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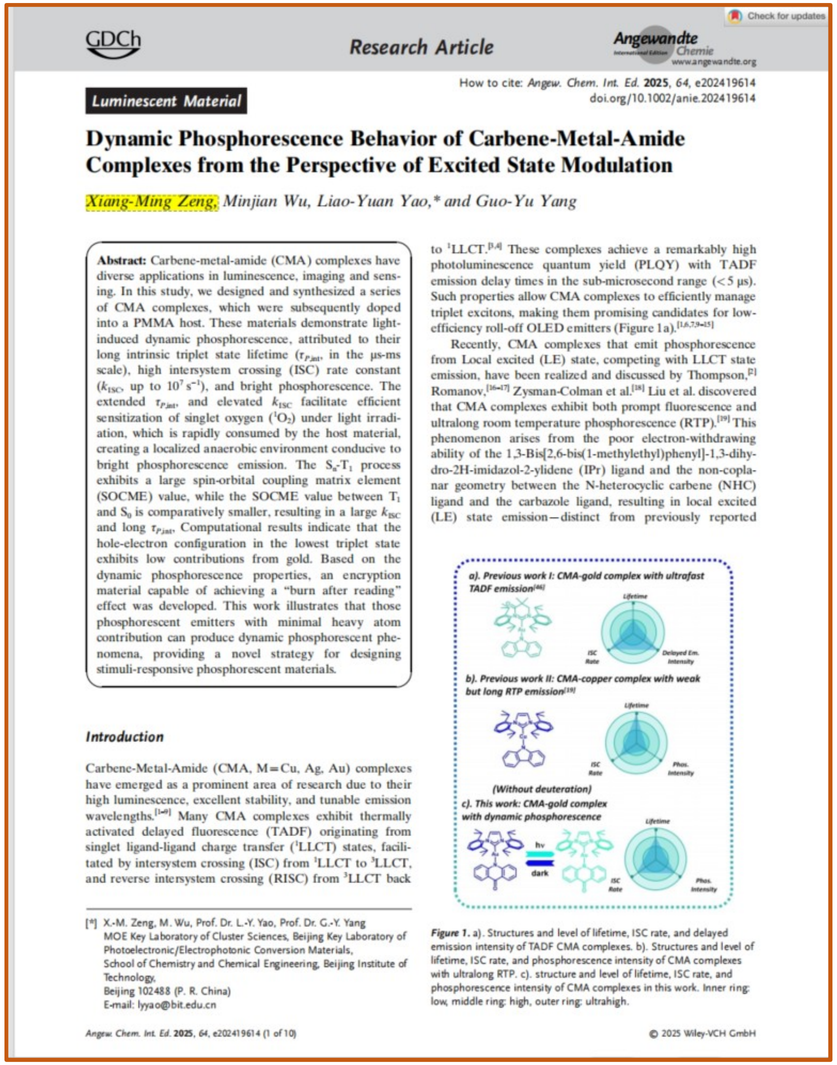

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Luminescent Material

Dynamic Phosphorescence Behavior of Carbene-Metal-Amide Complexes from the Perspective of Excited State Modulation

Xiang-Ming Zeng, Minjian Wu, Liao-Yuan Yao, and Guo-Yu Yang*

Abstract: Carbene-metal-amide (CMA) complexes have diverse applications in luminescence, imaging and sensing. In this study, we designed and synthesized a series of CMA complexes, which were subsequently doped into a PMMA host. These materials demonstrate light-induced dynamic phosphorescence, attributed to their long intrinsic triplet state lifetime ($\tau_{P,int}$, in the μs-ms scale), high intersystem crossing (ISC) rate constant (k_{ISC}, up to $10^7\,s^{-1}$), and bright phosphorescence. The extended $\tau_{P,int}$, and elevated k_{ISC} facilitate efficient sensitization of singlet oxygen ($^1O_2$) under light irradiation, which is rapidly consumed by the host material, creating a localized anaerobic environment conducive to bright phosphorescence emission. The S_n-T_1 process exhibits a large spin-orbital coupling matrix element (SOCME) value, while the SOCME value between T_1 and S_0 is comparatively smaller, resulting in a large k_{ISC} and long $\tau_{P,int}$. Computational results indicate that the hole-electron configuration in the lowest triplet state exhibits low contributions from gold. Based on the dynamic phosphorescence properties, an encryption material capable of achieving a "burn after reading" effect was developed. This work illustrates that those phosphorescent emitters with minimal heavy atom contribution can produce dynamic phosphorescent phenomena, providing a novel strategy for designing stimuli-responsive phosphorescent materials.

Introduction

Carbene-Metal-Amide (CMA, M=Cu, Ag, Au) complexes have emerged as a prominent area of research due to their high luminescence, excellent stability, and tunable emission wavelengths.[1–9] Many CMA complexes exhibit thermally activated delayed fluorescence (TADF) originating from singlet ligand-ligand charge transfer (^{1}LLCT) states, facilitated by intersystem crossing (ISC) from ^{1}LLCT to ^{3}LLCT, and reverse intersystem crossing (RISC) from ^{3}LLCT back to ^{1}LLCT.[3,4] These complexes achieve a remarkably high photoluminescence quantum yield (PLQY) with TADF emission delay times in the sub-microsecond range (<5 μs). Such properties allow CMA complexes to efficiently manage triplet excitons, making them promising candidates for low-efficiency roll-off OLED emitters (Figure 1a).[1,6,7,9–15]

Recently, CMA complexes that emit phosphorescence from Local excited (LE) state, competing with LLCT state emission, have been realized and discussed by Thompson,[2] Romanov,[16–17] Zysman-Colman et al.[18] Liu et al. discovered that CMA complexes exhibit both prompt fluorescence and ultralong room temperature phosphorescence (RTP).[19] This phenomenon arises from the poor electron-withdrawing ability of the 1,3-Bis[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-2H-imidazol-2-ylidene (IPr) ligand and the non-coplanar geometry between the N-heterocyclic carbene (NHC) ligand and the carbazole ligand, resulting in local excited (LE) state emission—distinct from previously reported

Figure 1. a). Structures and level of lifetime, ISC rate, and delayed emission intensity of TADF CMA complexes. b). Structures and level of lifetime, ISC rate, and phosphorescence intensity of CMA complexes with ultralong RTP. c). structure and level of lifetime, ISC rate, and phosphorescence intensity of CMA complexes in this work. Inner ring: low, middle ring: high, outer ring: ultrahigh.

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Topochemical synthesis of an atomic Pt modified plasmonic yolk–shell nanostructure for enhanced photocatalytic hydrogen evolution†

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The combination of plasmonic metals with semiconductors, driven by the hot injection effect and enhanced electromagnetic field effects, enables the improved absorption of incident light energy and the separation of photogenerated charge carriers. Among various metal–semiconductor topological structures, yolk–shell (Y–S) architectures are ideal photocatalysts due to their light-scattering capabilities and large surface area, but with unmanageable photocarrier dynamics. Building on this, we introduced single-atom dispersed Pt sites (Pt-SA) to increase surface catalytic sites for directional migration of charge carriers in photocatalytic hydrogen evolution reactions. By employing cation exchange and galvanic replacement, Y–S nanostructures with an Au-core and a Pt-SA modified CdS shell (namely Au@Pt-SA/CdS Y–S) were synthesized. The as-prepared catalyst exhibits an enhanced photocatalytic hydrogen evolution rate of 10.9 mmol g^{-1} h^{-1} under visible light (λ > 420 nm) irradiation, which is twice that of Au@CdS Y–S nanostructures. This work provides new insights into the topochemical synthesis of Y–S structures and the engineering of plasmonic metals and atomic sites for enhanced photocatalysis.

Introduction

The utilization of solar energy is commercially advantageous to maintain the sustainability of human society and alleviate the consumption of fossil fuels.[1,2] Photocatalysis, directly converting solar energy to storable chemical fuels, has been regarded as an ideal strategy for energy production.[3–7] To optimize the energy conversion efficiency of photocatalysis, rationally designed photocatalysts with engineered composition, geometry and carrier dynamics are imperative.[8–11] Compared to pristine semiconductor and metal based photocatalysts, the synthesis of plasmonic metal–semiconductor hybrid nanostructures has gained considerable interest due to the plasmon-mediated electron-transfer (PMET).[12,13] Typically, the integrated metal–semiconductor hybrid nanostructure could facilitate the injection of localized surface plasmon resonance (LSPR) hot carriers with optimized charge dynamics for improved carrier utilization.[14–17] The efficiency of this energy transfer is highly dependent on the proximity between the metal and semiconductor components, underscoring the critical need for precise geometric alignment of these elements within the nanostructures to optimize various photocatalytic performance parameters.[18–22]

The metal/semiconductor core–shell nanostructure has been widely investigated in photocatalysis,[23–25] due to the "antenna effect" facilitated enhanced charge transfer and efficient plasmon enhancement.[26,27] While retaining the benefits of traditional core–shell structures,[28,29] plasmonic yolk–shell nanostructures (Y–S NSs) could provide new opportunities with maintained carrier dynamics and increased specific surface area.[30] In particular, light undergoes multiple instances of reflection and scattering within the void between the yolk and the shell, which serves to amplify the capacity for capturing light.[31] Besides, the Y–S structure offers a substantial specific surface area that supplies ample active sites for surface redox reactions and allows for the introduction of cocatalysts on the surface, thereby improving the photocatalytic performance.[32] However, due to the irregular morphologies and crystallinities of the plasmonic Y–S NSs, it could be a challenge to manipulate the charge dynamics especially considering the complex LSPR under light irradiation for efficient photocatalysis.[33]

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† Electronic supplementary information (ESI) available: Details of the synthesis strategies, photocatalytic procedures and characterization methods; characterization of NSs by TEM, HRTEM, EDS, and XRD; product identification by GC; and EXAFS fitting curves. See DOI: https://doi.org/10.1039/d5ta00271k

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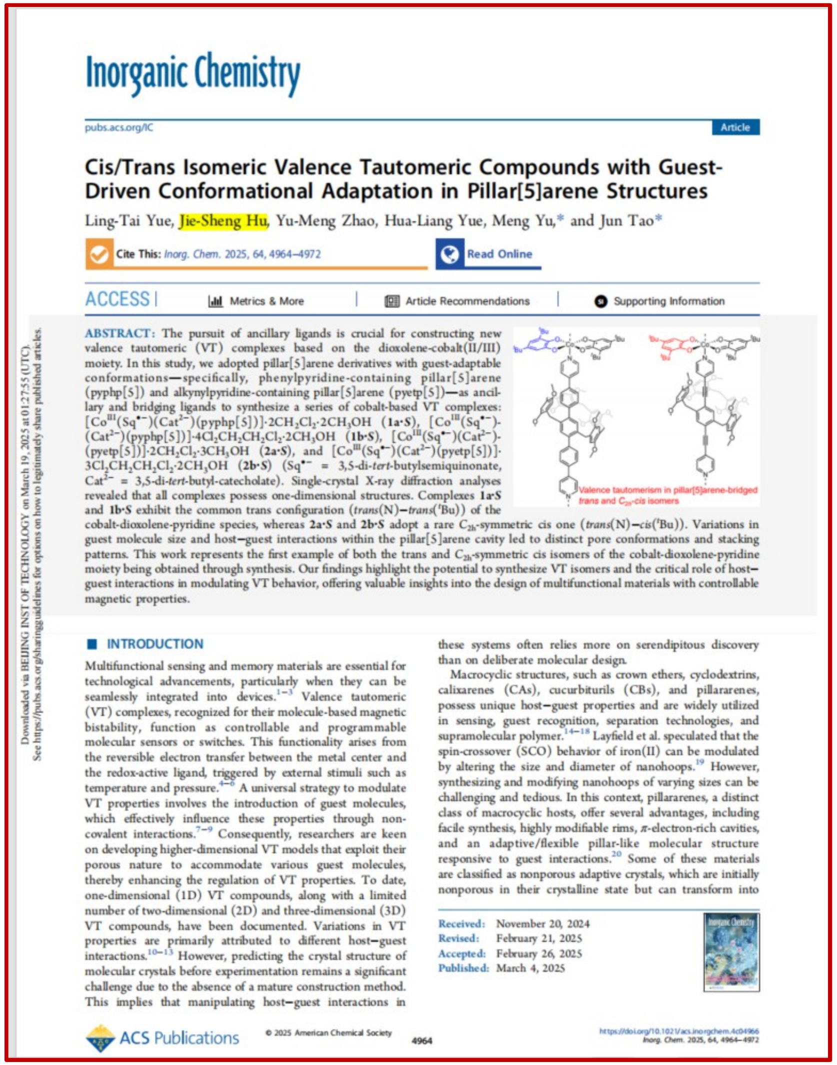

Inorganic Chemistry

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Cis/Trans Isomeric Valence Tautomeric Compounds with Guest-Driven Conformational Adaptation in Pillar[5]arene Structures

Ling-Tai Yue, Jie-Sheng Hu, Yu-Meng Zhao, Hua-Liang Yue, Meng Yu,* and Jun Tao*

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ABSTRACT: The pursuit of ancillary ligands is crucial for constructing new valence tautomeric (VT) complexes based on the dioxolene-cobalt(II/III) moiety. In this study, we adopted pillar[5]arene derivatives with guest-adaptable conformations—specifically, phenylpyridine-containing pillar[5]arene (pyphp[5]) and alkynylpyridine-containing pillar[5]arene (pyetp[5])—as ancillary and bridging ligands to synthesize a series of cobalt-based VT complexes: $[Co^{III}(Sq^{\bullet-})(Cat^{2-})(pyphp[5])]\cdot 2CH_2Cl_2\cdot 2CH_3OH$ (**1a·S**), $[Co^{III}(Sq^{\bullet-})(Cat^{2-})(pyphp[5])]\cdot 4Cl_2CH_2CH_2Cl_2\cdot 2CH_3OH$ (**1b·S**), $[Co^{III}(Sq^{\bullet-})(Cat^{2-})(pyetp[5])]\cdot 2CH_2Cl_2\cdot 3CH_3OH$ (**2a·S**), and $[Co^{III}(Sq^{\bullet-})(Cat^{2-})(pyetp[5])]\cdot 3Cl_2CH_2CH_2Cl_2\cdot 2CH_3OH$ (**2b·S**) ($Sq^{\bullet-}$ = 3,5-di-*tert*-butylsemiquinonate, Cat^{2-} = 3,5-di-*tert*-butyl-catecholate). Single-crystal X-ray diffraction analyses revealed that all complexes possess one-dimensional structures. Complexes **1a·S** and **1b·S** exhibit the common trans configuration (*trans*(N)−*trans*(^{t}Bu)) of the cobalt-dioxolene-pyridine species, whereas **2a·S** and **2b·S** adopt a rare C_{2h}-symmetric cis one (*trans*(N)−*cis*(^{t}Bu)). Variations in guest molecule size and host−guest interactions within the pillar[5]arene cavity led to distinct pore conformations and stacking patterns. This work represents the first example of both the trans and C_{2h}-symmetric cis isomers of the cobalt-dioxolene-pyridine moiety being obtained through synthesis. Our findings highlight the potential to synthesize VT isomers and the critical role of host−guest interactions in modulating VT behavior, offering valuable insights into the design of multifunctional materials with controllable magnetic properties.

Valence tautomerism in pillar[5]arene-bridged *trans* and C_{2h}-*cis* isomers

INTRODUCTION

Multifunctional sensing and memory materials are essential for technological advancements, particularly when they can be seamlessly integrated into devices.[1−3] Valence tautomeric (VT) complexes, recognized for their molecule-based magnetic bistability, function as controllable and programmable molecular sensors or switches. This functionality arises from the reversible electron transfer between the metal center and the redox-active ligand, triggered by external stimuli such as temperature and pressure.[4−6] A universal strategy to modulate VT properties involves the introduction of guest molecules, which effectively influence these properties through noncovalent interactions.[7−9] Consequently, researchers are keen on developing higher-dimensional VT models that exploit their porous nature to accommodate various guest molecules, thereby enhancing the regulation of VT properties. To date, one-dimensional (1D) VT compounds, along with a limited number of two-dimensional (2D) and three-dimensional (3D) VT compounds, have been documented. Variations in VT properties are primarily attributed to different host−guest interactions.[10−13] However, predicting the crystal structure of molecular crystals before experimentation remains a significant challenge due to the absence of a mature construction method. This implies that manipulating host−guest interactions in these systems often relies more on serendipitous discovery than on deliberate molecular design.

Macrocyclic structures, such as crown ethers, cyclodextrins, calixarenes (CAs), cucurbiturils (CBs), and pillararenes, possess unique host−guest properties and are widely utilized in sensing, guest recognition, separation technologies, and supramolecular polymer.[14−18] Layfield et al. speculated that the spin-crossover (SCO) behavior of iron(II) can be modulated by altering the size and diameter of nanohoops.[19] However, synthesizing and modifying nanohoops of varying sizes can be challenging and tedious. In this context, pillararenes, a distinct class of macrocyclic hosts, offer several advantages, including facile synthesis, highly modifiable rims, π-electron-rich cavities, and an adaptive/flexible pillar-like molecular structure responsive to guest interactions.[20] Some of these materials are classified as nonporous adaptive crystals, which are initially nonporous in their crystalline state but can transform into

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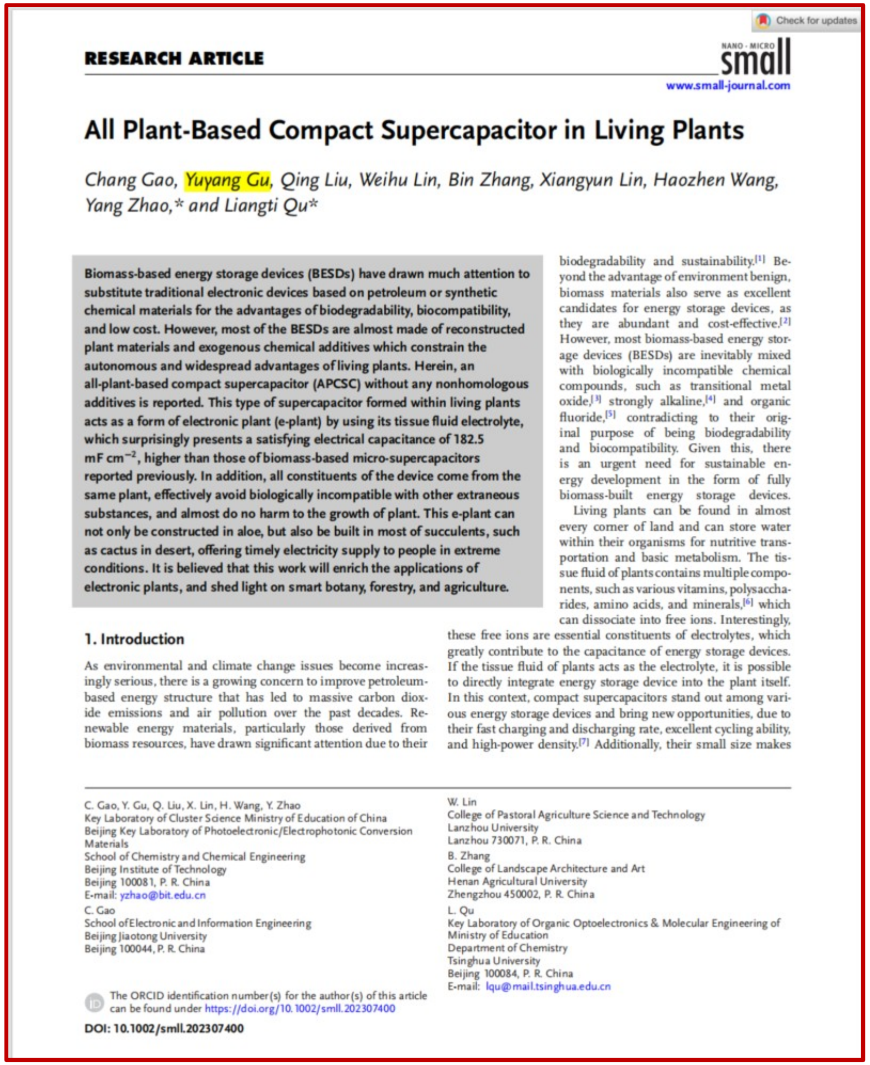

RESEARCH ARTICLE

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All Plant-Based Compact Supercapacitor in Living Plants

Chang Gao, Yuyang Gu, Qing Liu, Weihu Lin, Bin Zhang, Xiangyun Lin, Haozhen Wang, Yang Zhao, and Liangti Qu**

Biomass-based energy storage devices (BESDs) have drawn much attention to substitute traditional electronic devices based on petroleum or synthetic chemical materials for the advantages of biodegradability, biocompatibility, and low cost. However, most of the BESDs are almost made of reconstructed plant materials and exogenous chemical additives which constrain the autonomous and widespread advantages of living plants. Herein, an all-plant-based compact supercapacitor (APCSC) without any nonhomologous additives is reported. This type of supercapacitor formed within living plants acts as a form of electronic plant (e-plant) by using its tissue fluid electrolyte, which surprisingly presents a satisfying electrical capacitance of 182.5 mF cm^{-2}, higher than those of biomass-based micro-supercapacitors reported previously. In addition, all constituents of the device come from the same plant, effectively avoid biologically incompatible with other extraneous substances, and almost do no harm to the growth of plant. This e-plant can not only be constructed in aloe, but also be built in most of succulents, such as cactus in desert, offering timely electricity supply to people in extreme conditions. It is believed that this work will enrich the applications of electronic plants, and shed light on smart botany, forestry, and agriculture.

1. Introduction

As environmental and climate change issues become increasingly serious, there is a growing concern to improve petroleum-based energy structure that has led to massive carbon dioxide emissions and air pollution over the past decades. Renewable energy materials, particularly those derived from biomass resources, have drawn significant attention due to their biodegradability and sustainability.[1] Beyond the advantage of environment benign, biomass materials also serve as excellent candidates for energy storage devices, as they are abundant and cost-effective.[2] However, most biomass-based energy storage devices (BESDs) are inevitably mixed with biologically incompatible chemical compounds, such as transitional metal oxide,[3] strongly alkaline,[4] and organic fluoride,[5] contradicting to their original purpose of being biodegradability and biocompatibility. Given this, there is an urgent need for sustainable energy development in the form of fully biomass-built energy storage devices.

Living plants can be found in almost every corner of land and can store water within their organisms for nutritive transportation and basic metabolism. The tissue fluid of plants contains multiple components, such as various vitamins, polysaccharides, amino acids, and minerals,[6] which can dissociate into free ions. Interestingly, these free ions are essential constituents of electrolytes, which greatly contribute to the capacitance of energy storage devices. If the tissue fluid of plants acts as the electrolyte, it is possible to directly integrate energy storage device into the plant itself. In this context, compact supercapacitors stand out among various energy storage devices and bring new opportunities, due to their fast charging and discharging rate, excellent cycling ability, and high-power density.[7] Additionally, their small size makes

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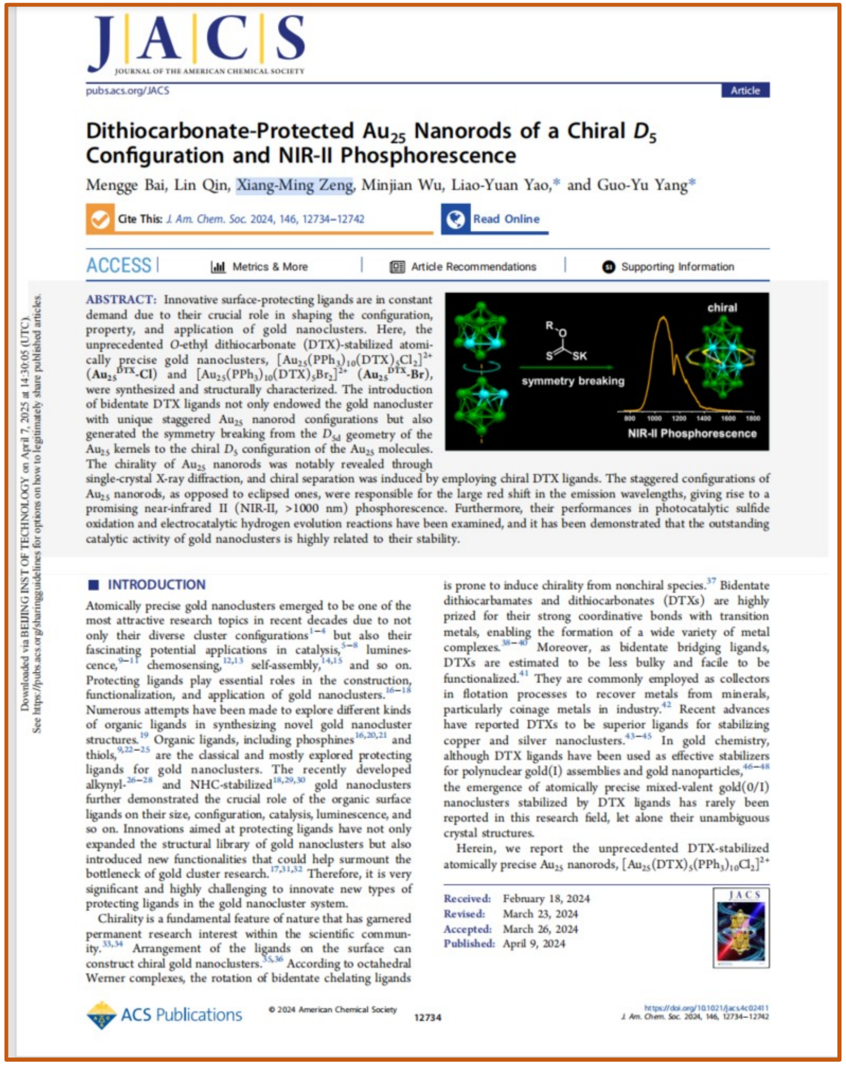

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Dithiocarbonate-Protected Au_{25} Nanorods of a Chiral D_5 Configuration and NIR-II Phosphorescence

Mengge Bai, Lin Qin, Xiang-Ming Zeng, Minjian Wu, Liao-Yuan Yao,* and Guo-Yu Yang*

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ABSTRACT: Innovative surface-protecting ligands are in constant demand due to their crucial role in shaping the configuration, property, and application of gold nanoclusters. Here, the unprecedented O-ethyl dithiocarbonate (DTX)-stabilized atomically precise gold nanoclusters, $[Au_{25}(PPh_3)_{10}(DTX)_5Cl_2]^{2+}$ (**Au_{25}^{DTX}-Cl**) and $[Au_{25}(PPh_3)_{10}(DTX)_5Br_2]^{2+}$ (**Au_{25}^{DTX}-Br**), were synthesized and structurally characterized. The introduction of bidentate DTX ligands not only endowed the gold nanocluster with unique staggered Au_{25} nanorod configurations but also generated the symmetry breaking from the D_{5d} geometry of the Au_{25} kernels to the chiral D_5 configuration of the Au_{25} molecules. The chirality of Au_{25} nanorods was notably revealed through single-crystal X-ray diffraction, and chiral separation was induced by employing chiral DTX ligands. The staggered configurations of Au_{25} nanorods, as opposed to eclipsed ones, were responsible for the large red shift in the emission wavelengths, giving rise to a promising near-infrared II (NIR-II, >1000 nm) phosphorescence. Furthermore, their performances in photocatalytic sulfide oxidation and electrocatalytic hydrogen evolution reactions have been examined, and it has been demonstrated that the outstanding catalytic activity of gold nanoclusters is highly related to their stability.

■ INTRODUCTION

Atomically precise gold nanoclusters emerged to be one of the most attractive research topics in recent decades due to not only their diverse cluster configurations[1−4] but also their fascinating potential applications in catalysis,[5−8] luminescence,[9−11] chemosensing,[12,13] self-assembly,[14,15] and so on. Protecting ligands play essential roles in the construction, functionalization, and application of gold nanoclusters.[16−18] Numerous attempts have been made to explore different kinds of organic ligands in synthesizing novel gold nanocluster structures.[19] Organic ligands, including phosphines[16,20,21] and thiols,[9,22−25] are the classical and mostly explored protecting ligands for gold nanoclusters. The recently developed alkynyl-[26−28] and NHC-stabilized[18,29,30] gold nanoclusters further demonstrated the crucial role of the organic surface ligands on their size, configuration, catalysis, luminescence, and so on. Innovations aimed at protecting ligands have not only expanded the structural library of gold nanoclusters but also introduced new functionalities that could help surmount the bottleneck of gold cluster research.[17,31,32] Therefore, it is very significant and highly challenging to innovate new types of protecting ligands in the gold nanocluster system.

Chirality is a fundamental feature of nature that has garnered permanent research interest within the scientific community.[33,34] Arrangement of the ligands on the surface can construct chiral gold nanoclusters.[35,36] According to octahedral Werner complexes, the rotation of bidentate chelating ligands is prone to induce chirality from nonchiral species.[37] Bidentate dithiocarbamates and dithiocarbonates (DTXs) are highly prized for their strong coordinative bonds with transition metals, enabling the formation of a wide variety of metal complexes.[38−40] Moreover, as bidentate bridging ligands, DTXs are estimated to be less bulky and facile to be functionalized.[41] They are commonly employed as collectors in flotation processes to recover metals from minerals, particularly coinage metals in industry.[42] Recent advances have reported DTXs to be superior ligands for stabilizing copper and silver nanoclusters.[43−45] In gold chemistry, although DTX ligands have been used as effective stabilizers for polynuclear gold(I) assemblies and gold nanoparticles,[46−48] the emergence of atomically precise mixed-valent gold(0/I) nanoclusters stabilized by DTX ligands has rarely been reported in this research field, let alone their unambiguous crystal structures.

Herein, we report the unprecedented DTX-stabilized atomically precise Au_{25} nanorods, $[Au_{25}(DTX)_5(PPh_3)_{10}Cl_2]^{2+}$

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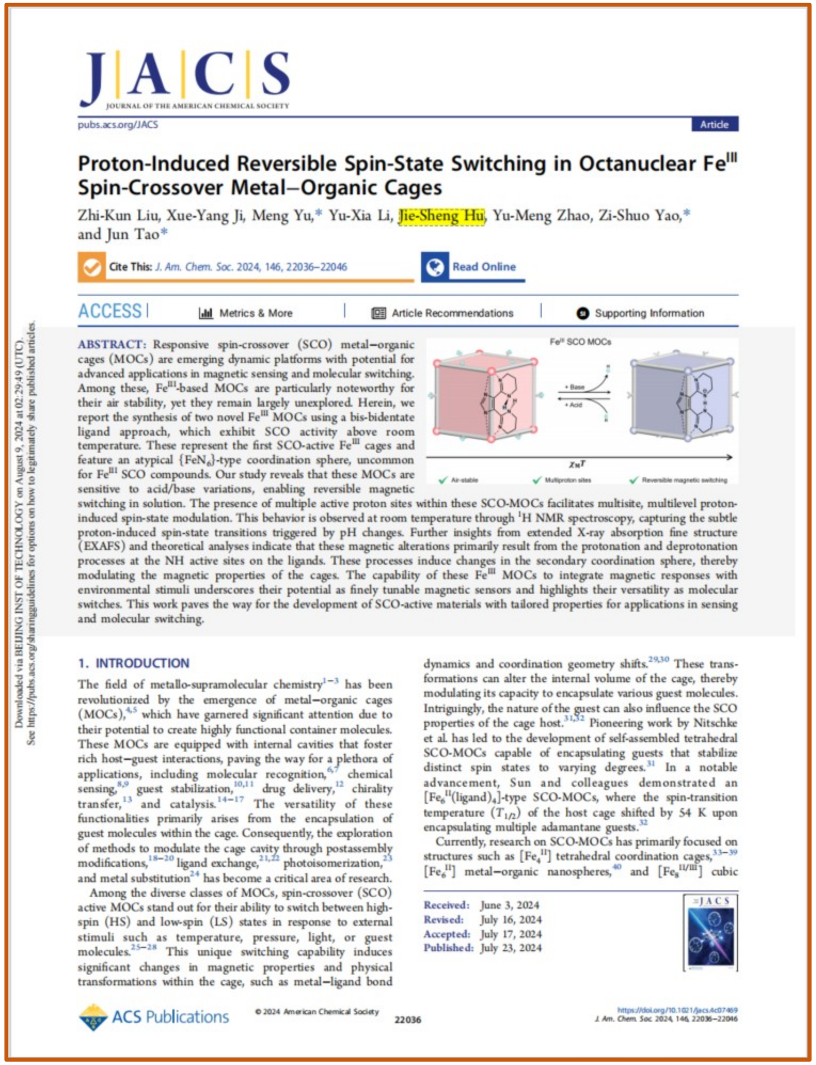

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Proton-Induced Reversible Spin-State Switching in Octanuclear Fe^{III} Spin-Crossover Metal−Organic Cages

Zhi-Kun Liu, Xue-Yang Ji, Meng Yu,* Yu-Xia Li, Jie-Sheng Hu, Yu-Meng Zhao, Zi-Shuo Yao,* and Jun Tao*

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ABSTRACT: Responsive spin-crossover (SCO) metal−organic cages (MOCs) are emerging dynamic platforms with potential for advanced applications in magnetic sensing and molecular switching. Among these, Fe^{III}-based MOCs are particularly noteworthy for their air stability, yet they remain largely unexplored. Herein, we report the synthesis of two novel Fe^{III} MOCs using a bis-bidentate ligand approach, which exhibit SCO activity above room temperature. These represent the first SCO-active Fe^{III} cages and feature an atypical $\{FeN_6\}$-type coordination sphere, uncommon for Fe^{III} SCO compounds. Our study reveals that these MOCs are sensitive to acid/base variations, enabling reversible magnetic switching in solution. The presence of multiple active proton sites within these SCO-MOCs facilitates multisite, multilevel proton-induced spin-state modulation. This behavior is observed at room temperature through ^1H NMR spectroscopy, capturing the subtle proton-induced spin-state transitions triggered by pH changes. Further insights from extended X-ray absorption fine structure (EXAFS) and theoretical analyses indicate that these magnetic alterations primarily result from the protonation and deprotonation processes at the NH active sites on the ligands. These processes induce changes in the secondary coordination sphere, thereby modulating the magnetic properties of the cages. The capability of these Fe^{III} MOCs to integrate magnetic responses with environmental stimuli underscores their potential as finely tunable magnetic sensors and highlights their versatility as molecular switches. This work paves the way for the development of SCO-active materials with tailored properties for applications in sensing and molecular switching.

1. INTRODUCTION

The field of metallo-supramolecular chemistry[1−3] has been revolutionized by the emergence of metal−organic cages (MOCs),[4,5] which have garnered significant attention due to their potential to create highly functional container molecules. These MOCs are equipped with internal cavities that foster rich host−guest interactions, paving the way for a plethora of applications, including molecular recognition,[6,7] chemical sensing,[8,9] guest stabilization,[10,11] drug delivery,[12] chirality transfer,[13] and catalysis.[14−17] The versatility of these functionalities primarily arises from the encapsulation of guest molecules within the cage. Consequently, the exploration of methods to modulate the cage cavity through postassembly modifications,[18−20] ligand exchange,[21,22] photoisomerization,[23] and metal substitution[24] has become a critical area of research.

Among the diverse classes of MOCs, spin-crossover (SCO) active MOCs stand out for their ability to switch between high-spin (HS) and low-spin (LS) states in response to external stimuli such as temperature, pressure, light, or guest molecules.[25−28] This unique switching capability induces significant changes in magnetic properties and physical transformations within the cage, such as metal−ligand bond dynamics and coordination geometry shifts.[29,30] These transformations can alter the internal volume of the cage, thereby modulating its capacity to encapsulate various guest molecules. Intriguingly, the nature of the guest can also influence the SCO properties of the cage host.[31,32] Pioneering work by Nitschke et al. has led to the development of self-assembled tetrahedral SCO-MOCs capable of encapsulating guests that stabilize distinct spin states to varying degrees.[31] In a notable advancement, Sun and colleagues demonstrated an $[Fe_6^{II}(ligand)_4]$-type SCO-MOCs, where the spin-transition temperature ($T_{1/2}$) of the host cage shifted by 54 K upon encapsulating multiple adamantane guests.[32]

Currently, research on SCO-MOCs has primarily focused on structures such as $[Fe_4^{II}]$ tetrahedral coordination cages,[33−39] $[Fe_6^{II}]$ metal−organic nanospheres,[40] and $[Fe_8^{II/III}]$ cubic

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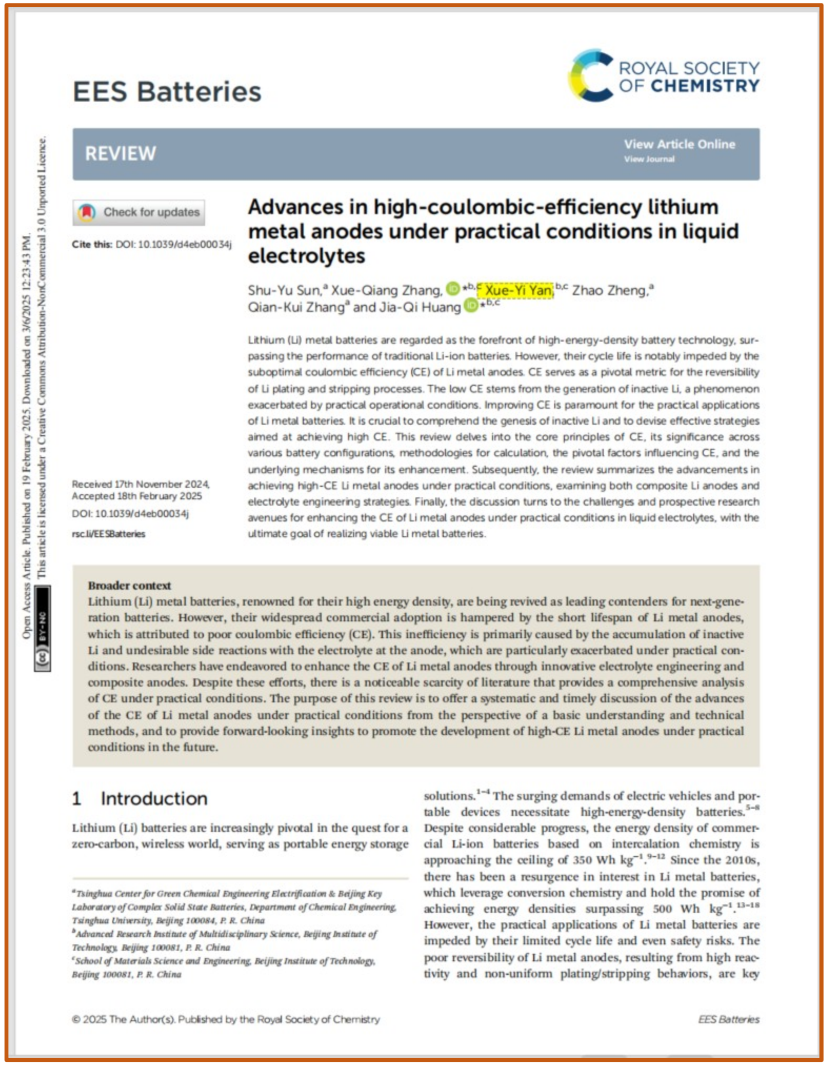

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REVIEW

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Advances in high-coulombic-efficiency lithium metal anodes under practical conditions in liquid electrolytes

Shu-Yu Sun,[a] Xue-Qiang Zhang, *[b,c] Xue-Yi Yan,[b,c] Zhao Zheng,[a] Qian-Kui Zhang[a] and Jia-Qi Huang *[b,c]

Lithium (Li) metal batteries are regarded as the forefront of high-energy-density battery technology, surpassing the performance of traditional Li-ion batteries. However, their cycle life is notably impeded by the suboptimal coulombic efficiency (CE) of Li metal anodes. CE serves as a pivotal metric for the reversibility of Li plating and stripping processes. The low CE stems from the generation of inactive Li, a phenomenon exacerbated by practical operational conditions. Improving CE is paramount for the practical applications of Li metal batteries. It is crucial to comprehend the genesis of inactive Li and to devise effective strategies aimed at achieving high CE. This review delves into the core principles of CE, its significance across various battery configurations, methodologies for calculation, the pivotal factors influencing CE, and the underlying mechanisms for its enhancement. Subsequently, the review summarizes the advancements in achieving high-CE Li metal anodes under practical conditions, examining both composite Li anodes and electrolyte engineering strategies. Finally, the discussion turns to the challenges and prospective research avenues for enhancing the CE of Li metal anodes under practical conditions in liquid electrolytes, with the ultimate goal of realizing viable Li metal batteries.

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Broader context

Lithium (Li) metal batteries, renowned for their high energy density, are being revived as leading contenders for next-generation batteries. However, their widespread commercial adoption is hampered by the short lifespan of Li metal anodes, which is attributed to poor coulombic efficiency (CE). This inefficiency is primarily caused by the accumulation of inactive Li and undesirable side reactions with the electrolyte at the anode, which are particularly exacerbated under practical conditions. Researchers have endeavored to enhance the CE of Li metal anodes through innovative electrolyte engineering and composite anodes. Despite these efforts, there is a noticeable scarcity of literature that provides a comprehensive analysis of CE under practical conditions. The purpose of this review is to offer a systematic and timely discussion of the advances of the CE of Li metal anodes under practical conditions from the perspective of a basic understanding and technical methods, and to provide forward-looking insights to promote the development of high-CE Li metal anodes under practical conditions in the future.

1 Introduction

Lithium (Li) batteries are increasingly pivotal in the quest for a zero-carbon, wireless world, serving as portable energy storage solutions.[1–4] The surging demands of electric vehicles and portable devices necessitate high-energy-density batteries.[5–8] Despite considerable progress, the energy density of commercial Li-ion batteries based on intercalation chemistry is approaching the ceiling of 350 Wh kg^{-1}.[9–12] Since the 2010s, there has been a resurgence in interest in Li metal batteries, which leverage conversion chemistry and hold the promise of achieving energy densities surpassing 500 Wh kg^{-1}.[13–18] However, the practical applications of Li metal batteries are impeded by their limited cycle life and even safety risks. The poor reversibility of Li metal anodes, resulting from high reactivity and non-uniform plating/stripping behaviors, are key

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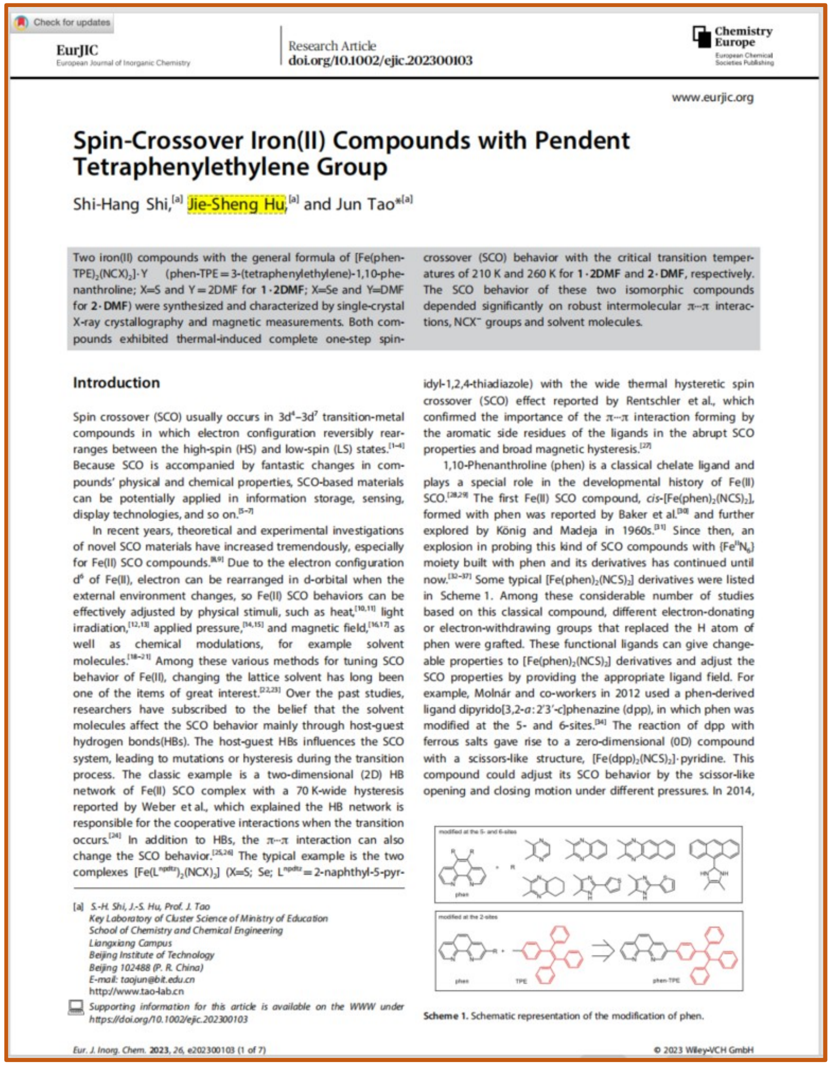

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Spin-Crossover Iron(II) Compounds with Pendent Tetraphenylethylene Group

Shi-Hang Shi,[a] Jie-Sheng Hu,[a] and Jun Tao*[a]

Two iron(II) compounds with the general formula of $[Fe(phen\text{-}TPE)_2(NCX)_2]\cdot Y$ (phen-TPE = 3-(tetraphenylethylene)-1,10-phenanthroline; X=S and Y = 2DMF for **1·2DMF**; X=Se and Y=DMF for **2·DMF**) were synthesized and characterized by single-crystal X-ray crystallography and magnetic measurements. Both compounds exhibited thermal-induced complete one-step spin-crossover (SCO) behavior with the critical transition temperatures of 210 K and 260 K for **1·2DMF** and **2·DMF**, respectively. The SCO behavior of these two isomorphic compounds depended significantly on robust intermolecular $\pi\cdots\pi$ interactions, NCX^- groups and solvent molecules.

Introduction

Spin crossover (SCO) usually occurs in $3d^4$–$3d^7$ transition-metal compounds in which electron configuration reversibly rearranges between the high-spin (HS) and low-spin (LS) states.[1–4] Because SCO is accompanied by fantastic changes in compounds' physical and chemical properties, SCO-based materials can be potentially applied in information storage, sensing, display technologies, and so on.[5–7]

In recent years, theoretical and experimental investigations of novel SCO materials have increased tremendously, especially for Fe(II) SCO compounds.[8,9] Due to the electron configuration d^6 of Fe(II), electron can be rearranged in d-orbital when the external environment changes, so Fe(II) SCO behaviors can be effectively adjusted by physical stimuli, such as heat,[10,11] light irradiation,[12,13] applied pressure,[14,15] and magnetic field,[16,17] as well as chemical modulations, for example solvent molecules.[18–21] Among these various methods for tuning SCO behavior of Fe(II), changing the lattice solvent has long been one of the items of great interest.[22,23] Over the past studies, researchers have subscribed to the belief that the solvent molecules affect the SCO behavior mainly through host-guest hydrogen bonds(HBs). The host-guest HBs influences the SCO system, leading to mutations or hysteresis during the transition process. The classic example is a two-dimensional (2D) HB network of Fe(II) SCO complex with a 70 K-wide hysteresis reported by Weber et al., which explained the HB network is responsible for the cooperative interactions when the transition occurs.[24] In addition to HBs, the $\pi\cdots\pi$ interaction can also change the SCO behavior.[25,26] The typical example is the two complexes $[Fe(L^{npdtz})_2(NCX)_2]$ (X=S; Se; L^{npdtz} = 2-naphthyl-5-pyridyl-1,2,4-thiadiazole) with the wide thermal hysteretic spin crossover (SCO) effect reported by Rentschler et al., which confirmed the importance of the $\pi\cdots\pi$ interaction forming by the aromatic side residues of the ligands in the abrupt SCO properties and broad magnetic hysteresis.[27]

1,10-Phenanthroline (phen) is a classical chelate ligand and plays a special role in the developmental history of Fe(II) SCO.[28,29] The first Fe(II) SCO compound, *cis*-$[Fe(phen)_2(NCS)_2]$, formed with phen was reported by Baker et al.[30] and further explored by König and Madeja in 1960s.[31] Since then, an explosion in probing this kind of SCO compounds with $\{Fe^{II}N_6\}$ moiety built with phen and its derivatives has continued until now.[32–37] Some typical $[Fe(phen)_2(NCS)_2]$ derivatives were listed in Scheme 1. Among these considerable number of studies based on this classical compound, different electron-donating or electron-withdrawing groups that replaced the H atom of phen were grafted. These functional ligands can give changeable properties to $[Fe(phen)_2(NCS)_2]$ derivatives and adjust the SCO properties by providing the appropriate ligand field. For example, Molnár and co-workers in 2012 used a phen-derived ligand dipyrido[3,2-*a*:2′3′-*c*]phenazine (dpp), in which phen was modified at the 5- and 6-sites.[34] The reaction of dpp with ferrous salts gave rise to a zero-dimensional (0D) compound with a scissors-like structure, $[Fe(dpp)_2(NCS)_2]\cdot$pyridine. This compound could adjust its SCO behavior by the scissor-like opening and closing motion under different pressures. In 2014,

Scheme 1. Schematic representation of the modification of phen.

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New flexible 3D POSS-based COF simultaneously strengthens and toughens epoxy resin (EP) at extreme temperatures

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ABSTRACT

This study introduces a novel approach by designing a flexible three-dimensional Covalent Organic Framework (COFs), specifically NH_2-POSS-COF, which serves as a uniform cross-linking site within the EP system. This framework provides substantial internal free volume and mitigates stress concentrations by enabling effective energy dissipation during mechanical loading. The research demonstrates that the integration of NH_2-POSS-COF significantly enhances the fracture toughness and tensile strength of EP at both RT and cryogenic. These findings open new avenues for optimizing EP performance in low-temperature applications, contributing to the development of high-performance composite materials for aerospace missions.

1. Introduction

As the global aerospace industry continues to advance and evolve, Carbon Fiber Reinforced Epoxy (CFRP) has originated as a pivotal material in spacecraft engineering, prized for its lightweight attributes, considerable specific strength, and substantial modulus of elasticity [1–3]. Nevertheless, the extreme thermal conditions prevalent in space, where temperatures can plummet to −200 °C or below, exacerbate the disparity in the thermal expansion coefficient between the epoxy matrix and the carbon fibers. This disparity engenders significant residual thermal stresses [4–6]. Additionally, at such cryogenic temperatures, the molecular chains within the epoxy matrix tend to become immobilized, culminating in a more brittle, cross-linked network structure [7,8]. These factors critically impede the operational lifespan of CFRP materials and constitute a potential hazard to the safety and reliability of spacecraft missions.

Currently, in the field of toughening EP at cryogenics, commonly utilized materials include rubber or polyurethane elastomers [9,10] thermoplastic polymers [11,12], hyperbranched polymers [13,14], and nanoparticles [15–17]. These materials play a substantial role in enhancing the low-temperature properties of EP. However, several key technical challenges limit the effectiveness and application of these methods. Firstly, elastomers and thermoplastic polymers face compatibility issues during integration with EP, which adversely affects the uniformity and performance of the materials [18]. Secondly, the dispersion of nanoparticles within the epoxy matrix and their thermal matching with the resin pose another significant challenge [19]. Additionally, although hyperbranched polymers hold potential, their practical application is limited by process feasibility [20].

More importantly, existing toughening modifications have not fundamentally optimized the cross-linked network structure of EP. It's well-known that the primary failure mode of EP at cryogenics is due to the freezing and breaking of molecular chains under stress [7,21]. If the structure of the cross-linked network could be optimized by strategically controlling the distribution of free volume, it would be possible to uniformly dissipate fracture energy across the network under stress, thereby avoiding areas where molecular chains are disproportionately stressed [22]. This approach is expected to significantly enhance the mechanical performance and durability of EP at cryogenics. Therefore, developing new toughening techniques, particularly those that focus on optimizing the cross-linked network, is crucial for improving the performance of EP in cryogenics applications.

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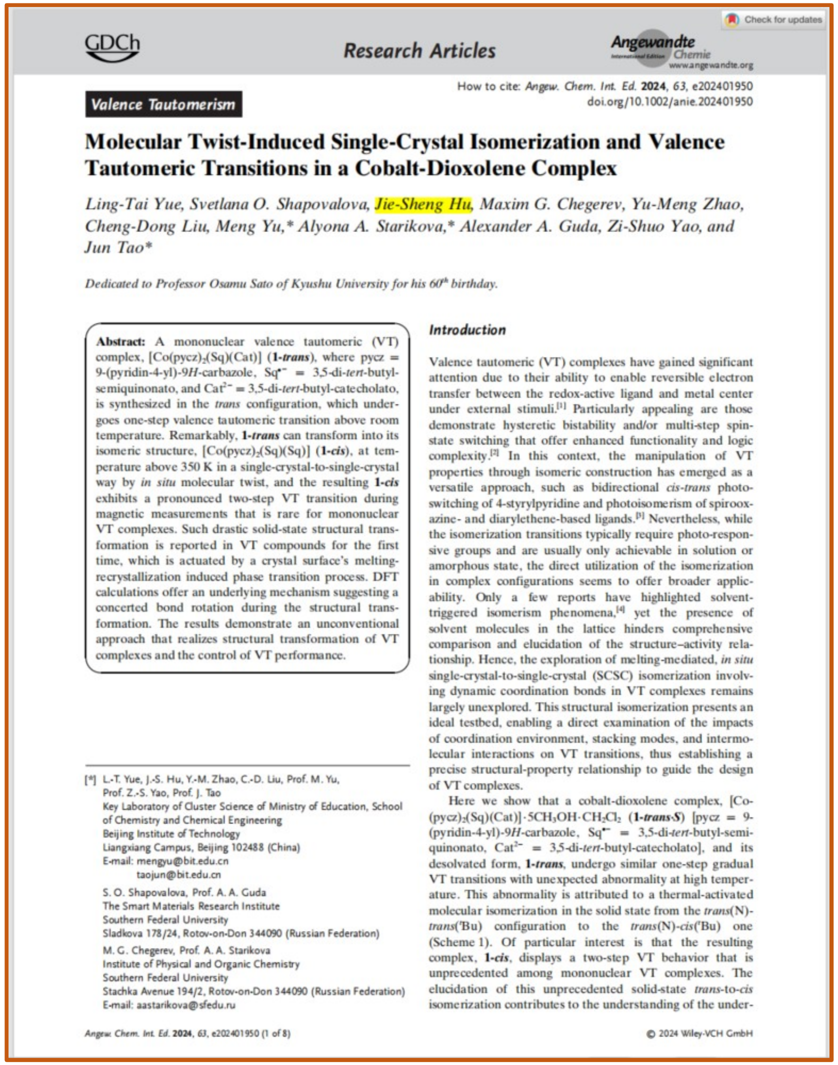

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Valence Tautomerism

Molecular Twist-Induced Single-Crystal Isomerization and Valence Tautomeric Transitions in a Cobalt-Dioxolene Complex

Ling-Tai Yue, Svetlana O. Shapovalova, Jie-Sheng Hu, Maxim G. Chegerev, Yu-Meng Zhao, Cheng-Dong Liu, Meng Yu, Alyona A. Starikova,* Alexander A. Guda, Zi-Shuo Yao, and Jun Tao**

Dedicated to Professor Osamu Sato of Kyushu University for his 60th birthday.

Abstract: A mononuclear valence tautomeric (VT) complex, $[Co(pycz)_2(Sq)(Cat)]$ (**1-*trans***), where pycz = 9-(pyridin-4-yl)-9*H*-carbazole, $Sq^{\bullet -}$ = 3,5-di-*tert*-butyl-semiquinonato, and Cat^{2-} = 3,5-di-*tert*-butyl-catecholato, is synthesized in the *trans* configuration, which undergoes one-step valence tautomeric transition above room temperature. Remarkably, **1-*trans*** can transform into its isomeric structure, $[Co(pycz)_2(Sq)(Sq)]$ (**1-*cis***), at temperature above 350 K in a single-crystal-to-single-crystal way by *in situ* molecular twist, and the resulting **1-*cis*** exhibits a pronounced two-step VT transition during magnetic measurements that is rare for mononuclear VT complexes. Such drastic solid-state structural transformation is reported in VT compounds for the first time, which is actuated by a crystal surface's melting-recrystallization induced phase transition process. DFT calculations offer an underlying mechanism suggesting a concerted bond rotation during the structural transformation. The results demonstrate an unconventional approach that realizes structural transformation of VT complexes and the control of VT performance.

Introduction

Valence tautomeric (VT) complexes have gained significant attention due to their ability to enable reversible electron transfer between the redox-active ligand and metal center under external stimuli.[1] Particularly appealing are those demonstrate hysteretic bistability and/or multi-step spin-state switching that offer enhanced functionality and logic complexity.[2] In this context, the manipulation of VT properties through isomeric construction has emerged as a versatile approach, such as bidirectional *cis-trans* photo-switching of 4-styrylpyridine and photoisomerism of spirooxazine- and diarylethene-based ligands.[3] Nevertheless, while the isomerization transitions typically require photo-responsive groups and are usually only achievable in solution or amorphous state, the direct utilization of the isomerization in complex configurations seems to offer broader applicability. Only a few reports have highlighted solvent-triggered isomerism phenomena,[4] yet the presence of solvent molecules in the lattice hinders comprehensive comparison and elucidation of the structure–activity relationship. Hence, the exploration of melting-mediated, *in situ* single-crystal-to-single-crystal (SCSC) isomerization involving dynamic coordination bonds in VT complexes remains largely unexplored. This structural isomerization presents an ideal testbed, enabling a direct examination of the impacts of coordination environment, stacking modes, and intermolecular interactions on VT transitions, thus establishing a precise structural-property relationship to guide the design of VT complexes.

Here we show that a cobalt-dioxolene complex, $[Co(pycz)_2(Sq)(Cat)]\cdot 5CH_3OH\cdot CH_2Cl_2$ (**1-*trans*·*S***) [pycz = 9-(pyridin-4-yl)-9*H*-carbazole, $Sq^{\bullet -}$ = 3,5-di-*tert*-butyl-semiquinonato, Cat^{2-} = 3,5-di-*tert*-butyl-catecholato], and its desolvated form, **1-*trans***, undergo similar one-step gradual VT transitions with unexpected abnormality at high temperature. This abnormality is attributed to a thermal-activated molecular isomerization in the solid state from the *trans*(N)-*trans*(^{t}Bu) configuration to the *trans*(N)-*cis*(^{t}Bu) one (Scheme 1). Of particular interest is that the resulting complex, **1-*cis***, displays a two-step VT behavior that is unprecedented among mononuclear VT complexes. The elucidation of this unprecedented solid-state *trans*-to-*cis* isomerization contributes to the understanding of the under-

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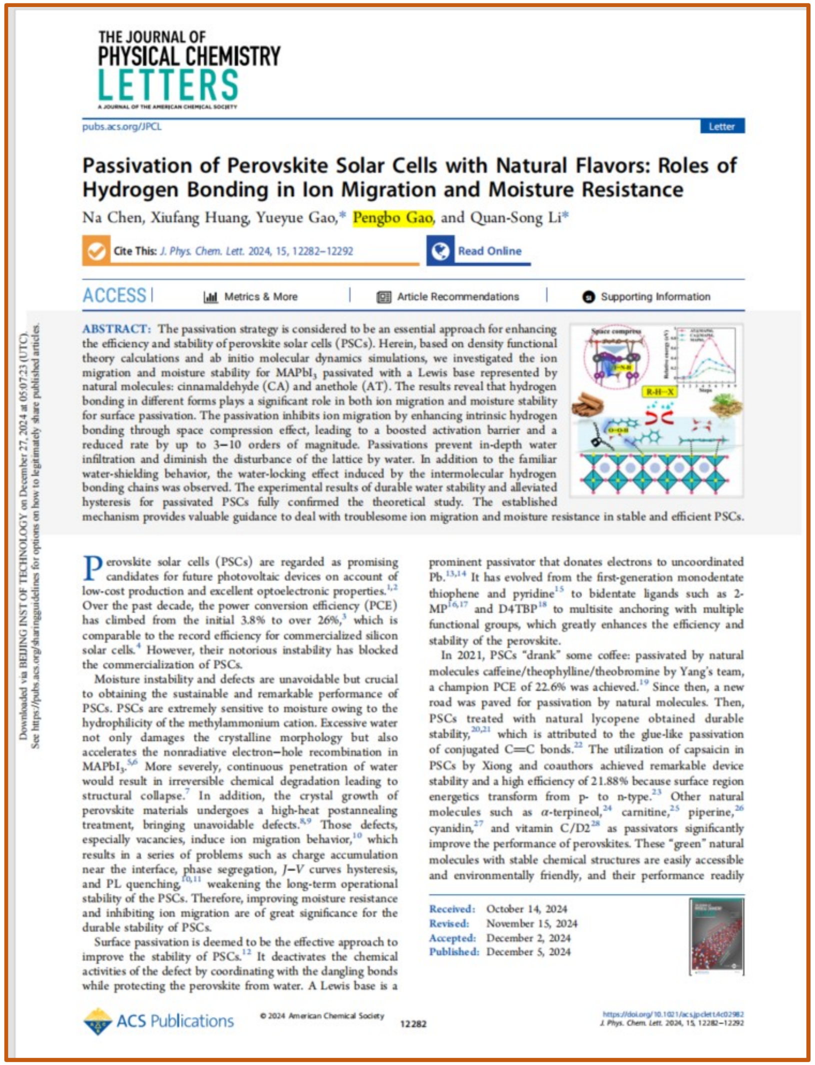

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Passivation of Perovskite Solar Cells with Natural Flavors: Roles of Hydrogen Bonding in Ion Migration and Moisture Resistance

Na Chen, Xiufang Huang, Yueyue Gao,* Pengbo Gao, and Quan-Song Li*

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ABSTRACT: The passivation strategy is considered to be an essential approach for enhancing the efficiency and stability of perovskite solar cells (PSCs). Herein, based on density functional theory calculations and ab initio molecular dynamics simulations, we investigated the ion migration and moisture stability for $MAPbI_3$ passivated with a Lewis base represented by natural molecules: cinnamaldehyde (CA) and anethole (AT). The results reveal that hydrogen bonding in different forms plays a significant role in both ion migration and moisture stability for surface passivation. The passivation inhibits ion migration by enhancing intrinsic hydrogen bonding through space compression effect, leading to a boosted activation barrier and a reduced rate by up to 3−10 orders of magnitude. Passivations prevent in-depth water infiltration and diminish the disturbance of the lattice by water. In addition to the familiar water-shielding behavior, the water-locking effect induced by the intermolecular hydrogen bonding chains was observed. The experimental results of durable water stability and alleviated hysteresis for passivated PSCs fully confirmed the theoretical study. The established mechanism provides valuable guidance to deal with troublesome ion migration and moisture resistance in stable and efficient PSCs.

Perovskite solar cells (PSCs) are regarded as promising candidates for future photovoltaic devices on account of low-cost production and excellent optoelectronic properties.[1,2] Over the past decade, the power conversion efficiency (PCE) has climbed from the initial 3.8% to over 26%,[3] which is comparable to the record efficiency for commercialized silicon solar cells.[4] However, their notorious instability has blocked the commercialization of PSCs.

Moisture instability and defects are unavoidable but crucial to obtaining the sustainable and remarkable performance of PSCs. PSCs are extremely sensitive to moisture owing to the hydrophilicity of the methylammonium cation. Excessive water not only damages the crystalline morphology but also accelerates the nonradiative electron−hole recombination in $MAPbI_3$.[5,6] More severely, continuous penetration of water would result in irreversible chemical degradation leading to structural collapse.[7] In addition, the crystal growth of perovskite materials undergoes a high-heat postannealing treatment, bringing unavoidable defects.[8,9] Those defects, especially vacancies, induce ion migration behavior,[10] which results in a series of problems such as charge accumulation near the interface, phase segregation, $J-V$ curves hysteresis, and PL quenching,[10,11] weakening the long-term operational stability of the PSCs. Therefore, improving moisture resistance and inhibiting ion migration are of great significance for the durable stability of PSCs.

Surface passivation is deemed to be the effective approach to improve the stability of PSCs.[12] It deactivates the chemical activities of the defect by coordinating with the dangling bonds while protecting the perovskite from water. A Lewis base is a prominent passivator that donates electrons to uncoordinated Pb.[13,14] It has evolved from the first-generation monodentate thiophene and pyridine[15] to bidentate ligands such as 2-MP[16,17] and D4TBP[18] to multisite anchoring with multiple functional groups, which greatly enhances the efficiency and stability of the perovskite.

In 2021, PSCs "drank" some coffee: passivated by natural molecules caffeine/theophylline/theobromine by Yang's team, a champion PCE of 22.6% was achieved.[19] Since then, a new road was paved for passivation by natural molecules. Then, PSCs treated with natural lycopene obtained durable stability,[20,21] which is attributed to the glue-like passivation of conjugated C=C bonds.[22] The utilization of capsaicin in PSCs by Xiong and coauthors achieved remarkable device stability and a high efficiency of 21.88% because surface region energetics transform from p- to n-type.[23] Other natural molecules such as α-terpineol,[24] carnitine,[25] piperine,[26] cyanidin,[27] and vitamin C/D2[28] as passivators significantly improve the performance of perovskites. These "green" natural molecules with stable chemical structures are easily accessible and environmentally friendly, and their performance readily

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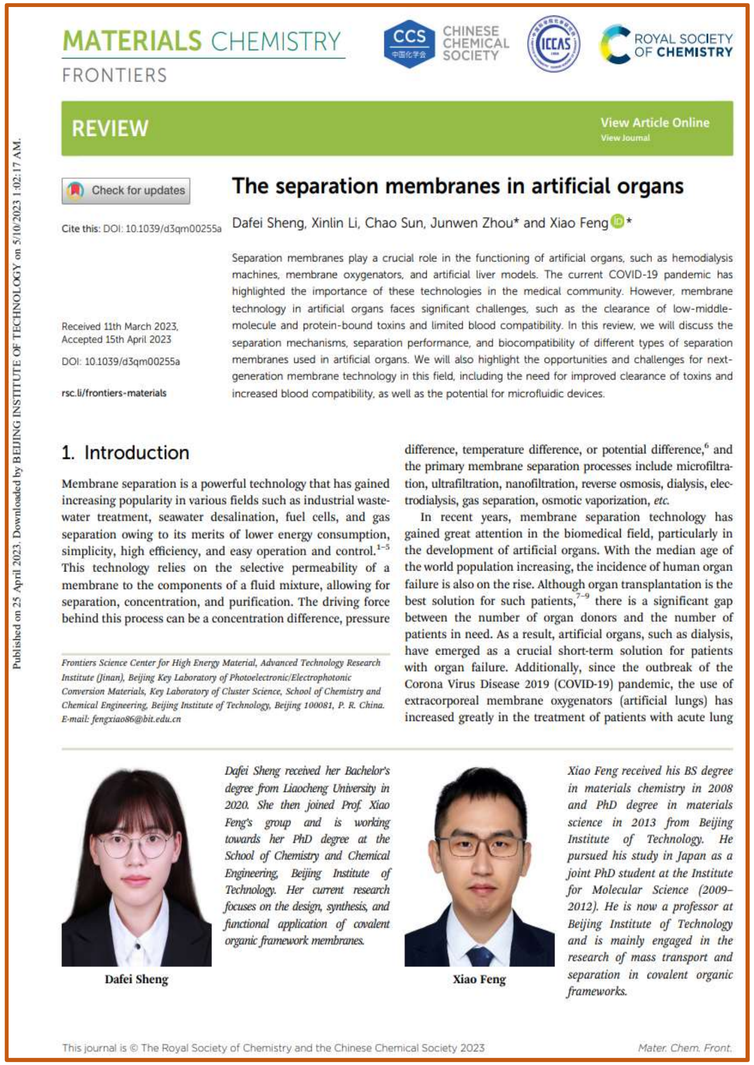

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The separation membranes in artificial organs

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Separation membranes play a crucial role in the functioning of artificial organs, such as hemodialysis machines, membrane oxygenators, and artificial liver models. The current COVID-19 pandemic has highlighted the importance of these technologies in the medical community. However, membrane technology in artificial organs faces significant challenges, such as the clearance of low-middle-molecule and protein-bound toxins and limited blood compatibility. In this review, we will discuss the separation mechanisms, separation performance, and biocompatibility of different types of separation membranes used in artificial organs. We will also highlight the opportunities and challenges for next-generation membrane technology in this field, including the need for improved clearance of toxins and increased blood compatibility, as well as the potential for microfluidic devices.

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1. Introduction

Membrane separation is a powerful technology that has gained increasing popularity in various fields such as industrial wastewater treatment, seawater desalination, fuel cells, and gas separation owing to its merits of lower energy consumption, simplicity, high efficiency, and easy operation and control.[1–5] This technology relies on the selective permeability of a membrane to the components of a fluid mixture, allowing for separation, concentration, and purification. The driving force behind this process can be a concentration difference, pressure difference, temperature difference, or potential difference,[6] and the primary membrane separation processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, dialysis, electrodialysis, gas separation, osmotic vaporization, *etc.*

In recent years, membrane separation technology has gained great attention in the biomedical field, particularly in the development of artificial organs. With the median age of the world population increasing, the incidence of human organ failure is also on the rise. Although organ transplantation is the best solution for such patients,[7–9] there is a significant gap between the number of organ donors and the number of patients in need. As a result, artificial organs, such as dialysis, have emerged as a crucial short-term solution for patients with organ failure. Additionally, since the outbreak of the Corona Virus Disease 2019 (COVID-19) pandemic, the use of extracorporeal membrane oxygenators (artificial lungs) has increased greatly in the treatment of patients with acute lung

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