

## Synthesis, Structure, and Chiroptical Properties of Indoloand Pyridopyrrolo-Carbazole-Based C<sub>2</sub>-Symmetric Azahelicenes

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Dedicated to Professor Christian Bruneau

Abstract: Treatment of 11,12-bis(1,1'-biphenyl-3-yl or 6phenylpyridin-2-yl)-substituted 11,12-dihydro-indolo[2,3-a]carbazole with an oxidizing system of Pd(II)/Ag(I) induced effective double dehydrogenative cyclization to afford the corresponding  $\pi$ -extended azahelicenes. The optical resolutions were readily achieved by a preparative chiral HPLC. It was found that the pyridopyrrolo-carbazole-based azahelicene that contains four nitrogen atoms exhibits ca. 6 times larger dissymmetry factors both in circularly dichroism (CD) and circularly polarized luminescence (CPL),  $|g_{CD}|$  and  $|g_{CPL}|$ values being  $1.1 \times 10^{-2}$  and  $4.4 \times 10^{-3}$ , respectively, as compared with the parent indolocarbazole-based azahelicene. Theoretical calculations at the RI-CC2 level were employed to rationalize the observed enhanced chiroptical responses. The (chir)optical properties of the former helicene was further tuned by a protonation leading to remarkable red-shift with a considerable enhancement of the  $|g_{CPL}|$  value.

Polycyclic heteroaromatic compounds have recently attracted significant attention as they are often relatively robust and tractable compared with similarly  $\pi$ -extended aromatic hydrocarbons and their optical, chiroptical, and electronic properties can be tuned by the introduction of different heteroatoms as well as the extent of  $\pi$ -systems. In particular, nitrogencontaining polycyclic aromatic compounds are of special interest as both pyridine- and pyrrole-types of nitrogen can be involved and they contrastively act as electron-withdrawing and -donating functions, respectively, within the structurally similar aromatic  $\pi$ -systems.<sup>[1-4]</sup>

Meanwhile,  $\pi$ -extended helicenes with screw-shaped structures have helical handedness and exhibit unique (chir)optical properties including high level of circular dichroism (CD) and, in

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particular, circularly polarized luminescence (CPL).<sup>[5]</sup> Organic luminescent materials with CPL characteristics are of valuable uses for various applications such as three-dimensional displays,<sup>[6]</sup> information storage systems,<sup>[7]</sup> biological probes,<sup>[8]</sup> and photocatalysis.<sup>[9]</sup> Thus, their synthesis, enantiomer separation, and chiroptical studies have been the subjects of intense investigations in the last two decades. Nitrogen-doped helicenes, i.e., azahelicenes, have been often the extensive target molecules among various heterohelicenes, due to the synthetic accessibility and stability of both pyridine- and pyrrole-containing scaffolds.<sup>[5g,10,11]</sup>

As for the construction of azahelicenes containing a pyrroletype nitrogen, a carbazole skeleton is often employed and typically located in the center of helicene molecules (Scheme 1a, Cz-helicene),<sup>[5g,11a-e]</sup> while some related less symmetrical azahelicenes have been known.<sup>[11f-i]</sup> On the other hand, we have been interested in indolo[3.2.1,-jk]carbazole as another carbazole motif (Scheme 1b, ICz),<sup>[12]</sup> as the derivatives of ICz are highly fluorescent and can also be appended with donor moieties to form D- $\pi$ -A-type dyes for applications in dyesensitized solar cells<sup>[13]</sup> and host materials for phosphorescent organic diodes.<sup>[14]</sup> The ICz skeleton is apparently strained and should be a promising core scaffold of azahelicenes of the twisted nature. Consequently, we designed a new ICz-based azahelicene with  $C_2$ -symmetry that contains a pair of ICz units (Scheme 1c, ICz-helicene). Among two possible key routes for the construction of the ICz-helicene by means of recently developed step-economic palladium-catalyzed dehydrogenative coupling, we chose a double dehydrogenation route of 11,12-



Scheme 1. Structures of (a) Cz-helicene, (b) ICz, and (c) ICz-helicene and (d) possible routes to ICz-helicene.

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dihydro-11,12-diphenyl-indolo[2,3-*a*]carbazole, as the similar reaction of 1,2-di(9*H*-carbazol-9-yl)benzene underwent monocyclization between the carbazole moieties and did not afford the ICz-helicene structure (Scheme 1d).<sup>[12,15]</sup> Herein, we report the successful preparation and optical resolution of diphenylsubstituted ICz-helicene and its pyridopyrrolo derivatives, together with their structural, (chir)optical, and electronic features. Remarkably, while keeping the comparable structure, chiroptical responses are considerably enhanced in pyridopyrrolo-helicenes as compared with the parent ICz-helicene.

The synthesis of ICz-helicene **7** (R=H, X=CH) was started from the Ullmann-type reaction of 11,12-dihydro-indolo[2,3*a*]carbazole (**1a**) with 3-bromo-1,1'-biphenyl (**2a**) to give the corresponding 11,12-bis(1,1'-biphenyl-3-yl)-substituted indolocarbazole **3** (Scheme 2).<sup>[16]</sup> Then, this was subjected to double dehydrogenative cyclization with a combination of Pd(TFA)<sub>2</sub>/ AgOAc as an oxidant system to furnish the target helicene **7**.<sup>[12]</sup> The pyridopyrrolo-type helicene **8** was similarly constructed with use of **1a** and 2-bromo-6-phenylpyridine (**2b**) as the starting materials. The methoxy- and chloro-substituted helicenes **9** and **10** were also obtained by the similar reactions with the corresponding indolocarbazoles **1b** and **1c**. The chlorofunction in **10** was reacted with di(4-*tert*-butylphenyl)amine under palladium catalysis to provide the D- $\pi$ -A helicene **11**.<sup>[17]</sup>



Scheme 2. Synthesis of racemic azahelicenes 7–11 {For clarity, (*M*)-configurations are shown as the representatives}. Reaction conditions: (x) Cu (2.5 eq.),  $K_2CO_3$  (4.0 eq.), 18-crown-6 (10 mol%) in *o*-dichlorobenzene at 185 °C for 48 h, (y) Pd(TFA)<sub>2</sub> (30 mol%), AgOAc (6.0 eq.) in PivOH at 130 ~ 160 °C for 24 h, (z) [(allyl)PdCl]<sub>2</sub> (20 mol%), Mophos (80 mol%), *tert*-BuONa (2.5 eq.) in *o*-xylene at 130 °C for 15 h, [Mo-Phos = di-*tert*-butyl(2,2-diphenyl-1-methyl-1-cyclopropyl)phosphine].

The highly twisted helical structures of racemic 7 and 8 were confirmed by X-ray crystallography (Figure S14 and S15). As anticipated, the angle between the two planes of the terminal rings A and G ( $\theta_{AG}$ ) for **8** (42.0°) is slightly reduced from that of 7 (50.6°), while their twist angles along the helical inner rim ( $\langle \phi_{AG} \rangle$ ) defined as average of five dihedral angles at the rim are almost identical (ca. 20°), inferring the comparable strength of aromatic conjugations between the azahelicenes 7 and 8 (Figure 1). The distance between a centroid of A ring and a least-squares plane for rings C, D, and E ( $d_{A-CDE}$ ) was considerably smaller for 8 (1.00 Å) than for 7 (1.44 Å), implying that the substantial twists being evoked at the terminal rings (rather than overall helix structure) in the latter helicene, primary due to the steric hindrance of C-H hydrogens (X=CH in 7). The optical resolutions of helicenes 7, 8, 9, and 11 to the corresponding (P)- and (M)-enantiomers were accomplished by preparative HPLC using conventional chiral stationary phases (see the Supporting Information for details), while 10 was not separable due to its low solubility into the mobile phase solvent. The absolute configurations of the latter elutes of 7 and 8 were ambiguously determined as (M)-configuration by the X-ray crystallographic analyses on the crystals of enantiomerically pure samples (Figure S18 and S19). Despite of different packing pattern, structures of the individual molecules were essentially similar to those found for the racemic crystals. The Flack parameters for (M)-7 and (M)-8 were found -0.0017 and -0.10, respectively.

The racemization was completely prohibited for optically resolved **7** and **8** at an ambient temperature. However, interconversion between the enantiomers was observed for **7** upon heating in 1,2-dichloroethane (DCE) at 60 °C and for **8** in toluene at 90 °C. The activation energies for racemization of azahelicenes **7** and **8** were determined to be 26.9 and 27.8 kcal/mol, respectively (Figure S13). As in the related systems,<sup>[18]</sup> the terminal phenyl rings indeed provide a medium configurational stability for the present azahelicenes.<sup>[19]</sup> It was somewhat surprising that the activation energy for **8** was slightly, but



**Figure 1.** Comparison of X-ray crystal structures of (a) *rac*-**7** and (b) *rac*-**8**. The angle between the two planes of the terminal rings A and G ( $\theta_{AG}$ ) is highlighted in green. The distance between a centroid of A ring and a least-squares plane defined by central three rings C, D, and E ( $d_{A-CDE}$ ) is highlighted in blue. The twist angle along the helical inner rim ( $\langle \phi_{AG} \rangle$ ) is defined as average of five dihedral angles at inner rim and highlighted in red.

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Table 1. Photophysical properties of ICz-helicenes.							
lCz	$\lambda_{ m abs}~({ m nm})^{ m [a]}~({ m log}~oldsymbol{arepsilon})$	$\lambda_{_{(em)fl}}$ (nm) $^{[a,b]}$	$arPsi^{[a,b]}$	$\Delta  u$ (cm $^{-1}$ ) <sup>[c]</sup>			
7	310 (5.00), 357 (4.53), 404 (4.15)	429	0.24	1440			
8	323 (4.79), 405 (3.43)	420, 439 (sh)	0.14	880			
9	325 (4.81), 352 (sh, 4.45), 407 (4.11)	436, 457 (sh)	0.21	1630			
11	323 (4.96), 443 (3.82)	521	0.26	3380			
[a] Measured in	n CHCl <sub>3</sub> (1.0×10 <sup>-5</sup> M). [b] Excitation wavelength: 7 300 n	m; <b>8</b> 323 nm; <b>9</b> 330 nm; <b>11</b> 330 nr	n. [c] Stokes shift.				

ICz CD <sup>[a]</sup> CPL <sup>[a,b]</sup>	
$\lambda$ (nm) $\Delta \varepsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) $g_{\rm CD}$ (10 <sup>-3</sup> ) $\lambda$ (nm)	$arPhi^{\mathrm{[a,b]}}$ $g_{\mathrm{CPL}}$ (10 <sup>-3</sup> )
7 369 -62 -1.9 436	0.24 -0.76
<b>8</b> 360 -198 -11 429	0.14 -4.4
<b>8</b> <sup>(c)</sup> 373 -176 -11 509	0.05 -5.8
<b>9</b> 408 -112 -8.6 447	0.21 -2.7
<b>11</b> 355 -11 -5.3 530	0.26 -1.1

meaningfully higher than that for 7, that may be ascribed to more twisted geometry of the phenyl substituents in 7, but the exact reason is obscure at the present stage.

The lowest-energy absorption bands measured in chloroform (CHCl<sub>3</sub>) solutions were red-shifted in an order of 8<7<  $9 \ll 11$  and the corresponding fluorescence emissions were also in the same order (Figure 2 and Table 1). An introduction of electron-donor substituent on the indolocarbazole skeleton (9 and 11) lead to a considerable bathochromic shift due to their D-A structure. As expected from the CT nature, helicene 11 showed an apparent solvatochromism in the exited state, exhibiting blue, green, and yellow emissions in cyclohexane, CHCl<sub>3</sub>, and DMSO, respectively (Figure S20 and Table S5). A large dipole moment of 11 in the exited state ( $\mu_e$ ) was estimated to be 23.7 D, using the experimental differential dipole moments between the excited and ground states ( $\Delta \mu =$  $\mu_{e}$ - $\mu_{g}$ =22.9D) from the Lippert-Mataga plot,<sup>[20]</sup> and the ground state dipole moment ( $\mu_{q}$ ) of 0.8 D calculated at the B3LYP/6-31G(d) level of theory. The fluorescence quantum yields for azahelicenes 7, 8, 9, and 11 for CHCl<sub>3</sub> solutions were in a range of 0.14-0.26 that are at least one order of magnitude larger than those of pristine carbohelicenes of the similar size.<sup>[21]</sup> Notably, azahelicene 11 exhibited the emission with a relatively high quantum yield of 0.50 in DMSO (Table S5). A moderate Stokes shift of 1440 cm<sup>-1</sup> was observed for azahelicene **7**, which was further enhanced by the introduction of the D-A character (in 9 and 11). The smaller value observed for 8 (880 cm<sup>-1</sup>) indicates the relatively minor structural relaxation of this helicene in its exited state. A relatively rigid nature of pyridopyrrolo-helicenes 8 and 9 is in accord with the structured fluorescence spectra (Figure 2b).

The results of the CD and CPL spectral measurements for the chiral ICz-helicenes are compared in Figure 3 and Table 2. All the azahelicenes provided mirror-imaged spectra between the (*M*)- and (*P*)-enantiomers. While a very complex signal of multiple negative and positive Cotton effects was apparent in the CD spectra for all the helicene derivatives investigated, they all provided a quite comparable pattern with some differences in intensities and excitation energies. Apparently, the intensities of CD and CPL were found generally stronger in the pyridopyrrolo-helicene **8** (and **9** in moderate degrees). It is also to note that the signs of the CPL and the lowest-energy CD bands are always the same, as is typically observed for the  $\pi$ - $\pi$ \* transition of the rigid aromatic systems.<sup>[22]</sup> As for the typical pristine helicenes, the absolute configurations were assigned as (+) $\leftrightarrow$ P and (-) $\leftrightarrow$ M,<sup>[5c]</sup> that are in accord with those determined by the anomalous X-ray scattering described above.

Dissymmetry factors for CD and CPL spectra are frequently used for more accurately evaluating the degree of molecular



Figure 2. (a) UV-vis and (b) fluorescence spectra of ICz-helicenes in  $CHCI_{3}$  (1.0  $\times$  10  $^{-5}$  M).



Figure 3. (a) CD and (b) CPL spectra of ICz-helicenes in  $CHCl_3$  ( $1.0 \times 10^{-5}$  M).



chirality, that are defined as  $g_{CD} = \Delta \varepsilon$  ( $\lambda$ ) / $\varepsilon$  ( $\lambda$ ) { $\varepsilon$  ( $\lambda$ ) = 1/2 [ $\varepsilon_L$  $(\lambda) + \varepsilon_{R} (\lambda)$  and  $g_{CPL} = 2 \times \Delta I (\lambda)/I (\lambda) \{\Delta I (\lambda) = I_{L} (\lambda) - I_{R} (\lambda)\},\$ respectively,<sup>[22]</sup> where  $\boldsymbol{\varepsilon}_{L}$  and  $\boldsymbol{\varepsilon}_{R}$  denote the molecular extinction coefficients for left and right circularly polarized light, and  $\Delta I$  is the intensity difference between the left  $(I_1)$  and right  $(I_2)$ circularly polarized spontaneous emissions from a fluorophore at a given wavelength. The  $|g_{\rm CD}|$  and  $|g_{\rm CPL}|$  values of helicene derivatives are usually in a range of  $10^{-4}$  to  $10^{-3}$ , and only occasionally becomes  $10^{-2}$  in the order. As such, the  $|g_{CD}|$  value of **7** at 369 nm was found in an ordinal value of  $1.9 \times 10^{-3}$ , and interestingly, a 5.8 times larger value of  $1.1 \times 10^{-2}$  was observed for the pyridopyrrolo helicene 8, despite of the negligible structural differences (vide supra). The  $|g_{CPL}|$  value of helicene 8 was also 5.8 times larger than that of 7, being  $4.4 \times 10^{-3}$  and  $7.6 \times 10^{-4}$ , respectively. In a view of CPL-responsive materials science, the CPL brightness<sup>[22e]</sup> or luminocity<sup>[22f]</sup> shall better gauge the quantitative performance of the relevant chiral molecules. While the pyridine moiety generally reduces molecular absorptivity, the value was estimated to be around 3 times improved in the pyridopyrrolo-helicene 8 than that of parent helicene 7.

It is worth citing that a pyridine-containing *S*-shaped azahelicene was reported to show a relatively large (absolute) dissymmetry factor value compared with the corresponding carbohelicene,<sup>[23]</sup> for which none of a possible rationale was discussed. A simultaneous introduction of electron-withdrawing and -donating functions to<sup>[7]</sup> helicene was found to significantly enhance its CPL features, which was ascribed to a proper control of the relevant molecular orbitals.<sup>[24a]</sup> In chiral carbazolophanes, the relative geometries of two carbazole moieties were recently shown to impact on the chiroptical responses and excimer emission in particular.<sup>[24b]</sup>

Consequently, we performed the theoretical calculations by the approximate coupled cluster singles and doubles model at the RICC2/def2-TZVP level to explain the enhanced CPL responses for 8 against 7 (see the Supporting Information for details).<sup>[25]</sup> The electronic transition relevant for the CPL response was determined as the A-symmetry for both of the helicenes, which means the transition is along the Z-axis. The calculated transition energies for 8 (422 nm vs 429 nm) and a relative shift between helicenes **7** and **8** ( $\Delta\lambda = +3$  nm vs +7 nm) all well reproduced the experimental observations. It is to note that a considerable amount (~15%) of double excitation character was identified for both of the helicenes, which somewhat justifies our failure of the (conventional) TD-DFT method to reproduce the experimental results. The dissymmetry factor can be theoretically approximated as  $g_{CPL} =$  $4|\mu||m|\cos\theta/(|\mu|^2+|m|^2)$ , where  $\mu$  and m are the electric and magnetic dipole transition moments of the relevant electronic transitions.<sup>[22]</sup> The calculation predicted very well the experimental CPL spectra both for helicenes 7 and 8, the dissymmetry factor for the latter being calculated to be 4.2 times higher than that of the former (Table 3), again satisfactorily reproduced the observation. This is attributed to the introduction of pyridine-nitrogens, for which a considerable enhancement of  $|\mathbf{m}|$  and slight reduction of  $|\mathbf{\mu}|$  are responsible, while the angles between both dipole transition moments

Table 3. Transition energy, dipole transition moments, and dissymmetry
factor for the $S_1 \rightarrow S_0$ transition of ( <i>M</i> )-7 and ( <i>M</i> )-8 calculated at the RI-CC2/
def2-TZVP level.

Transition energy (eV)2.92 (425 nm)2.94 (422 nm) $ \boldsymbol{\mu} ^{[a]}$ 266.4179.0 $ \boldsymbol{m} ^{[b]}$ 17.451.0 $\cos \theta^{[c]}$ -1.0-1.0 $q_{CP}^{[d]}$ -2.6 × 10^{-4}-1.1 × 10^{-3}	Parameter/ICz	7	8	1
	Transition energy (eV) $ \mu ^{[a]}$ $ m ^{[b]}$ $\cos\theta^{[c]}$ $g_{CPL}^{[d]}$	2.92 (425 nm) 266.4 17.4 1.0 2.6×10 <sup>-4</sup>	2.94 (422 nm) 179.0 51.0 −1.0 −1.1×10 <sup>-3</sup>	

[a] Magnitude of electric dipole transition moment in  $10^{-20}$  esu cm units. [b] Magnitude of magnetic dipole transition moment in  $10^{-23}$  erg G<sup>-1</sup> units. [c]  $\theta$ : angle between the electric and magnetic dipole transition moments. [d] Dissymmetry factor,  $g_{CPL} = 4 |\boldsymbol{\mu}| |\boldsymbol{m}| \cos\theta/(|\boldsymbol{\mu}|^2 + |\boldsymbol{m}|^2)$ .

remain antiparallel. A configurational analysis on **8** revealed that a considerable amount (4%) of HOMO-1 to LUMO contribution is apparent in addition to the HOMO-LUMO (87%), while the former contribution was completely missing in **7** (nearly pure HOMO-LUMO transition). The A-symmetry nature of HOMO-1 orbital (while HOMO and LUMO orbitals are both B-symmetry) seems responsible for the enhanced magnetic dipole transition moment in pyridopyrrolo-helicene **8** (Figure S22).

In order to externally control the chiroptical responses by modifying electron-withdrawing effect of pyridine-nitrogen,<sup>[26]</sup> we performed the CD and CPL spectral examination for **8** with a gradual addition of trifluoroacetic acid (TFA) (Figure 4). As expected, a slight red-shift was observed in the absorption spectra upon an increased addition of the acid. In addition, the fluorescence spectra are more significantly red-shifted with a decrease of emission intensity. The original blue emission was completely disappeared and the green emission became apparent in the presence of an 80 mM of TFA. Nevertheless, the observed CPL was remained in the comparable intensity, implying that the (absolute) dissymmetry factor value considerably increased in the protonated form. Such a phenomenon



**Figure 4.** (a) UV-vis and (b) fluorescence spectral changes of 8 in CHCl<sub>3</sub>  $(1.0 \times 10^{-5} \text{ M})$  by an incremental addition of TFA. (c) CD and (d) CPL spectra of 8 in CHCl<sub>3</sub>  $(1.0 \times 10^{-5} \text{ M})$  in the presence (80 mM) and absence of TFA.

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may be quite valuable for possible applications in the chiroptical switching devices.<sup>[27]</sup> It is to note that an azahelicene involving an imidazole moiety was reported to show a decreased dissymmetry factor upon an addition of TFA.<sup>[26d]</sup> Thus, the effect of protonation to basic nitrogen on chiroptical responses, in particular the  $|g_{CPL}|$  values, is not straightforward and details of observed enhancement in the current system are remain to be elucidated.

Finally, we paid our attention to the molecular packing modes of helicenes **7** and **8** in their solid states. The molecules of helicene **7** was found to make a unique one-directional columnar structure in a helical manner, while those of **8** showed a completely different packing mode (Figure S16 and S17). As such, a semiconducting behavior was anticipated for the former helicene in the solid thin-film state. Indeed, an apparent hole-transporting property was demonstrated in a field effect transistor (FET) characteristics measurements, a hole mobility being found  $1.5 \times 10^{-5}$  cm<sup>2</sup>/Vs (Figure S24).<sup>[11f]</sup> The HOMO level estimated by photoelectron yield spectroscopy (PYS) measurement was -5.70 eV (Figure S25), which is in accord with the calculated one (-5.38 eV) at the B3LYP/6-31G(d) level of theory (Figure S23).

In summary, we successfully obtained the enantiomerically pure forms of a series of  $C_2$ -symmetic  $\pi$ -extended azahelicenes bearing the double indolo[3.2.1,-jk]carbazole scaffold by means of palladium-mediated double dehydrogenative cyclization, followed by chiral HPLC. The chiral helicene 8 possessing pyridopyrrolo-carbazole moieties exhibited much improved chiroptical responses with ca. 6 times higher  $|g_{CD}|$  and  $|g_{CPL}|$ values compared with those from the non-pyridine azahelicene 7. Theoretical calculations confirmed that the pyridine nitrogen effectively increases the magnetic versus electric contribution in the relevant electronic transition, and thus, enhances the dissymmetry factor values. Upon protonation of 8, a remarkable red-shift of the emission with a considerable increase of the |  $g_{CPL}$  value was observed, facilitating the chiroptical switching applications. Besides, a p-type FET response was established with helicene 7, due to its semiconducting property through the columnar structure in its solid state. Our findings and implications detailed above would provide valuable information for designing novel azahelicenes and derivatives, with superior optical, chiroptical, as well as electronic properties.

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## **Conflict of Interest**

The authors declare no conflict of interest.

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