

## SUPPORTING INFORMATION

### **Altering the Polymorphic Accessibility of Polycyclic Aromatic Hydrocarbons with Fluorination**

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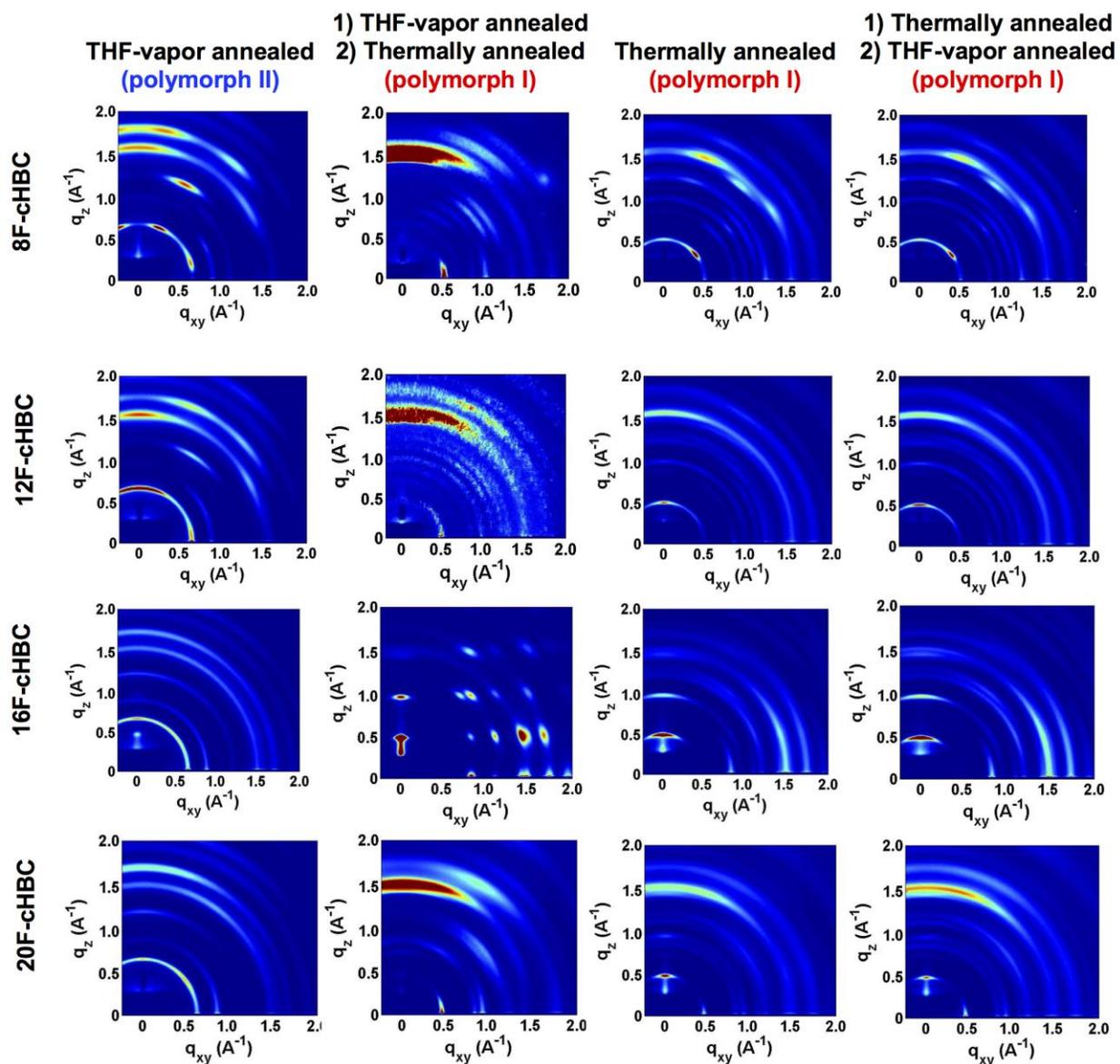
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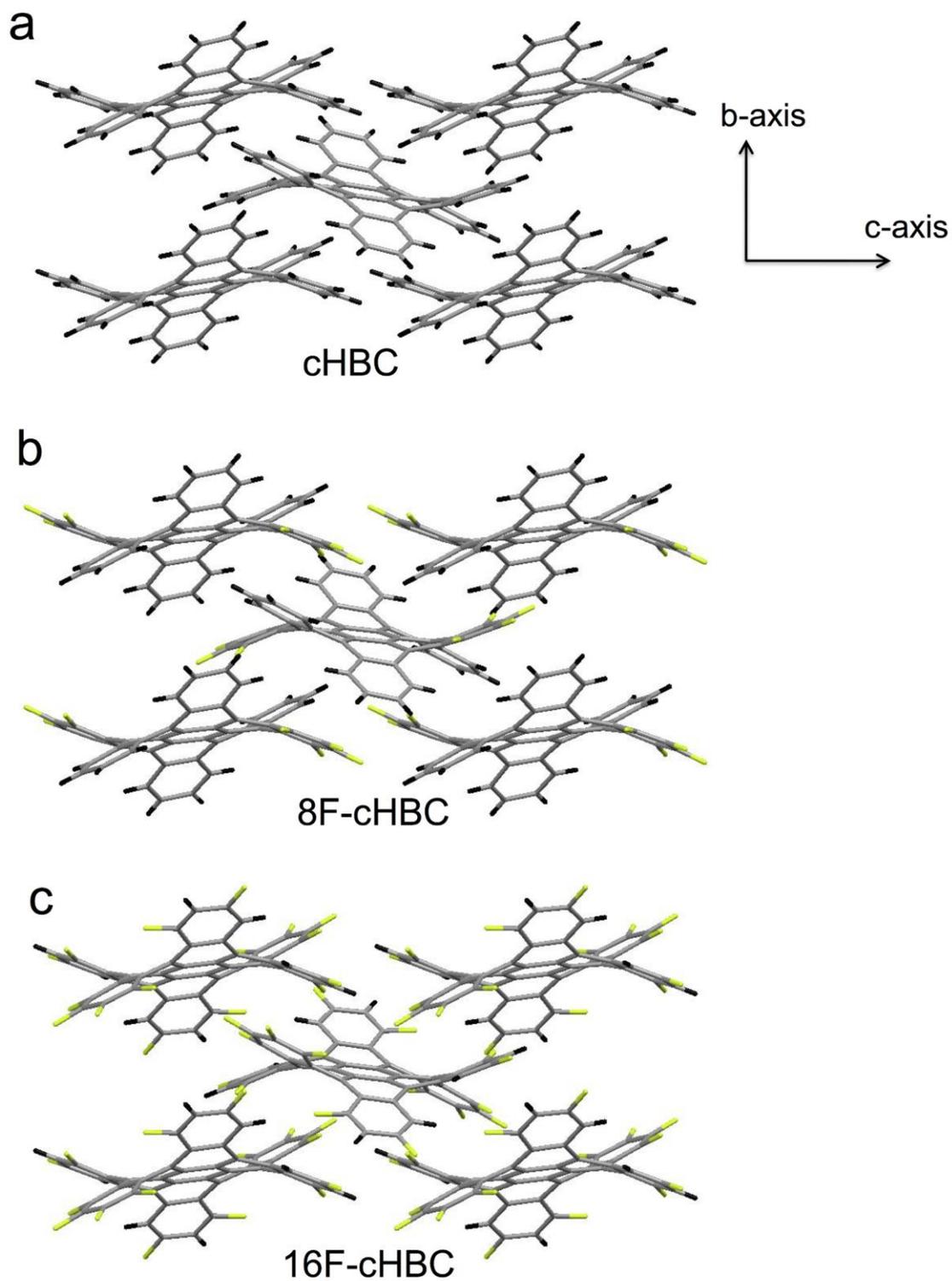
## Experimental Details

cHBC and its fluorinated derivatives were synthesized as previously reported.<sup>1-2</sup> Films of fluorinated cHBC derivatives were thermally evaporated on hexamethyldisilazane-treated silicon (100) wafers with thermally grown, 300 nm thick oxide layers (Process Specialties, Inc.). The silicon wafers were first cleaned by sequential sonication for 5 minutes each in acetone, isopropyl alcohol, and deionized water and were then dried with nitrogen. Hexamethyldisilazane, HMDS, was then deposited at 150 °C and 2-4 Torr in an HMDS deposition chamber to passivate the surface. Approximately 100 nm-thick films of the fluorinated cHBC derivatives were then thermally evaporated atop the cleaned and treated silicon wafers. The base pressure prior to evaporation typically was  $2 \times 10^{-6}$  mbar, and an evaporation rate of 1 Å/s was targeted. *Ex-situ* post-deposition thermal annealing was performed in-air at temperatures between 200 to 315 °C depending on the fluorinated cHBC derivative. For post-deposition THF-vapor annealing, samples were placed in a covered Petri dish with a 10 mL reservoir of THF for a specified period of time, typically 4 hours. To limit the number variables, we maintained a constant thickness of ca. 100 nm for all films of cHBC derivatives in this study. However, we note that we previously explored thermal annealing of amorphous cHBC films having thicknesses between ca. 20 to 250 nm and that those films always adopted polymorph I, i.e., the  $P2_1/c$  crystal structure.<sup>3</sup>

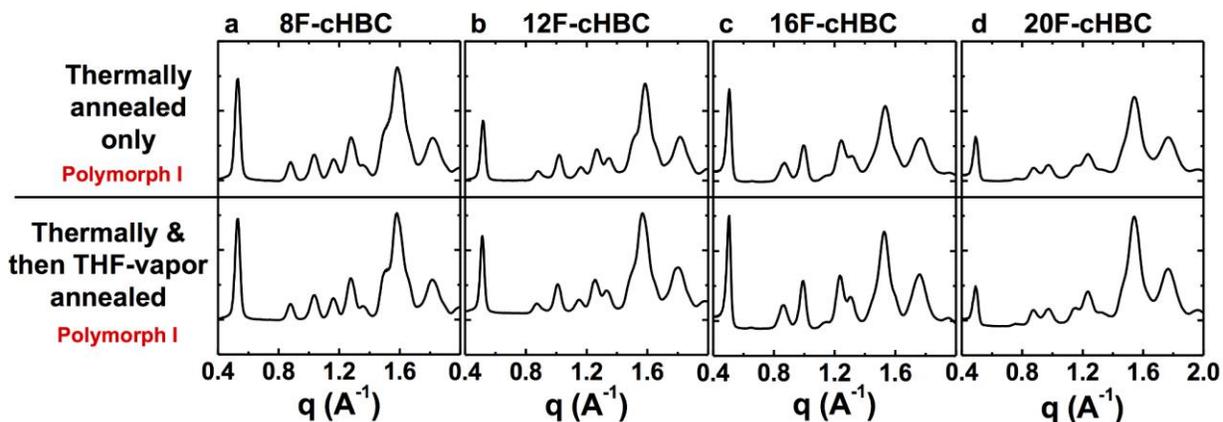
Two-dimensional grazing-incidence X-ray diffraction, 2D-GIXD, experiments were conducted at the G1-Line (9.9 keV) of the Cornell High Energy Synchrotron Source. Synthetic multilayer optics (W/B4C, 23.6 Å spacing) were used to select the beam energy. The incident beam was approximately 0.05 mm tall and 1 mm wide, and the samples were chosen to be 0.5 cm wide in order to reduce geometric smearing effects. A custom “SabreTube” furnace (Absolute Nano, Wixom, MI) with Mylar windows was used for *in-situ* thermal annealing studies, as described previously.<sup>4-5</sup> We noticed that in the presence of air, simultaneous heating and exposure of samples to X-ray radiation caused their degradation, but in the presence of nitrogen gas, no degradation was observed. Thus, we continuously flowed nitrogen gas through the enclosed “SabreTube” furnace while performing kinetics experiments. A piece of silicon serving as the substrate holder was rapidly heated by resistive heating and reached the target temperatures in the range of ca. 200-315 °C within 12 seconds. At elevated temperatures of ca. 280 °C and above, we observed sublimation of the films of fluorinated cHBC derivatives from the substrate surface.



**Figure S1.** 2D-GIXD images of thin-films of 8F-, 12F-, 16F-, and 20F-cHBC after processing by THF-vapor annealing, THF-vapor annealing followed by thermal annealing, thermal annealing, and thermal annealing followed by THF-vapor annealing.



**Figure S2.** The  $P2_1/c$  crystal structures (i.e., polymorph I) of **(a)** cHBC, **(b)** 8F-cHBC, and **(c)** 16F-cHBC. Crystal structures of cHBC and 16F-cHBC are reproduced from Refs. <sup>4</sup> and 1, respectively.



**Figure S3.** Diffraction traces of (a) 8F-, (b) 12F-, (c) 16F-, (d) 20F-cHBC films after thermal annealing (top panels) and of the same films after undergoing an additional processing step of THF-vapor annealing for six hours (bottom panels). Unlike cHBC, thermally annealed films of 8F-, 12F-, 16F-, and 20F-cHBC show no change in their X-ray diffraction patterns with THF-vapor annealing.

## References

1. Loo, Y.-L.; Hiszpanski, A. M.; Kim, B.; Wei, S.; Chiu, C.-Y.; Steigerwald, M. L.; Nuckolls, C., Unusual Molecular Conformations in Fluorinated, Contorted Hexabenzocoronenes. *Org. Lett.* **2010**, *12*, 4840-4843.
2. Plunkett, K. N.; Godula, K.; Nuckolls, C.; Tremblay, N.; Whalley, A. C.; Xiao, S., Expedient Synthesis of Contorted Hexabenzocoronenes. *Org. Lett.* **2009**, *11*, 2225-2228.
3. Saylor, J. L. S. Structure-Function Relationships of Organic Semiconductors in Electronic Devices. B.S.E. Dissertation. Princeton University, Princeton, NJ, 2013.
4. Hiszpanski, A. M.; Baur, R. M.; Kim, B.; Tremblay, N. J.; Nuckolls, C.; Woll, A. R.; Loo, Y.-L., Tuning Polymorphism and Orientation in Organic Semiconductor Thin Films via Post-deposition Processing. *J. Am. Chem. Soc.* **2014**, *136*, 15749-15756.
5. van Laake, L.; Hart, A. J.; Slocum, A. H., Suspended heated silicon platform for rapid thermal control of surface reactions with application to carbon nanotube synthesis. *Rev. Sci. Instrum.* **2007**, *78*, 083901.