Helicenes

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A Facile and Versatile Approach to Double N-Heterohelicenes: Tandem Oxidative C–N Couplings of N-Heteroacenes via Cruciform Dimers**

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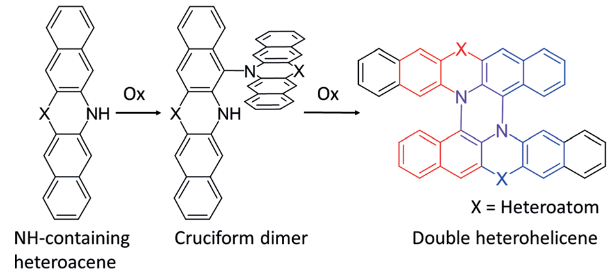
Abstract: *Novel double N-hetero[5]helicenes that are composed of two nitrogen-substituted heteropentacenes are synthesized by tandem oxidative C–N couplings via the cruciform heteropentacene dimers. The developed method is very facile and enables the synthesis of a double helicene in only two steps from commercially available naphthalene derivatives. These double N-hetero[5]helicenes have larger torsion angles in the fjord regions than typical [5]helicenes, and optical/electrochemical measurements revealed a significant increase in the electronic communication between the two heteropentacene moieties of the double helicenes compared with their cruciform dimers. The optical resolution of one of the double helicenes was successfully carried out, and their stability towards racemization was remarkably higher than those of typical [5]helicenes. The synthetic strategy proposed in this paper should be versatile and widely applicable to the preparation of double helicenes from other N-containing π-conjugated planar molecules.*

Azaacenes, the nitrogen-substituted analogues of acenes, have attracted much attention in the field of organic electronics as promising candidates for charge-transport materials because of their facile syntheses and higher chemical stability compared with larger acenes, such as pentacene.[1] Over the past decade, several research groups have reported the synthesis of novel azaacene derivatives by means of chemical modification of azaacene skeletons, for example, by introducing functional groups[2,3] and/or extending the π-plane.[4] However, there have been few attempts to construct complicated structures by combining azaacene molecules, in spite of their potential for three-dimensional π-conjugated molecular bricolages. Herein, we report the shortest synthesis of double N-hetero[5]helicenes by a direct oxidative coupling of N-substituted pentacenes via their cruciform dimers to demonstrate the usefulness of these compounds as building blocks for novel three-dimensional (3D) π-systems (Scheme 1).



Scheme 1. Synthesis of double heterohelicenes via cruciform heteroacene dimers by tandem oxidative couplings.

The oxidative coupling is one of the most straightforward strategies to connect π-systems.[5] Recently, we found that a 6,13-dihydro-6,13-diazapentacene (DP) with an alkyl substituent on one of the nitrogen atoms (**5a** and **5b**) could be easily oxidatively dimerized in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; Scheme 2a). X-ray single-crystal analysis revealed the cruciform structure of these dimers with a single bond between the N13 and C12′ positions of each monomer, and the two diazapentacene moieties were found to be almost perpendicular to each other (Supporting Information, Figure S1). It is well-known that DP is converted into 6,13-diazapentacene by chemical oxidation,[1] and this reaction could be understood as the formation of a pyrazine moiety resulting from the removal of two electrons and two protons. On the other hand, **5a** and **5b** have only one NH group, and therefore, the formation of a pyrazine moiety is impossible; instead, oxidation results in the dimerization between the N13 and the C12′ positions, which have a large spin density in the radical cation state (Figure S2). The oxidative dimerization of 13*H*-dibenzo[*b*,*i*]phenoxazine (**6**), which is regarded as the nitrogen- and oxygen-substituted analogue of pentacene and contains only one NH group, also gave a cruciform dimer, namely compound **4** (Scheme 2a). In contrast to the previously reported oxidative dimerizations of phenoxazines, which provided mixtures of two structural isomers,[6] the dimerizations of **5a**, **5b**, and **6** proceeded with high regioselectivity, giving only the N13–C12′ connected dimers because the fused benzene rings prevent reactions at the *para* positions with

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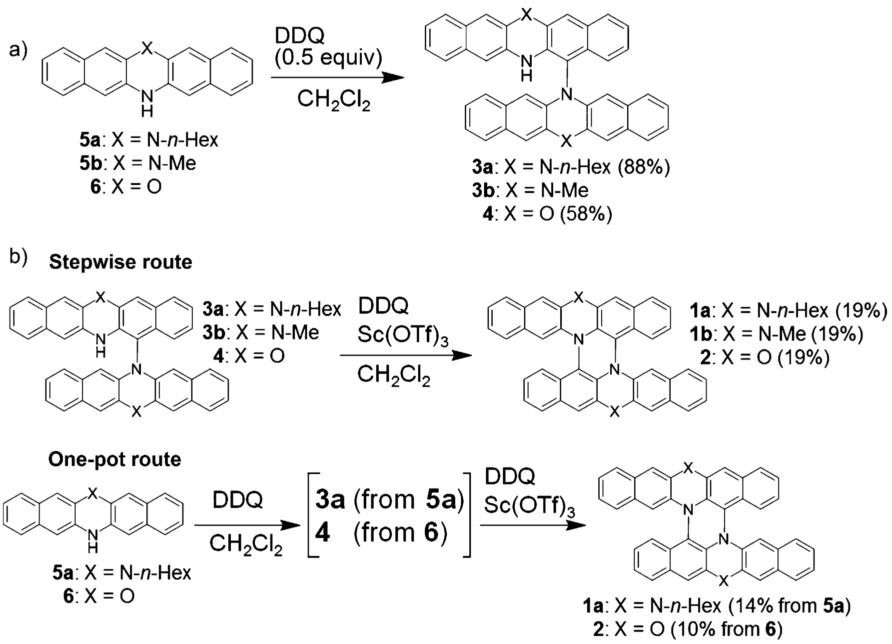

Scheme 2. Synthesis of a) cruciform dimers and b) double N-hetero[5]helicenes.

respect to the nitrogen atoms, which are the carbon atoms with the largest spin density in the radical cation state.

An important feature of these cruciform dimers is the presence of an intact NH group, which enables further chemical modifications. It is easily predicted that the oxidation of these cruciforms will result in ring-fusion reactions affording double N-hetero[5]helicene structures (Scheme 1).[7–9] First, we tried to further oxidize the cruciform dimers with DDQ, but the ring-fused products were not obtained. After screening some oxidation conditions, we found that a combination of DDQ and Sc(OTf)$_3$ resulted in the ring-fusion reaction (Scheme 2b).[5] Moreover, we succeeded to reduce the number of synthetic steps required for the formation of **1a** and **2** by developing a method for the one-pot tandem oxidation of **5a** and **6**. To the best of our knowledge, these are the shortest syntheses of double helicenes to date, as only two and three steps are required to obtain **1a** and **2** from commercially available 2,3-disubstituted naphthalene derivatives, respectively. Rajca et al. have reported the synthesis of double N-hetero[5]helicenes by three oxidative homocouplings (one C–C and two N–N couplings) between two planarized *meta*-phenylenediamine derivatives.[8] However, because the helical structure was maintained by the weak N–N single bonds, Rajca's double helicene could be reverted back to its non-helical precursor by chemical reduction and the dissociation of two N–N bonds. In our case, on the other hand, the two heteroacenes are connected by two C–N bonds, and therefore, our double helicenes are thought to have higher chemical stability. Furthermore, because our strategy does not require any premodifications of the starting heteroacenes, such as the introduction of reactive substituents, it should be widely applicable to the construction of double helicenes from other planar π-conjugated monomers with an NH group, such as phenothiazine and carbazole derivatives.[10]

Fortunately, the structures of **1b** and **2** were confirmed by single-crystal X-ray crystallography (Figure 1), which revealed their double helicene structure consisting of two N-hetero[5]helicene moieties with the same helicity in a molecule. The two enantiomers (the *P*,*P′* and *M*,*M′* isomers) were found to be present in the unit cell in a ratio of 2:2. The torsion angles, which are defined as the dihedral angles between three successive purple bonds in Figure 1, were determined to be 54.7° and 51.8° for **1b** and 50.1° and 41.4° for **2**; these values are significantly larger than the dihedral angle of [5]helicene (ca. 30°).[11] We could not observe the formation of the achiral *P*,*M′* isomer. These results were explained by DFT calculations.[12] The achiral isomers of **1b** and **2** were calculated to be unstable with respect to the chiral isomers by 10.1 and 8.6 kcal mol^{-1}, respectively, probably because of the large strain energy that results from the highly bent structure of the heteropentacene moieties in the central hexagons (Figures S3 and S4). All of the double helicenes are well soluble in

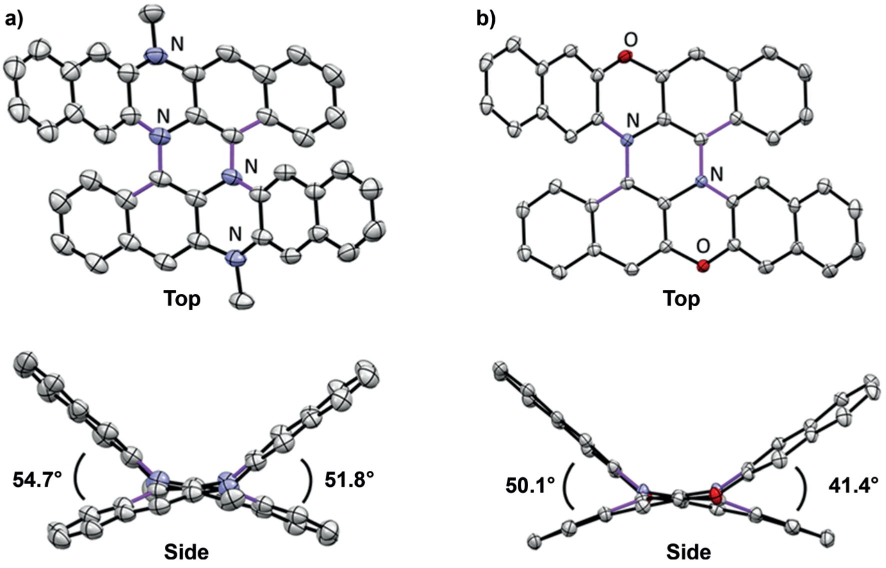

Figure 1. X-ray crystal structures of a) (*P*,*P′*)-**1b** and b) (*P*,*P′*)-**2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. The torsion angles are defined as the dihedral angles between three successive purple bonds.

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common organic solvents, such as toluene, dichloromethane, chloroform, and THF, which reflects their distorted molecular structures, whereas the cruciform dimers **3b** and **4** with short or no side chains showed low solubilities.

The absorption spectra of **1a**, **3a**, and 6,13-dihexyl-6,13-dihydro-6,13-diazapentacene[3] (**7**) are shown in Figure 2a. The spectral shape for cruciform dimer **3a** was very similar to that of **7**, and therefore, the two DP units in **3a** basically maintain their monomeric electronic properties because of their perpendicular arrangement. On the other hand, the absorption of DP double helicene **1a** was globally broadened and red-shifted. The same trend was observed in the spectra of **2**, **4**, and **6**, suggesting an increase in the π-conjugation between the two heteroacene moieties in the double helicenes. The ring fusion to the double helicenes also affected the emission properties (see the Supporting Information).

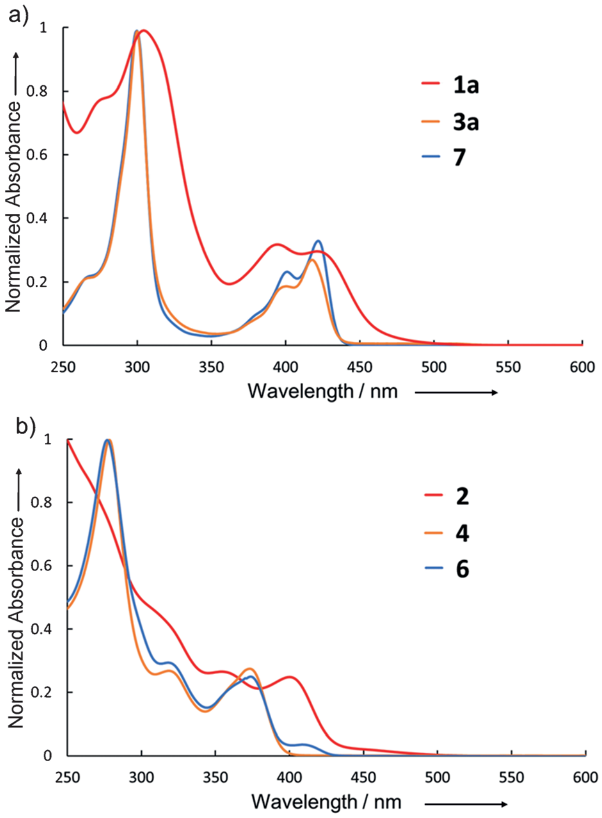

Figure 2. Absorption spectra of a) **1a**, **3a**, and **7** and of b) **2**, **4**, and **6** in CH_2Cl_2.

Electrochemical measurements revealed that the double helicenes show three (**1a** and **1b**) and two (**2**) couples of reversible one-electron oxidation processes (Table 1; for the voltammograms see Figure S10–S14). Interestingly, for the double helicenes, the difference between the first and the second oxidation potential ΔE (E_2-E_1), which relates to the magnitude of the electronic interaction between two redox sites, is much larger than for their cruciform precursors. For example, the ΔE values of the cruciform DP dimers (**3a**: 0.121 V; **3b**: 0.101 V) increased substantially to 0.578 V (**1a**) and 0.574 V (**1b**) in the double N-heterohelicenes.[13] These results also suggest that the ring fusion of two heteroacene moieties greatly enhances the electronic communication between the two azaacene units. The forth oxidations of **1a** and **1b** were prohibited probably because of the increased Coulomb repulsion in their highly oxidized states resulting from the ring fusion. The absorption spectra of $\mathbf{1a}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ showed that the generated radical spin was fully delocalized over the whole molecular skeleton (see the Supporting Information).

Table 1: Oxidation potentials (V vs. Fc^0/Fc^+) of the double N-hetero[5]-helicenes **1a**, **1b**, and **2** and the cruciform dimers **3a** and **3b** in CH_2Cl_2 (0.1 M nBu_4NBF_4), determined by differential pulse voltammetry (DPV) measurements and simulations.[14]

	E_1	E_2	E_3	E_4	E_2-E_1
1a	−0.103	0.475	0.802		0.578
3a	0.044	0.165	0.190	0.725	0.121
1b	−0.065	0.509	0.820		0.574
3b	0.057	0.158	0.220	0.696	0.101
2	0.152	0.717			0.565

We succeeded in the optical resolution of double helicene **2** by using an HPLC column with a chiral stationary phase. The circular dichroism (CD) spectra of the fractions that eluted more rapidly and more slowly were mirror images of each other (Figure 3a), and it was confirmed that these two fractions consisted of enantiomers with opposite helicity. The CD spectra of (*P*,*P*′)-**2** and (*M*,*M*′)-**2** that were simulated by time-dependent density functional theory (TD-DFT) calculations were in good agreement with the observed spectra, and it is strongly suggested that the faster eluting enantiomer has *P*,*P*′ helicity and the more slowly eluting enantiomer *M*,*M*′ helicity (Figure 3b). The CD spectrum of enantiopure **2** remained unchanged after heating in toluene at 100 °C for 13 hours (Figure S20), showing that double hetero[5]helicene **2** has a much higher stability towards racemization than [5]helicene, which racemizes with a half-life of 62.7 minutes at 57 °C.[15]

In conclusion, we have successful developed a facile and straightforward approach for the preparation of novel double N-hetero[5]helicenes that consist of two fused heteropentacenes by employing tandem oxidative coupling reactions of heteropentacenes that proceed via the cruciform dimers. X-ray single-crystal analysis confirmed the structures of the double helicenes and the cruciform intermediates.[16] The absorption and emission spectra, electrochemical measurements, and DFT calculations revealed an increase in π-conjugation between the two heteroacene moieties in the double helicenes compared to the cruciform precursors. The optical resolution of **2** was accomplished by preparative HPLC on a chiral stationary phase, and the helical structures were shown to be stable reflecting their rigid molecular structure. The synthetic strategy towards double helicenes that we propose in this paper is thought to be highly general and applicable to various heteroacenes. The physical properties of the heteroacenes, such as their charge transport and circular polarized luminescence (CPL) properties, will be discussed in detail in our future work, and further investiga-

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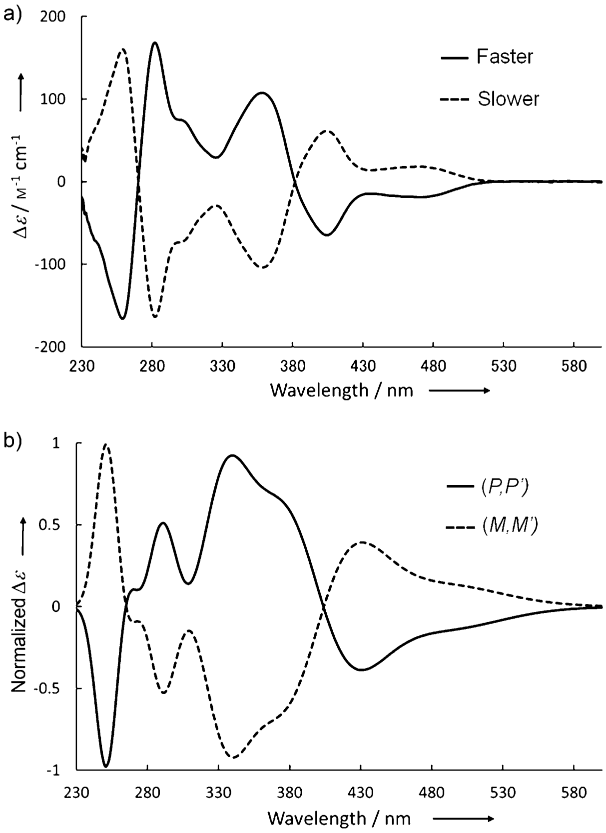

Figure 3. a) CD spectra of the faster and the more slowly eluting enantiomers of **2** in $CHCl_3$ at 298 K. b) Simulated CD spectra of (*P*,*P*')-**2** and (*M*,*M*')-**2** based on TD-DFT calculations at the B3LYP/6-311+G*//B3LYP/6-31G* level of theory.

tions to construct double helicenes from other heteroacenes or with higher helicity are in progress.

Keywords: electrochemistry · electron transfer · helicenes · heteroacenes · oxidation

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[16] CCDC 1028660 (**3a**), 1028661 (**4**), 1040766 (**2**), and 1040767 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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