

Improving performance of polymer semiconductors with metal-ligand based mechanophores

By [Andy Tay](#)

With the rise of wearable electronics, it becomes increasingly crucial to develop electronic materials that can resist mechanical strain caused by deformations without compromising electrical properties. One of the most important electrical components in wearable electronics is the polymer-based field-effect transistor (FET), a type of polymer semiconductor (PSC) device that uses electric field to control the flow of current in a semiconductor.

However, PSCs are usually brittle due to rigid conjugated chemical backbones and ordered molecular packing, which are necessary for charge carrier transport and high stretchability. While methods like strain engineering can improve mechanical properties, they require additional and cumbersome processing steps.

In a recent [paper](#) published in *Advanced Functional Materials*, a team of researchers led by [Professor Zhenan Bao](#) and [Dr. Hung-Chin Wu](#) in the Department of Chemical Engineering at Stanford University made use of metal-ligand based mechanophores to improve the mechanical and electrical performance of their PSCs commonly found in wearable electronics.

“We wanted to develop a polymer semiconductor, without blending secondary elastomers or incorporating additives, that possesses both high mechanical robustness and electronic performance under strain. We discovered that the molecular ordering of semiconducting polymers can be effectively manipulated by the dynamic of metal-ligand coordination bonds, leading polymer semiconductors to be highly stretchable without sacrificing charge transporting,” says Wu.

What are mechanophores?

Mechanophores are dynamic areas in a polymer network that contain either adaptive covalent or weak non-covalent bonds, such as metal-ligand coordination bonds, that can dissipate mechanical stress under strain by breaking and reforming. Mechanophores have been exploited for use of stretchable and self-healing elastomeric polymers. Amongst them, metal-ligand coordination is particularly useful. A variety of stretchable polymers with different mechanical features can be created by varying the type and oxidation state of the metal center, and the class and denticity, i.e., number of donor groups in a single ligand that bind to a central atom in a coordination complex, of the coordinating ligands.

Wu and colleagues made use of iron metal-ligand based mechanophores to improve the mechanical robustness and charge transport performance of PSCs (**Figure 1**). The team cross-linked a donor-acceptor polymer with iron (Fe)-ligand mechanophores. A variety of materials were created by copolymerizing DPP [1] and TVT [2], which are two of the most commonly used polymers in PSCs, with either Py [3] or BPy [4] units. Next, the authors added FeX₂ (X = Cl, B(Ph₄)) to these ligands to form Wolf type-II metallopolymers before characterizing their mechanical properties.

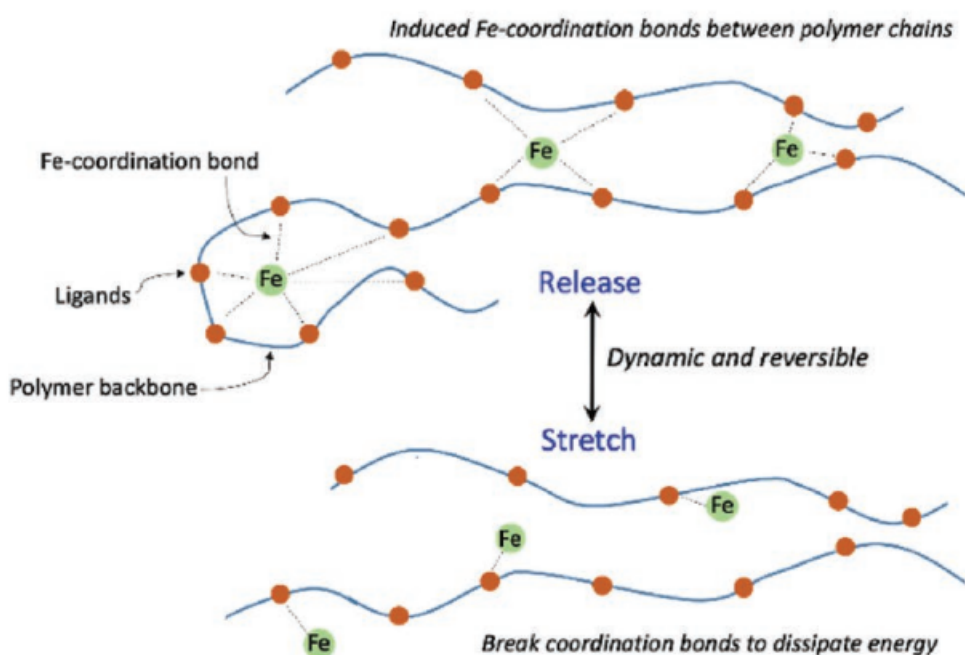


Figure 1 Schematic showing iron-ligand coordination-based mechanophores in polymer semiconductors. The metallated bonds can break to dissipate energy and are also reversible for self-healing properties. Image credit: Adv Funct Materials, Volume: 31, Issue: 11, First published: 12 January 2021, DOI: (10.1002/adfm.202009201)

Optimizing mechanical properties

The team observed that the incorporation of relatively weak PyFeB bonds resulted in crack-free films even at 75% strain and that metallated polymers with PyFeB mechanophore showed better mechanical robustness. The authors reasoned that in conventional PSC films, the rigid crystalline domains caused brittleness in films, and this is a conundrum as the crystalline domains are essential for interchain charge transport. However, by introducing heterocyclic spaces such as the Py ligand, the crystallinity and size of the rigid crystallites can be tailored to modify mechanical properties. For instance, adding more Py moieties reduced the elastic modulus of the thin film by decreasing polymer aggregation, hence making the films more stretchable. When there were too many iron ions, there was a decline in stretchability in films with a higher degree of Fe-coordination due to excessive cross-linking between polymer chains.

Optimizing electrical properties

Using a bottom-gate/top-contact FET device, the team then tested the electrical properties of their materials and surprisingly found that mechanophores enhanced charge carrier mobility, likely because the coordinated iron ions might have doped the semiconducting layer. However, when there were too many iron ions, the high degree of cross-linking could disrupt crystalline ordering between polymer chains and discourage charge transport.

Increasing the robustness of polymer semiconductors

Comparing PyFeB material with a widely studied PSC - DPPTVT, which consists of electron-withdrawing DPP and electron-donating TVT moieties, the authors found that the introduction of Py-FeB bonds improved electrical performance under deformation. However, when strain increased, there was noticeable strain-induced physical damage that interrupted charge transport. Using molecular simulations, the authors showed that when forces were applied on PSC chains, weaker

metallated bonds tended to break to release energy. However, the bonds could reform, creating a self-healing effect, and the reversibility was influenced by the density of metal ion coordination.

“Our work provides a viable approach to enhance both the mechanical and the electronic performance of polymer-based soft devices. Additionally, a fully self-healable device is expected to be developed for wearables with such semiconducting polymers that possess dynamic and reversible Fe-coordination bonds,” says Wu.

A promising film material for wearables

In this paper, Wu and colleagues showed that the incorporation of metal-ligand coordination bonds into PSCs can modify molecular ordering and boost charge transport efficiency while improving thin film deformability. Specifically, the metallated DPPTVT-Py-FeB film had two-fold better field-effect charge mobility than the parent polymer, DPPTVT. In the future, such polymers with metallated mechanophores can be used to create stretchable electronic devices for wearables with robust mechanical and electrical performance.

End Notes

[1] DPP: 3,6-bis(5-bromothiophene-2-yl)-*N,N'*-bis(5-decyl-1-pentadecyl)-1,4-dioxopyrrolo[3,4-c]pyrrol; ketopyrrolopyrrole

[2] TVT: 1,2-(E)-bis(5'-trimethylstannyl-2'-C-thienyl)ethene; thiophene-vinyl-thiophene

[3] Py: 3,5-dibromopyridine

[4] BPy: 5,5'-dibromo-2,2'-bipyridine

Source article

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