# Electron Transport Across Hexa-*peri*-hexabenzocoronene Units in a Metal–Self-Assembled Monolayer–Metal Junction**

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The fabrication of functional electronic devices based on ultrathin organic films, such as self-assembled monolayers (SAMs), requires the understanding and control of electron transport across organic molecules. Our group and others have shown that the electron-transfer rate, measured by the current flow through metal–molecule–metal junctions, sensitively depends on the structure of the molecules.[1,2] Electron transfer through molecules is commonly described by a simple relation used for electron tunneling mechanisms:

$$j = j_0 \exp^{-\beta d} \tag{1}$$

where $j$ is the magnitude of the current density flowing through the molecules, $d$ is the length of the molecule, and $\beta$ is the correlation or decay factor, which depends on the structure of the molecule. The decay factor, $\beta$, for organic molecules has been reported to decrease with an increasing degree of electron delocalization along the molecular backbone, suggesting that highly conjugated molecules should exhibit very small values of $\beta$, i.e., high molecular "conductivity".[1c,2]

Materials based on phenyl-derived molecules have been extensively used for charge-transport studies and organic electronic devices.[3] A family of nanographene molecules, the smallest members of which are hexa-*peri*-hexabenzocoronene (HBC) derivatives, have recently attracted special attention due to their unique electronic characteristics.[4] The strong π–π interaction between the hexabenzocoronene discs gener-ates well-ordered supramolecular aggregates, even in solutions of low concentration.[5] The charge-mobility values measured along the stacking axis of the columnar structures formed by the HBC moieties is among the highest reported so far for organic molecules ($0.5–1 \text{ cm}^2 \text{V}^{-1}\text{s}^{-1}$).[6] The strong π–π interaction between the HBC cores also dominates the organization of the amphiphilic molecules in Langmuir and Langmuir–Blodgett (LB) films.[7] X-ray reflectivity studies of the LB monolayers show that i) the film thickness is well defined, ii) the aromatic cores are organized in columnar structures, and iii) the lateral aliphatic chains are mostly disordered.[8] Scanning tunnelling microscopy (STM) studies have revealed that the strong interaction of HBC with graphite surfaces leads to the formation of highly ordered mono- and multilayers with attractive electronic properties. Charge transport rates across the columnar HBC structure and electron transfer rates across mono- and multilayers of HBC have been measured.[9]

The aim of this work is to study electron transport across the hexabenzacoronene disc by using a metal–molecules–metal junction. To the best of our knowledge, this is the first attempt to measure electron transport across highly conjugated, polycyclic, aromatic hydrocarbons. For such measurements, an upright orientation of the molecular plane with respect to the metal electrodes is required. For this purpose, we have synthesized a new compound incorporating the hexabenzocoronene units, 2-(5-[1,2]dithiolan-3-yl-pentanoic acid dodecyl ester)-5,8,11,14,17-(3,7-dimethyloctanyl) HBC, which is able to form a SAM (Fig. 1). The molecule carries branched alkyl side chains to increase solubility, and has a terminal 1,2-dithiolan-3-yl-pentanoic acid dodecyl ester moiety to bind to the gold surface. The experimental work presented here is focused on i) characterization of the SAM incorporating the HBC units and ii) measurement of current flow through the HBC SAM (denoted as HBCS in device configurations) by using a metal–SAM//SAM–metal junction.

The HBC SAMs are formed by immersing gold substrates (~ 20 nm Au) in a 10 mM solution of HBC in ethanol for 36 h with subsequent rinsing and drying (see Experimental). The samples have been characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The results show that densely packed and contamination-free HBC SAMs have been formed. The S 2p XPS spectra (see Supporting Information) suggest that binding of the HBC molecules

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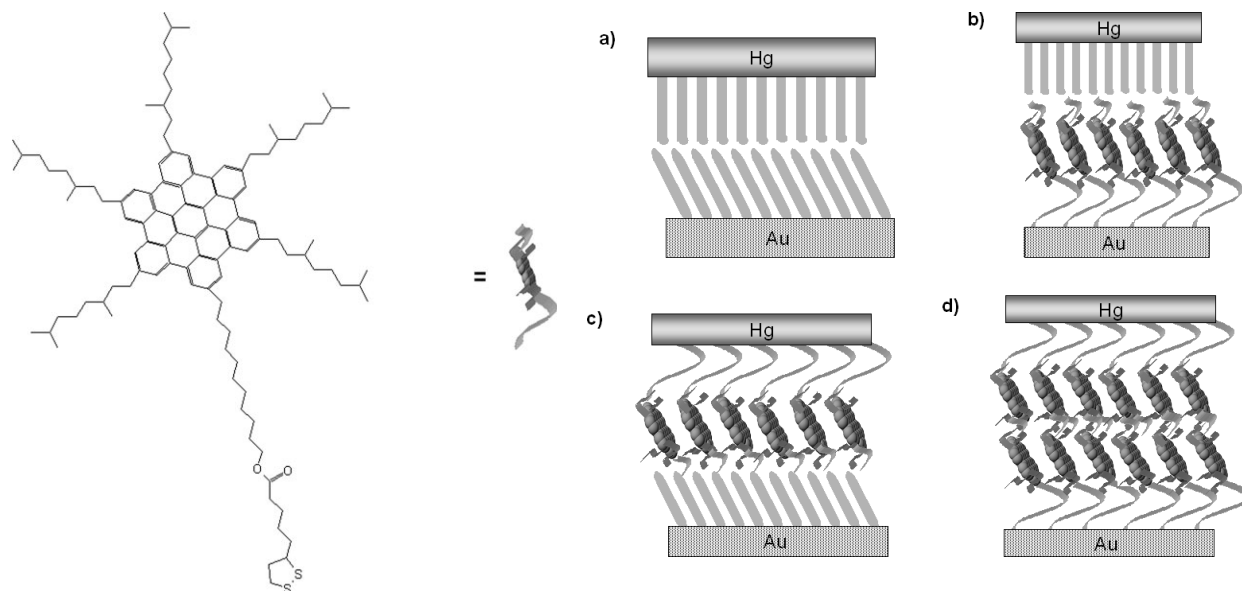12 Oxford Street, Cambridge, MA 02138 (USA)

**Figure 1.** Left: Molecular structure of 2-(5-[1,2]dithiolan-3-yl-pentanoic acid dodecyl ester)-5,8,11,14,17-(3,7-dimethyloctanyl) HBC in the extended configuration. Right: schematic illustrations of the assembled junctions. a) Au–$C_n$//$C_{12}$–Hg; b) Au–HBCS//$C_n$–Hg; c) Au–$C_n$//HBCS–Hg; and d) Au–HBCS//HBCS–Hg.

to the substrate occurs through a thiolate bond formed by one of the sulfur atoms in the dithiolan moiety. The second sulfur atom remains unbound. This binding geometry implies that the aliphatic chain attached to the dithiolane moiety is partially stretched (trans-extended), keeping the aromatic core away from the substrate. According to the XPS and NEXAFS data (Supporting Information), the HBC cores in the SAM are densely packed and well ordered with an average tilt angle of 30–35°. The overall film thickness is estimated to be about 3.0 nm (values of $2.98 \pm 0.05$ and $2.89 \pm 0.05$ nm were determined using ellipsometry and XPS data, respectively). Assuming that the molecules assemble in this extended conformation with a 30° tilt angle and a length of 4.4 nm (Fig. 1), the thickness of the monolayer is expected to be 3.71 nm, which is noticeably higher than the XPS- and ellipsometry-derived values. This discrepancy suggests that the HBC molecules are either not in the extended conformation and/or the 30° tilt is not applicable to the entire molecule. In this context, it is important to note that the thickness of the HBC SAMs and the orientation of the HBC units in the film are similar to values obtained by X-ray reflectivity measurements for LB monolayers formed by amphiphilic hexabenzocoronene molecules of the same length on glass substrates.[8,10] We infer from this analogy that the HBC SAMs have a similar organization to that of the HBC LB films, i.e., highly ordered HBC units with a tilt angle of 30–35° and poorly organized aliphatic chains (Fig. 1). While it is not possible to distinguish between the spectral contributions of the individual chains, their average orientation can be determined from the NEXAFS data, which indicates a preferable upright orientation of the aliphatic chains in the HBC films (based on the dichroism of the characteristic absorption resonance of the aliphatic part; see Sup-

porting Information). Considering that the side chains should be arbitrarily oriented, it is reasonable to assume that the anchoring chain is stretched upright on the substrate.

Electron-transport measurements through HBC SAMs have been performed by using junctions based on Au and Hg electrodes, as previously described.[11] The junctions are based on a Au surface electrode and a Hg drop electrode both covered by similar or different SAMs (see Experimental). A schematic depiction of interfaces formed at the junctions is shown in Figure 1.

In junction a, Au–$C_n$//$C_{12}$–Hg, the gold electrode bears SAMs formed by methyl-terminated alkanethiols (ATs) of different lengths, $CH_3(CH_2)_{n-1}SH$ ($C_n$: $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$), and the Hg electrode is covered by a $C_{12}$ SAM. The I–V curves measured for these junctions are shown in Figure 2. By using Equation 1, the decay factor for the ATs was calculated to be $0.76 \pm 0.05$ Å$^{-1}$ at 0.5 V (Fig. 2a), in good agreement with literature data.[10] This result indicates that interpenetration of the alkyl chains of the two facing SAMs does not occur or is very limited in our experimental setup (long, well-ordered alkyl chains result). For comparison (see below), we have also measured the current across a junction in which both SAMs are formed by $C_{18}$, Au–$C_{18}$//$C_{18}$–Au. At 0.5 V, the measured current density in this junction is as high as $10^{-8} \pm 0.7 \times 10^{-8}$ A cm$^{-2}$.

Junction b, Au–HBCS//$C_n$–Hg, incorporates the HBC SAMs formed on the Au substrate and AT SAMs of different lengths ($C_{10}$, $C_{12}$, $C_{14}$, and $C_{18}$) on Hg. Importantly, we observed that these junctions are very mechanically stable, thus allowing several consecutive, reproducible measurements to be made. The I–V curves measured for junction b are shown in Figure 2b. To calculate the correlation factor, $\beta$, the value of
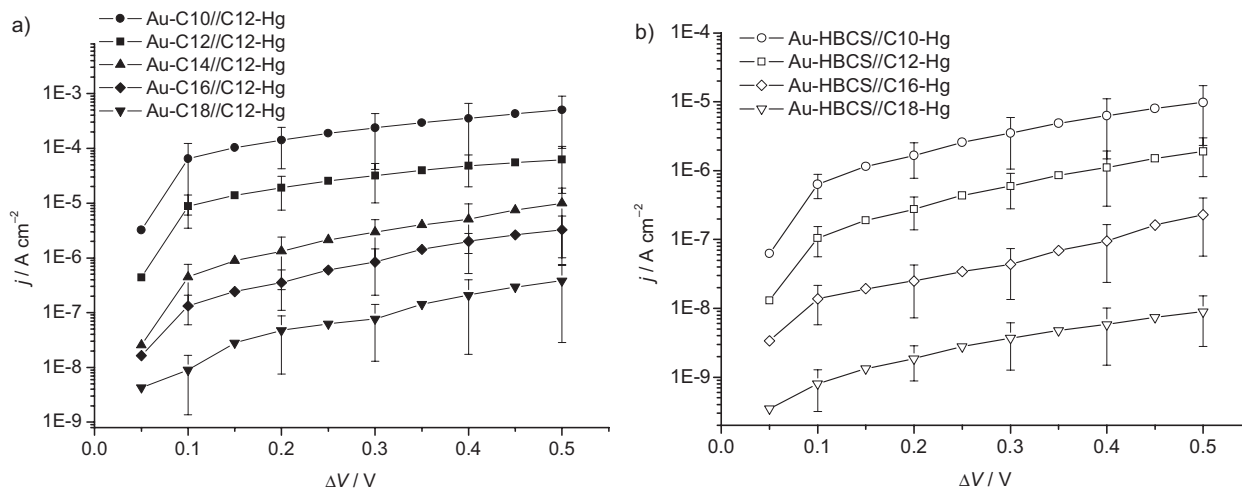
**Figure 2.** Plots of current density $j$ as a function of applied voltage for a) junction a, Au–C$_n$//C$_{12}$–Hg and b) junction b, Au–HBCS//C$_n$–Hg.

the current density, $j$, at 0.5 V, has been plotted versus the chain lengths of the ATs, $d$. The obtained value, $\beta = 0.73 \pm 0.05$ Å$^{-1}$, is in agreement with values previously reported in the literature,[1c] and with those obtained from junction a. We note that the values of the current density at 0.5 V in junction b, Au–HBCS//C$_{18}$–Hg, and junction a, Au–C$_{18}$//C$_{18}$–Hg, are similar, both being $10^{-8} \pm 0.7 \times 10^{-8}$ A cm$^{-2}$.

Junction c, Au–C$_n$//HBCS–Hg, includes AT SAMs on Au, along with an HBC SAM on the Hg surface. Junctions of this type showed low mechanical stability even after long incubation to form HBC monolayers on Hg (more than 16 h). Many junctions failed under applied voltage due to rapid amalgamation of the Hg and Au electrodes. The few successful Au–C$_{12}$//HBCS–Hg junctions showed current densities of $1 \times 10^{-6}$ Å cm$^{-2}$ at 0.5 V. These values are similar to those obtained for junction b, Au–HBCS//C$_{12}$–Hg, at 0.5 V.

In junction d, Au–HBCS//HBCS–Hg, HBC SAMs were formed on both the Au and Hg electrodes. The current density flowing across the junction is shown in Figure 3 (open hexagons). For comparison, $I$–$V$ curves for junction a, Au–C$_{18}$//C$_{18}$–Hg (solid triangles), and junction b, Au–HBCS//C$_{18}$–Hg (open triangles), are also plotted in the same figure.

The $I$–$V$ curves shown in Figure 3 show that the current densities across these three junctions are similar, and that the current density values for junctions incorporating the HBC unit are similar to those measured for the Au–C$_{18}$//C$_{18}$–Hg junction. These comparisons lead to the conclusion that the HBC units are transparent to electrons as compared to the aliphatic chains. This conclusion is confirmed by the observation that the current density value across junction b, Au–HBC//C$_{12}$–Hg, is intermediate between that measured across two junction a configurations, Au–C$_{16}$//C$_{12}$–Hg and Au–C$_{18}$//C$_{12}$–Hg.

According to studies of electron transfer through molecules,[1,2] the current is expected to decrease exponentially as the molecule length increases. Comparison of the current densities obtained in junctions a, b, c, and d indicates that the
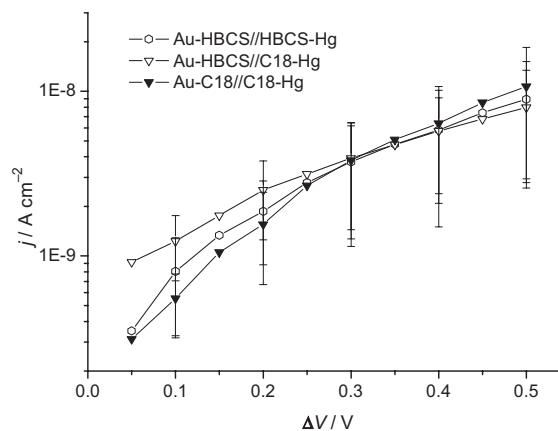


**Figure 3.** Plots of current density $j$ as a function of applied voltage for junction d, Au–HBCS//HBCS–Hg (open hexagons), junction b, Au–HBC//C$_{18}$–Hg (open triangles), and junction a, Au–C$_{18}$//C$_{18}$–Hg (solid triangles).

HBC aromatic core has an attenuation factor, $\beta$, much smaller than that of the aliphatic chains. In particular, the data shown in Figure 3 indicates that the 30 Å thick HBC SAM exhibits the same current density as a 20 Å thick C$_{18}$ aliphatic SAM. Based on the electrical measurements and spectroscopic data, the HBC SAMs are seen to behave as if they are composed of two layers. According to the NEXAFS data, the HBC units are well organized with an average tilt angle of 30° and estimated diameter of 12 Å for the HBC unit; we estimate an average thickness of 10 Å for the HBC cores inside the HBC SAMs. Therefore, the 30 Å thick HBC SAM can be considered to be effectively composed of two parts: a "highly conductive" HBC layer with a thickness of 10 Å, and a "less conductive" aliphatic part with a thickness of 20 Å. The aliphatic chains are predominantly responsible for the cumulative barrier to electron transport in the HBC monolayer, whereas the HBC cores are relatively "transparent" to electrons.

The organization of the lateral aliphatic chains, both in HBC SAMs on metal surfaces, and when sandwiched between electrodes, is not known. The NEXAFS data (see Supporting Information) indicates that the transition dipole moments of the R* resonance are oriented perpendicular to the plane of the axis of alkyl chains, indicating that, on average, the aliphatic chains have an upright orientation. A well-ordered orientation of the lateral alkyl chains in a direction orthogonal to the surface has been reported for LB films formed from similar HBC molecules upon the application of a large lateral pressure to the film.[11] In principle, the aliphatic chains of the HBC units could interpenetrate the SAM formed on the opposite electrode. The similarity of the $\beta$ factors of the aliphatic chains calculated from junctions a and b ($0.76 \pm 0.05$ Å$^{-1}$ and $0.73 \pm 0.05$ Å$^{-1}$, respectively) indicates that, regardless of the organization of the aliphatic chains in the HBC SAM, they contribute a constant barrier to the electron transfer process in every junction. This finding indicates that the aliphatic chains of the HBC monolayer either do not interpenetrate the aliphatic SAMs, or that the extent of the interpenetration is almost independent of the length of the AT molecules. The former hypothesis seems more likely when the results from Slowinski and Majda[12] are taken into account.

In summary, the results obtained in this study show that the thiol derivative of HBC forms SAMs on gold with exceptional robustness to mechanical stress; almost 100 % of the junctions formed from the HBC SAMs successfully endured applied voltages as high as 2 V. XPS and NEXAFS characterization of the monolayers indicates that the HBC units inside the SAMs are densely packed and well oriented (due to the lateral interactions between them), while the anchoring aliphatic chains are partly stretched, holding the HBC unit away from the substrate. Electrical measurements across the HBC SAMs, and comparison of the current-density values in a series of junctions incorporating the HBC and/or aliphatic SAMs indicate that electron transport through the HBC core is extremely efficient, when compared to the aliphatic part of the monolayer. Differences in the electron-transfer efficiency due to a "gauche" rather than a "trans" alkyl chain configuration,[13] and through chains containing an ester group as opposed to pure alkyl chains,[14] do not alter our conclusions. The 30 Å thick HBC SAM behaves electronically as a monolayer formed from two components: a 10 Å thick part consisting of highly conjugated hexabenzocoronene units that are almost transparent to electrons, and a 20 Å thick aliphatic part, which acts as the current-limiting electronic barrier.

While several reports in the literature focus on measuring the "conductivity" of single molecules, there have been very few experimental studies of the electrical behavior of organic SAMs. This work has reported the first quantitative and comparative measurements of I–V curves for current flowing across the plane of a HBC aromatic core. The high mechanical stability and electrical "conductivity" of the HBC unit indicates that this material may be a promising building block for molecular electronics.

## Experimental

*Materials*: The dithiolane-substituted HBC was synthesized by a carbodiimide promoted esterification reaction: 45 mg of thioctic acid, 42 mg of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride, and a catalytic amount of dimethylaminopyridine in 2 mL dry dichloromethane were stirred for 30 min under an argon atmosphere. 50 mg of 2-(11-hydroxy-undecyl)-5,8,11,14,17-penta-(3,7-dimethyloctyl) HBC [10] was then added and the mixture was stirred overnight. Subsequently, 20 mL of methanol was added and a yellow precipitate of the final product was obtained. The precipitate was washed with methanol and dried under vacuum. The reaction yield was around 70–80 %. Field desorption mass spectrum (8 kV): *m/z* (%) 1583.0 (100) [M]$^+$, 791.9 (50) [M]$^{++}$, 1056.7 (6) [M$_2$]$^{+++}$, 3175.6 (50) [M$_2$]$^+$. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 8.26 (s, 12H; Ar–H), 3.96 (t, 2H; –CH$_2$–O), 3.49 (dd, 1H; –CH–), 3.07 (m, 14H; –CH$_2$–), 2.34–0.88 (m, 123H).

*Assembly of the Junctions*: SAMs on gold were prepared by immersing a freshly evaporated thin film of gold in a solution of the appropriate thiol (10 mM) in either ethanol or dichloromethane. The SAMs were allowed to form at room temperature over 24 h as previously described. The gold film was prepared by thermal evaporation (Edwards Auto 306) of an adhesion layer of chromium (~ 20 Å) onto glass followed by a layer of gold (~ 200 Å). After the evaporation chamber was filled with argon gas, the metal film was removed and immediately immersed in the thiol solution. The SAM-coated gold surfaces were removed from the thiol solution, rinsed with ethanol, and dried under a stream of dry nitrogen. These surfaces were then ready for incorporation into junctions. SAMs on mercury were formed by extruding a drop of liquid mercury from a capillary (~5 L) and exposing it to an aerated solution of thiol (10 mM) in ethanol or hexadecane for ~ 5 min. After the SAM had formed on the drop of mercury, it was removed from the thiol and rinsed with hexadecane; the SAM-coated mercury was then used to assemble the junction.

The junctions were obtained as described: a SAM-coated gold film was placed in a beaker and covered with a solution of hexadecane The Au–SAM was connected to an electrometer by using an alligator clip in contact with the gold surface. The SAM-coated hanging mercury drop, supported by a gas-tight syringe (1 mL, Hamilton), was immersed in the hexadecane solution above the Au–SAM. A tungsten wire protruding from the Teflon tip of the syringe plunger provided an electrical connection between the mercury electrode and an electrometer. The syringe suspending the mercury drop was held by a micromanipulator, and the micromanipulator was used to bring the SAM-coated drop of mercury into contact with the surface of the SAM on Au. The contact areas were determined by video microscopy; a video camera with a 50× objective was used to image the junction and display the image on a video monitor. The diameter of the circular area of interfacial contact between the two organic films was estimated on the video screen with calipers; this diameter was compared to the magnified diameter of the syringe tip to estimate the real diameter of the contact. I–V curves were measured with the electrodes attached to an electrometer (Keithley 617 programmable electrometer). The electrometer was used both to apply the potential and to measure the current through the junction. The voltage ramp was applied as a staircase function with steps of 50 mV and with an interval of at least 5 s between steps.

*Preparation of HBC SAMs*: During the preparation of HBC SAMs on gold we have observed the following: i) the formation of an HBC SAM of adequate quality to allow fabrication of the junction and the completion of electrical measurements requires more time (36–48 h) than the formation of robust aliphatic SAMs (24 h), and ii) during the electrical measurements, the HBC SAM appears to be more robust than the aliphatic SAM (more than 20 cycling I–V measurements were possible on the same spot without any change in the current intensities). The formation of HBC SAM layers on the mercury electrode also required a longer time in comparison to aliphatic SAMs

(several seconds). For assembling the junctions, it took more than 1 h for the HBC SAMs to be of adequate quality, while at least 16 h incubation was required to obtain junctions suitable for electrical measurements. We assume that the lateral aliphatic chains prevent rapid organization and require a longer time to form a well-packed SAM.

*Characterization of HBC SAMs*: The HBC monolayers were characterized by XPS, NEXAFS spectroscopy, and ellipsometry. The XPS and NEXAFS spectroscopy measurements were carried out under ultra high vacuum (UHV) conditions at a base pressure $< 1.5 \times 10^{-9}$ mbar (1 bar $= 10^5$ Pa). The acquisition time for these measurements was chosen in such a way that no noticeable X-ray damage occurred during spectral acquisition [15].

The XPS and NEXAFS experiments were performed at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin, Germany. The XPS measurements were carried out using a VG CLAM 2 analyzer with synchrotron light as the X-ray source. The photon energy was varied depending on the range of interest. The spectral acquisition was carried out in a normal emission geometry with an energy resolution of 0.4–0.5 eV.

The acquisition of NEXAFS spectra was performed at the carbon K-edge in the partial-electron-yield mode with a retarding voltage of –150 V. Linearly polarized synchrotron light with a polarization factor of $\approx 82$ % was used. The energy resolution was $\approx 0.40$ eV. The incident angle of the light was varied from 90° ($E$ vector in the surface plane) to 20° ($E$ vector nearly normal to the surface), in steps of 10–20°, to monitor the orientational order of the HBC molecules within the films.

The ellipsometry measurements were carried out using an AutoEL-II Ellipsometer (Rudolph Research, Flanders, NJ) with a He–Ne laser ($\lambda = 632.8$ nm). The data was analyzed with appropriate software. The angle of incidence was set at 70° and calibrated using a silicon wafer as the reference. A refractive index of 1.45 was assumed for all films while calculating their thickness [16].

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