Strength in Weakness: The Role of Weak Interactions in Shaping Optical and Electrical Properties of Thiazole-Based Molecular and Coordination Materials

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The performance of functional molecular materials depends not only on molecular composition but also on the organization of molecules in the solid state. While covalent and coordination bonds define molecular identity, weak intermolecular interactions (including hydrogen bonding, π–π stacking, chalcogen bonding, metallophilic contacts, halogen interactions, and weak coordination modes) govern crystal packing, electronic coupling, excited-state dynamics, and charge transport. Understanding these interactions is therefore essential for the rational design of semiconductors, luminescent materials, and memristive devices.

This work compares three closely related classes of thiazole-based materials: (i) organic thiazolothiazole (TzTz) derivatives [1], (ii) Cu(I)-cyanothiazole coordination polymers [2], and (iii) Ag(I)-cyanothiazole [3] coordination networks. Although these systems differ in composition and dimensionality, they reveal a common principle: weak interactions are key structure-directing factors that determine optical response, electronic structure, and electrical switching behavior.

The first family comprises symmetrically substituted thiazolothiazoles containing a planar electron-deficient TzTz core. Minor changes in substituent type lead to profound differences in crystal packing, producing herringbone, parallel, or grid-like arrangements despite nearly identical molecular geometries. These architectures arise from competing π–π stacking, hydrogen bonding, chalcogen-chalcogen contacts, chalcogen–pnictogen interactions, and halogen-mediated interactions. Density functional theory calculations show that intermolecular orbital overlap depends strongly on packing, resulting in significant differences in electronic coupling and predicted charge-transfer rates. These structural variations are directly reflected in the optical properties. The TzTz derivatives display broad absorption and emission bands, large solid-state Stokes shifts approaching 1 eV, and photophysical behavior that is highly sensitive to crystal packing. Time-resolved fluorescence measurements demonstrate that both radiative and non-radiative relaxation pathways are controlled by the local supramolecular environment. Several derivatives also exhibit reproducible memristive behavior. Charge transport proceeds predominantly through hopping between localized states, and its efficiency is governed by intermolecular coupling established through π-stacking and short heteroatom contacts. Favorable packing arrangements improve conductivity modulation, endurance, and synaptic-like potentiation/depression characteristics, highlighting the potential of these materials for neuromorphic electronics.

The second class consists of Cu(I)-cyanothiazole coordination polymers obtained from three positional isomers of cyanothiazole. Relocation of a single nitrile group induces substantial structural reorganization. Whereas the 2- and 4-cyanothiazole ligands form Cu_2I_2 cluster-based frameworks connected through nitrile bridges, 5-cyanothiazole generates one-dimensional CuI ribbon structures coordinated mainly through the thiazole nitrogen atom. In all cases, the architectures are stabilized by π–π interactions, C–H···I hydrogen bonds, S···I contacts, and chalcogen–pnictogen interactions. These coordination polymers behave as luminescent semiconductors with band gaps of approximately 2.5–3.1 eV. Their electronic structures arise from hybrid CuI- and ligand-derived states, while supramolecular organization controls orbital overlap, luminescence efficiency, and electrical transport. All compounds exhibit memristive behavior, although the switching characteristics depend on crystal architecture. The 5-cyanothiazole derivative shows gradual analog switching suitable for neuromorphic applications, whereas the 2- and 4-cyanothiazole analogues display more abrupt transitions between conductive states. These results demonstrate that weak interactions regulate electrical performance by controlling local electronic coupling and trap-state distribution.

The Ag(I)-cyanothiazole family provides the clearest illustration of the functional importance of weak interactions. Competition between coordination bonding and secondary intermolecular forces generates structures ranging from discrete molecular complexes to one-, two-, and three-dimensional coordination polymers. Small structural modifications, such as changing the nitrile position or replacing nitrate with nitrite, produce dramatic differences in crystal architecture and physical properties. The resulting frameworks are stabilized by hydrogen bonding, π–π stacking, Ag···S contacts, chalcogen bonding, chalcogen–pnictogen interactions, and weak cation–anion contacts, while vibrational spectroscopy reveals that nitrile coordination exists along a continuum rather than as a simple coordinated/non-coordinated state. Electronic-structure calculations identify all Ag(I) complexes as semiconductors with band gaps between approximately 1.7 and 2.9 eV. Charge transport is dominated by localized electronic states and hopping mechanisms, making weak interactions crucial for carrier localization, trap formation, and charge redistribution. The observed resistive switching is consistent with a coupled ionic-electronic mechanism involving trapped charges and field-induced rearrangements of the flexible Ag(I) coordination environment. Among the investigated compounds, the 4CNTz-$AgNO_3$ coordination polymer exhibits the best combination of structural stability, electronic tunability, retention, reproducibility, and synaptic performance, demonstrating the benefits of an optimized network of weak interactions.

Comparison of all three material families reveals several general trends. Small molecular modifications produce disproportionately large changes in crystal packing because weak interactions respond sensitively to molecular topology. Supramolecular organization controls orbital overlap and therefore governs charge transport, excited-state relaxation, and luminescence. The best-performing materials rely on the cooperative action of multiple weak interactions rather than on a single dominant structural motif. Across all systems, memristive behavior is closely associated with localized electronic states generated and stabilized by weakly coupled molecular or coordination networks. Thus, weak interactions are not merely secondary crystallographic features but active functional elements that determine the optical and electrical properties of thiazole-based molecular and coordination materials. By tailoring π-stacking geometry, hydrogen-bond networks, chalcogen bonding, metallophilic contacts, and weak coordination modes, it is possible to tune band gaps, luminescence efficiency, charge transport, electrical hysteresis, retention, and synaptic plasticity without extensive synthetic modification. Strong bonds define the structural building blocks, whereas weak interactions determine how these building blocks communicate, providing a versatile strategy for the rational design of next-generation optoelectronic, sensing, and neuromorphic materials.

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