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Synthesis, Photophysical Characterization, and Self-Assembly of Hexa-*peri*-hexabenzocoronene/Benzothiadiazole Donor–Acceptor Structure

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Abstract: Hexa-*peri*-hexabenzocoronene (HBC) substituted by six benzothiadiazole (BTZ) units with ethynylene bridges was synthesized as a new donor-acceptor (D-A) motif. The C≡C bridges significantly reduce the dihedral angles between HBC and BTZ, and thus lead to a planar molecular conformation as predicted by density functional theory (DFT) calculations. The optoelectronic properties were investigated by UV-vis absorption and emission spectroscopies with absorption and emission maxima at 424 and 650 nm, respectively, indicating tunable electronic structures of HBC by attaching electron-withdrawing BTZ units. Two-dimensional wide-angle X-ray scattering (2D-WAXS) analysis manifested that the molecules self-assembled into liquid crystalline columns with high stability over a wide temperature range. Scanning tunneling microscopy (STM) revealed the formation of ordered bilayers of the D-A molecules with star-shaped structures.

Hexa-*peri*-hexabenzocoronene (HBC) and its derivatives have been widely investigated over the past two decades as an important class of organic functional materials with superior self-assembling and mesophase-forming properties, as well as high intrinsic charge-carrier mobility.^[1] The functionalization of its aromatic core plays a significant role in modulating the physicochemical properties of HBC, depending on the nature and position of the substituents.^[2] For instance, the installation of various alkyl chains on HBC allows controlling the self-assembly behavior, giving rise to highly stable liquid crystalline phases and

unique supramolecular nanostructures such as nanofibers and nanotubes.^[2a, 2c, 3] On the other hand, the optoelectronic properties of HBCs could be well tuned by substitution of the core with electron-donating or -withdrawing moieties.^[4] In particular, the introduction of π -conjugated electron-withdrawing groups onto the electron-rich HBC disc has been demonstrated to be an effective strategy to tune the energy levels of molecular orbitals and broaden the absorption spectra. This is essential for applications in organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).^[4b, 4c, 4g, 4h] Nevertheless, there have been few reports on HBC-based donor-acceptor (D-A) systems.^[4a-c, 4g]

Benzo[*c*][1,2,5]thiadiazole (BTZ) is a widely used acceptor unit for the construction of high-performance organic semiconductors in electronic devices.^[5] Previously, we reported HBC-BTZ D-A structures, where one or two BTZ units were directly linked with HBC by C-C σ -bonds, and observed intramolecular charge-transfer character as well as liquid-crystalline columnar assemblies.^[4b] However, the steric hindrance most probably leads to a twist between BTZ and HBC cores, which significantly reduced the conjugation. Herein, we introduce ethynylene units as conjugated linkers between BTZ and HBC aiming to mitigate the steric repulsion and increase the molecular planarity. Furthermore, we install six BTZ units to maximize the electron-withdrawing effect, affording an ethynylene-bridged six-fold BTZ-substituted HBC derivative, namely, HBC-6BTZA (Scheme 1). Density functional theory (DFT) calculations were performed to yield energy-optimized geometries of HBC-6BTZA as well as HBC-6BTZ without the ethynylene linkers for comparison (Figure S1). HBC-6BTZA appears to have a much more planar conjugated structure relative to its analogue HBC-6BTZ without the ethynylene spacers

Encouraged by the predicted planar D-A geometry, HBC-6BTZA was synthesized according to the route depicted in Scheme 1. The asymmetrically substituted BTZ precursor **4** was achieved from the commercially available 4,7-dibromobenzothiadiazole (**1**) by a three-step procedure. First, functionalization of **1** with one dodecyl chain was accomplished through a stoichiometric Negishi coupling to obtain **2** in 54% yield. Then, the C≡C triple bond was introduced by a Sonogashira-Hagihara coupling of **2** with an excess of trimethylsilyl (TMS)-acetylene, followed by deprotection of the TMS group using tetrabutylammonium fluoride (TBAF), affording **4** in 76% yield over two steps. Herein, the linear dodecyl chain was installed on **4** to enhance the solubility and self-assembly behavior of the resulting HBC-6BTZA. Hexaiodo-*peri*-hexabenzocoronene (HBC-6I) was prepared according to our previous report.^[1f] In the final step, a six-fold Sonogashira-Hagihara cross-coupling reaction of HBC-6I with **4** was performed adapting a synthetic protocol previously reported for HBC-PDI dyads.^[4a] After purification by recycling preparative gel permeation chromatography (GPC), HBC-6BTZA was obtained

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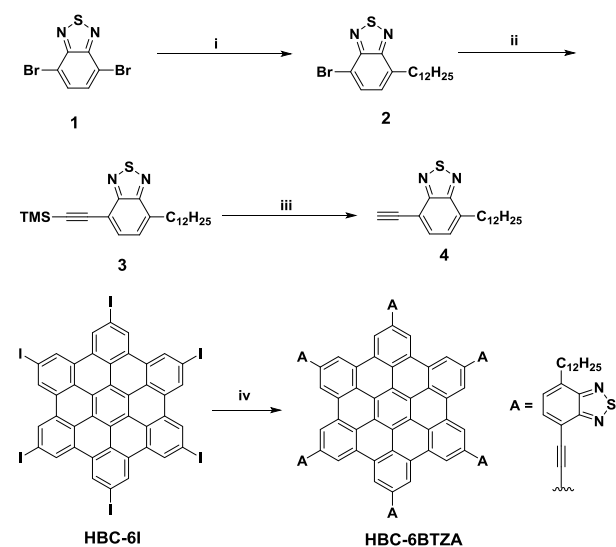
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Scheme 1. Synthesis of HBC-6BTZA. Reagents and conditions: i) $C_{12}H_{25}Br$, Zn, Pd(dppf)Cl₂, *N,N*-Dimethylacetamide, 50 °C, 15 h, 52%; ii) TMS-acetylene, Pd(PPh₃)₄, CuI, piperidine/THF, 50 °C, 14 h, 84%; iii) TBAF, THF, rt, 91%; iv) 4, Pd(PPh₃)₄, CuI, piperidine, 60 °C, 14 h, 64%

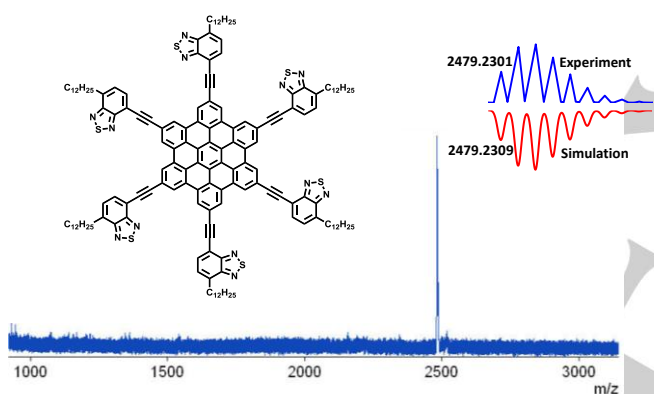


Figure 1. MALDI-TOF mass spectrum of HBC-6BTZA. Inset: HR MALDI-TOF MS spectrum, showing isotopic distribution (blue: experiment, red: simulation).

in a high yield of 64% for a six-fold reaction. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis of HBC-6BTZA showed a group of isotopic signals with the accurate mass $m/z = 2479.2301$, consistent with calculated $m/z = 2479.2309 [M]^+$, as well as a perfect agreement of the isotopic distribution with the simulation, proving the formation of the desired structure (Figure 1). Moreover, the absence of other mass signals supported the full removal of incompletely substituted byproducts and other impurities after purification via recycling GPC. In addition, the ¹H-NMR spectrum of HBC-6BTZA was achieved in tetrachloroethane-*d*₂ at 140 °C (Figure S5). The aromatic proton signals of HBC and BTZ subunits could be clearly assigned, in spite of the signal broadening due to strong aggregation, further corroborating the formation of the title compound HBC-6BTZA.

DFT calculations were performed to evaluate the frontier molecular orbitals and energy levels of HBC-6BTZA, where all the dodecyl chains were replaced by methyl groups for computational simplicity. As shown in Figure 2a, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of HBC-6BTZA were calculated as -5.27 and -2.60 eV, respectively, with the HOMO-LUMO gap of 2.67 eV. As expected for HBC-incorporated D-A systems, this value is reduced by 0.93 eV compared to that of the parent HBC.^[6] For comparison, HBC-6BTZ was also calculated using the same method, showing relatively higher HOMO and LUMO levels at -5.15 and -2.43 eV, respectively, as well as a slightly wider HOMO-LUMO gap of 2.72 eV (Figure S2). This could be explained by the more planar molecular backbone and larger π -conjugation length of HBC-6BTZA versus those of HBC-6BTZ due to the installation of ethynylene spacers. Additionally, the doubly degenerate LUMO of HBC-6BTZA is distributed mostly over the BTZ units, whereas the corresponding degenerate HOMO is mainly located on the HBC moiety.

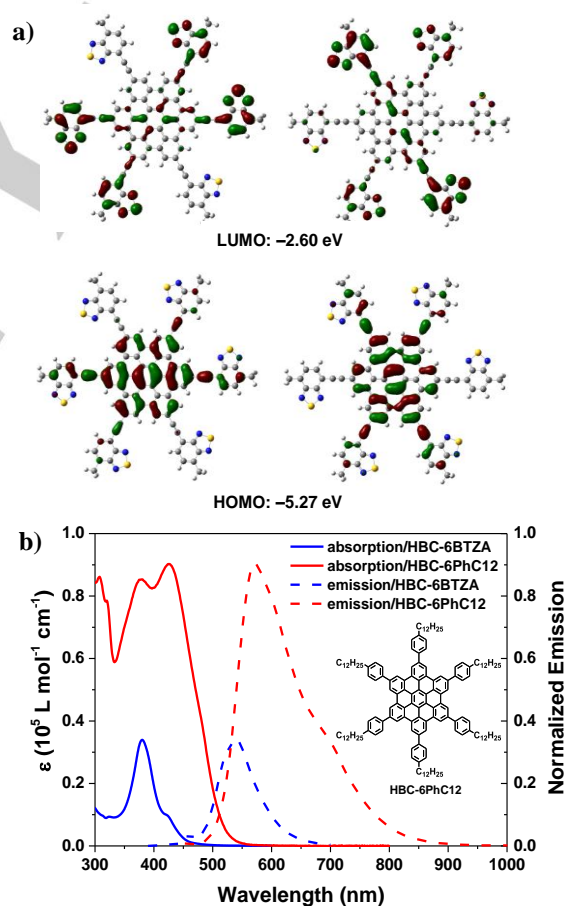


Figure 2. a) Frontier molecular orbitals and related energy levels of HBC-6BTZA calculated by DFT at the B3LYP/6-31G(d,p) level. b) UV-Vis absorption and emission spectra of HBC-6BTZA and HBC-6PhC12 in chloroform at a concentration of 10^{-5} mol L⁻¹.

The optical properties of HBC-6BTZA were next investigated by UV-Vis absorption and emission spectra which are shown in Figure 2b, including the absorption and emission of hexakis(4-dodecylphenyl)-HBC (HBC-6PhC12) for comparison.^[7] HBC-6BTZA displays absorption bands centered at 320 and 379 nm^[8], which coincide with those of the BTZ^[9] and HBC-6PhC12, respectively, as well as a pronounced low-energy band between 400 and 550 nm with the maximum at 424 nm. Compared with HBC-6PhC12, the latter transition could be attributed to the extension of π -conjugation of HBC to the BTZ moieties through the ethynylene linkers. The optical gap estimated from the onset absorptions is 2.39 eV for HBC-6BTZA in contrast to 2.73 eV for HBC-6PhC12, demonstrating the efficiency of energy gap modulation via introducing HBC into D-A systems. Interestingly, the relative intensity of the band at 424 nm decreased compared to that at 379 nm, when the solvent was changed from chloroform (good solvent) to hexane (bad solvent) or methanol (bad solvent) mixed with chloroform, which suggested the H-aggregation of HBC-6BTZA.^[10] (Figures S5 and S6)

The fluorescence spectrum of HBC-6BTZA exhibited an emission peak at 570 nm, which was red-shifted compared to that of HBC-6PhC12 emitting at 540 nm. (Figure 2b) Cyclic voltammetry analyses of HBC-6BTZA provided reversible reductive processes, whereas no oxidation could be observed scanning up to 1.5 V (Figure S4). The LUMO energy estimated from the first half-wave reduction is -2.84 eV, while the HOMO energy could then be calculated to be -5.23 eV using the optical energy band gap. This is in good agreement with the theoretical results.

The supramolecular organization of HBC-6BTZA in bulk was investigated by two-dimensional wide-angle X-ray scattering (2D-WAXS). The solid sample of HBC-6BTZA was extruded into a macroscopically aligned fiber at 90 °C, which was positioned vertically towards the 2D detector for the measurement. As shown in Figure 3, a typical 2D-WAXS pattern of HBC-6BTZA was recorded at 30 °C, indicating a discotic hexagonal columnar liquid-crystalline organization with the disc-shaped molecules stacking on top of each other. The intracolumnar π - π stacking distance is 0.35 nm derived from the meridional wide-angle scattering intensities, while the equatorial ones determined the intercolumnar distance of 3.0 nm. The structural analysis has proven that the packing of the HBC-6BTZA molecules is not disturbed by attaching BTZ units. It is noteworthy that the alternating donor-acceptor arrangement along the columns was not observed, which was the case with a donor-acceptor dyad HBC-PDI.^[4a] Furthermore, differential scanning calorimetry (DSC) measurement revealed no phase transition in the temperature range from -100 to 250 °C, indicating that the liquid-crystalline phase is stable over a broad temperature range (Figure S4). This is in agreement with other HBCs substituted with relatively bulky and rigid units (eg. phenyl), which typically show an extremely stable mesophase over a large temperature range as in the previous cases of hexaphenyl HBC and HBC-BTZ arrays.^[4b, 11]

To image HBC-6BTZA with molecular resolution and further study its self-assembly behaviors, scanning tunneling microscopy (STM) was performed at the solution-solid interface, which revealed that HBC-6BTZA formed ordered adlayers at the 1,2,4-trichlorobenzene (TCB)/highly oriented pyrolytic graphite

(HOPG) interface. Figure 4 shows large- and small-scale STM images, where ordered bright disk-like features can be discerned. Large-scale STM images revealed that the molecular domains extend several hundred square nanometers. The STM data indicate plausible bilayer formation where the HBC-6BTZA molecules adsorbed in the adlayer exhibit two different types of contrast. The areas highlighted by black arrows in Figure 4a point toward molecules adsorbed in the lower layer and show lower apparent height than the rest of the adlayer which appears relatively bright. This observation indicates that the adlayer formed at the TCB/HOPG interface is a bilayer with a few defects in the upper layer. Smaller scale images indicate that the

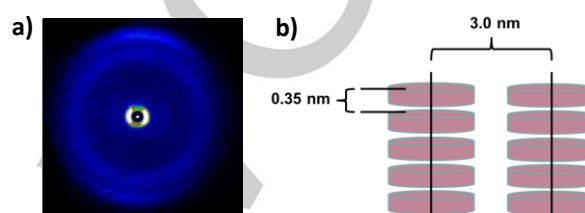


Figure 3. a) 2D-WAXS of HBC-6BTZA recorded at 30 °C; b) Schematic illustration of the columnar organization (each disc represents the whole molecule).

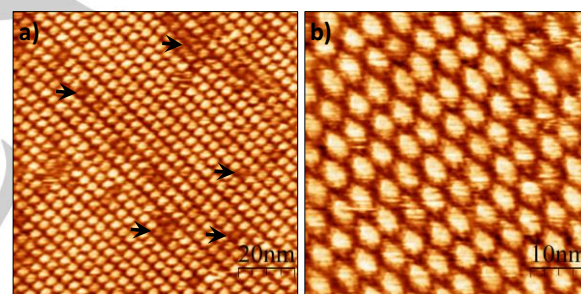


Figure 4. STM images of bilayer formed by HBC-6BTZA at the TCB/HOPG interface. a) Large-scale STM image of the bilayer showing missing molecule defects in the upper layer (black arrows). (b) Small-scale STM image. Imaging parameters: Tunneling current, $I_T = 80$ pA, Sample bias, $V_S = -800$ mV.

bright discs, which correspond to the aromatic HBC core, are separated by darker regions where the alkyl chains are adsorbed. The peripheral BTZ units could not be resolved possibly due to their mobility on the time-scale of STM measurements. The observation of bilayer formation is in line with two-dimensional wide-angle X-ray scattering (2D-WAXS) measurements which also show stacking of the molecular discs on top of each other. Similar stacking was reported for a related HBC derivative upon adsorption on the gold surface.^[4a]

In summary, an ethynylene-bridged donor-acceptor molecule HBC-6BTZA was synthesized by a six-fold Sonogashira coupling reaction. By introducing these linkers, steric hindrance between HBC and BTZ could be reduced, resulting in a significantly more planar π -conjugated skeleton and declined

HOMO/LUMO levels relative to those of HBC-6BTZ without similar linkages as calculated by DFT. Investigation of the photophysical properties revealed modulation of the energy gap by attaching BTZ units onto the HBC core via C≡C triple bonds. These results provide new insight into the design of HBC-based and other π -conjugated donor-acceptor molecules with tunable electronic structures. STM revealed the formation of ordered bilayers at the solution-graphite interface. 2D-WAXS studies exhibited that the star-shaped HBC-6BTZA molecules self-assembled into liquid crystalline columnar structures, which are stable over a wide temperature range, encouraging its further application in organic electronic devices such as OFET, OPV, and optical sensors.

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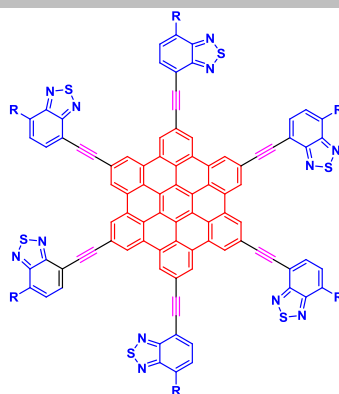
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Keywords: hexa-*peri*-hexabenzocoronene • benzothiadiazole • donor-acceptor structures • charge transfer • optoelectronic properties

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COMMUNICATION

An ethynylene-bridged Hexa-*peri*-hexabenzocoronene (HBC) /benzothiadiazole (BTZ) donor-acceptor molecule was achieved by a six-fold Sonogashira coupling reaction. The ethynylene-linkers could reduce the dihedral angles between HBC and BTZ units, resulting in a more planar conjugated π -system, and modulated electronic properties. In bulk phase, the molecule could self-assemble into liquid crystalline columnar structures, encouraging its further applications in organic electronics.



Ethynylene-Bridged HBC/BTZ Donor-Acceptor Structure

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Synthesis, Optical Characterization, and Self-Assembly of Hexa-*peri*-hexabenzocoronene/Benzothiadiazole Donor-Acceptor Structures