

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

- XAS
- Heterogeneous Catalysis, Metal–organic Frameworks

Reference

1. J. A. Peña Prada, T. A. Huertas Navarro, S. L. Chua, A. M. Granados, C.-W. Pao, A. M. Fracaroli, N. M. Bedford, *Angew. Chem. Int. Ed.* **64**, e202424540 (2025).

How Subtle Atomic Asymmetry Makes Polymers Both Stretchable and Electrically Fast

Through a dipole-tailored polymer design, high stretchability and fast charge transport are achieved for soft, high-performance electronic materials.

Flexible and wearable electronic devices that can stretch, bend, and conform to human skin are rapidly advancing the frontier of biomedical sensing and human–machine interfaces. However, designing polymers that are both mechanically stretchable and electronically conductive has remained a challenge. Typically, increasing flexibility tends to reduce crystalline order, which in turn slows down charge transport. A research team led by Chien-Chung Shih at National Yunlin University of Science and Technology has now addressed this dilemma through smart molecular design. Their study introduces a “dipole-tailoring strategy” that decouples polymer aggregation from crystallinity, allowing a single material to be soft, strong, and electronically agile.¹

The key innovation lies in dipole-tailored isomeric linkers (DTL) that subtly rearrange the position of an alkoxy group on a benzene ring. By shifting this group from the 2,6- and 3,5- positions to the asymmetric 2,4- position, the researchers created polymers with progressively stronger internal dipoles. This seemingly minor atomic change dramatically reshapes how polymer chains pack, aggregate, and respond to mechanical stress. Through a series of carefully controlled syntheses, the team incorporated each DTL isomer into a diketopyrrolopyrrole (DPP)–thiophene polymer backbone. Spectroscopic and computational analyses showed that the asymmetric 2,4-

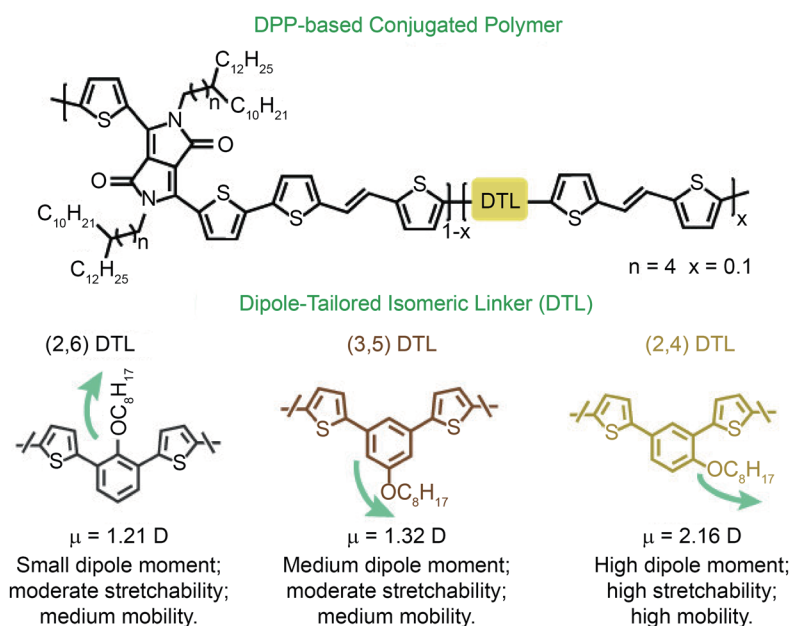


Fig. 1: Chemical structures of the DPP-based conjugated polymers and their isomeric linkers. The parent polymer backbone incorporates a DPP unit and thiophene spacers, while the DTL modulates the local dipole moment through positional variation of the alkoxy substituent on the benzene ring. The three isomers—(2,6)-DTL, (3,5)-DTL, and (2,4)-DTL—exhibit increasing dipole moments ($\mu = 1.21, 1.32,$ and 2.16 D, respectively), corresponding to progressively enhanced chain polarity and electrostatic interactions. This dipole engineering enables tunable mechanical and electronic properties: higher dipole moments lead to greater stretchability and improved charge mobility, as demonstrated in the 2,4-DTL polymer. [Reproduced from Ref. 1]

DTL possesses the highest dipole moment (2.16 D) and the most distorted geometry, thus promoting local electrostatic attraction between chains.

To confirm how these dipolar modifications affect molecular organization, the team relied heavily on synchrotron-based grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements. GIWAXS is uniquely suited to probing the nanometer-scale order

of thin polymer films, revealing how chains stack, twist, and crystallize. Using this high-flux synchrotron X-ray technique, the team discovered that long-range crystallinity decreased as the dipole moment increased, reducing rigid lamellar domains that normally limit flexibility. In addition, short-range aggregation was enhanced, forming compact local clusters that preserve efficient π - π charge transport. The synchrotron GIWAXS data confirmed that these improvements arise not from conventional crystallization but from dipole-induced local ordering.

After establishing the structural origin of flexibility, the team demonstrated real-world device performance. When blended with a non-fullerene acceptor (Y7), PDPP-(2,4)-DTL formed a stretchable bulk-heterojunction photodiode that exhibited the following key parameters: an external quantum efficiency of 45%, detectivity (D^*) exceeding 10^{12} Jones, stable operation even under 80% mechanical strain, and retention of photoresponse after 1000 stretching cycles. These results mark a breakthrough for skin-compatible optoelectronics, such as wearable heart-rate sensors, pulse oximeters, and biomedical photoplethysmography (PPG) systems. Indeed, the team demonstrated a working on-skin PPG sensor capable of recording human pulse signals in real time without any degradation under repeated bending.

By merging molecular dipole design with synchrotron X-ray characterization, the research team achieved what was long thought to be contradictory: polymers that are simultaneously soft like skin and conductive like silicon. This study establishes a new principle in polymer science: dipole engineering can be used to control local aggregation independently of long-range order, breaking the long-standing trade-off between electrical performance and mechanical stretchability. Their findings open new possibilities for stretchable transistors, photodiodes, and biomedical sensors, redefining how we design materials for the next era of flexible electronics. (Reported by Yu-Jong Wu)

This report features the work of Chien-Chung Shih and his co-workers published in J. Am. Chem. Soc. 147, 29282 (2025).

TLS 13A1 X-ray Scattering

- GIWAXS
- Materials Science, Soft matters

Reference

1. C.-C. Kang, T.-M. Hung, S.-T. Lu, T.-C. Lu, C.-C. Shih, J. Am. Chem. Soc. 147, 29282 (2025).

Turning Nitrate Waste into Useful Ammonia Fertilizer: Custom-Built Copper Molecules for Clean Catalysis

A team developed enhanced activity and selectivity of molecular Cu(I) catalysts for electrocatalytic nitrate reduction reaction (NO_3RR) by incorporating electrically charged prosthetic groups on catenane ligands.

A research team led by Ho Yu Au-Yeung and Edmund Tse at the University of Hong Kong (HKU, China) has developed a new family of copper-based molecular catalysts.¹ These catalysts efficiently convert harmful nitrate pollutants in water into valuable ammonia fertilizers. The discovery, made at the HKU-CAS Joint Laboratory on New Materials, demonstrates that precisely designed molecular structures called catenanes can enhance the selectivity and durability of catalysts used in green chemistry (Fig. 1).

Nitrate contamination from agricultural runoff, industrial discharge, and household wastewater is one of the world's most pressing water-quality problems. Traditional removal techniques often consume excessive energy and generate unwanted by-products. Converting nitrate back into ammonia provides a sustainable alternative. Ammonia is a valuable fertilizer and a potential hydrogen carrier. However, developing a low-cost, non-precious metal catalyst that can convert nitrate selectively and efficiently without causing side reactions remains a challenge.

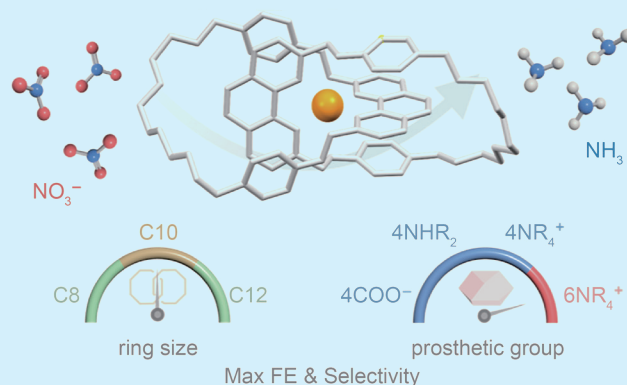


Fig. 1: Influence of prosthetic groups in Cu(I) catenane complexes and the size of interlocked macrocycles in the entangled ligands on NO_3RR . [Reproduced from Ref. 1]