

RESEARCH ARTICLE

Synthetic Control of Structure and Magnetism in Low-Dimensional Organic Copper(II) Chloride Hybrids

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ABSTRACT

Low-dimensional (LD) organic metal halide hybrids (OMHHs) have attracted widespread attention owing to their exceptional structural versatility and emergent photophysical and spin-dependent properties. While hundreds of LD OMHHs have been reported to date, systematic investigations into how organic cations influence structural dimensionality and magnetic behavior remain limited. Here, we report a steric-engineering strategy to control structural dimensionality and magnetism in LD OMHHs. By systematically tuning methyl substitution in 1,3-propanediamine (PDA), we achieve a structural progression from two-dimensional (2D) Dion-Jacobson (DJ) and Ruddlesden-Popper (RP) phases to a mixed one-dimensional/zero-dimensional (1D/0D) structure, and ultimately isolated 0D structures in a series of organic copper(II) chloride hybrids. This structural evolution modulates magnetic exchange pathways, giving rise to coexisting ferromagnetic (FM) and antiferromagnetic (AFM) interactions in 2D OMHHs, dual AFM transitions in the mixed-dimensional (MD) system, and paramagnetic (PM) behavior in 0D compounds. Density functional theory (DFT) calculations reveal spin configurations consistent with experimentally observed magnetic behavior. This work presents a unique approach to precisely controlling the dimensionality and magnetism of OMHHs, paving the way for the rational design of ionically bonded organic–inorganic hybrid materials for spintronic applications.

1 | Introduction

Low-dimensional (LD) organic metal halide hybrids (OMHHs) are a versatile class of ionically bonded organic–inorganic hybrid materials composed of organic cations and metal halide anions, offering exceptional tunability in both structure and properties. A defining feature of OMHHs is their ability to adopt diverse structural dimensionalities, which can be modulated through the choice of organic cations that act as structure-directing agents, governing the connectivity and spatial extension of metal halide polyhedra [1]. In contrast to conventional three-dimensional (3D) metal halide perovskites, where predictive guidelines such as the Goldschmidt tolerance factor [2] enable

rational structural design, no general framework currently exists for directing dimensionality in LD OMHHs through organic cation selection [3]. Consequently, despite the extensive library of reported LD OMHHs spanning two-dimensional (2D) [4, 5], one-dimensional (1D) [6–8], and zero-dimensional (0D) structures [9–11], their discovery has largely relied on empirical approaches, and a fundamental understanding of how organic cations dictate structural dimensionality remains limited. Establishing such insight is critical as the potential of LD OMHHs for emerging technologies continues to expand, given that their properties are strongly governed by dimensionality. For instance, reducing dimensionality enhances quantum confinement and structural distortion, often leading to broadband emissions with large

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Stokes shifts [10], but also suppresses charge transport due to increased isolation of the inorganic framework. While such structure-property relationships have been extensively explored in optoelectronic contexts, their implications for magnetic behavior remain comparatively underdeveloped. Addressing this gap is particularly important in the context of emerging spintronic technologies, where establishing a clear structure-magnetism relationship in LD OMHHs could open up exciting avenues for designing next-generation magnetic materials with tailored functionalities.

Magnetic properties in LD OMHHs arise from exchange interactions between paramagnetic (PM) metal centers, which are highly sensitive to structural dimensionality, connectivity, and local coordination environments. Early studies, dating back to the 1960s [12], primarily focused on 2D hybrids incorporating transition metal ions such as Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Cu^{2+} , where layered structures enable tunable magnetic anisotropy and a range of magnetic ground states, including ferromagnetic (FM) [13, 14], antiferromagnetic (AFM) [15, 16], co-existing FM/AFM [17–20], and PM behaviors [21]. Canted antiferromagnetism with significant anisotropy between the in-plane and out-of-plane directions has also been reported in such structures [22]. More recently, increasing attention has been directed toward 1D and 0D analogs, where reduced dimensionality and enhanced quantum confinement can give rise to distinct magnetic phenomena. We previously reported AFM ordering in a 1D organic copper(II) chloride hybrid, $(\text{C}_8\text{H}_{22}\text{N}_2)\text{Cu}_2\text{Cl}_6$, with a Néel temperature of 24 K [7]. Nevertheless, only a small number of Mn^{2+} , Co^{2+} , and Cu^{2+} based 1D and 0D OMHHs have been systematically investigated to date [23–25], highlighting the need for broader exploration. The strong potential of LD OMHHs for studying magnetism in low dimensions stems from the exceptional tunability of structural parameters that govern magnetic exchange interactions, including metal-halide-metal bond angles, bond lengths, coordination geometries, interatomic distances, and connectivity of paramagnetic centers. Depending on the metal ion and synthetic conditions, the inorganic metal halide polyhedra can adopt diverse coordination environments, such as octahedral [9], square-pyramidal [9], tetrahedral [25], see-saw [10], and square-planar configurations [26], and assemble into architectures ranging from layered sheets and corrugated structures [27] in 2D hybrids to chains [28], nanoribbons [29], and nanotubes in 1D hybrids [30], and isolated mononuclear species or clusters in 0D hybrids [31, 32]. Mixed-dimensional (MD) hybrids that contain both metal halide chains and individual polyhedra within a single structure are also possible. This rich structural variability, combined with the sensitivity of magnetic interactions to local geometry, makes LD OMHHs an ideal platform for investigating magnetism in low dimensions and for developing structure-property relationships that can guide the design of new functional magnetic materials.

Here, we demonstrate a substituent-driven strategy to systematically tune the structural dimensionality and magnetic properties of a series of LD diammonium copper(II) chloride hybrids, spanning 2D, MD, and 0D regimes. The reaction of the parent molecule, 1,3-propanediamine (PDA), with copper(II) chloride (CuCl_2) forms a Dion-Jacobson (DJ) 2D hybrid $(\text{C}_3\text{H}_{12}\text{N}_2)\text{CuCl}_4$ ((PDA) CuCl_4). Stepwise methyl substitution on PDA induces a structural evolution from the

initial DJ phase to a Ruddlesden-Popper (RP) type with N-Methyl-1,3-propanediamine (MPDA) in $(\text{C}_4\text{H}_{14}\text{N}_2\text{Cl})_2\text{CuCl}_4$ ((MPDA) $_2\text{CuCl}_4$), followed by a unique MD structure with N,N'-Dimethyl-1,3-propanediamine (DMPDA) in $(\text{C}_5\text{H}_{16}\text{N}_2)_3\text{Cu}_6\text{Cl}_{18}$ ((DMPDA) $_3\text{Cu}_6\text{Cl}_{18}$) that contains both 1D $[\text{Cu}_2\text{Cl}_6^{2-}]_\infty$ chains and 0D $\text{Cu}_2\text{Cl}_6^{2-}$ dimers, and ultimately to fully isolated 0D structures with N,N,N'-Trimethyl-1,3-propanediamine (TriMPDA) and N,N,N',N'-Tetramethyl-1,3-propanediamine (TMPDA) in $(\text{C}_6\text{H}_{18}\text{N}_2)\text{CuCl}_4$ ((TriMPDA) CuCl_4) and $(\text{C}_7\text{H}_{20}\text{N}_2)\text{CuCl}_4$ ((TMPDA) CuCl_4), respectively. This systematic structural transformation enables direct correlation between dimensionality and magnetic exchange interactions. Magnetic susceptibility measurements reveal coexisting FM and AFM interactions in the 2D hybrids, governed by intra- and interlayer coupling, whereas the MD hybrid exhibits AFM ordering with two distinct transition temperatures arising from the chain and dimer sublattices. In contrast, the 0D hybrids display PM behavior due to the large spatial separation between Cu^{2+} centers, which suppresses magnetic coupling. Density functional theory (DFT) calculations further elucidate the spin arrangements and exchange pathways, supporting the experimentally observed magnetic behaviors. Together, these results establish a molecular-level structure-magnetism relationship and provide a general strategy for designing LD OMHHs with tunable magnetic properties.

2 | Results and Discussion

2.1 | Synthesis and Structural Characterization

To investigate the effect of substituents on dimensionality, we synthesized single crystals of five copper-based OMHHs using PDA and its methyl-substituted derivatives as organic cations. Single crystals of (PDA) CuCl_4 , (DMPDA) $_3\text{Cu}_6\text{Cl}_{18}$, (TriMPDA) CuCl_4 , and (TMPDA) CuCl_4 were obtained via a solvent evaporation method, in which methanol was slowly evaporated at room temperature from precursor solutions containing the corresponding amine, HCl, and CuCl_2 . In contrast, (MPDA) $_2\text{CuCl}_4$ single crystals were grown by slow cooling of a hot, acidified methanolic solution containing MPDA and CuCl_2 (see Supporting Information for experimental details). The crystal structures of all compounds were determined by single-crystal x-ray diffraction (SCXRD). Figure 1a–e show the crystal structures and representative crystal images of 2D (PDA) CuCl_4 and (MPDA) $_2\text{CuCl}_4$, MD (DMPDA) $_3\text{Cu}_6\text{Cl}_{18}$, and 0D (TriMPDA) CuCl_4 and (TMPDA) CuCl_4 . SCXRD data and refinement details of all five materials are provided in Table S1 (CIFs have been deposited with the CCDC under deposition numbers 2477917, 2449443, 2333801, 2440959, and 2429616).

Brown, plate-shaped single crystals of (PDA) CuCl_4 (Figure 1a) crystallize in the orthorhombic Pnma space group with lattice parameters $a = 7.15951(15)$ Å, $b = 18.2595(4)$ Å, and $c = 7.49161(17)$ Å, as determined by SCXRD. These crystallographic data are in good agreement with those previously reported by Phelps et al. for (PDA) CuCl_4 , which also crystallizes in the orthorhombic Pnma space group with lattice parameters $a = 7.200(2)$ Å, $b = 18.246(6)$ Å, and $c = 7.451(2)$ Å [19]. The structure adopts a layered DJ phase, in which corner-sharing CuCl_6^{4-} octahedra form 2D sheets separated by monolayers of PDA^{2+} cations. Within the inorganic layers, adjacent Cu centers are

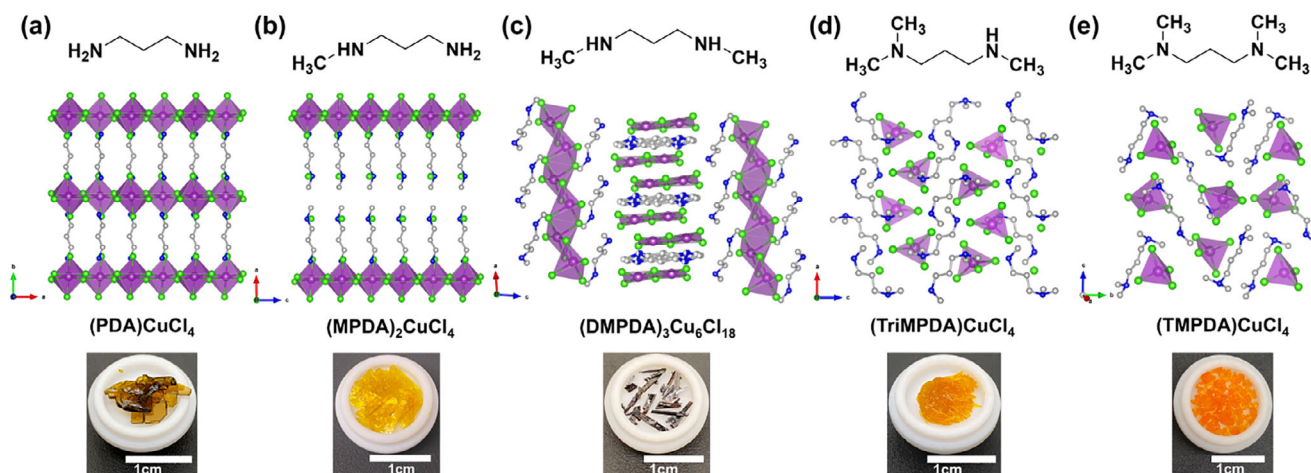


FIGURE 1 | Crystal structures and representative images of (PDA)CuCl₄(a), (MPDA)₂CuCl₄(b), (DMPDA)₃Cu₆Cl₁₈(c), (TriMPDA)CuCl₄(d), and (TMPDA)CuCl₄(e), along with the corresponding amines used for their synthesis. Color scheme: C, light gray; N, blue; Cu, purple; Cl, green; H atoms are omitted for clarity.

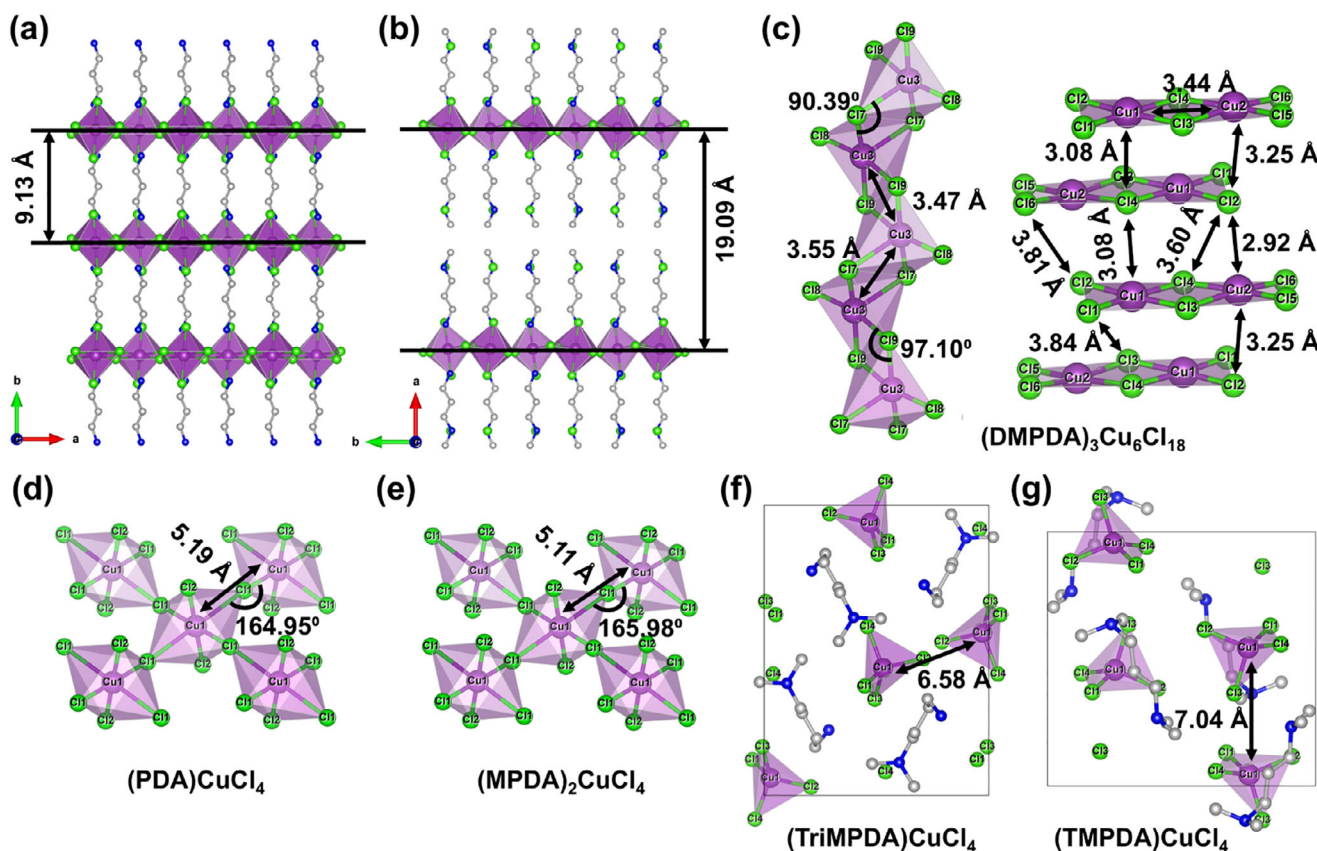


FIGURE 2 | Structural metrics of the organic copper(II) chloride hybrids. Interlayer distances in (PDA)CuCl₄(a) and (MPDA)₂CuCl₄(b), showing the increased spacing upon methyl substitution of PDA. The isolated chain of [Cu₂Cl₆]²⁻ in MD (DMPDA)₃Cu₆Cl₁₈(c), showing the arrangement of edge-sharing CuCl₅³⁻ polyhedra and the Cu...Cl and Cl...Cl distances between adjacent dimers in (DMPDA)₃Cu₆Cl₁₈. Cu-Cu distance and Cu-Cl-Cu bond angle within the layer of (PDA)CuCl₄(d) and (MPDA)₂CuCl₄(e). Shortest Cu-Cu distance in 0D (TriMPDA)CuCl₄(f) and (TMPDA)CuCl₄(g).

connected through Cu-Cl-Cu bridges with an intralayer Cu...Cu distance of 5.19 Å and a bond angle of 164.95° (Figure 2d). Detailed Cu-Cl bond lengths and Cu-Cl-Cu bond angles for all compounds are listed in Tables S3-S12. The related 2D hybrid, (MPDA)₂CuCl₄, crystallizes in the monoclinic C2/c space

group with lattice parameters $a = 38.20(2)$ Å, $b = 7.327(8)$ Å, $c = 7.122(5)$ Å, and $\beta = 90.88(7)^\circ$. In contrast to (PDA)CuCl₄, (MPDA)₂CuCl₄ adopts a 2D RP-type structure, where layers of corner-sharing CuCl₆⁴⁻ octahedra are separated by bilayers of MPDA²⁺ cations (Figure 1b). Consistent with this structural

change, the unit cell of (PDA)CuCl₄ contains three [CuCl₄²⁻]_∞ layers, whereas the unit cell of (MPDA)₂CuCl₄ contains only two (Figure S1). The interlayer spacing increases significantly from around 9.13 Å in (PDA)CuCl₄ to around 19.09 Å in (MPDA)₂CuCl₄ (Figure 2a,b). Notably, despite these differences in interlayer separation and stacking, the intralayer Cu...Cu distance (5.11 Å) and Cu—Cl—Cu bond angle (165.98°) (Figure 2e) remain nearly unchanged, suggesting that the [CuCl₄²⁻]_∞ sheets are structurally analogous in both 2D hybrids. The Cu²⁺ ions in both 2D structures exhibit pronounced Jahn-Teller distortions, leading to significant variations in Cu—Cl bond lengths and distortion of the CuCl₆⁴⁻ octahedra. The degree of distortion is quantified using the bond length distortion index (D) and bond angle variance (σ²). Both (PDA)CuCl₄ and (MPDA)₂CuCl₄ exhibit comparable D values of 0.114 and 0.104, and σ² values of 6.41 and 4.98, respectively (Table S2). These values deviate significantly from the zero value for an ideal octahedron, indicating substantial structural distortion within the inorganic frameworks. In addition, the Cu—Cl—Cu bond angles of 164.95° in (PDA)CuCl₄ and 165.98° in (MPDA)₂CuCl₄ deviate from the ideal 180°, further evidencing significant interoctahedral distortion in both structures.

The synthesized (DMPDA)₃Cu₆Cl₁₈ single crystals are thin, blade-like, and dark red in color (Figure 1c). They crystallize in the triclinic P-1 space group with lattice parameters *a* = 6.14660(10) Å, *b* = 9.3925(2) Å, *c* = 19.9678(3) Å, α = 96.7900(10)°, β = 96.2460(10)°, and γ = 106.967(2)°. As shown in Figure 1c, the structure comprises 1D anionic [Cu₂Cl₆²⁻]_∞ chains and 0D Cu₂Cl₆²⁻ dimers, which are separated and charge-balanced by DMPDA²⁺ cations, giving rise to a unique MD structure. The 1D chains are constructed from edge-sharing square-pyramidal CuCl₅³⁻ units, whereas the dimers consist of edge-sharing square-planar CuCl₄²⁻ units. Along the chains, Cu...Cu distances range from 3.47 to 3.55 Å depending on the bridging chloride, accompanied by variations in Cu—Cl—Cu bond angles (Figure 2c), with values of 97.10° (Cu3-Cl9-Cu3) and 90.39° (Cu3-Cl7-Cu3). Within the dimers, the Cu...Cu distance is ~3.44 Å, with Cu—Cl—Cu bond angles of 97.34° (Cu1-Cl3-Cu2) and 95.69° (Cu1-Cl4-Cu2). The dimers are closely packed, with multiple Cu...Cl and Cl...Cl distances in the range of 2.92–3.25 Å and 3.60–3.84 Å, respectively, providing pathways for Cu-Cl...Cu and Cu-Cl...Cl-Cu superexchange interactions that are essential for magnetic coupling. Single crystals of both (TriMPDA)CuCl₄ and (TMPDA)CuCl₄ are orange in color (Figure 1d,e) and crystallize in the orthorhombic P₂₁2₁2₁ and monoclinic P₂₁/c space groups, respectively. The crystal structures reveal that the CuCl₄²⁻ tetrahedra are completely isolated and surrounded by their respective organic cations, resulting in a 0D structure at the molecular level. The shortest Cu...Cu distance is 6.58 Å in (TriMPDA)CuCl₄ (Figure 2f) and 7.04 Å in (TMPDA)CuCl₄ (Figure 2g), indicating negligible magnetic coupling between Cu²⁺ centers.

We demonstrate that the dimensionality of copper (II) chloride-based OMHHs can be systematically tuned from 2D to a unique MD structure and ultimately to 0D through systematic methyl substitution on the PDA cation. In the absence of substitution, PDA reacts with CuCl₂ to form a 2D DJ phase, (PDA)CuCl₄. Introduction of a single methyl group yields MPDA, which still forms a 2D hybrid but adopts an RP phase in (MPDA)₂CuCl₄. This transition is accompanied by a reduction in the spacing between adjacent organic cations from 4.165 Å

in (PDA)CuCl₄ to 2.429 Å in (MPDA)₂CuCl₄ (Figure S1), which disrupts the packing required for DJ-type connectivity and drives the phase change. Further methyl substitution at both ends of PDA produces DMPDA, leading to the formation of a unique MD structure in (DMPDA)₃Cu₆Cl₁₈ that contains both 1D [Cu₂Cl₆²⁻]_∞ chains and 0D Cu₂Cl₆²⁻ dimers. The increased steric hindrance and altered packing of the DMPDA cations promote partial separation of the inorganic framework, resulting in the coexistence of extended and isolated motifs. Addition of a third methyl group (TriMPDA) introduces complete separation of the metal halide polyhedra, yielding a fully 0D structure in (TriMPDA)CuCl₄. Further methylation does not alter the dimensionality, and (TMPDA)CuCl₄ also adopts a 0D structure. This behavior suggests that a critical steric threshold is reached at the TriMPDA stage, beyond which additional substitution does not further influence inorganic connectivity. These results highlight a clear steric-control mechanism in which progressive substitution of the organic cation modulates intermolecular packing and inorganic framework connectivity, providing a rational pathway for tuning dimensionality in OMHHs and enabling the design of hybrid materials with targeted structural and functional properties.

2.2 | Magnetic Properties

The temperature-dependent magnetic susceptibility (χ) of all the synthesized hybrids was measured on single crystals over the range of 2.0–300 K under an applied magnetic field of 500 Oe, while the field-dependent magnetization (M-H) was recorded at 2 K. For (PDA)CuCl₄, both in-plane and out-of-plane susceptibilities exhibit PM behavior at high temperatures, followed by a maximum at ~15 K and a sharp drop in the in-plane χ below the transition temperature, indicating the presence of AFM ordering (Figure 3a). In contrast, the out-of-plane susceptibility remains nearly constant below the transition temperature, consistent with the expected perpendicular susceptibility response of an antiferromagnet. The inverse susceptibility (χ⁻¹ vs. T) is approximately linear above the transition temperature for both orientations (Figure S2). Fitting the high-temperature region (T > 100 K) to the Curie-Weiss equation, $\chi = \frac{C}{T - \theta}$ (where *C* is the Curie constant and θ is the Curie-Weiss temperature), yields positive θ values of approximately 25 K (in-plane) and 5 K (out-of-plane), indicating dominant FM interactions within the layers. These results suggest competing intralayer FM and interlayer AFM interactions that collectively govern the magnetic behavior, consistent with related Cu²⁺-based 2D systems [18]. No magnetic hysteresis is observed in the M-H curves for either in-plane or out-of-plane directions, and the magnetization saturates at ~45 KOe (Figure 3b). The magnetic properties of this hybrid have also been previously investigated by Phelps et al. and von Känel et al. [19, 20]. The reported magnetic behavior, including the in-plane and out-of-plane susceptibilities and the magnetic ordering at approximately 15 K, is consistent with our measurement. Similarly, the saturation field and saturation magnetization obtained in the present study agree well with the previously reported values. The intralayer FM coupling in (PDA)CuCl₄ is primarily attributed to nearly orthogonal, non-overlapping magnetic d orbitals in the corner-sharing CuCl₆⁴⁻ octahedra, arising from Jahn-Teller distortions [18]. In contrast, the interlayer AFM interaction is mediated by

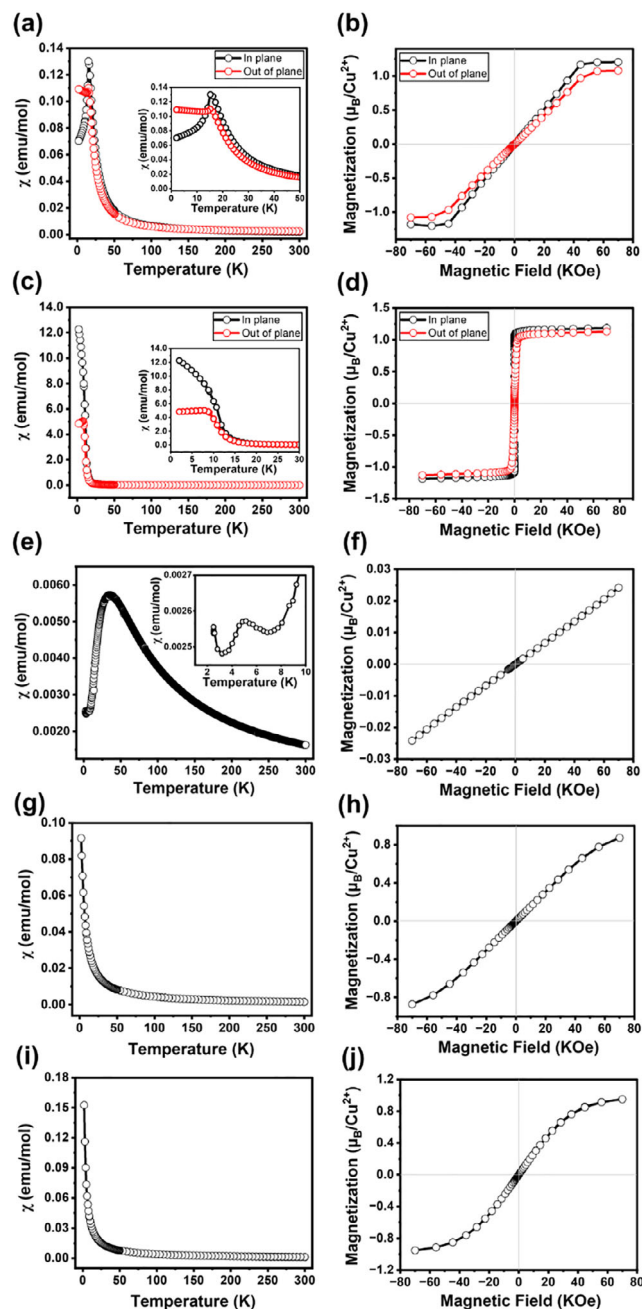


FIGURE 3 | Temperature-dependent magnetic susceptibility (χ) under an applied field of 500 Oe for single crystals of (PDA)CuCl₄(a), (MPDA)₂CuCl₄(c), (DMPDA)₃Cu₆Cl₁₈(e), (TriMPDA)CuCl₄(g), and (TMPDA)CuCl₄(i), and field-dependent magnetization of (PDA)CuCl₄(b), (MPDA)₂CuCl₄(d), (DMPDA)₃Cu₆Cl₁₈(f), (TriMPDA)CuCl₄(h), and (TMPDA)CuCl₄(j) measured at 2 K. The insets show an enlarged view of the low-temperature magnetic susceptibility data.

superexchange and dipolar coupling through apical Cl⁻ ions and is highly sensitive to the interlayer separation. The relatively short interlayer separation (9.13 Å) in (PDA)CuCl₄ therefore facilitates appreciable interlayer AFM coupling, leading to the observed anisotropic magnetic behavior.

The impact of interlayer separation on magnetic properties is more pronounced in (MPDA)₂CuCl₄, where the interlayer distance increases to 19.09 Å, nearly twice that of (PDA)CuCl₄,

due to the methyl substituent. As a result, the χ vs. T profiles for both in-plane and out-of-plane directions exhibit a clear PM to FM transition at ~13 K, below which the susceptibility rises sharply and approaches saturation (Figure 3c). In contrast to (PDA)CuCl₄, no AFM ordering is observed, consistent with significantly weakened interlayer coupling at larger separations. Curie-Weiss fittings to χ^{-1} vs. T plots yield positive θ values of ~33 and 4 K for the in-plane and out-of-plane directions, respectively, confirming dominant FM interactions. Field-dependent magnetization measurements further support this behavior: M-H curves reach saturation at ~1 μ_B per Cu²⁺, with distinct saturation fields of ~100 Oe (in-plane) and ~3 kOe (out-of-plane), indicating that the magnetic easy axis lies within the [CuCl₄]²⁻ layers (Figure 3d). A clear hysteresis loop is observed for the in-plane orientation (Figure S3), with a very small coercive field of 35 Oe, characteristic of soft ferromagnetism. The effect of interlayer separation on the magnetic behavior of layered Cu(II) halide hybrids has been previously demonstrated using different organic cations of varying sizes [18]. In contrast, the present work shows that a simple substitution of the organic cation is sufficient to substantially increase the interlayer separation and suppress interlayer AFM coupling. This provides a simple synthetic strategy for tuning magnetic interactions through subtle modifications of the organic cation.

For the MD hybrid (DMPDA)₃Cu₆Cl₁₈, the magnetic susceptibility exhibits paramagnetic behavior at high temperatures, followed by a broad maximum at ~25 K and a sharp decrease upon further cooling, indicative of long-range AFM ordering (Figure 3e). The inverse susceptibility (χ^{-1} vs. T) is approximately linear above the transition temperature (Figure S2), and fitting the high-temperature region (>100 K) to the Curie-Weiss equation yields a negative θ value of -51 K, consistent with dominant AFM interactions. Field-dependent magnetization measurements show no hysteresis and no saturation up to 70 kOe, further confirming the AFM nature of the hybrid. This primary magnetic transition is attributed to AFM coupling within the 1D [Cu₂Cl₆]²⁻ chains, consistent with our previous report on the structurally analogous 1D (C₈H₂₂N₂)Cu₂Cl₆ hybrid, which exhibits a Néel temperature of 24 K [7]. In both systems, the chains are composed of edge-sharing square-pyramidal CuCl₅³⁻ units connected through chloride bridges, enabling strong superexchange interactions that drive AFM ordering. Notably, (DMPDA)₃Cu₆Cl₁₈ exhibits a second magnetic feature at lower temperature: a weak upturn in susceptibility near ~5 K followed by a sharp decrease, indicative of an additional AFM transition. This secondary transition is confirmed by measurements under a higher applied field (70 kOe; Figure S4b). We attribute this low-temperature ordering to weaker intra- and inter-dimer interactions arising from multiple Cu-Cl...Cl-Cu and Cu-Cl...Cu superexchange pathways, facilitated by the close spatial arrangement of the Cu₂Cl₆²⁻ dimers [33].

The χ vs. T profiles of both 0D hybrids, (TriMPDA)CuCl₄ and (TMPDA)CuCl₄, exhibit typical PM behavior, characterized by a gradual increase in χ upon cooling with no evidence of long-range magnetic ordering (Figure 3g,i). The inverse susceptibility (χ^{-1} vs. T) shows a linear dependence over the range 2–300 K, extrapolating close to the origin. Fitting the high-temperature region (>100 K) to the Curie-Weiss law yields C values of 0.44

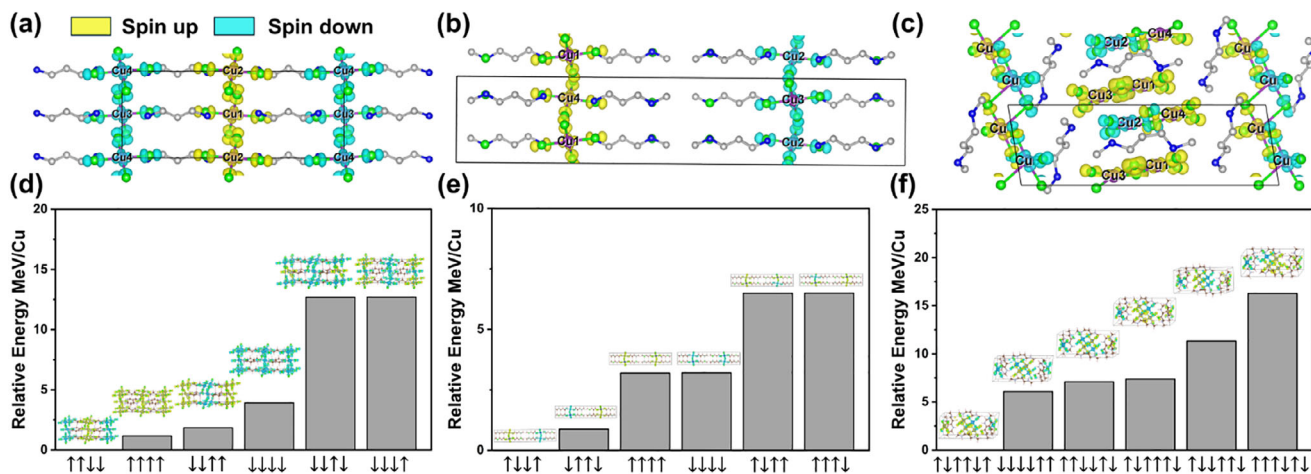


FIGURE 4 | Calculated spin-density distributions in the copper chloride frameworks of 2D (PDA)CuCl₄(a), 2D (MPDA)₂CuCl₄(b), and MD (DMPDA)₃Cu₆Cl₁₈(c), showing the magnetic arrangements within the layers, chains, and dimers. The relative energies of magnetic ordering of Cu atoms in 2D (PDA)CuCl₄(d), 2D (MPDA)₂CuCl₄(e), and MD (DMPDA)₃Cu₆Cl₁₈(f).

and 0.38 and corresponding effective magnetic moments (μ_{eff}) of 1.88 μ_{B} and 1.75 μ_{B} per Cu²⁺ for (TriMPDA)CuCl₄ and (TMPDA)CuCl₄, respectively, in good agreement with the expected spin-only value for Cu²⁺ ($\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$). Field-dependent magnetization measurements show no hysteresis for either compound, and the magnetization does not reach saturation even at a field of 70 KOe (Figure 3h,j), which is in good agreement with the PM nature of the hybrids. Similar PM behavior has been reported for other structurally isolated CuCl₄²⁻-based OMHHs [34]. The absence of magnetic ordering is attributed to the complete isolation of CuCl₄²⁻ tetrahedra by the organic cations, which leads to large Cu...Cu separations and effectively suppresses magnetic exchange interactions between Cu²⁺ centers. A comparison of the key structural parameters and magnetic properties of all LD diammonium-copper(II) chloride hybrids synthesized in this study is provided in Table S13.

2.3 | Computational Studies

To elucidate the spin arrangements in these systems, density functional theory (DFT) calculations were performed to evaluate the magnetic configurations of the metal halide frameworks in 2D (PDA)CuCl₄ and (MPDA)₂CuCl₄, as well as chains and dimers in (DMPDA)₃Cu₆Cl₁₈ (Figure 4). All possible magnetic orderings within the unit cell of the hybrids were enumerated to generate the corresponding DFT energies. Given that there are 4 symmetrically inequivalent Cu atoms in the unit cell of both (PDA)CuCl₄ and (MPDA)₂CuCl₄ (Figure S5a,c), the enumeration results in a total of 16 different configurations for each hybrid. Using the lowest-energy structure as the reference, representative magnetic orderings are shown in Figure 4d,e, with full energetics summarized in Tables S14 and S15. Structural optimization reveals that the ground state in both hybrids exhibits parallel spin alignment within the 2D layers, corresponding to intralayer FM ordering, while adjacent layers are coupled antiferromagnetically through antiparallel spin alignment (Figure 4a,b). These results are in good agreement with the experimentally observed coexistence of in-plane FM and out-of-plane AFM interactions.

For the MD (DMPDA)₃Cu₆Cl₁₈, 6 symmetrically inequivalent Cu atoms are present in the unit cell (Figure S5b), giving rise to 64 possible magnetic configurations. Representative configurations and their relative energies are shown in Figure 4f and Table S16. After structural optimization, the lowest-energy state exhibits antiparallel spin alignment along the 1D [Cu₂Cl₆²⁻]_∞ chains, indicating dominant intrachain AFM ordering (Figure 4c). This behavior arises from superexchange interactions mediated by dichloro-bridged Cu-(Cl)-Cu pathways and is consistent with the higher-temperature AFM transition ($T_{\text{N}} = 25$ K) as well as prior observations in structurally analogous 1D systems [7]. In addition, antiparallel spin alignment is found within the Cu₂Cl₆²⁻ dimers, reflecting weaker AFM coupling between Cu²⁺ ions, which likely accounts for the lower-temperature AFM transition ($T_{\text{N}} = 5$ K).

3 | Conclusions

In summary, we have synthesized and characterized a series of methyl-substituted diammonium copper(II) chloride hybrids and showed that the position and number of methyl substituents systematically govern both structural dimensionality and magnetic behavior. Detailed structural analysis reveals that progressive methyl substitution introduces increasing steric bulkiness, which drives the isolation of metal halide polyhedra and enables a controlled evolution from 2D to MD and ultimately 0D structures. Magnetic susceptibility measurements show that these structural changes strongly modulate magnetic exchange interactions through variations in inorganic sublattice connectivity. Specifically, the 2D hybrids (PDA)CuCl₄ and (MPDA)₂CuCl₄ exhibit coexisting FM and AFM interactions governed by interlayer coupling; the MD hybrid displays AFM ordering with two distinct transition temperatures arising from chain and dimer sublattices, and the 0D hybrids exhibit PM behavior due to the complete isolation of magnetic centers. These findings establish a clear structure-magnetism relationship linking inorganic framework connectivity to magnetic exchange interactions. Our work establishes a rational molecular design strategy for achieving structural tunability of LD OMHHs and controlling their magnetic

properties through targeted structural modifications, thereby paving the way toward LD magnetic materials based on OMHHs for fundamental studies of magnetism and next-generation spintronic applications.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Deposition numbers [2477917](#) (for (PDA)CuCl₄), [2449443](#) (for (MPDA)₂CuCl₄), [2333801](#) (for (DMPDA)₃Cu₆Cl₁₈), [2440959](#) (for (TriMPDA)CuCl₄), and [2429616](#) (for (TMPDA)CuCl₄) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <http://www.ccdc.cam.ac.uk/structures/service>.

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