

Iron-Coordinating π -Conjugated Semiconducting Polymer

Rational side-chain engineering was performed on a semicrystalline semiconducting conjugated polymer based on DPP to incorporate metal-chelating moieties without disruption of the π -conjugation.

Conjugated polymers constitute an intriguing class of materials, particularly promising to replace silicon as semiconducting materials in next-generation stretchable and portable electronics. This ability is due not only to their inherently effective charge-transport properties but also to their solubility in common organic solvents, opening new avenues for solution deposition and fabrication of electronic devices at large scale and decreased cost. Their favourable optoelectronic properties have been exploited so far to fabricate various electronic devices, including organic photovoltaics and organic light-emitting diodes. In more recent years, new strategies and approaches for a conjugated polymer, directly developed through chemical design and material engineering, have been utilized to increase the charge-transport and device efficiencies. Among other approaches, the utilization of supramolecular chemistry is particularly promising to enhance the packing interaction between polymer chains. Although hydrogen bonds have been used to improve the charge transport and the softness of diverse conjugated polymers, there have been few examples of polymer designs based on metal-chelation chemistry.¹⁻³

This work by Yu-Cheng Chiu (National Taiwan University of Science and Technology), Simon Rondeau-Gagné (University of Windsor, Canada), Bi-Hsuan Lin (NSRRC) and their joint team members focuses on the use of dynamic metal-ligand (M-L) interactions to influence the electronic properties of a high-performance conjugated polymer, as illustrated in Fig. 1. Through metal chelation, diverse parameters can be fine-tuned, including the optoelectronic properties, solubility in organic solvents and stability of the materials. These non-covalent interactions can also be further explored, through use of a plethora of ligand motifs that have been developed, in tandem with an appropriate metal salt.

The new conjugated polymer system is based on diketopyrrolopyrrole (DPP) semiconducting π -conjugated polymers containing benzimidazole pyridine (MeBZIMPY) pincer ligands in the side chains of the polymer. These ligands facilitate the complexation of Fe(II), to generate a metal-coordinated polymer, which was completely characterized with various techniques to evaluate the optoelectronic properties of the new materials. Importantly, metal complexation by the conjugated polymers was found to be particularly challenging. As a result, X-ray fluorescence spectra and X-ray near-edge absorption spectra experiments for the semiconducting thin film were undertaken at TPS 23A to confirm that Fe was successfully coordinated in the ligands, as shown in Fig. 2. (see next page). The selection of this specific salt is due to its vast exploitation in M-L systems, which are utilized in polymer catalysis, bioimaging, fluorescence, dielectric systems, and chemical or mechanical sensors. The selection of the pincer ligand was due to its ability to be functionally tuned through the amines present in the benzimidazole pendant arms. Functionalizing these areas allows for changes in solubility to occur, making this system more easily processable. (Reported by Yu-Cheng Chiu, National Taiwan University of Science and Technology)

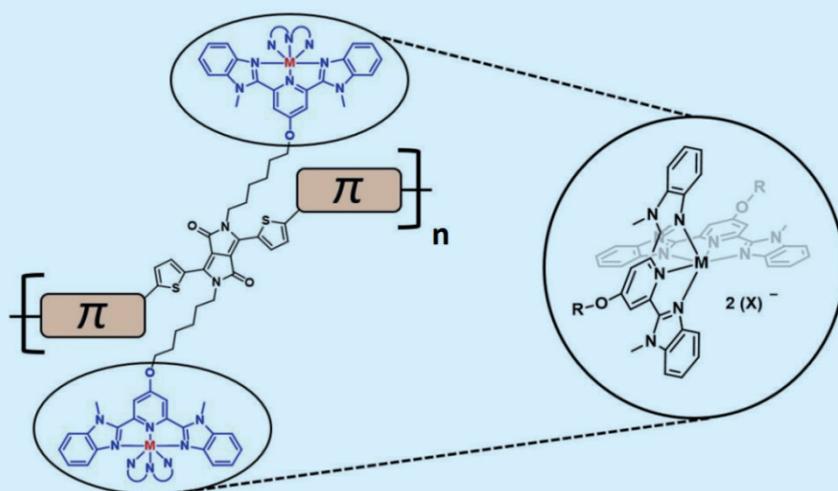


Fig. 1: DPP-based polymer with methylbenzimidazole (MeBZIMPY) ligand-containing side chains for coordination of Fe(II). [Reproduced from Ref. 2]

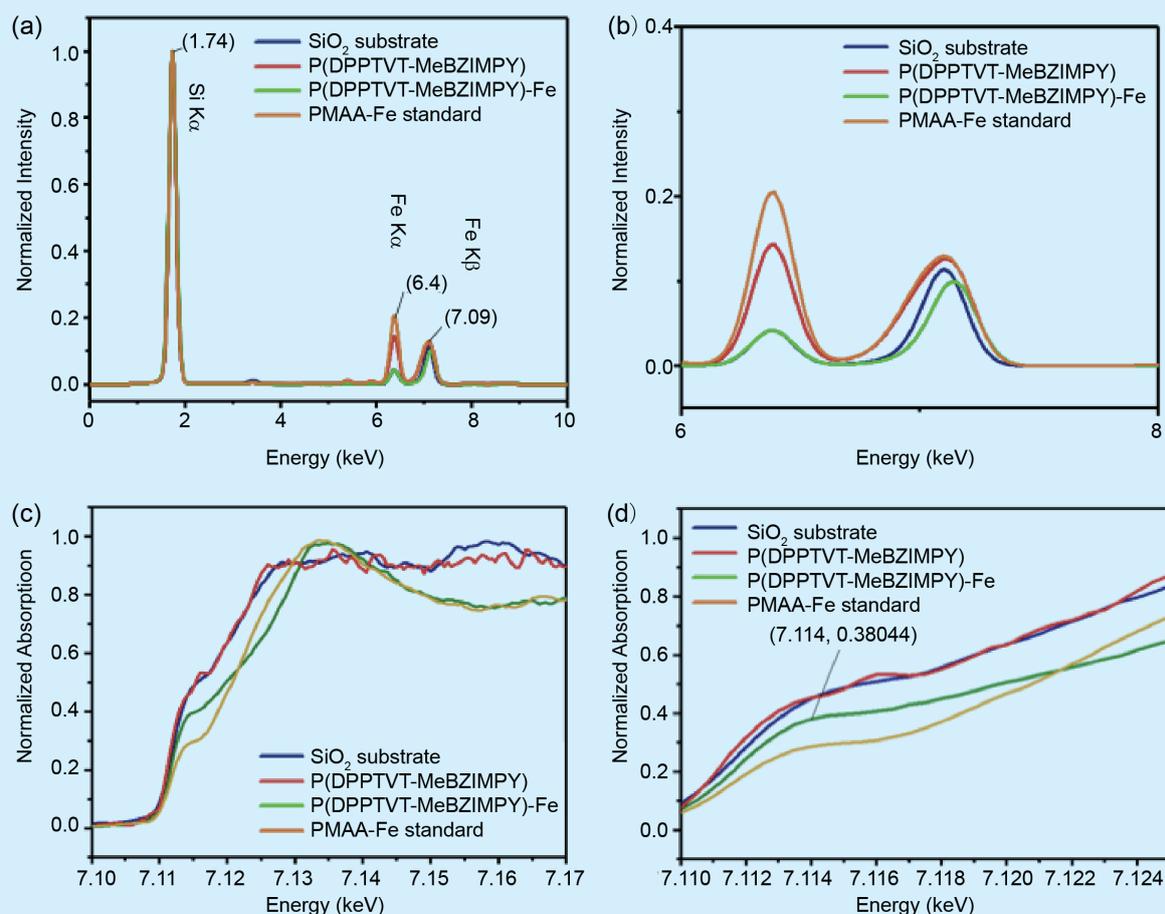


Fig. 2: (a) X-ray fluorescence spectra (full spectra) of SiO₂, P(DPPTVT-MeBZIMPY), P(DPPTVT-MeBZIMPY)-Fe and PMAAFE standard; (b) X-ray fluorescence spectra of SiO₂, P(DPPTVT-MeBZIMPY), P(DPPTVT-MeBZIMPY)-Fe and PMAAFE standard expanded in region 6–8 keV. The spectra have been normalized relative to the Si K α signal; (c) fluorescence yield (FY) Fe K-edge X-ray-absorption near-edge structure (XANES) spectra of SiO₂, P(DPPTVT-MeBZIMPY), P(DPPTVT-MeBZIMPY)-Fe and PMAAFE standard, and (d) fluorescence-yield Fe K-edge XANES spectra of SiO₂, P(DPPTVT-MeBZIMPY), P(DPPTVT-MeBZIMPY)-Fe and PMAAFE standard expanded in region 7.110–7.124 keV. [Reproduced from Ref. 2]

This report features the work of Yu-Cheng Chiu, Simon Rondeau-Gagné and their collaborators published in *J. Mater. Chem. C* **8**, 8213 (2020).

TPS 23A X-ray Nanoprobe

- XRF, XANES
- Materials Science, Semiconducting Polymer, Organic Transistor, Metal Coordination

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