Ligand size effects in two-dimensional hybrid copper halide perovskites crystals

Arramel Arramel¹ [✉], Angga Dito Fauzi^{1,2} , Xinmao Yin^{1,2,11}, Chi Sin Tang^{1,2,3,12}, Muhammad Haris Mahyuddin^{4,5} , Muhammad Fauzi Sahdan¹, Mimin Aminah⁶, Djulia Onggo⁶, Ganes Shukri^{4,5}, Caozheng Diao² , Hong Wang^{7,8} , Muhammad Danang Birowosuto⁷ , Andrew Thye Shen Wee^{1,9} & Andriwo Rusydi^{1,2,3,10}[✉]

Intensive effort to tailor photophysics of lead-free perovskites is appealing in recent years. However, their combined electronic and optical property elucidations remain elusive. Here, we report spectroscopic observations of the coexistence Zhang-Rice singlet state and exotic electronic transitions in two-dimensional copper-based perovskites. Herein, several perovskites with different alkylammonium spacers are investigated to unravel their correlated electronic systems and optical responses. Namely, methylammonium, ethylammonium, phenylmethylammonium and phenethylammonium. Using temperature dependent high-resolution X-ray absorption spectroscopy, we observe distinct electronic features highlighting the impact of short spacer chains compared to long-conjugated ligands, demonstrating a pronounced $3d^9$ and $3d^9L$ signature linewidth variation. Corroborated by density functional theory calculations, the transient dynamics evolution of copper-based hybrid perovskites is influenced by the strong interplay of electron-phonon interactions and geometric constrictions. This finding sheds light on tuning the electronic and optical properties of hybrid perovskites towards efficient photoactive-based devices.

¹Department of Physics, National University of Singapore, Singapore, Singapore. ²Singapore Synchrotron Light Source (SSLS), National University of Singapore, Singapore, Singapore. ³NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, Singapore, Singapore. ⁴Research Group of Advanced Functional Materials, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung, Indonesia. ⁵Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, Bandung, Indonesia. ⁶Inorganic and Physical Chemistry Research Group, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Bandung, Indonesia. ⁷CINTRA UMI CNRS/NTU/THALES 3288, Research Techno Plaza, Singapore, Singapore. ⁸School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore. ⁹Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore, Singapore. ¹⁰NUSNNI-NanoCore, National University of Singapore, Singapore, Singapore. ¹¹Present address: Shanghai Key Laboratory of High Temperature Superconductors, Physics Department, Shanghai University, Shanghai, China. ¹²Present address: Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), Innovis, Singapore. ✉email: phyarr@nus.edu.sg; phyandri@nus.edu.sg

Two-dimensional hybrid organic–inorganic perovskites (2D-HOIPs) materials have demonstrated promising progress in photovoltaics and light-emitting diodes applications, such as their excellent performance as active-light absorbers and carrier transporters^{1–5}. These materials deserve special attention in the field of unconventional 2D hybrid materials due to their tunable dielectric confinements, charge carrier dynamics, and their structural diversities. Initially, the research progress is motivated by a large number of seminal papers in the 1980s and 1990s^{6–9}. To date, several classes of 2D-HOIPs have emerged with a diversity concerning their structure–property relationships^{3–5,10}.

An intrinsic quantum well structure in 2D-HOIPs is composed of ammonium cations connected to the halide ions of inorganic sheets via hydrogen bonding. The hybrid perovskite framework has unique alternation of bilayer chains of spacers comprising alkyl- or aromatic ammonium cations and inorganic perovskite layers held by corner-sharing $[\text{BX}_4]^{2-}$ octahedra^{9,11}. B element represents typical metals such as lead or tin with formal oxidation state of 2^+ , and X^- is a halide anion. The inorganic sheets have potentially active sites due to their high charge carrier mobility¹². The organic spacer ligands that occupy the A-site of the crystal structure with tunable length afford superior hydrophobicity and large dielectric confinement¹³. As a result, the formation of quantum well-like structure manifests high excitonic binding energies at room temperature and high radiative decay rate^{2,5,7,14–21}. Pressure, electric field, and temperature serve as potential external stimulus owing to the weak hydrogen-bonding interactions between organic and inorganic moieties, which are tunable via thermally activated motion of the cations.

A fundamental challenge in the advancement of 2D-HOIPs is the toxicity issue and material stability^{2–4}. The environmental toxicity originates from the lead that occupies the B-site of 2D-HOIPs crystal structure, which is a roadblock in commercialization. In this regard, 2D lead-free halide perovskites are particularly useful for future commercial applications^{15,19}. For example, Cortecchia and coworkers explored the optical properties of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$ series by tuning Br/Cl ratio to widen the optical absorption to the near-infrared regime¹⁵. Polyakov et al.²² and Nugroho et al.²³ investigated copper-based 2D-HOIPs with longer alkylammonium chains $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{CuCl}_4$, and they showed the coexistence of ferromagnetic and ferroelectric orders within a hybrid material. With regard to the unstable humidity issue, several strategies have been employed such as the replacement of hygroscopic methylammonium (MA) functional group with a hydrophobic cation in the A-site of 2D-HOIPs crystals such as butylammonium (BA)²⁴ and phenethylammonium (PEA). The work of Li et al.¹⁹ involving the case of $(\text{PMA})_2\text{CuBr}_4$ ($\text{PMA} = \text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+$; phenylmethylammonium) suggests the importance of copper as the lead substitute that suitable for light-harvesting in thin-film solar cells.

Several experimental^{25,26} and theoretical^{27,28} studies have demonstrated that the organic ligand size of 2D-confined spacer layer plays a significant role in determining their charge carrier dynamics. In particular, Zhang–Rice singlet state has a crucial role in the low-energy signature of A-site ordered cuprate perovskites such as hole-doped high-T_c superconductivity^{29,30}. Santoso et al.³¹ outline that a strong competition between spin singlet and triplet states occurs in the hole-doped cuprates, manifesting an anomalous spectral-weight transfer in their high-energy optical conductivity measurements³¹. Owing to the similar layered structure, the question arises as to whether the copper hybrid perovskites could exhibit such intriguing correlated electron–electron interactions. To date, a systematic study on the charge recombination profile as a function of alkylammonium spacers in a lead-free hybrid perovskite is still lacking.

Here, we systematically investigate the electronic transition across the unoccupied electronic state and emission properties of copper-based 2D-HOIPs with tunable insulating layers using high-resolution synchrotron X-ray absorption (XAS) and steady-state photoluminescence (PL) spectroscopies, supported by density functional theory (DFT) calculations. In this study, we unravel the correlation of the core-hole transition to its unoccupied states and the choice of ligand size. Apart from the conventional $L_{2,3}$ absorption threshold peaks³², we attribute the emergence of four well-defined electronic transitions based on the XAS lineshape analyses. For example, the compounds containing short ligand such as MA and ethylammonium (EA) exhibit pronounced transitions originating from Cu $2p$ states to the respective $3d^9L$ (~ 936.6 eV, where L denotes for chlorine hole), $3d^8$ configuration (~ 939.9 eV) and Cu $4s$ – $3d$ hybridized states (~ 942.4 and ~ 946.0 eV). In addition, the admixture spin singlet and triplet states of these Cu-perovskite series is largely influenced by the annealing temperature. Furthermore, a photo-induced charge transfer dynamics investigation of A_2CuCl_4 compounds at the perovskite phase transition temperature suggests that different compositional ratio of free exciton and self-trapped exciton is achieved. The Stokes shifts of these compounds vary as the cation size increases, suggesting a modulation of the activation energy barrier between free exciton and self-trapped exciton states. DFT results reveal that the role of octahedral distortion is pronounced in $(\text{PMA})_2\text{CuCl}_4$.

Results and discussion

Temperature-dependent XAS of copper-based hybrid perovskite with short chain spacers. We perform temperature-dependent XAS measurements at the Cu $L_{2,3}$ edge on $(\text{MA})_2\text{CuCl}_4$ single crystal as depicted in Fig. 1a. Prior to examine the samples in the synchrotron measurements, we have characterized the structure, vibrational mode, and chemical state of the compounds (X-ray diffraction patterns, Raman spectra and X-ray photoemission spectroscopy) in Supplementary Figs. 1–3 respectively. The intense peak centered at ~ 932.9 eV is attributed to the Cu $2p_{3/2} \rightarrow 3d$ transition (Cu L_3), while the absorption peak at ~ 952.7 eV corresponds to the Cu $2p_{1/2} \rightarrow 3d$ transition (Cu L_2). These two peaks are the main features of the Cu $L_{2,3}$ edge emerging from the $2p$ spin-orbit coupling interaction. Apart from those well-known absorption electronic transitions, we also observed other emergent peaks that centered at ~ 936.6 eV, ~ 939.9 eV, ~ 942.4 eV, and ~ 946.0 eV labeled as A1–A4, respectively. The first peak (A1) can be associated with the electronic transition from the Cu $2p$ states that resemble the signature of Zhang–Rice singlet state^{29,33–35}.

Here, we rationalize the observed peak due to the electronic transition of the ground state $3d^9L$ to the $cd^{10}L$ excited state. L and c represent ligand hole and core hole, respectively. The second peak can be attributed to the typical signature of Cu in the high energy region ($3d^8$ configuration) and the third peak correspond to the Cu $2p \rightarrow 4s$ – $3d$ transition^{36,37}, while the fourth broaden peak is related to the electronic transition from the Cu $2p$ hybridized with the ligand p states to the Cu $4s$ – $3d$ hybridized orbital³⁸. As the samples were annealed at a higher temperature, we observed that the absorption intensities of the main features (Cu L_2 and Cu L_3 peaks) were decreased. However, this trend does not hold for the other emergent peaks, indicating that $3d^9L$, $3d^8$, and s – d hybridization are sensitive to the temperature variations. Here we notice that the line shape of $3d^8$ signature in $(\text{MA})_2\text{CuCl}_4$ Cu L -edge XAS spectrum changed its intensity as the annealing temperature was lowered down to 200 K, whereas the core hole contribution (d^9L) was slightly perturbed. Based on these findings, we attribute the spin singlet states to be prominently pronounced in the short chain spacer of copper perovskites.

Fig. 1 Temperature-dependent XAS spectra of Cu $L_{2,3}$ edge in different A_2CuCl_4 compounds. Inset represent each of the optimized geometrical structure. **a** $(MA)_2CuCl_4$ absorption L -edge profile, indicating the coexistence of L_2 and L_3 absorption peak accompanied by the presence of $d^9 L$ and d^9 signals. **b** $(EA)_2CuCl_4$ absorption L -edge with a pronounced spectral weight transfer. **c** $(PMA)_2CuCl_4$ absorption L -edge with strong suppression as the higher spectral feature are diminished. **d** $(PEA)_2CuCl_4$ absorption L -edge are depicted the L_3 and $d^9 L$ competing interaction within the elevated temperatures. The temperature data represent 200 K (blue), 300 K (red), green (320 K), and magenta (340 K) respectively.

We further discuss the evolution of emergent features of the Cu L_3 and L_2 edges in XAS spectra of $(EA)_2CuCl_4$ as shown in Fig. 1b. Interestingly, the absorption intensity of $(EA)_2CuCl_4$ has a substantial enhancement compared to the previous discussion on short chain spacer compounds. Particularly, these well-defined electronic transitions are strongly pronounced at 200 K. Thus, the intensities were gradually decreased when the annealing temperature reached ~ 340 K, coincided with the estimated transition temperature for Cu-series hybrid perovskites. Here we propose that the majority contribution originating from the spin triplet states rather than the singlet states within the experimental conditions. This effort introduces a strong and yet localized hybridization between $3d$ Cu and Cl $3p$ orbitals, accompanied by the weak coupling between the neighboring $CuCl_6$ octahedron sheets. Structurally, the CH_2 (methylene) moiety consists of two hydrogen atoms bound to a carbon atom. The covalent C–H bonding is dominated by the p character where the orbital is perpendicular with respect to the molecular plane, whereas the in-plane (σ -bond) direction is dominated by s character³⁹. As the organic spacer is extended from MA to EA ligands, the extra sigma bond in the latter constructively increases its impact led to spectral changes as shown in the temperature-dependent XAS measurements. Based on these findings, we tentatively proposed that the additional $-CH_2$ moiety span the organic ligand length inducing extra s states in this lead-free correlated hybrid perovskite electronic system.

Temperature-dependent XAS of copper-based hybrid perovskite with long chain spacers. We have performed a

comparable XAS investigation on a longer conjugated organic spacer, namely, $(PMA)_2CuCl_4$ as shown in Fig. 1c. In contrast to $(MA)_2CuCl_4$ and $(EA)_2CuCl_4$ cases, the curvature of $(PMA)_2CuCl_4$ exhibited the weaken Zhang-Rice singlet states and featureless signals in the high energy range of 940–950 eV. Here, we consider that the absence of such signatures could be mediated by the substitution of a short chain spacer with a highly conjugated organic ligand. Moreover, the peak position of the Cu L_3 and L_2 features is shifted even further by ~ 0.4 eV to the higher energy compared to the corresponding features in $(MA)_2CuCl_4$. Here, we tentatively propose that mixed covalency character can be moderately controlled by increasing the ligand size of the organic spacer, thereby promoting strong localization on the core hole signals.

Interestingly, the incorporation of an extra CH_2 -chain onto the conjugated ligand spacer structure displayed a significant outcome as depicted in the temperature-dependent XAS measurements of $(PEA)_2CuCl_4$ in Fig. 1d (inset shown the corresponding structural arrangement). We notice that qualitatively, the line shape of the XAS spectra of $(PEA)_2CuCl_4$ is strikingly different compared to its counterpart ($(PMA)_2CuCl_4$), exhibiting a pronounced temperature-induced of Cu L_3 intensity variation. Here, the curvature variation between L_3 and $d^9 L$ transitions strikingly depends on the temperature. For example, L_3 signal is much more pronounced than that of $d^9 L$ feature at 200 K (blue spectrum) and the absence of higher spectral signatures (beyond 940 eV). On the contrary, the reversal intensities on these signatures were observed at elevated temperatures. For example, $d^9 L$ core holes are substantially increased with respect to the L_3

Fig. 2 FWHMs and peak positions extracted from XAS spectra, demonstrating the implication of short versus long ligand size on their linewidth spectral analyses. The FWHM profile corresponds to the d^9L (red circles) and d^9 (blue squares) of (MA)₂CuCl₄ (a) and (PMA)₂CuCl₄ (b), respectively. The peak position variation corresponds to the d^9L (top) and d^9 (bottom) of (MA)₂CuCl₄ (c) and (PMA)₂CuCl₄ (d), respectively. Error bars are collected from the respective fitting results.

features. We attribute these observations due to the competing interactions that arise between spin triplet and singlet states, which triggers the former to become dominant at 300 K and 340 K. Furthermore, these spectral weight transfer infers that Cu spins arrangements within the CuCl₆ octahedron inducing local antiferromagnetic ordering at low temperature.

We further analyzed the full-width half maximum (FWHM) and peak positions to shed some light on the spectral weight

transfer in this system as shown in Fig. 2a–d. For instance, we observe that the FWHM of d^9 (blue square) and d^9L (red circle) in short chain spacer (i.e. (MA)₂CuCl₄) increased as a function of temperatures as depicted in Fig. 2a, whereas the opposite trend was found in the long chain spacer (PMA)₂CuCl₄ as outlined in Fig. 2b. Similar behaviors were also pronounced in the peak positions profile shown in Fig. 2c, d. Interestingly, a plot of the integrated area of the short chains (Fig. 3a, b) and long chains

Fig. 3 The overview of integrated area acquired from the XAS spectra of A_2CuCl_4 compounds. The evolution of $d^9 L$ (red circles) and d^9 (blue circles) of $(MA)_2CuCl_4$ (a), $(EA)_2CuCl_4$ (b), $(PMA)_2CuCl_4$ (c), and $(PEA)_2CuCl_4$ (d), respectively. Error bars are collected from the respective fitting results. (e) Schematic representation of spectral weight transfer of the short and long ligand spacers compounds. The arrows indicate the respective electronic transitions.

Fig. 4 Room-temperature photoluminescence of A_2CuCl_4 compounds. PL spectra and the deconvoluted excitonic signatures of $(MA)_2CuCl_4$ (a), $(EA)_2CuCl_4$ (b), $(PMA)_2CuCl_4$ (c), and $(PEA)_2CuCl_4$ (d), respectively. Raw PL data (black), donor bound exciton (red), free exciton (blue), self-trapped exciton (green), and fitting peak (cyan). Error bars are collected from the respective fitting results.

(Fig. 3c, d) Cu-perovskites share comparable findings. It is obvious that temperature greatly influenced the proportion of respective electronic transitions, exhibiting abrupt spectral changes above 300 K. According to these extracted parameters, we believe careful consideration is required to shed some light on the role of mixed covalence states and spectral weight transfer governing the ground state d^9L to the $cd^{10}L$ excited state transitions. Such a finding could be useful to tailor the electronic properties of copper-hybrid perovskite using the organic ligand size effects^{5,16,19,26,27,40}. In summary, we proposed that peculiar energetic transitions can be realized between the short versus long organic ligand spacer of copper-hybrid perovskite as schematically depicted in Fig. 3e. We further extend the investigations through optical measurement in the following sections.

Optical response of copper-based hybrid perovskites as a function of temperatures. Steady-state PL measurements of these alkylammonium-based perovskite series suggest that the emission peak of $(MA)_2CuCl_4$ and $(EA)_2CuCl_4$ crystals do not vary significantly (Fig. 4a, b). On the contrary, the maxima of PL peak for the perovskite with a conjugated ligand spacer was blueshifted from 586 nm (2.12 eV) for $(PMA)_2CuCl_4$ to 537 nm (2.31 eV) for $(PEA)_2CuCl_4$ as depicted in Fig. 4c, d, respectively. This finding is in accordance with the previous reports on the lead iodide hybrid perovskite crystals^{25,40–43} and the corresponding theoretical works^{28,44–46}. Furthermore, the FWHM of $(PMA)_2CuCl_4$ is determined to be ~48 nm, evidencing a narrow-band emission attributed to the recombination of free excitons¹². On the other hand, the linewidth broadening of the other three

cases shows typical FWHM in the range of 200 nm, which is comparable to the previous HOIPs reports^{15,40,47,48} and our recent work⁴⁹. We associate that the occurrence of such broad-band emission arises from the self-trapped excitons caused by strong carrier-phonon interaction within 2D-HOIPs structure^{25,41–43,50–52}. The physical origin of such self-trapped excitons emission in 2D-alkylammonium copper halides is highly correlated to the Jahn-Teller effect resulted from the out-of-plane distortion within the Cu octahedra^{52,53}. In addition, we also discuss further the absorption profile of the compounds in supplementary note 1 and Supplementary Fig. 4.

To shed some light on the excitonic recombination of the copper-based perovskites, the extracted integrated area from the temperature-dependent PL spectra of A_2CuCl_4 crystals are illustrated in Fig. 5. For example, the Gaussian fittings are implemented to deconvolute PL peaks with three components in Fig. 5a. For instance, we note that the PL measurement acquired in 200 K resulted in the first PL peak centered at 518 nm (FWHM = 102 nm and integrated area = 85050) and the second peak at 637 nm (FWHM = 247 nm and integrated area = 51252), respectively. The former signal corresponds to the formation of free-exciton emission, while the latter is considered as self-trapped exciton emissions. In addition, the red triangles correspond to the presence of donor-bound excitons. Here, we find that the free-exciton emission (blue squares, Fig. 5a–d) of alkylammonium and conjugated organic spacers do not change dramatically as a function of temperature. On the other hand, we observe that the corresponding self-trapped exciton emissions (green triangles) is slightly decreased close to 320 K for EA-, PMA-, and PEA-cases. Whereas the shortest chain (MA) displays a reasonable

Fig. 5 The overview of integrated area acquired from the PL spectra of A_2CuCl_4 compounds. (MA) $_2CuCl_4$ (a), (EA) $_2CuCl_4$ (b), (PMA) $_2CuCl_4$ (c), and (PEA) $_2CuCl_4$ (d), respectively. Self-trapped exciton (green circles), free exciton (blue squares), and donor bound exciton (red triangles). Error bars are collected from the respective fitting results.

fluctuation at high temperature. Here, we reconcile that the self-trapping of photogenerated carriers within the $CuCl_6$ octahedra is comprised of mutual interaction between emissive states and recombination pathways, which is much more feasible for the long spacers in these hybrid copper perovskites.

We further investigate the linewidth of the PL trends by comparing their FWHMs as a function of temperature (Fig. 6). In the case of free excitons signals, the FWHMs are gradually increasing for all samples. This can be rationalized due to the localized exciton at low temperature that thermally activated as temperature increases, which promotes the broadening of the spectral line shape. In contrast, self-trapped excitons emissions exhibit the absence of FWHM broadening as the temperature increases. With the exception, the longest chain compound in this study displays a reduction of ~ 50 nm in its FWHM. Moreover, the large Stokes shift can be realized between free-exciton and self-trapped exciton emissions. In addition, we note that such a Stoke difference becomes larger as the alkylammonium cation size increases (Supplementary Tables 1–4). For comparison, we include the extracted fitting parameters of donor bound excitons in Supplementary Tables 5 and 6 for alkyl-chains-ligand spacers and conjugated-chains-ligand spacers, respectively. Based on these findings, we consider that the organic spacer length of the A-site in copper-hybrid perovskites could be used to tune the activation energy barrier of the free excitons and self-trapped excitons states.

First principle calculations on the length-dependent of copper-based hybrid perovskites. To corroborate our experimental

findings, we perform DFT calculations on (MA) $_2CuCl_4$, (EA) $_2CuCl_4$, (PMA) $_2CuCl_4$, and (PEA) $_2CuCl_4$. The optimized geometry, band structure, and projected density of states (PDOS) of each compound are summarized in Fig. 7. As previously discussed by Cortecchia et al.¹⁵, the lowest unoccupied molecular orbital (LUMO) which renders a conduction band in the minority spin is mainly comprised of Cu $3d$ orbital as Cu^{2+} involves an unpaired electron in its outer shell as outlined in Fig. 7a, b for (MA) $_2CuCl_4$ and (EA) $_2CuCl_4$, respectively. Here, we note that for (PMA) $_2CuCl_4$ and (PEA) $_2CuCl_4$ (Fig. 7c, d), there is a distinctive state above the LUMO originating from the C $2p$ orbital of the benzene ring. This indicates that the long organic spacers have more significant contributions to the charge carrier dynamics organic than the short ones⁴⁶. In addition, the calculated electronic band gaps for (MA) $_2CuCl_4$, (EA) $_2CuCl_4$, (PMA) $_2CuCl_4$ and (PEA) $_2CuCl_4$ (1.83, 1.90, 1.85, and 1.89 eV, respectively) are in agreement with the UV-Vis absorption spectra and the calculated band structure (Supplementary Fig. 5). Therefore, we deduce that the chemical composition of the organic ligand in 2D-HOIPs structure does not change the band gaps significantly.

Table 1 summarizes the calculated lattice and geometrical parameters of (MA) $_2CuCl_4$, (EA) $_2CuCl_4$, (PMA) $_2CuCl_4$, and (PEA) $_2CuCl_4$ crystals. We find that the above parameters are in excellent agreement with the experimental values^{21,54–56}. In this particular 2D-HOIPs structure, the coordinated Cu atoms to neighboring six Cl ligands form two type bonding, i.e., short and long equatorial Cu–Cl bonds that oriented perpendicular with respect to the apical (axial) Cu–Cl bonds. These bonds are strongly related to the formation of Cu–Cl–Cu bond angle, which

Fig. 6 The overview of FWHM extracted from the PL spectra of A_2CuCl_4 compounds. (MA) $_2CuCl_4$ (a), (EA) $_2CuCl_4$ (b), (PMA) $_2CuCl_4$ (c), and (PEA) $_2CuCl_4$ (d), respectively. Self-trapped exciton (green circles), donor bound exciton (red triangles), and free exciton (blue squares). Error bars are collected from the respective fitting results.

indicates the presence of $CuCl_6$ octahedron distortion and therefore act as a descriptor for a carrier lifetime of HOIPs²⁸. It is generally accepted that a carrier lifetime of HOIPs can be predicted through the Cu–Cl–Cu angle as a parameter of the $CuCl_6$ octahedron distortion. We note that the Cu–Cl–Cu angle of (PMA) $_2CuCl_4$ (157.2°) is the smallest among the studied compounds. Accordingly, (PMA) $_2CuCl_4$ is predicted to have the largest octahedral distortion and thus promotes the shortest carrier lifetime within the reported series. We also hypothesize that the previous discussion on the competing d^9-d^9L components and PL response resulted from direct consequence of the expansion of second equatorial bond length that more pronounced in (PMA) $_2CuCl_4$ crystals as schematically shown in Supplementary Fig. 6.

To strengthen our argument on the interplay of the electron-phonon couplings, we have performed molecular dynamics (MD) simulations to calculate the MSD for Cu, Cl, C atoms. As suggested by Gong et al.¹⁷, atomic displacements (essentially optical phonons) are important indicators of crystal rigidity, which is inversely proportional to the variation of electronic bandgap. Thus, this relation could be used to estimate the electron-phonon interactions within the two-dimensional perovskite structures. We have performed MD simulations to calculate the mean squared displacement (MSD) for Cl and Cu atoms, which respectively determine the valence band maxima and conduction band minima in the studied perovskites, along with a timeframe of 5 ps (Supplementary Fig. 7). For example, a

hybrid perovskite crystal that exhibits a slow molecular motion leads to a greater rigidity, and thereby results in weaker electron-phonon interactions. According to our MD simulations, we found that (MA) $_2CuCl_4$ and (EA) $_2CuCl_4$ exhibit a lower MSD value (<2 Å²) than (PMA) $_2CuCl_4$ and (PEA) $_2CuCl_4$ (>2 Å²), inferring that the electron-phonon interactions in the short-spacer copper hybrid perovskite crystals are weak.

Conclusion

In conclusion, we summarize that the synchronous emergence of the structural transition, optical signature, and electronic modulation are present in the A_2CuCl_4 single crystals under variable temperature using combined photoluminescence and high-resolution synchrotron spectroscopies. The high-resolution XAS spectra at Cu $L_{2,3}$ edge demonstrated that the implication of ligand size is clearly pronounced within the observed temperature range. Here, we observe peculiar linewidth variation of the d^9 and d^9L signature, involving the role of short-chain spacer (i.e. (MA) $_2CuCl_4$) as a function of temperatures. In the contrary, the opposite spectral weight transfer was found in the long-chain spacer (PMA) $_2CuCl_4$. Moreover, the reversal intensity ratio between d^9L and L_3 signal unambiguously suggests the presence of local-induced antiferromagnetic interaction between the neighboring Cu-inorganic sheets at 200 K.

Based on the temperature-dependent PL analyses, the hybrid compound with long conjugated organic ligand induces order-disorder structural phase transition resulting in the shift of

Fig. 7 Computed density of states of A_2CuCl_4 compounds. $(MA)_2CuCl_4$ (a), $(EA)_2CuCl_4$ (b), $(PMA)_2CuCl_4$ (c), and $(PEA)_2CuCl_4$ (d), respectively. Total DOS (black), C 1s and 2p (blue), Cu 3d (green), and Cl 3p (red). Majority (minority) spin represent by the positive (negative) DOS.

Table 1 Calculated lattice and geometrical parameters of $(MA)_2CuCl_4$, $(EA)_2CuCl_4$, $(PMA)_2CuCl_4$, and $(PEA)_2CuCl_4$.						
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>β</i> (°)	<i>d</i> _{Cu-Cl} (Å) ^a	∠ _{Cu-Cl-Cu} (°)
$(MA)_2CuCl_4$	7.534	7.394	10.283	111.4	2.332 (ap), 2.309 (eq), 2.924 (eq)	172.4
	7.257	7.350	9.959	111.2		
	7.155	7.424	9.814	110.9	2.311 (ap), 2.287 (eq), 2.902 (eq)	
$(EA)_2CuCl_4$	22.067	7.441	7.535	90	2.333 (ap), 2.291 (eq), 3.068 (eq)	161.9
	21.18	7.47	7.35	90	2.285 (ap), 2.277 (eq), 2.975 (eq)	169.7
					2.353 (ap), 2.277 (eq), 3.211 (eq)	157.2
$(PMA)_2CuCl_4$	7.806	7.419	33.834	90		
	7.59	7.38	31.30	90		
$(PEA)_2CuCl_4$	7.483	7.483	38.834	90	2.315 (ap), 2.301 (eq), 3.052 (eq)	162.0
	7.210	7.266	38.238	90	2.304 (ap), 2.288 (eq), 2.853 (eq)	169.1

^aap and eq stand for apical and equatorial bonds, respectively.
The referenced experimental values are also shown for comparison.

emission peak close to room temperature. As a result, we observe large Stokes shift manifests large separation of free excitons and self-trapped excitons emission signals. In addition, the Stoke difference becomes larger as the organic spacer size increases. We attribute such optical response can be realized by tuning the activation energy barrier among the abovementioned defect states. This finding suggests that the geometric constriction argument promotes reduced structural fluctuations that unambiguously present in a longer conjugated organic space, thus it improves the carrier lifetime extensively. To strengthen the findings, DFT calculations and MD simulations shared similar insight in which the anomalous behavior is mainly influenced by

the electronic properties of A_2CuCl_4 system due to the presence of large octahedral distortion. The future outcome from this study is promising since a tunable and yet correlated spin system can be realized via odd-even effects of the organic spacer. Further implication of this study is appealing to tailor the admixture spin singlet and triplet states towards the advancement of lead-free two-dimensional hybrid perovskites.

Methods

Synthetic growth of copper(II) hybrid-compounds. The method to grow $(PEA)_2CuCl_4$ perovskite single crystals were based on published literature⁵⁷. A solution of copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 1.70 g) in 10 mL of distilled

water was mixed with 2-phenylethylamine hydrochloride (PEA, $\text{C}_8\text{H}_{12}\text{NCl}$, 3.15 g) containing 3–4 mL of 32% HCl. The mixture was stirred and heated up to 70 °C to achieve a homogeneous solution. After one hour, the solution was cooled down naturally to room temperature after which the crystallization emerged. This process was repeated until good-quality single crystals were obtained. A similar procedure was carried out to fabricate $(\text{PMA})_2\text{CuCl}_4$, $(\text{EA})_2\text{CuCl}_4$, and $(\text{MA})_2\text{CuCl}_4$ by replacing the PEA precursor with PMA (phenylmethylamine hydrochloride, $\text{C}_7\text{H}_{10}\text{NCl}$, 2.86 g), EA (ethylamine hydrochloride, $\text{C}_2\text{H}_8\text{NCl}$, 1.67 g) and MA (methylamine hydrochloride CH_3NCl , 1.35 g), respectively.

XAS measurements. Temperature-dependent X-ray absorption spectra at Cu $L_{2,3}$ edge were examined within the photon energy range of 920–970 eV. A linearly polarized X-ray light was impinged onto a sample and the total electron yield method was implemented to collect the spectra. The measurements were performed under grazing incidence geometry, which can be varied by rotating the polar angle of the sample. The spectra were normalized to the integrated intensity spectra after subtracting an energy-independent background. The linear polarization factor of the X-ray beam was determined to be more than 90% with a photon energy resolution of 100 meV. XAS spectra were first normalized to the incident photon intensity (I_0) monitored by a refocusing mirror. The penetration depth of soft X-ray measured with the total electron yield method is generally obtained in 2–4 nm range set by the mean free path of low energy ($E < \sim 10$ eV) secondary electrons created in the scattering process⁵⁸. The temperature-dependent XAS measurements were carried out in the soft X-ray and ultraviolet (SUV) beamline of Singapore Synchrotron Light Source (SSLS)⁵⁹.

PL and optical absorption measurements. Temperature-dependent PL measurements were performed at a temperature range of 200–350 K using free-space excitation and collection through a visible-near-infrared microscope objective (5×, NA = 0.15). The samples were excited with a ps-pulsed ytterbium fiber laser emitting at a high harmonic generation of 266 ± 1 nm wavelength with 10 MHz repetition rate. Photoluminescence spectra were detected using thermoelectric-cooled Avaspec HERO spectrometer. Absorption spectra were obtained using ultraviolet-visible light (UV-Vis) spectrometer (Shimadzu, Model UV-2450).

X-ray diffraction measurements. High-resolution X-ray diffractometry characterization for the samples was performed at the X-ray Demonstration and Development beamline at SSLS. All diffraction measurements were carried out at room temperature. X-ray diffractograms data acquisition was done in two-axis mode with a step size of 0.02° over a Bragg angle range of 10–80°.

High-resolution X-ray photoemission measurements. Room temperature X-ray photoemission experiments were carried out in an ultrahigh vacuum chamber with a typical base pressure of 1×10^{-10} mbar in the Surface, Interface, and Nanostructure Science beamline at the Singapore Synchrotron Light Source. The photon energy of 60 eV was used to determine the valence band spectra. The photoemission spectra were acquired in normal emission geometry and collected using a VG Scienta R4000 analyzer^{60,61}.

Raman spectroscopy. The Raman vibration modes were measured using Alpha 300 R (WITec focus innovations) with an excitation wavelength of 532 nm and 37 μW continuous-wave laser at room temperature. The microscope objective has a numerical aperture of NA = 0.8 (Olympus 100×). The Raman microscope was operated at the diffraction limit with a laser spot size of fewer than 1 μm. The measurements were carried out in backscattering geometry.

DFT calculations. Spin-polarized calculations were performed with relaxed spin-multiplicity under the Kohn–Sham formulation^{62,63} as implemented in the Vienna Ab-initio Simulation Package (VASP)^{54,55}. The projector augmented wave (PAW) method^{56,64} was employed to describe the interaction between ion cores and electrons. The electron exchange-correlation was treated by the generalized gradient approximation (GGA) based on the Perdew–Burke–Ernzerhof (PBE) functional⁶⁵. A rotationally invariant GGA + U approach introduced by Dudarev et al.⁶⁶ was used with an effective Hubbard parameter U_{eff} being 7.5 eV for the Cu d orbital, as suggested by Cortecchia et al.¹⁵. The plane-wave basis sets with cut-off energy of 500 eV were employed for all calculations. Brillouin zone sampling centered at the Γ point was set to $2 \times 2 \times 2$, $1 \times 2 \times 2$, $2 \times 2 \times 1$, and $2 \times 2 \times 1$, respectively for $(\text{MA})_2\text{CuCl}_4$, $(\text{EA})_2\text{CuCl}_4$, $(\text{PMA})_2\text{CuCl}_4$ and $(\text{PEA})_2\text{CuCl}_4$. The conjugate gradient method was employed for cell optimizations and the calculations were considered to converge when the maximum forces on each atom were less than 0.01 eV/Å. During calculations, all atoms were allowed to fully relax. One monoclinic unit-cell of $(\text{MA})_2\text{CuCl}_4$ and one orthorhombic unit-cell of the corresponding $(\text{EA})_2\text{CuCl}_4$, $(\text{PMA})_2\text{CuCl}_4$, and $(\text{PEA})_2\text{CuCl}_4$ were used for the calculations. MD simulations were carried out with a time step of 1 fs within the NVT ensemble using the Nosé–Hoover thermostat as implemented in the VASP package. All atoms were allowed to equilibrate for 2 ps at a temperature of 300 K. Subsequent statistical sampling was then carried out for another 3 ps. Mean squared displacement (MSD) were obtained from the MD simulations using the following

formula:

$$\text{MSD}(t) = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \quad (1)$$

Data availability

All data generated or analyzed during this study are included in the published article and the Supplementary Information and are available from the corresponding authors upon reasonable request.

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Author contributions

A.A. and A.R. conceived the project. M.A. and D.O. synthesized the perovskite single crystals. A.D.F., X.Y., C.S.T., C.D., and A.R. performed X-ray absorption spectroscopy measurements. M.D.B. carried out photoluminescence and optical absorption experiments. A.A., X.Y., and C.S.T. carried out X-ray photoemission spectroscopy measurements. A.A. and M.F.S. carried out Raman scattering experiments. M.H.M. performed density functional theory calculations. G.S. calculated MD simulations. H.W. and A.T.S. W. contributed to the fruitful discussions. All the authors were involved in the discussion and manuscript preparation. All authors have given their approval for the final version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to A.A. or A.R.

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