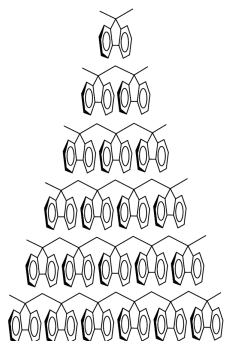


ELECTRONIC COMMUNICATION IN COVALENTLY vs. NON-COVALENTLY BONDED POLYFLUORENE SYSTEMS: THE ROLE OF THE COVALENT LINKER.

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The covalently linked polyfluorene molecules F1-F6 (see left) are prototypical molecular wires by virtue of their favorable electron/hole transport properties brought about by π -stacking. To understand the role of the covalent linker in facilitating electron transport in these systems, we have investigated several van der Waals (vdW) analogues by resonant mass spectroscopy. Electronic spectra and ion yield curves are reported for jet-cooled vdW clusters containing up to six fluorene units. The near-coincidence of the electronic band origins for the dimer and larger clusters suggests that a structure containing a central dimer chromophore is the predominant conformational motif. As for F1-F6, the threshold ionization potentials extracted from the ion yield measurements decrease linearly with inverse cluster size. Importantly, however, the rate of decrease is significantly smaller in the vdW clusters, indicating more efficient hole stabilization in the covalently bound systems. Results for similar vdW clusters that are locked into specific conformations by steric effects will also be reported.