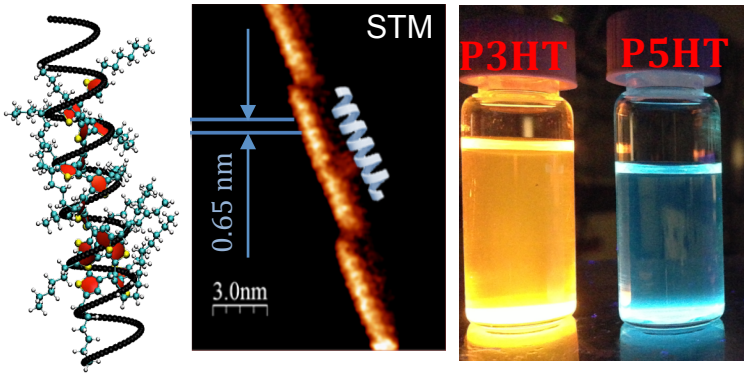
Designing Functional Molecules to Remove Interactions that Cause Aggregation

Achievement: Poly(5-alkyl-2,3-thiophene)s (P5AT), an *ortho*-connected isomer of poly(3-alkyl-2,5-thiophene)s (P3AT), was synthesized for the first time.

Significance and Impact: P5ATs show distinct helical structures with different optoelectronic properties compared to their P3AT isomeric counterparts and are representative of a new class of potential optoelectronic materials.



Left: Computational modeling predicted structure for P5BT. **Middle**: STM image of P5BT on HOPG showing a 0.65 nanometer helical pitch. **Right**: Photographs of the THF solutions of P3HT and P5HT under 360 nm UV light showing that P5HT has green photoluminescence under irradiation.

Research Details:

- Synthesis via Chain-growth Suzuki cross-coupling polymerization
- P5ATs characterized using computational modeling, NMR, small angle x-ray scattering (SAXS) and scanning tunneling microscopy (STM)

Sponsor/Facility: This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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Overview:

Conjugated polyarylenes have found a wide range of applications including optical sensors, electrochromic devices, field effect transistors, and organic solar cells. However often the interactions driven by the conjugated pi-backbone causes difficulties in solution processing due to strong aggregation of the polymer chains. One approach to uncouple these backbone interactions between polymer chains to mediate aggregation is to introduce a helix geometry for the backbone. This could be done by using ortho-connected isomers, poly(5-alkyl-2,3-thiophene)s (P5AT) but such polyarylenes have never been reported because of the difficulty in their syntheses. This work marks the first synthesis of regioregular P5AT; achieved via controlled Suzuki cross-coupling polymerization with PEPPSI-IPr as catalyst, affording the polymers with tunable molecular weight, narrow polydispersity (PDI), and well-defined functional end groups at the gram scale. The helical geometry of the P5ATs predicted by computational modeling was confirmed by a combination of NMR, small-angle X-ray scattering (SAXS), and scanning tunneling microscopy (STM). Since the Suzuki cross-coupling polymerization tolerates a wide range of functionalized aromatic monomers, this method can be applicable for the synthesis of poly(**o**-arylene)s

with aromatic rings other than thiophene and thus opens access to a new class of poyarylenes where the combination of helical structure, conjugated backbone, and photoluminescence properties make P5ATs good candidates for a range of applications in optoelectronics and related field applications.