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Oxa-[7]-superhelicene: A π -extended helical chromophore based on HBCs

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Abstract: Herein, we report on the synthesis of a novel π -extended "superhelicene" based on hexa-peri-hexabenzocoronenes (HBC) via an efficient four-step synthetic procedure starting from diphenylether. Comprehensive structural analyses were performed by means of NMR-spectroscopy and mass spectrometry measurements together with X-ray analysis. Physico-chemical analysis of the superhelicene and suitable HBC references revealed among others outstanding fluorescent features with quantum yields of over 80%.

Polycyclic aromatic hydrocarbons (PAHs) have evolved as important benchmarks in the study of graphene. Here, their smaller, modular sizes and their size-tunable features stand out.^[1] Not only the more common, planar PAHs have drawn significant attention among chemists, physicists, and material scientists. But, also the design, synthesis, and study of nonplanar PAHs is of great interest. Deviation from planarity offers novel ways and means in the fields of organic materials and electronics.^[2] Alteration of conjugated π -systems towards the third dimension is enabled by the introduction of non-sixmembered rings, by the "roll-up" of individual π -systems, or by the institution of helicity. In the latter approach, π -systems are placed in a screw-shaped arrangement.^[3]

Discovered more than 100 years ago, helical, contorted aromatics were among the first of these systems to be described in the literature.^[4] Ever since, this family of molecules has always ignited the curiosity of chemists^[5] and has found its way into a large variety of applications. By virtue of their inherent chirality they have been applied in enantioselective catalysis; both in the form of ligands to afford catalytically active metal complexes^[6] as well as in the field of organocatalysis.^[7] Notable are also their roles in light emitting devices,^[8] solar cell devices,^[9] chiroptical switches,^[10] organic field-effect transistors (OFETs)^[11] and non-linear optics.^[12]

At the forefront of contemporary research is the π -extension of helicenes to afford novel materials with unique and tailorable

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properties. Important is also the solubility of helicenes, which exceeds that of the planar analogous by far, and, which constitutes a milestone in the realization of solution-processable materials.^[13]

In the context of converting non-planar PAHs into three dimensional carbon allotropes, helical building blocks are considered as key precursors. Promising is in this context the fact that several π -extended helical structures have recently been reported.^[14]

Herein, we report on the synthesis and the characterization of a first member of a new class of HBC-based helicenes, namely "superhelicenes".^[15] The synthesis – scheme 1 – started from diphenylether 1, which was converted into its 3,6-di-brominated derivative 2 by aromatic halogenation. A double Sonogashira coupling with 4-tert-butylphenyl-acetylene followed by a Diels-Alder reaction with 2.5 eq. of 2,3,4,5-tetrakis(4-(tertbutyl)phenyl)cyclopenta-2,4-diene-1-one 8 yielded bis-HAB-ether 4. Helical 6 was obtained after reaction with 2,3-dichloro-5,6dicyano-1,4-benzoquinone DDQ / triflic acid in CH₂Cl₂ creating an overall number of 13 C-C bonds, including the formation of the furan ring. To the best of our knowledge formation of a furan ring under such experimental conditions is unprecedented. We have reason to believe that the closure of the furan ring is the final step of the cascade, as shorter reaction times like, for example, 2 h, furnished mixtures of helicene 6 and bis-HBCether 5. Interestingly, changing the reagents to $FeCl_3$ in nitromethane/CH₂Cl₂ assisted in avoiding the closure of the furan ring and in forming bis-HBC-ether 5 selectively. 5 serves as a perfect reference as it is structurally related to the π -extended helicene 6 but lacking HBCs in a helical arrangement. Notably, bis-HBC-ether 5 is light sensitive and transforms into helicene 6 via photocyclization. This phenomenon was observed during photophysical measurements but was not further studied yet. In consequence, such measurements with bis-HBC-ether 5 always show minor amounts of 6. Therefore, two other references, that is, pentakis-tert-butyl-mono-methoxy-HBC 7 and hexakis-tertbutyl-HBC 23, were synthesized and characterized - for details see SI, chapter 2.

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Scheme 1: Synthesis of the oxa-[7]-superhelicene 6: a) Br_2 (2 eq.), 1,2-dichloroethane, 1 h at 0 °C, 17 h at r.t., yield 99 %; b) 4-*tert*-butylphenylacetylene (2.1 eq.), Pd(PPh₃)₂Cl₂ (3 mol%), Cul (1.5 mol%), THF/disopropylamine (1:1), N₂, 19 h at 100 °C, yield 51 %; c) tetra-(4-*tert*-butylphenyl)-cyclopentadienone (2.5 eq.), toluene, N₂, 23 h at 220 °C (pressure flask), yield 86 %; d) FeCl₃ anhydrous (35 eq.), MeNO₂, CH₂Cl₂, N₂, 25 min at 0 °C, 20 h at r.t., yield 60 %; e) DDQ (15 eq.), triflic acid (30 eq.), CH₂Cl₂, N₂, 25 min at 0 °C, 20 h at r.t., yield 60 %; e) acaculated (DFT-calculation carried out on B3LYP/6-31G* level). Hydrogen atoms omitted for clarity.

Crystals suitable for x-ray diffraction analysis were grown by slow diffusion of ethanol into a benzene solution of 6 at room temperature. Only small, twinned crystals were obtained and the crystal structure was of moderate quality - for x-ray analysis details see SI, chapter 11. Fortunately the quality of the measurement was good enough to present a preliminary structural analysis of the superhelicene 6. It reveals that 6 crystallizes in a triclinic crystal system with a P-1 space group and most importantly, the connectivity between the two HBCs is validated. Also the stacking of the helicenes in the solid state can be deduced. The M and P isomers pair off and form π - π stacks between two HBCs with a distance of ~ 3.4 Å. Such a distance is in very good agreement with those seen for π - π stacks of hexakis-tert-butyl-HBC 23.[16] Since the crystal structure was of only moderate quality we also performed DFT calculations on the structure and the molecular frontier orbitals of the superhelicene - see scheme 1 and SI, chapter 10. Considering the overall sum of the five torsion angles of the seven rings forming the helicene we derived values of 86.4 ° (xray structure) and 94.1 ° (DFT-calculation) - for details see SI, chapter 11 - which are both larger than 78.9 ° seen in the x-ray structure for oxa-[7]-helicene,^[17] prompting to a more distorted helical system.

The structure is also reflected in the NMR spectra. The signals of the "inner" *tert*-butyl groups, which are positioned above and below the other HBC are high-field shifted and appear in the ¹H NMR spectrum at 0.18 ppm. With the help of HSQC, HMBC, COSY and nuclear Overhauser effect (NOE) measurements it was possible to assign all signals in the ¹H NMR and a majority of signals in the ¹³C NMR – for details see SI, chapter 3.

Comparative assays on the basis of photophysical investigations between hexakis-*tert*-butyl-HBC **23**, pentakis-*tert*-butyl-monomethoxy-HBC **7**, bis-HBC-ether **5** and helicene **6** shed light onto the impact of twisting and extended π -conjugation. The absorption of, for example, **6** features signatures in the UV and the visible regions. In accordance with Clar's rule for PAHs, the absorption features at 355 / 365, 393 / 433 nm, and 480 / 515 nm are ascribed to β -, p-, and α -band absorptions, respectively.^[13] At first glance, the β -, p-, and α - band absorptions are, due to the larger π -conjugated system, redshifted respectively by 14, 3, and 50 nm relative to those of 23, 7, and 5 - Figure 1. A closer look reveals additional differences: The α -band absorptions in the long wavelength range are more intense in superhelicene 6 than in 5 and 7, while the β -band absorptions in the short wavelength range are less intense. In principle, p- and α-band absorptions are symmetry-forbidden and, as such, should be unobservable. On one hand, the p-absorption bands are enabled by intensity borrowing from the energetically close lying β-absorption bands. On the other hand, symmetrybreaking substituents and or structural alterations affect the αband absorptions. The functional groups assist in lowering the symmetry from D_{6h} in 23 to C_{2v} in 7 and 5, and in intensifying the α -band absorptions. In **6**, it is the extended π -conjugation and the helical structure that both alter the HBC structure. As a matter of fact, it is hardly surprising that the α -band absorptions in the helicene 6 are even more intense than in 5 and 7 and overall red-shifted.[18]





Strong fluorescence evolves for superhelicene **6** in the 490 to 670 nm region, with vibrational fine structure that includes 525, 565, and 620 nm maxima, as well as fluorescence quantum yields in the range of 80% to 85%. – see SI, chapter 7. Notable is the small Stokes shift of 10 nm when contrasting the long wavelength absorption maximum with the short wavelength fluorescence maximum. The fluorescence features of **7** and **5** are 50 nm blue-shifted relative to those of **6** in sound agreement with the findings gathered in the absorptions measurements. They are also vibrationally better resolved as a reflection of

10.1002/anie.201800585

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structural rigidity. The fluorescence quantum yields of **23** and **7** with 4.1% and 6.9% are more than ten times weaker than those of **6**.^[19] In time-resolved fluorescence experiments a decay rate of 2.3×10^8 s⁻¹ for **6** signifies a significant acceleration relative to **23**, **7**, and **5** with 0.21 × 10⁸, 0.26 × 10⁸ and 0.28 × 10⁸ s⁻¹, respectively.^[20]

From the absorption and fluorescence measurements we derive singlet excited state energies for **23**, **7**, **5**, and **6** of 2.8, 2.6, 2.6, and 2.4 eV, respectively. To investigate the energetics of the triplet excited state, emission measurements were conducted at 80 K. In contrast to the references, which reveal phosphorescence features in the 550 to 700 nm range, oxa-[7]-superhelicene **6** is non-phosphorescent – for details see SI chapter 4.

The redox features were determined by cyclic voltammetry and differential pulse voltammetry in CH_2CI_2 with Fc/Fc^+ as reference and 0.2 M TBAPF₆ as supporting electrolyte. **6** gives rise to two reductions at -1.5 and -1.8 V as well as three oxidations at +0.9, +1.2, and +1.5 V – Figure 2. **23** features only one reduction at -1.7 V and only one oxidation at +1.1 V. **5** exhibits two reductions at -1.6 and -1.9 V and three oxidations at +1.1, +1.3 and +1.4 V, while **7** possesses only one reduction at -1.8 V and two oxidations at +0.9 and +1.1 V – for details see SI, chapter 6.



Figure 2: Differential pulse voltammetry (left) and cyclic voltammetry (right) of 6 in CH₂Cl₂ with Fc/Fc⁺ and 0.2 M TBAPF₆ as reference and supporting electrolyte, respectively.

Considering the first reduction and the first oxidation, the HOMO – LUMO gaps of **23**, **7**, **5**, and **6** are 2.8, 2.7, 2.7, and 2.4 eV, respectively. All of them are in sound agreement with the singlet excited state energies – vide supra.

The signatures of **6** upon oxidation were elaborated in spectroelectrochemical experiments. Upon applying a bias of +1.0 V versus Ag/Ag⁺, prominent maxima develop at 600, 650 and 700 nm and are ascribed to the one-electron oxidized form of **6** – Figure 5 – for more details see SI, chapter 6.



Figure 3: Species associated spectra (left) and time profiles (right) of 6 in THF received by Target Analysis.

Femtosecond transient absorption spectroscopy in combination with global and target analyses stood at the forefront to shed light onto the time-dependent excited state features and kinetics. Figure 3 shows that 387 nm excitation of **6** leads to the instantaneous formation of its singlet excited state with characteristic maxima at 420, 650, 740, and 860 nm – for more details see SI chapter 5, figure 21. By means of intersystem crossing, the singlet excited state transforms into triplet excited state. Fingerprint absorption of the latter is a 700 nm maximum. The underlying rates of singlet excited state decay / triplet excited state formation and triplet excited state decay were determined for **6** as 2.3×10^8 and 1.3×10^4 s⁻¹, respectively.

In comparison, **23**, **7**, and **5** show different behaviors. Upon 387 nm excitation of the references, the singlet excited state forms with maxima at 544 and 1350 nm – for more details see SI chapter 5, figure 22 - 24. In the following, transformation into the triplet excited state by intersystem crossing with characteristic maxima at 500 and 980 nm is observed. The deactivation rates of the singlet excited states are in the range from 0.21 x 10^8 to 0.28 x 10^8 s⁻¹, while those of the triplet excited states range from 0.71 x 10^4 to 1.5 x 10^4 s⁻¹.

Probing 6 in the presence of TCNE led to the formation of the one-electron oxidized form of 6 with transients evolving at 645 and 705 nm - Figure 4 - for more details see SI, chapter 5, figure 20. As far as the signature of the TCNE radical anion is concerned, it is discernable in the 400 to 450 nm range in accordance with literature, where it has been reported to appear at 430 nm.^[21] It is, however, the triplet excited state of 6, which undergoes charge separation with a bimolecular rate constant of $2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ – for more details see SI, chapter 5, figure 25. On a timescale of up to 10 µs, the corresponding charge separated state deactivates via reinstatement of the ground state. The addition of TCNE to solutions of 23, 7, and 5 led to similar results. Here, the one-electron oxidized form evolved in the form of 430, 555, and 860 nm signatures. The corresponding bimolecular rate constant for charge separation starting from the triplet state are between 0.9 x 10^{10} and 1.2 x 10^{10} M⁻¹s⁻¹ – for more details see SI, chapter 5, figure 26 - 27.







Figure 5: Comparison of TA spectrum of **6** in THF upon addition of TCNE with 0.06 μ s time delay with SEC spectrum of **6** in THF upon applying of 1.0 V with TBAPF₆ as electrolyte vs. Ag/Ag⁺.

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In summary, we synthesized and in depth characterized the first member of a novel family of π -extended helical chromophores. A straightforward four-step synthetic protocol was developed starting from diphenylether. We documented the outstanding photophysical properties of helical rather than planar HBC relatives. Currently, we perform complementary investigations with these novel π -extended helicenes including the tailored synthesis of even more intriguing members of this molecular family. Additionally, we are focusing on the enantiomeric separation and device fabrication such as light emitting devices.

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Keywords: Helical structures • π -extension • Polycyclic aromatic hydrocarbons • Fluorescence • Photophysics

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- [18] Footnote: The auto-oxidation of 5 results in an absorption spectrum, which also features the characteristics of 6.
- [19] Footnote: As 5 auto-oxidizes under illumination the fluorescence quantum yields of 5 feature contributions from 6. Uncorrected, the quantum yield is then 12.1 %. Corrections of the absorption and fluorescence spectra by subtracting the absorption and fluorescence features of 6 lead to quantum yields of 6.4 %.
- [20] Footnote: In line with the energy gap law of the fluorescence, the redshifted fluorescence of superhelicene 6 is linked to shorter lifetimes as non-radiative deactivation channels start to dominate. This stands, however, in sharp contrast to the fluorescence quantum yields of superhelicene, which are higher than those noted for the in the blue region emitting HBCs 5 and 7. A likely rationale is the lower symmetry of superhelicene 6 when compared to the parent HBCs.
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Entry for the Table of Contents (Please choose one layout)

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The fusion of oxa-[7]-helicene with HBC subunits in a straight forward synthesis gave a novel structural motif for π -extended helical chromophores with outstanding photophysical properties (e.g. fluorescence quantum yields $\Phi_{\rm f} > 80$ %).



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Page No. – Page No.

Oxa-[7]-superhelicene: A π -extended helical chromophore based on HBCs