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Fluorescence of a Chiral Pentaphene Derivative Derived from the Hexabenzocoronene Motif

Received 00th January 20xx, Accepted 00th January 20xx Philipp Rietsch,^[a] Jan Soyka,^[a] Steffen Brülls,^[d] Jasmin Er,^[a] Katrin Hoffmann,^[b] Julia Beerhues,^[C] Biprajit Sarkar,^[c] Ute Resch-Genger,^{[b]*} and Siegfried Eigler^{[a]*}

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A new fluorescent pentaphene derivative is presented that differs from hexabenzocoronene (HBC) by one carbon atom in the basal plane skeleton. A 500% increased fluorescence quantum yield is measured compared to the HBC derivative. The pentaphene compound, obtained by a modified Scholl oxidation, is also emissive in the solid-state, due to the packing motif in the crystal.

Hexabenzocoronenes (HBCs), a subgroup of polyaromatic hydrocarbons (PAHs), have 42 sp²-carbon atoms assembled by linking seven benzene rings. The resulting properties make them interesting for optical and electronic applications,^[1-5] self-assembly,^[2, 6] surface functionalisation^[7] and the bottom-up synthesis of graphene.^[8-10] The HBC scaffold has D₆ symmetry. Through the variation and arrangement of the substituents, a plethora of derivatives with a wide range of different chemical properties and of well-defined symmetry (C₃, C₂ and C₁) were synthesized.^[7, 11-12]

Pentaphenes, another interesting subgroup of PAHs, have been synthesized since the 1940s, mostly by cycloaddition reactions and subsequent oxidation.^[13-17] The fluorescence properties of pentaphene derivatives, which emit light between 400 and 500 nm, were studied by Fetzer *et al.*^[18-19] However, neither the fluorescence quantum yields ($\Phi_{\rm Fl}$) nor an emission in the solid-state were reported.^[18-19] The pentaphene motif can also be found in HBCs, which show a red-shifted fluorescence with a

^{a.} M. Sc. Philipp Rietsch, Prof. Dr. Siegfried Eigler; Institute of Chemistry and Biochemistry Freie Universität Berlin Takustraße 3, 14195 Berlin, Germany.

^c M. Sc. Julia Beerhues, Prof. Dr. Biprajit Sarkar

similar vibronic fine structure at about 500 nm.^[5, 7] Another dye class related to HBCs are hexapyrrolohexaazacoronenes or hybrids with HBC as reported by Müllen et al. in 2013.^[20] In 2017, Jux et al. prepared a racemic [5]helicene, structurally closely related to HBCs, that contains one pyrrole moiety.[21] Recently, high $\Phi_{\rm Fl}$ values exceeding 80% were found for two oxa[7]superhelicenes, realized by ether-bridging hexaphenylbenzene moieties, followed by oxidation. This yielded a chiral fluorescent oxa[7]superhelicene. Another strategy that can lead to a high fluorescence are push-pull systems. This was as e.g. reported for HBCs substituted by B-, Ncontaining diaminodicyanoquinonemoieties and derivatives.[22-23]

Herein, we present the synthesis and optical-spectroscopic characterization of an enantiomeric pentaphene derivative 4, with 41 sp²-carbon atoms. Compound **4** could be prepared by implementing an unprecedented Scholl oxidation step (Fig. 4).^[24] First, a Diels-Alder reaction^[25-26] between 1,4-bis(4-(tertbutyl)phenyl)buta-1,3-diyne 2 and 1 was performed to yield hexaarylbenzene 3. Under Scholl oxidation conditions compound **3** (conditions: CH_3NO_2 , 12 eq. $FeCl_3$, room temperature (RT), 15 h) was transformed into compound 4 in 80% yield, due to an unprecedented ring- closing reaction. The ring-closing reaction between the alkyne moiety and the benzene ring (Fig. 1A step iii) proceeds in analogy to the synthesis of, e.g. corannulenes, HBCs or naphthalenes.^[27-30] The analytical characterization of **4** including single-crystal X-ray analysis, is given in the Supporting Information (SI). We tested the reproducibility of this reaction by synthesizing the phenanthrene derivative, 9-(4-methoxyphenyl)phenanthrene, starting from 2-((4-methoxyphenyl)ethynyl)-1,1'-biphenyl (SI). This reaction was performed in dry dichloromethane with 0.9 eq. FeCl₃ with a yield of 69%. In addition, for our photophysical property studies, HBC 5 was synthesized as reference compound by a reported one pot reaction of hexaphenylbenzene and tert-BuCl with FeCl₃ acting as oxidant and Lewis acid catalyst.[31]

E-mail: siegfried.eigler@fu-berlin.de

^{b.} Dr. Ute Resch-Genger, Dr. Katrin Hoffmann; Bundesanstalt für Materialforschung und -prüfung (BAM), Department 1, Division Biophotonics, Richard Willstätter Straße 11, 12489 Berlin, Germany, E-Mail: ute.resch@bam.de

Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin, Germany

^{d.} Chamlers University of Technology SE-412 96 Gothenburg, Sweden

⁺ Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Compared to the HBC core with 42 sp²-carbon atoms, the missing carbon atom in compound **4** induces chirality as shown by the structural analysis. Moreover, **4** reveals a strong fluorescence, both in solution, as well as in the solid-state.

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Fig. 1. A) Synthetic route to the pentaphene derivative **4** and hexabenzocoronene (HBC) **5**. A Diels-Alder reaction between **1** and dialkyne **2** leading to hexaphenylbenzene **3** was used. Trimerization of alkyne **2'** leads to hexaphenylbenzene **3'**. Cyan: pentaphene moiety; green: pyrene moiety. i) 24 h, 250 °C in diphenylether; ii) Co(CO)₈, dioxane, 24 h, reflux; iii/iv) CH₃NO₂, 12 eq. FeCl₃, 15 h, RT. The inset shows solutions of the respective compound in dichloromethane under irradiation at 366 nm. The respective $\Phi_{\rm FI}$ is given below each compound. B) Single-crystal X-ray structures of **4** and **5**. Ellipsoids are drawn at 50% probability.

To gain first insights into the photophysics of these compounds, we analyzed the photophysical characteristics of **4** in comparison to **5** in three solvents of varying polarity and proticity, here cyclohexane (CH; apolar and aprotic), dichloromethane (DCM; medium polarity, aprotic) and ethanol

(EtOH; polar and protic). The absorption spectra and normalized fluorescence spectra of both compounds in CH are shown if **Fig. 2**. Whereas the molar absorption coefficients reach values of about 60,000 L mol⁻¹ cm⁻¹ at 360 nm for both compounds, the $\Phi_{\rm FI}$ of **4** is about five times higher than that of compound **5** (**Table 1** and **Fig. 2**).



Fig. 2. Absorption spectra (black) and fluorescence spectra (blue, normalized and multiplied by the correspondingly measured $\Phi_{\rm Fi}$) of compound **4** (solid) and **5** (dashed) in cyclohexane. The fluorescence quantum yield of **4** ($\Phi_{\rm FI}$ = 11%) in cyclohexane is about five times higher than that of HBC **5** ($\Phi_{\rm FI}$ = 2 %) in this solvent. Both compounds were measured at a concentration of 4x10⁻⁶ mol/L and excited at 375 nm.

In addition, we measured fluorescence maps (excitation emission matrices (EEM); see **Fig. S12** and **SI**, **Fig. S11** and **Fig. S12**). For both compounds, excitation at 370 nm leads to the highest fluorescence (**Fig. S12**) with the fluorescence maxima being located between 470 and 500 nm. The emission spectrum of **4** reveals a more pronounced vibrational fine structure compared to **5** and resembles, with its two main peaks and shoulders, the emission spectra of the pentaphene derivatives investigated by Fetzer *et al.*.^[18-19]

An overview of the absorption and emission maxima together with the Stokes shift, which is between 100-130 nm for both compounds, is given in Table S2.* The $\Phi_{\rm FI}$ and the mean fluorescence lifetimes τ (derived from the multiexponential decay kinetics) of 4 and 5 in the three solvents used are summarized in **Table 1**. Obviously, Φ_{FI} of **4** always exceeds that of 5, reaching a maximum of 16% in DCM compared to 3% obtained for 5. The mean fluorescence lifetimes of 4 are also always longer than those of 5 with values of 17.2 ns (CH) and 21.4 ns (DCM) compared to 11.0 ns (CH) and 14.2 ns (DCM), respectively. Temperature-dependent studies of the decay kinetics of both compounds in the temperature range of -100 °C to 50 °C (see SI, Fig. S14) reveal an increase in mean fluorescence lifetime by about a factor of 3.5 when comparing mean lifetimes recorded at 50 °C (4: 18.02 ns, 5: 7.93 ns) and -100 °C (4: 63.23 ns, 5: 27.67 ns), respectively. An increase in fluorescence lifetime upon cooling has been observed for many dye classes including rhodamines^[32] and the recently analyzed diaminodicyanoquinones.^[22] It typically suggests that

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^{*} As the absorption and emission spectra are in a similar wavelength region, the Stokes shifts are provided on a wavelength scale and not on an energy scale.

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at least one non-radiative decay channel involves a rotation that is slowed down or even completely hindered at very low temperatures.^[33]

Table 1. Φ_{FI} and amplitude-weighted mean fluorescence lifetimes τ of **4** and **5** in solvents of different polarity. Values for the normalized Dimroth-Reichardt Parameter Er^N were taken from Ref. ^[34].

		2	4	5		
Ετ ^Ν	Solvent	Φ _{FI} [%]	τ [ns]	Φ _{FI} [%]	τ [ns]	
0.207	СН	11	17.2	2	12.4	
0.386	DCM	16	21.4	3	14.2	
0.654	EtOH	11	17.8	2	11.0	
	Solid	11	-	2	-	

Surprisingly, **4** shows an intense solid-state fluorescence with $\Phi_{\rm FI}$ =11% (**Fig. 3** and **Fig. S15-S17** in the **SI**), while $\Phi_{\rm FI}$ of **5** is only 2% (**Table 1** and **Figure S15**). The solid-state fluorescence of **4** is bathochromically shifted by about 35 nm compared to the emission in DCM although the spectral shape and vibronic fine structure of the emission band is only slightly altered and broadened.



Fig. 3. Comparison of the solution (blue, in DCM) and solid-state fluorescence (green) of 4. The absorption spectra in solution (DCM) is shown in black. The excitation wavelength was 355 nm, respectively. The solid-state fluorescence, recorded with a spectral scanning Laser scanning microscope (CLSM), is bathochromically shifted by about 35 nm. The insets show the fluorescence in solution (left, blue frame) and in the solid-state (right, green frame).

The latter is often observed for solid-state emission (inhomogeneous broadening). The Stokes shift is thus increased from 130 nm in solution to 165 nm in solid-state. Whether this shift originates from polarity and/or crystal packing effects or a combination of is only 4 nm. In addition, the solid-state emission-band of **5** is broadened by about 100 nm and thereby extended from 600 nm in solution to 700 nm (**Fig. S15 and S17**). To correlate the solid-state fluorescence of **4** (see **Fig. 3**) with the molecular structure and the crystalline packing motif^[35], we studied the crystal structure of **4** and **5**. The pentaphene **4** crystallizes in a triclinic lattice with the space group P1, similar to the previously mentioned helicene-HBC hybrid.^[21] As discussed by Müllen *et al.* the π -system of **5** is slightly bent due to the sterically demanding *tert*-butyl groups.^[36] According to the four basic packing types of aromatic systems,^[37-38] the



structure of compound **5** is classified as a sandwich herringbone structure with an inter-planar distance of $9.44^{4}A^{039/C9CC05451K}$

Fig. 4. Arrangement of the molecules of 4 in the crystal. A) *Tert*-butyl groups in green and the helical moieties in red. The interplanar distance is 9.24 Å. B) Enantiomeric pair of 4. Blue M(-) and turquoise P(+).

The π - π interactions as well as C-H- π interactions determine this packing motif. This dense packing in the crystal might induce an aggregation induced quenching of the fluorescence. In contrast, the pentaphene **4** presents a θ -system with graphitic planes (**Fig. 4**) separated by 9.24 Å. The space between the π -planes is filled by the bulky *tert*-butyl groups (**Fig. 4**). The pentaphene derivatives published by Fetzer *et al.* have a distance of the π -planes of about 3.52 Å.^[17] As the inter-planar distance in **4** is induced by the helicene motif (**Fig. 5A**), which is absent for **5**, we compared the angles between the planes A-D of **4** with those of [4]helicene (**Fig. 5**, **Table 2**).^[39] The A-D angle of 32.46 ° of **4** compared to 26.68 ° ([4]helicene) indicates a stronger curvature of **4**, which is mainly induced by ring D, with 20% (A-D) up to almost 100% (C-D) increased angles compared to [4]helicene.



Fig. 5. A) Schematic presentation of the 4[helicene] moiety in compound **4** with the crucial benzene rings defined A-D. B) 4[Helicene]. C) Steric hindrance between hydrogen atoms in an extract of compound **4**.

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The reason for this is probably the sterically demanding phenyl ring, which is twisted around the dihedral angle D_{α} by 67.58 ° (**Fig. 5A**), and the three hydrogen atoms (**Fig. 5C**). In addition, the helical chirality is visible in the crystal structure as enantiomeric pairs (**Fig. 4B**). The enantiomers of [4]helicenes cannot be separated at RT as the racemisation barrier is below 25 kcal/mol.^[40-41] Nevertheless, we used density functional theory (DFT) at the B3LYP/6-31G(d) level of theory to calculate the racemisation barrier of **4**,^[42-43] which is about 10 kcal/mol (**Fig. S18**).

Table 2. Angles between planes A-D (Fig. 5A) of 4 and [4]helicene^{[39]} derived from crystallographic data.

	A-B	A-C	A-D	B-C	B-D	C-D
4	5.24°	16.76°	32.46°	11.86°	27.23°	16.54°
[4] helicene	10.26°	18.12°	26.68°	7.87°	16.55°	8.83°

In conclusion, we reported a novel pentaphene derivative, which is closely related to HBCs, however, with only 41 sp²carbon atoms, instead of 42. Consequently, the pentaphene **4** is chiral and crystallizes as enantiomeric pair with a distance of the π -planes of almost 1 nm. This substitution pattern results in an enhanced fluorescence in solution and the solid state compared to the HBC motif. The presented synthetic strategy to pentaphenes could lead to more advanced derivatives with improved photophysical properties.

Acknowledgement

Conflicts of interest

There are no conflicts to declare.

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