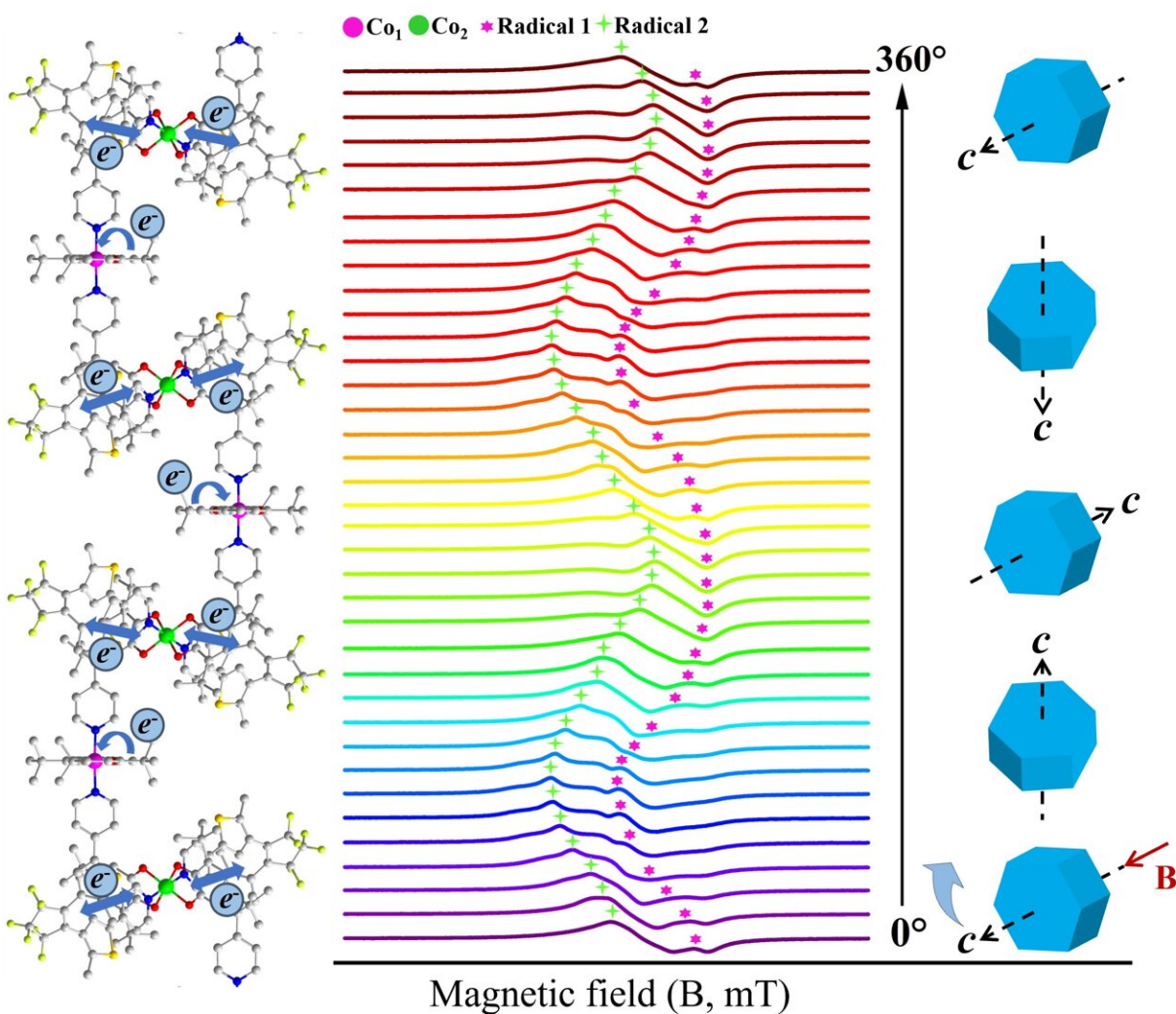


Dual-radical observation in a photoswitchable coordination polymer with synergy effect of semi-conductivity

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Dual radicals were observed directionally for the first time in a semiconductive

VT coordination polymer due to the presence of two crystallographically independent SQ^- radicals. The directional variations of these dual radicals, as well as their 180° periods were confirmed by the angle-dependent EPR spectroscopy. The conductive anomaly along the ab plane in the open-form complex is due to the electron transfer during the VT process. Credit: Science China Press

In a study published in the journal *National Science Review* and led by Dr. Zhao-Yang Li (School of Material Science and Engineering, Nankai University) and Prof. Masahiro Yamashita (Department of Chemistry, Graduate School of Science, Tohoku University), a photoisomerizable ligand was used to synthesize two VT coordination polymers, which display VT and photoconversion behavior.

Two crystallographically independent SQ^- radicals arranged along the 1D chain were observed in the open-form complex using SC-XRD. Therefore, two clearly distinct radical signals were observed in the high-field/-frequency single-crystal EPR spectra of a VT complex for the first time.

In their strategy, a pyridyl derivative of a diarylethene (DAE) ligand was used as the linker along with the Co-dioxolene unit, which is a classical VT building block, to form a VT CP with a chain structure. Light may promote the rearrangement of the crystal structure and further influence [magnetic properties](#) through modification of the ligand field (isomers differ substantially in shape and conjugation), leading to photocontrol and deep insight into organic radicals on a 1D chain.

An open-form and a closed-form complex were synthesized. Photoconversion between the open- and closed-form species (ligands and complexes) due to the effect of DAE ligand photoisomerization was

explored through UV/vis absorption spectroscopy.

Notably, the 1D chains in the two types of complexes differ due to the open and closed forms of the 6F-DAE-py₂ ligand. The open-form complex exhibits a zigzag 1D structure, while the closed-form complex displays quasi-linear characteristics. In the study of SC-XRD, two types of crystallographically distinct SQ⁻ radicals, referred to as Radical 1 and Radical 2, are observed in the chains of the open-form complex due to their zigzag configurations.

They used high-field (~13.3 T) and -frequency (~360 GHz) single-crystal EPR spectroscopy to significantly enhance the resolution of Zeeman splitting in the open-form complex, which led to the observation of a remarkable phenomenon. Dual SQ⁻ radical signals were directly visualized when the *c*-axis was aligned with the static field.

Furthermore, angle-dependent EPR spectroscopy was carried out. The directional variations of these dual radicals, as well as their 180° periods, were confirmed. To conveniently investigate the two directional radicals, they determined the face index of a single crystal of the open-form complex. In this way, they confirmed the g_z value of Radical 1 and distinguished the g_1 and g_2 values obtained in high-field and high-frequency EPR spectroscopy.

Interestingly, a synergistic effect between valence tautomerism and semi-conductivity was found in magnetic and electronic studies. Electrical conductivity increased with increasing temperature below the [transition temperature](#), which is a characteristic semiconductor behavior. However, electrical conductivity was observed to decrease with increasing temperature above 330 K, which is ascribable to [electron transfer](#) during valence tautomerism.

Such behavior was observed for the first time in a single-crystal VT

complex. The Arrhenius analysis determined the origin of the semiconductive behavior before 330 K, while DFT calculations helped illustrate the mechanism of the unusual change in [electrical conductivity](#) during the VT transition process.

This study presents the first example of dual-radical-based molecular anisotropy and charge-transfer-induced conductive anisotropy in a photoswitchable coordination polymer. It is of considerable significance with regard to the anisotropy and synthesis of multifunctional bistable magnetic materials in the molecular magnetism field.

More information: Jing-Wei Dai et al, Dual-radical-based molecular anisotropy and synergy effect of semi-conductivity and valence tautomerization in a photoswitchable coordination polymer, *National Science Review* (2023). [DOI: 10.1093/nsr/nwad047](https://doi.org/10.1093/nsr/nwad047)

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