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Title: Photochemical Synthesis and Spectroscopy of Large Polycyclic Aromatic Hydrocarbons  
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Polycyclic aromatic hydrocarbon (PAH) molecules with extended dimensions are interesting materials, whose electronic and optical properties provide extreme challenges for theory. These systems also allow the systematic investigation of properties as system size progresses toward nano-graphene materials. Larger PAH systems have been produced by wet-chemical synthetic polymerization of PAH monomers, or by their thermal processing, but the chemistry involved is neither efficient nor general. Our laboratory has discovered a promising new photochemical polymerization method that appears to overcome these problems. The work in this new directions project has explored the continued development of this method and the characterization of the PAH dimer and trimer materials that have been produced.

In the photochemical polymerization method, a pellet of powder pressed under high pressure from a selected PAH monomer is irradiated under vacuum with a pulsed UV excimer laser. Excitation of the thick material apparently causes both photochemistry and a high-pressure shock in the material, leading to hydrogen atom elimination and radical recombination reactions. Covalently bonded dimer and trimer species were detected initially by in situ mass spectrometry. Mass spectrometric detection has revealed the efficient formation of dimer and trimer ions for coronene, perylene, pyrene and benzopyrene. Figure 1 shows high-resolution mass spectra, which demonstrate the loss of hydrogen in the dimer ions, establishing that these polymer species have covalent linkages.

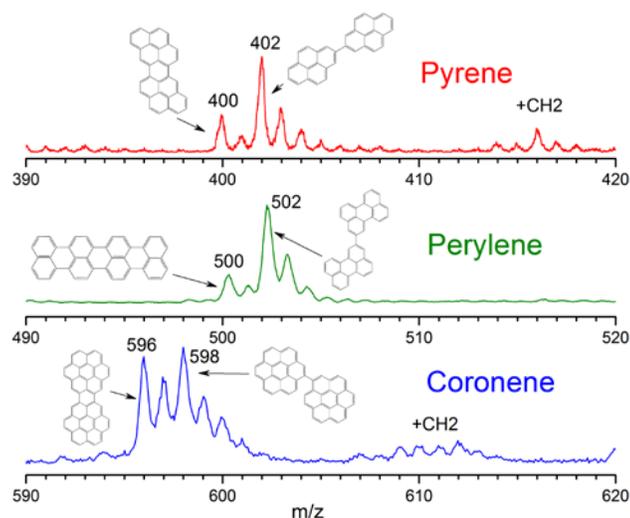


Figure 1. The laser desorption time-of-flight mass spectrum of pyrene, perylene and coronene, zooming in on the mass region of the dimer ions.

More recently, this process has been scaled up (400 Hz excimer laser) and the polymerization material has been collected and purified, allowing spectroscopic characterization. Figure 2 shows an example of the laser desorption mass spectrum of the material resulting from purification of pyrene dimer. In this process, the material was collected on a glass slide by photopolymerization and coincident ablation. It was purified with differential sublimation by heating the resulting powder to 100° C for 4 hours under vacuum, preferentially evaporating the monomers, and leaving the dimers behind. Similar results were obtained for coronene and perylene. Purification by HPLC shows some promise, but issues of product solubility and column type need to be addressed.

After purification, the resulting milligram quantities of material allow spectroscopic characterization. We have employed infrared, Raman, and UV-visible methods for these analyses. Infrared bands are weak and non-specific, but Raman spectra have been more informative. Figure 3 shows the UV-visible spectra of pyrene monomer and dimer compared to the predictions of time-dependent density functional theory (TD-DFT/CAM-B3LYP/def2-TZVP). As shown TD-DFT at this level reproduces the main features of the monomer spectrum, and predicts

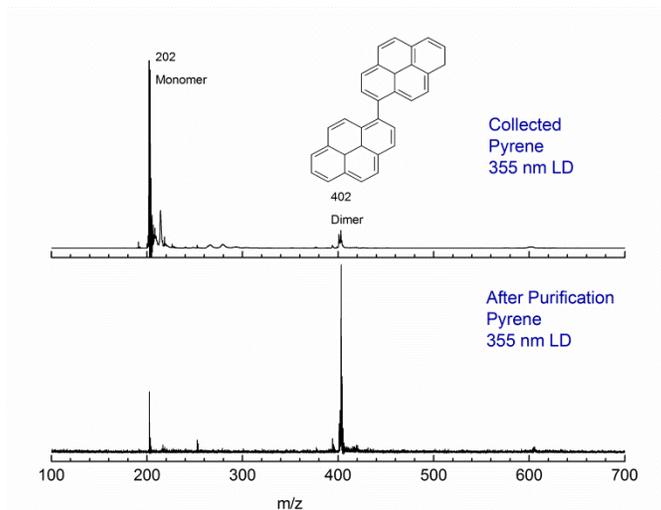


Figure 2. The laser desorption time-of-flight mass spectrum of pyrene polymerization before and after purification.

shifted features for the dimer spectrum. A monomer band near 334 nm is predicted to shift slightly to the red for the dimer, and indeed a doublet at 334 and 338 nm is observed. The observation of the 334 nm band in both spectra is consistent with a small amount of monomer still being present in the dimer sample, and the 338 nm band is therefore associated with the dimer. The most prominent new feature for the dimer spectrum, which is not found at all for the monomer, is predicted and observed near 300 nm.

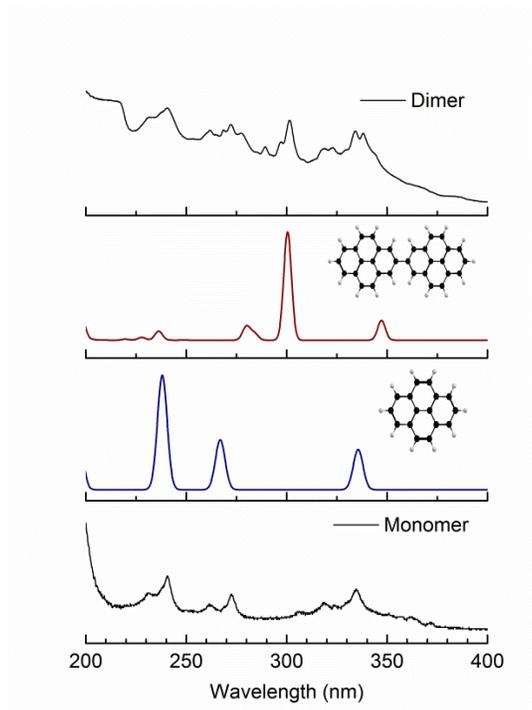


Figure 3. The UV-visible absorption spectrum of pyrene monomer and purified dimer samples dissolved in hexane compared to the spectra predicted by TD-DFT theory.

Ongoing experiments are attempting to extend these polymerization experiments to other PAH systems, and to optimize the purification and spectroscopy already measured for perylene, pyrene and coronene.

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