Modelling the Optical Properties of Benzochalcogenodiazole-based Copolymers using Tuned Range-Separated Hybrid Functionals.

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Since the discovery of organic semiconductors, these systems have been deeply investigated and many strategies to module their optical and electronic properties have been established. In this sense, Donor-acceptor (D−A) approach to conjugated polymer design has become a widely used method for preparing conjugated polymers with narrow band gaps. This approach involves synthesizing a polymer with a delocalized π-electron system that comprises alternating electron-rich (donor) and electron-deficient (acceptor) repeat units. The combination of high-lying HOMO levels (residing on the donor units) and low-lying LUMO levels (residing on the acceptor units) results in an overall narrow band gap for the polymer (see **Figure 1**).[1] In this sense, poly(cyclopentadithiophene)benzothiadiazole, (PS in Figure 1) is a D−A polymer for which power conversion efficiencies in solar cells of 5-6% are reported.[2] In this work, we use density functional theory (DFT) calculations to investigate the tuning of the electronic and structural properties of cyclopentadithiophene-benzochalcogenodiazole D−A polymers, wherein a single atom in the benzochalcogenodiazole unit is varied from sulfur to selenium to tellurium [3] (**Figure 1**). Resonance Raman (RR) spectroscopy is also used to describe the nature of the electronic excitations. Improved prediction of the optical properties has been obtained by using long-range corrected functionals, considering both tuned and default range-separation parameters, aiming at predicting their optical and charge transport properties.

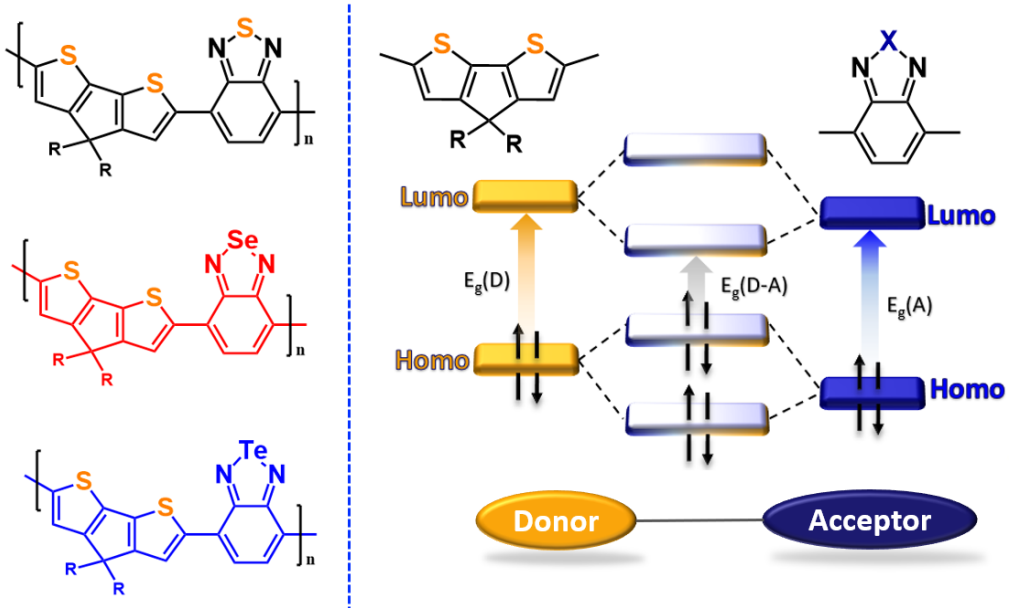

Figure 1. D-A copolymers under study (a). HOMO-LUMO gap decrease upon D-A approach.

References

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