Determination of the Electronic Properties of a Series of Copolymers using Raman Spectroscopy and QM Calculations

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Polymer-based photovoltaics and electro-luminescent devices have potential applications because of their easy solution processability but are hampered by their low efficiencies. Understanding the electronic structure and light interaction dynamics of the polymers is important in improving device efficiency. We have studied a series of copolymers that contain alternating electron-donor and acceptor units using both Raman spectroscopy and density functional theory (DFT) calculations. Each of the polymers in the series uses a carbazole donor unit and the acceptor unit is varied. The acceptors used are DBT (bis(2-thienyl)-2,1,3-benzothiadiazole)), FL (fluorene), SeBT (benzoselenadiazole) and BT (benzothiadiazole).

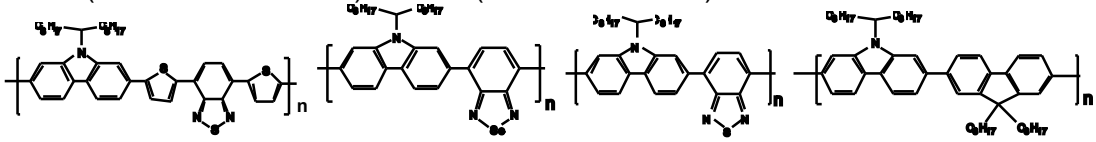

Figure 1: Structures of PC-DBT, PC-SeBT, PC-BT and PC-FL from left to right

Resonance Raman spectroscopy can give insight into the nature of electronic excitation as according to Tsuboi's rule[1], modes that mimic the geometry change from ground to excited state will be enhanced. For PC-BT, PC-DBT and PC-SeBT several modes are resonantly enhanced that are centred on the acceptor unit, indicating a charge transfer to the acceptor as the acceptor unit has increased distortion upon excitation. The charge transfer nature of the excitation was reinforced by TD-DFT calculations, which show electron density change from being evenly spread across the donor-acceptor unit in the ground state to being focused on the acceptor unit in the excited state.

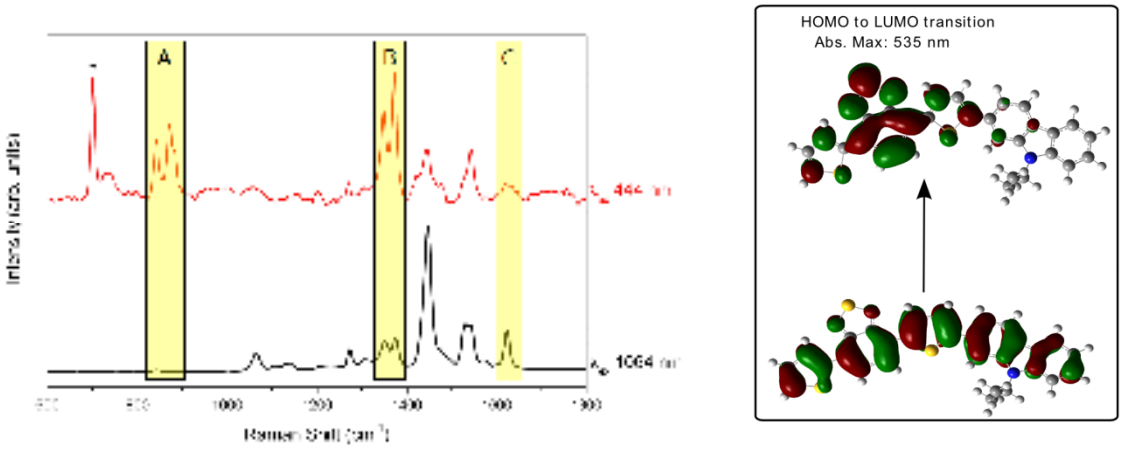

Figure 2: Left- The resonance (top) and non-resonance (bottom) spectra of PC-DBT. All modes in the boxes labelled A and B are modes involving the acceptor and are greatly enhanced while the mode labelled C is focused on the donor and is not enhanced (indicates a solvent band). Right- Electron Iso-density surfaces of the ground and lowest excited state show the charge transfer to the acceptor.*

Ref: 1.) Hirakawa, A. Y., Tsuboi, M. 1975. *Science* 188:359-61