25}_D$ = +3707°),[22] tentatively assigned (*P*,*P*)-**1** showed much smaller and opposite optical rotation ([α]$^{20}_D$ =

(a)

(b)
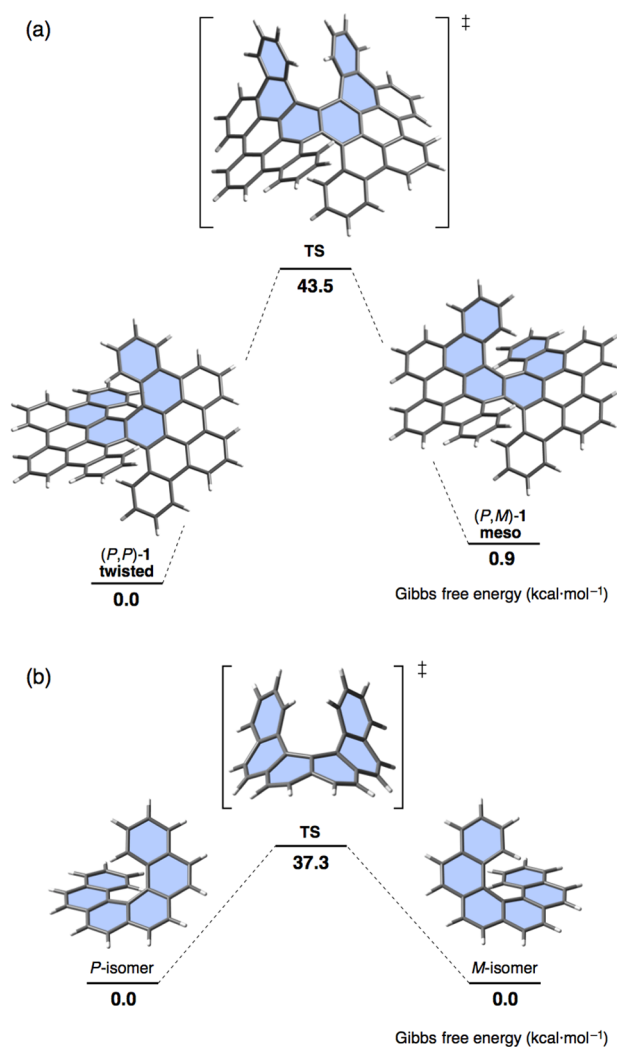
Figure 4. Isomerization (a) between (P,P)-**1** and (P,M)-**1**, and (b) between P-isomer and M-isomer of [6]helicene.
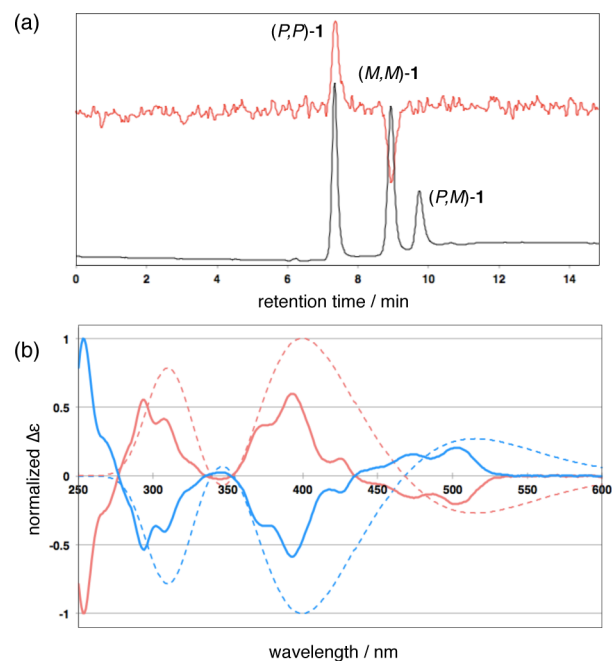
(a)

(b)

Figure 5. (a) Chiral HPLC analysis of the isomeric mixture of **1** with optical rotation, eluted by n-hexane/chloroform (3:7) using CHIRALPAK IF (black line: absorption intensity at 400 nm, red line: optical rotation) with tentative assignment of the peaks. (b) Circular dichroism spectra of the first peak (red solid line) and the second peak (blue solid line), and a simulated circular dichroism spectra of (P,P)-**1** (red dashed line) and (M,M)-**1** (blue dashed line) by B3LYP/6-31G(d).
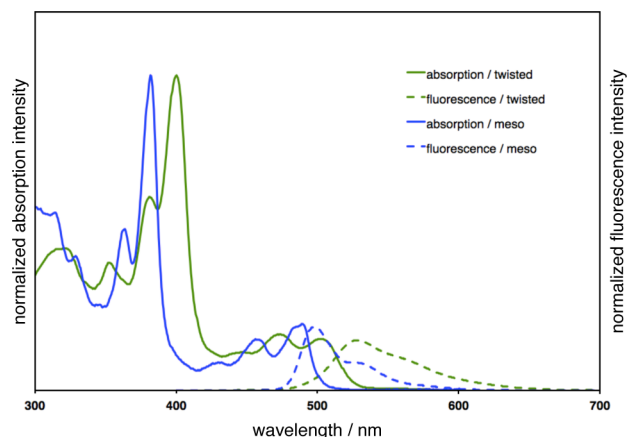
−81°, c 0.0036, chloroform). Comparison of circular dichroism spectra of (P)-[6]helicene[23] and (P,P)-**1** also suggested no clear correlation of π-conjugated double [6]helicene substructure of **1** and pristine [6]helicene on chiroptical properties.

As expected from the DFT calculation, the *twisted−meso* interconversion (isomerization) does not occur below 200 °C. For example, the diphenyl ether solution of *meso*-**1** was heated at various temperatures and analyzed periodically by HPLC. The isomerization was not observed below 200 °C. At higher temperatures over 230 °C, absorption intensities of *twisted*-**1** gradually increased.[21]

UV−vis Absorption, Fluorescence, and TD-DFT Study of *twisted*-1 and *meso*-1. UV−vis absorption and fluorescence spectra of *twisted*-**1** and *meso*-**1** were measured to elucidate the effect of the molecular geometry difference on the electronic state of **1**. Shown in Figure 6 is the spectra of *twisted*-**1** and *meso*-**1** in a chloroform solution. Finger-shaped absorption spectra as observed in typical PAHs were observed in both diastereoisomers. *Twisted*-**1** has longer maxima at 506, 476, and 450 nm, and the sharpest maximum at 401 nm. Meanwhile, *meso*-**1** shows a similar but blue-shifted absorption spectrum with the longer maxima at 491, 460, and 434 nm and the sharpest maximum at 382 nm. A blue shift was also observed in the fluorescence spectra of *meso*-**1** (λ_{em} = 496 nm,

Figure 6. UV−vis absorption spectra (solid lines) and fluorescence spectra (broken lines) of *twisted*-**1** (green lines) and *meso*-**1** (blue lines) in chloroform solution.

Φ_F = 0.42) compared to that of *twisted*-**1** (λ_{em} = 525 nm, Φ_F = 0.052). Fluorescence lifetimes (τ_s) of *twisted*-**1** and *meso*-**1** are 1.6 and 6.5 ns, respectively. According to the equations $\Phi = k_r \times \tau_s$ and $k_r + k_{nr} = \tau_s^{-1}$, the radiative ($k_r$) and nonradiative ($k_{nr}$) decay rate constants from the singlet excited state were determined (*twisted*-**1**: k_r = 3.3 × 10⁷ s⁻¹, k_{nr} = 5.9 × 10⁸ s⁻¹; *meso*-**1**: k_r = 6.5 × 10⁷ s⁻¹, k_{nr} = 8.9 × 10⁷ s⁻¹). Stokes shifts were 19 nm (716 cm⁻¹) and 5 nm (206 cm⁻¹) for *twisted*-**1** and *meso*-**1**, respectively.

In order to understand the nature of absorption, a TD-DFT study was performed at the B3LYP/6-31G(d) level. The energy diagrams of the dominant excitations are depicted in Figure 7.
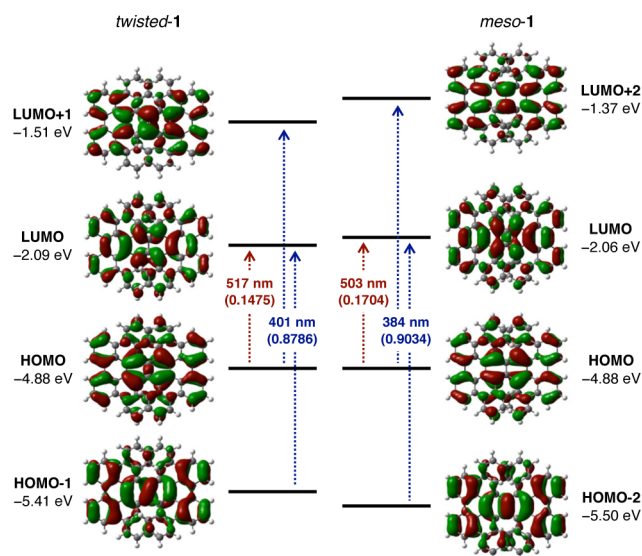
Figure 7. Energy diagrams of *twisted*-**1** and *meso*-**1** calculated at the B3LYP/6-31G(d) level of theory. Excitation energies were computed by TD-DFT at the same level. Values in parentheses represent the oscillator strengths (f).

In the case of *twisted*-**1**, it was estimated that longer maxima at around 500 nm are characterized by a large contribution of HOMO → LUMO and a small contribution of HOMO−1 → LUMO+1 transition (S_1, 517 nm, f_{calc} = 0.1475), and the sharpest maximum (401 nm) is characterized by almost equal contributions of HOMO−1 → LUMO and HOMO → LUMO+1 transitions (S_4, 401 nm, f_{calc} = 0.8786). On the other hand, the longer maxima at around 490 nm in the absorption of *meso*-**1** are characterized by a large contribution of HOMO → LUMO and a small contribution of HOMO−2 → LUMO+2 transition (S_1, 503 nm, f_{calc} = 0.1704). The sharpest maximum (382 nm) is characterized by almost equal contributions of HOMO−2 → LUMO and HOMO → LUMO+2 transitions (S_6, 384 nm, f_{calc} = 0.9034). The origin of the spectral shift was estimated by the calculated spatial distribution (see the Supporting Information) and the molecular energy, which suggested that *twisted*-**1** has low-lying LUMO and LUMO+1 orbitals and a high-lying HOMO−1 compared with the corresponding molecular orbitals of *meso*-**1** (LUMO, LUMO+1 and HOMO−1 of *twisted*-**1** correspond to LUMO, LUMO+2 and HOMO−2 of *meso*-**1** respectively).

CONCLUSION

In summary, we have achieved the concise synthesis of a new π-extended double helicene **1**. The three isomers resulting from the two [6]helicene substructures of **1** were successfully separated by chiral HPLC and their fundamental properties were investigated experimentally and computationally. The highly distorted π-conjugated system of racemic *twisted*-**1** was unambiguously confirmed by X-ray crystallography. The contorted three-dimensional lamellar packing structure suggested three-dimensional electronic interactions in contrast to one- or two-dimensional stacking of planar π-system. The established synthetic protocol here would allow us to rapidly access a variety of such fascinating molecules. To discover the unrevealed functionalities of the twisted and π-extended aromatic system, synthesis of other double helicenes with

substituents or with heteroaromatic substructures is currently ongoing.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization of data for all new compounds, crystallographic data of *twisted*-**1**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03118.

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Notes

The authors declare no competing financial interest.

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