Improved Prediction of the Optical Properties in pi-Conjugated Polymers: The case of Benzochalcogenodiazole-Based Copolymers with Different Heteroatom Substitution

Sergio Gámez Valenzuela,[1] Irene Badia-Domínguez,[1] D. Herrero-Carvajal,[1] G.L. Gibson,[2] D.S. Seferos,[2] J.T. López Navarrete[1] M. Carmen Ruiz Delgado[1]

[1]Department of Physical Chemistry, University of Málaga (Spain)
[2]Lash Miller Chemical Lab, Department of Chemistry, University of Toronto (Canada)
sergiogamez@uma.es

Donor−acceptor (D−A) approach to conjugated polymer design has become a widely used method for preparing conjugated polymers with narrow band gaps.[1] One outstanding D−A polymer is poly(cyclopentadithiophene)benzothiadiazole, PCPDTBT (P1 in Figure 1), for which power conversion efficiencies in solar cells of 4.5-5.5% are reported.[2] In this work, we use resonance Raman (RR) and 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 (Fig. 1).[3] Sophisticated DFT calculations have been carried out using long-range corrected functionals, considering both tuned and default range-separation parameters, aiming at predicting their optical and charge transport properties. In addition, the nature of the electronic excitation is described by analyzing the enhancement pattern in the RR spectra using Raman excitation wavelengths coincident with the various transitions in the copolymers.

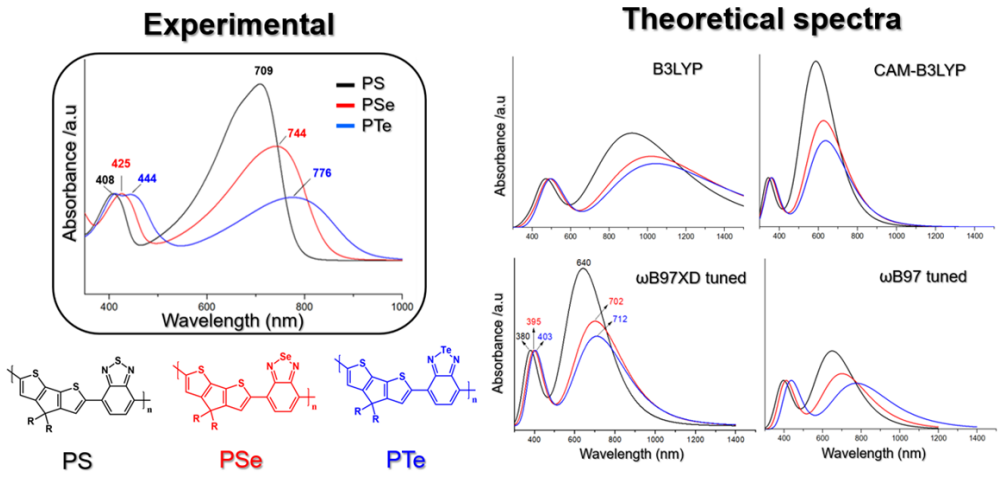

Figure 1. D-A copolymers under study. Their synthesis is reported In Ref. 4

References

[1] P. M. Beaujuge, C. M. Amb, J. R. Reynolds, *Acc. Chem. Res*. **2010**, *43*, 1396−1407.
[2] F. S. U. Fischer, K. Tremel, A. K. Saur, S. Link, N. Kayunkid, M. Brinkmann, D. Herrero-Carvajal, J.T. López Navarrete, M.C. Ruiz Delgado, S. Ludwigs, *Macromolecules* **2013**, *46*, 4924-4931.
[3] I. Badía-Domínguez, Sergio Gámez-Valenzuela, D. Herrero-Carvajal, G. L. Gibson, D. S. Seferos, S. Salman, V. Hernández, J.T. López Navarrete, M. Carmen Ruiz Delgado, *in preparation.*
[4] G. L. Gibson, T. M. McCormick, D. S. Seferos, *J. Am. Chem.Soc.* **2012**, *134*, 539−547.