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**).

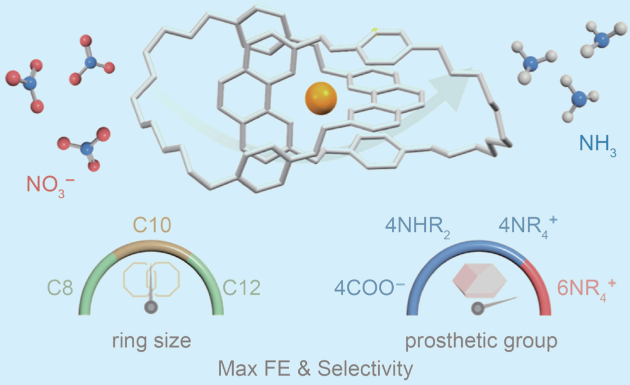
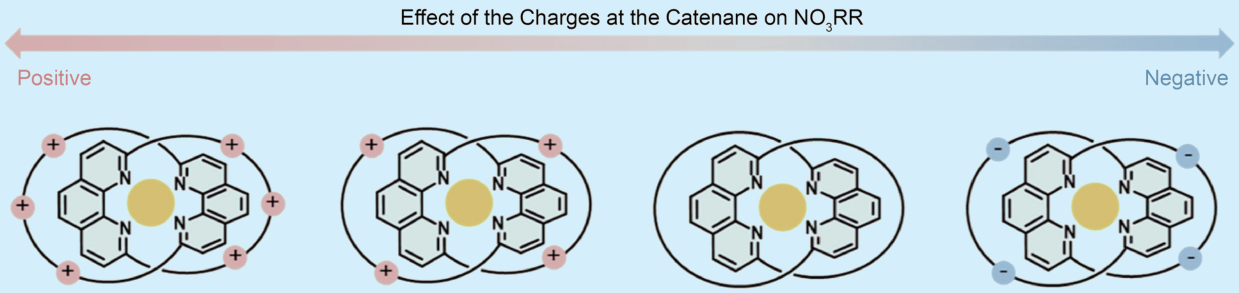


Fig. 1: Influence of prosthetic groups in Cu(I) catenane complexes and the size of interlocked macrocycles in the entangled ligands on NO_3RR. [Reproduced from Ref. 1]

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.



Mechanical Bond: Maintaining the integrity of the complex by overcoming the Coulombic repulsion

Positive Prosthetic Groups: Facilitate acceptance of anionic reactant NO_3^- and release of cationic product NH_4^+

Fig. 2: Effect of prosthetic groups of the Cu(I) catenane complexes on NO_3RR. [Reproduced from Ref. 1]

Au-Yeung and Tse addressed this challenge by designing a new set of mechanically interlocked Cu(I) complexes, known as catenanes. These structures resemble tiny molecular links—two or more rings intertwined—enabling precise control over metal atom interactions during reactions. Although copper (Cu) is an abundant and affordable metal for catalysis, conventional copper catalysts often face the “activity-selectivity-durability trilemma”: they may work quickly, but lack selectivity and degrade rapidly. The HKU researchers overcame this limitation by mechanically locking and chemically tuning the copper environment to create stable and highly selective catalysts.

Their approach combined two strategies:

- Mechanical Interlocking: using catenane ligands to secure the copper center, preventing unwanted structural changes during reactions.
- Covalent Modification: attaching positively charged groups to enhance attraction to negatively charged nitrate ions and facilitate the release of the positively charged ammonia product.

In the new catalysts, the copper center is positioned within an interlocked framework that resists distortion under reaction conditions. The charged groups on the catenane backbone help attract nitrate ions to the copper site, allowing electrons and protons to transfer efficiently (**Fig. 2**). According to the researchers, this design achieves two goals: it increases the conversion rate from nitrate to ammonia and reduces competing reactions, such as unwanted hydrogen evolution.

Laboratory tests showed that the best-performing compound—$[Cu(C_{6p})](PF_6)_7$—achieved a Faradaic efficiency of 86%. This means nearly nine out of ten electrons were used productively to make ammonia. This performance is among the highest reported for molecular copper catalysts operating in water at room temperature.

The process is the electrocatalytic nitrate reduction reaction. It involves passing an electrical current through a catalyst in a water-based system. Each nitrate ion (NO_3^-) accepts eight electrons and nine protons to become ammonia. The HKU team showed that by adjusting the number of positive charges and the tightness of the catenane rings, they could fine-tune the catalyst’s interaction with different reaction steps. Tighter rings enhanced stability, while more charged groups improved selectivity for ammonia.

Experiments also revealed that the mechanical bond helped maintain the copper center’s shape even during extended operation. Without this interlocking, typical copper complexes tend to decompose or convert into less active species. Copper can readily switch between +1 and +2 oxidation states during reactions, affecting catalyst performance. Therefore, confirming that the catalyst maintains Cu(I) is crucial. The team used Cu L-edge X-ray absorption spectroscopy (XAS), a soft X-ray technique, to examine the electronic structure and oxidation state of copper at **TLS 20A1**. The nearly identical spectra of $[Cu(C_{6p})](PF_6)_7$, its carbon-supported form, and the reference confirm that all species contain Cu(I) rather than Cu(II) (**Fig. 3**, see next page). These results demonstrate that the mechanical interlocking effectively stabilizes the Cu(I) environment, leading to the catalysts’ high selectivity and durability.

This research represents an important step toward closing the nitrogen cycle, a key sustainability goal in environmental chemistry. The method can both purify water and produce green fertilizers using renewable electricity. Additionally, the concept of mechanical interlocking introduces a new approach to catalyst design. Structural engineering at the molecular level can now achieve comparable performance with earth-abundant materials, reducing reliance on expensive metals such as platinum or palladium.

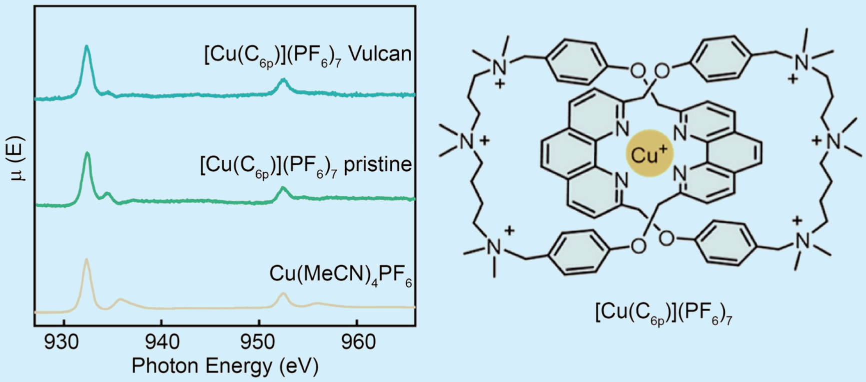


Fig. 3: Cu L_3-edge XAS of $Cu(MeCN)_4(PF_6)$ reference (orange), $[Cu(C_{6p})](PF_6)_7$ pristine (green), and $[Cu(C_{6p})](PF_6)_7$ supported on Vulcan (blue). XAS spectra were collected in total electron yield mode. [Reproduced from Ref. 1]

As Tse explained, the interlocked copper system "demonstrates that precision molecular design can solve long-standing challenges in catalysis—stability, selectivity, and efficiency—without relying on rare metals." The team plans to expand this approach to other catalytic reactions. They also aim to integrate their catalysts into scalable devices that could convert wastewater pollutants into useful resources on an industrial scale. According to Au-Yeung, "Mechanically interlocked ligands offer a powerful platform for tailoring catalysts at the molecular level. This work provides a blueprint for developing robust, efficient systems for sustainable chemical transformations."

Through innovative molecular design, Au-Yeung and Tse's team at HKU transformed an environmental challenge into an opportunity for clean chemical production. Their copper catenane catalysts convert nitrate pollution into useful ammonia and demonstrate how mechanical chemistry can redefine the future of sustainable catalysis. (Reported by Shu-Chih Haw)

TLS 20A1

- Soft X-ray Absorption Spectroscopy
- Energy-related Materials, Catalytic Materials, Electron-correlated Materials, Molecular Films, Biomaterials

Reference

1. Y. Deng, X. Mo, S. K.-M. Lai, S.-C. Haw, H. Y. Au-Yeung, E. C. M. Tse, J. Am. Chem. Soc. **147**, 14316 (2025).

When Order Defies Nature: Hexagonal High-Entropy Nanocrystals for Accelerated Hydrogen Evolution

Atomic engineering characterized by in situ X-ray diffraction and X-ray absorption spectroscopy leads to the design of novel catalysts for hydrogen production.

In the world of nanoscience, order and chaos often coexist in strange harmony. Imagine arranging five precious metals—ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), and iridium (Ir)—into a single, nanosized crystal. Each atom competes for space, but they somehow settle into a balanced configuration, forming what scientists call a high-entropy alloy (HEA). These materials, composed of multiple metallic elements in nearly equal proportions, have attracted enormous interest because of their unusual stability, catalytic properties, and resistance to degradation. There are three key questions in this field. First, how do these atoms organize themselves at the smallest scales? Second, can they form unconventional structures that nature rarely favors? Third, what forces allow such structures to persist? These are the questions driving a recent study on $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$ core–shell nanocrystals, where Tung-Han Yang (National Tsing Hua University) and his collaborators engineered a new type of high-entropy material with a hexagonal close-packed (HCP) shell, a crystal structure that is normally unstable for this combination of elements. Through cutting-edge X-ray experiments, this study offers a rare glimpse into how atomic architecture evolves and stabilizes under extreme conditions.