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Crystal Engineering of a 2D Lead-free Perovskite with Functional Organic Cation by Second Sphere Coordination**

Daniele Cortecchia, Cesare Soci, Massimo Cametti, Annamaria Petrozza,* Javier Martí-Rujas*

Abstract: Hybrid lead-halide perovskite semiconductors are attracting increasing attention for applications in optoelectronics. However, the high lead content calls for the development of greener and smarter alternatives by crystal engineering, which is extremely challenging since the use of functional cations often results in the disruption of the metal-halide framework. Here we show the rational design of a new lead-free, copper based hybrid perovskite following a second sphere coordination approach. Our synthetic strategy allows the incorporation of an organic cationic fluorophore within the two-dimensional Cu-Cl framework of a layered copper perovskite. The functionalization results in a moisture stable and near-UV/blue emitting copper perovskite. Jointly with the possibility of extending the emission in the visible range by further synthetic design, our approach paves the way for the development of a new class of Pb-free perovskites with potential applications in solid-state lighting.

Over the last four years, lead halide hybrid perovskites have been attracting major interest for applications in photovoltaic energy conversion,^[1] photo-detection and light emission.^[2] In particular, light emitting devices (LEDs),^[3] field effect light emitting transistors (LE-FETs)^[4] and tunable lasers^[5] were realized recently. Most of these technologies, however, rely heavily on Pb-based

perovskites, such as methylammonium lead iodide (MAPbI₃) or cesium lead bromide (CsPbBr₃), and due to the toxicity and strict regulations of lead based products^[6,7] their commercialisation could be strongly hampered. This urges the development of alternative lead-free perovskites.^[8]

Copper-based layered perovskites, which were well known for their ferromagnetic properties,^[9] have been recently studied for their piezochromism,^[10] as lithium cycling material in hybrid electrodes^[11] and sensitizers in solar cells.^[12] While these studies focused on transport and magnetic properties of the metal-halide inorganic scaffold, inclusion of functional organic cations is similarly important to design new tailor-made smart functional materials.^[13] In this regard, pioneering works have achieved efficient electroluminescence in 2D lead perovskites combining the transport properties of the metal halide framework with the optical properties of an oligothiophene chromophore.^[14,15] However, the use of bulky organic building blocks represents a big challenge as the steric hindrance is likely to disrupt the layered 2D nature of the metal halide networks, resulting in perovskite structures with different dimensionality, such as 1D or 0D.^[16,17]

Crystal engineering principles aim at the rational design of solid materials by combining building blocks via self-recognition processes into new materials whose properties differ from those of the starting components. Up to certain extent, crystal engineering allows the synthesis and also to control functional properties of solid materials such as porosity, magnetism and conductivity. Self-assembling of metal ions and organic cations via second sphere coordination involving reversible hydrogen bonding interactions can be used to design new materials with functional properties.^[18] Second sphere coordination, also known as outer sphere, refers to any intermolecular interaction with the ligands directly bound to the primary coordination sphere of a metal ion.^[19] Hence, first sphere ligands can form second sphere adducts with virtually the whole range of non-covalent bonding interactions, such as coordination bonds, electrostatic, hydrogen bonding, halogen bonding, charge transfer and Van der Waals interactions. In recent years, development of hybrid metal organic materials self-assembled via second sphere coordination have shown potential applications in gas adsorption,^[20,21] separation^[22] and non-linear optical properties.^[23]

In this work, we apply crystal engineering by second sphere coordination interactions using charge assisted hydrogen bonds to synthesise a new type of moisture resistant “green” copper based hybrid metal-organic perovskite that incorporates an optoelectronically active organic cation. The solution-based synthesis is straightforward and can be carried out in short time. As opposed to standard perovskites, where the cation has merely a structural function, the crystal engineering strategy applied here allows incorporation of a functional cation within the perovskite scaffold, conferring UV/blue photoluminescence (PL) and improved moisture stability. Being amenable to easy synthetic design of the organic cation, the newly designed material is an ideal platform to achieve optical properties on-demand, with great potential as

[*] Dr. J. Martí-Rujas, Dr. Annamaria Petrozza, Daniele Cortecchia, Istituto Italiano de Tecnologia, Centre for Nano Science and Technology (CNST@PoliMi), Via Pascoli 70/3, 20133 Milan, Italy
E-mail: javier.rujas@iit.it, annamaria.petrozza@iit.it

Prof. Dr. Cesare Soci, Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore

Daniele Cortecchia, Interdisciplinary Graduate School, Energy Research Institute at NTU, 639798 Singapore

Energy Research Institute @ NTU (ERI@N), Research Technoplane, Nanyang Technological University, Nanyang Drive, 637553 Singapore

Prof. Dr. Massimo Cametti, Dipartimento di Chimica Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Via Mancinelli 7, 20131 Milan, Italy.

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alternative lead-free perovskite for light emitting applications.

Figure 1. Synthesis of the 2D perovskite using the organic building block **L** and CuCl_2 (a). Perovskite **1** yellow powders (b) and SEM picture of a cluster of perovskite micro-crystals showing the plate-like crystal habit (scale bar = 5 μm).

Instead of using 4,4'-bipyridine, which is known to form similar type of 2D perovskite-like structures,^[24] we chose here the organic building block 4,4'-(1,1'-biphenyl-4,4'-diyl)di(4-aminophenyl) ether (**L**). This ligand, having a rigid rod-like geometry (*ca.* 19 Å length), can be seen as composed of a conjugated oligoaromatic core (the biphenyl group) linked to two aniline anchoring units (Figure 1a). These confer the ditopic nature and increase the hydrophobicity of the ligand thanks to their aromatic nature, balancing the hydrophilicity of the amino groups. In addition, the ether bridges and the biphenyl core allows the torsional flexibility to accommodate this bulky ligand in the final perovskite stabilising the layered structure. The single crystal X-ray (SC-XRD) structure of **L** shows the predisposition of the ligand to pack giving both $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ stacking interactions and the hydrophilic nature of the amino-groups coordinating water molecules in the hydrated structure (Figure S1).

By reacting in ambient atmosphere the pre-formed organic salt $[\text{H}_2\text{L}]\text{Cl}_2$ ^[25] (Figure S2, Supporting Information) with CuCl_2 in acid (*i.e.*, HCl) DMSO solution, a yellow fine powder was instantly obtained (Figure 1a, b). As shown by the SEM images, microcrystals with plate-like shape were obtained (Figure 1c). Single crystals of micrometric size were structurally characterized by SC-XRD, confirming the formation of the hybrid 2D perovskite with formula $[\text{H}_2\text{L}][\text{CuCl}_4]$ (**1**).

In the structure, in the asymmetric unit there is half cation and half $[\text{CuCl}_4]^{2-}$ anion, and there is no solvent included. The two amine groups in the organic cation are protonated and act as hydrogen bond donors. By means of second sphere coordination interactions, the organic ammonium groups interact with the $[\text{CuCl}_4]^{2-}$ metal ion via three $\text{N-H}\cdots\text{Cl}^-$ charge assisted hydrogen bonds with N-Cl distances ranging from 3.174 Å to 3.282 Å and $\text{N-H}\cdots\text{Cl}^-$ angles going from 145° to 169°, forming a well-defined organic layer (Figure 2a). The molecular packing in the hybrid material induces a nearly perfect planar conformation of the biphenyl (torsion angle = 2.718°), which allows the maximum electronic delocalization between the adjacent aromatic rings.^[26]

Regarding the inorganic part of the structure, $[\text{CuCl}_4]^{2-}$ units are arranged by alternating $\text{Cu}\cdots\text{Cl}-\text{Cu}$ bridges which ultimately forms an infinite 2D layer extending along the *bc* plane where each Cu(II) center adopts an octahedral coordination geometry, distorted by an evident Jahn-Teller effect. In fact, the distances are Cu-Cl1 (2.284 Å, 2.283 Å and 2.293 Å) while the longest one is the Cu-Cl2 (2.884

Å). The two longest distances correspond to the chloride-bridged Cl-

Figure 2. Crystal structure of the 2D hybrid perovskite **1** showing the layered nature (a). Enlarged view of the layered nature of the inorganic part of the second sphere adduct (b). Detailed view of part of the structure of **1** showing the second sphere charge assisted hydrogen bonding interactions established among the $-\text{NH}_3^+$ groups and the chloride ligands in the first sphere (c). Charge assisted hydrogen bonding interactions are shown in black dash lines. Colour code: carbon (orange); oxygen (red); nitrogen (blue); copper (brown); chloride (green); hydrogen (white).

μ -Cl bond. An important aspect is that the 2D perovskite can also be prepared as powders homogeneously. The X-ray powder diffraction pattern of the bulk powder is the same as that simulated from single crystal X-ray data indicating that the powder material has the same structure as the single crystal (Figure S3a).

Interestingly, the $\text{N-H}\cdots\text{Cl}^-$ charge assisted hydrogen bonds are strong enough to overcome the hydrogen bonding with water molecules (observed in the free ligand **L**, Figure S1 Supporting Information) obtaining a completely water-free material. The second sphere interactions, together with the aromatic character of the ligand, contribute to strongly protect the final material against

moisture, which is generally detrimental for the hybrid perovskite stability.^[27] Moreover, as observed in other iso-structural Pb-based compounds, the intrinsic layered structure of the 2D perovskite shall contribute to further obstruct water diffusion in the material as compared to the standard 3D perovskites.^[28] Indeed, this was confirmed by exposing the perovskite powders to air for one month, which did not cause significant changes in the powder X-ray diffraction pattern of the material (Figure S3).

The observed octahedral distortion is in agreement with the Cu^{2+} electronic configuration $3d^9$ ($t_{2g}^6 e_g^3$), particularly prone to undergo Jahn-Teller distortion in an octahedral crystal field. The coordination complex $[\text{CuCl}_6]^{4-}$, with distorted octahedral coordination, is therefore characterized by a series of $d-d$ transitions based on Cu^{2+} , schematically shown in Figure 3a, originating a broad absorption band in the near infrared region (NIR) between 8000-1600 cm^{-1} (625-1250 nm), Figure 3b.

Figure 3. Optical characterization of **1** in the NIR region. (a) Schematic energy diagram for a distorted octahedral coordination (D_{4h} symmetry) and corresponding allowed electronic transitions. (b) Details of $d-d$ transitions in the range 8000-1600 cm^{-1} (625-1250 nm) and principle component fitting showing the three electronic transitions contributing to the broadband NIR absorption in **1**.

Analysis of this broad band by principal component fitting yields the contribution of three components. These bands, peaking at 10893 cm^{-1} , 12281 cm^{-1} and 13286 cm^{-1} are respectively assigned to the electronic transitions $\text{Cu}_{d_{xz,yz}} \rightarrow \text{Cu}_{d_{x^2-y^2}}$, $\text{Cu}_{d_{xy}} \rightarrow \text{Cu}_{d_{x^2-y^2}}$, and $\text{Cu}_{d_{z^2}} \rightarrow \text{Cu}_{d_{x^2-y^2}}$,^[12,29] in agreement with the orbital energy levels of a d^9 configuration in octahedral field (O_h) and z-out distortion (D_{4h}) (Figure 3a). Accordingly, the coordination complex $[\text{CuCl}_6]^{4-}$ shows a splitting of the e_g levels $\Delta_e = 10893 \text{ cm}^{-1}$, $10Dq = 12281 \text{ cm}^{-1}$ and crystal field stabilization energy $\text{CFSE} = 0.6 \cdot 10Dq = 88.1 \text{ kJ/mol}$, which is in agreement with the values previously reported for similar hybrid copper perovskites.^[29,30]

The presence of the optoelectronically active building block H_2L^{2+} in the structure of the 2D perovskite prompted us to study the photoluminescence properties of **1**. Figure 4a shows the transformed Kubelka-Munk function $F(R)$ obtained from the powder reflectance R according to the equation $F(R) = (R-1)^2/2R$ (Figure S4, Supporting Information), which gives a spectrum proportional to the absorption coefficient of the material. The spectrum of the 2D perovskite **1** features two main absorption bands: one below 350 nm and a second peaking at 380 nm, with a shoulder at 440 nm. The latter, with a direct band-gap of 464 nm (2.67 eV, Figure S4d, Supporting Information) can be attributed to ligand-to-metal charge transfer (CT) transitions, in agreement with similar copper perovskites.^[12,31,32] Such CT states occur between the first sphere coordination ligands (Cl) and the highest antibonding of the d orbitals based on copper, and can be expressed as $\text{Cl}_{p\sigma} \rightarrow \text{Cu}_{d_{x^2-y^2}}$ and $\text{Cl}_{p\pi} \rightarrow \text{Cu}_{d_{x^2-y^2}}$. Conversely, the higher energy band fits well the absorption of $[\text{H}_2\text{L}]\text{Cl}_2$, with a band gap of 326 nm (3.80 eV, Figure 4a and S4b, Supporting Information), and can be assigned to electronic transitions in the organic component.

Figure 4. (a) Transformed powder reflectance spectrum of the organic salt precursor $[\text{H}_2\text{L}]\text{Cl}_2$ (red) and **1** (black). Photoluminescence properties of (b) $[\text{H}_2\text{L}]\text{Cl}_2$ and (c) **1**: photoluminescence (PL) spectrum at $\lambda_{\text{exc}} = 280 \text{ nm}$ (green) and photoluminescence excitation spectrum (PLE) at $\lambda_{\text{probe}} = 360 \text{ nm}$ (blue). (d) chromaticity coordinates (CIE 1931) of $[\text{H}_2\text{L}]\text{Cl}_2$ and **1**.

Moreover, $[\text{H}_2\text{L}]\text{Cl}_2$ shows bright photoluminescence peaked at 343 nm, with full width at half maximum $\text{FWHM} = 45 \text{ nm}$ and stoke shift of 17 nm (Figure 4b), in good agreement with the fluorescence of biphenyl and biphenyl derivatives.^[33, 34, 35, 36] Interestingly, the photoluminescence properties of the organic ligand are retained upon self-assembly of the perovskite framework: under excitation wavelength of 280 nm, the hybrid perovskite **1** shows

fluorescence with $\lambda_{\text{max}} = 336$ nm (Figure 4c). This emission is largely blue-shifted compared to the perovskite CT transitions, and therefore cannot be associated to emission from the perovskite band-edge (464 nm).

On the other hand, the excitation spectrum (λ_{em} 360 nm) measured in the perovskite (Figure 4c) perfectly matches the excitation spectrum of the organic salt $[\text{H}_2\text{L}]\text{Cl}_2$ as well as its absorption spectrum (Figure 4a, b), indicating the successful functionalization with the organic cation. The slight blue shift (7 nm) and narrowing (full width at half maximum -FWHM- decreases of 9 nm) of the emission band in the perovskite may be attributed to the different packing of the H_2L^{2+} cations in the constrained perovskite lattice. In fact, the molecular packing was found to vary in the three crystals based on the **L** ligand (Figure S4, Supporting Information). This involves slight differences in the torsion angle of the biphenyl (with consequent change in electronic delocalization) and modifications in the intermolecular forces holding the crystal (C-H... π and π ... π stacking interactions), which are likely to affect the collective excited state of the resulting solid.

The emission spectra from both the materials contain a visible component giving a nearly pure blue colour with CIE coordinates (0.148 ; 0.099) for $[\text{H}_2\text{L}]\text{Cl}_2$ and (0.125 ; 0.155) for the perovskite **1** (Figure 4d and Figure S6, Supporting Information). However, the main emission of the perovskite **1** falls in the UV-A range (320-400 nm), which is a challenging spectral region to cover with traditional semiconductors and is currently reached with AlGaIn quantum wells (<365 nm)^[37] and nanostructured ZnO in the near-UV/blue region.^[38] Ultraviolet LEDs are typically fabricated with these materials for applications in high density information storage, chemical biological analysis, or combined with phosphore mixtures to generate white light with high CRI (colour rendering index) values suitable for indoor applications.^[39, 40, 41] While the luminescence properties of **1** are potentially suitable for such a down-conversion approach, the possibility to chemically engineering the organic cation also allows the tuning of the optoelectronic properties of the hybrid material with the possibility to span across the visible spectrum, increasing its relevance for applications in solid-state lighting. For example, the biphenyl could be easily functionalized with nitro and sulfonate group to modulate its luminescence, or the conjugation increased including carbazole and anthracene derivatives, placing **1** as the first member of a big family of functional hybrid, lead-free perovskites.

In summary, we have shown the rational synthetic design of a new hybrid copper perovskite through second sphere coordination approach. The new layered material **1** is based on 4,4'-(1,1'-biphenyl-4,4'-diyl)dioxy)dianiline as organic building block and combines for the first time a two-dimensional copper chloride framework with an optoelectronically active bulky cation, achieving near-UV/blue photoluminescence and moisture resistance in the resulting hybrid. This study paves the way for the development of a new class of lead-free hybrid perovskites incorporating functional cations and allowing the tuning of optical properties through synthetic design by exploitation of second sphere coordination interactions. These characteristics make hybrid functional copper perovskites a valuable alternative to Pb-based perovskites, with great potential for applications in solid-state lighting.

Experimental Section

Single crystal X-ray diffraction experiments were carried out with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with a focusing mirror (Cu K α radiation, $\lambda = 1.54056$ Å).

Single-crystal XRD data for **L**: $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3$, $M_r = 384.42$, monoclinic, $P-1$, $a = 5.6806(6)$ Å, $b = 7.9232(8)$ Å, $c = 21.668(2)$ Å, $\alpha = 93.567(7)^\circ$, $\beta = 97.413(7)^\circ$, $\gamma = 90.187(7)^\circ$, $V = 965.16(17)$ Å³, $T = 296(2)$ K, $Z = 2$, $\rho_{\text{calcd}} = 1.323$ g cm⁻³, 3331 reflns measured, 2542 indep. reflns, 262 parameters, 0 restraints, $2.060^\circ < \theta < 66.367^\circ$, $R_1 [I > 2\sigma(I)] = 0.0845$ and $wR^2 [I > 2\sigma(I)] = 0.2909$.

Single-crystal XRD data for $[\text{H}_2\text{L}]\text{Cl}_2$: $\text{C}_{28}\text{H}_{34}\text{Cl}_2\text{N}_2\text{S}_2$, $M_r = 597.58$, triclinic, $P-1$, $a = 5.6713(5)$ Å, $b = 8.2899(7)$ Å, $c = 15.9733(14)$ Å, $\alpha = 85.385(7)^\circ$, $\beta = 81.832(7)^\circ$, $\gamma = 78.316(6)^\circ$, $V = 726.92(11)$ Å³, $T = 150(2)$ K, $Z = 2$, $\rho_{\text{calcd}} = 1.365$ g cm⁻³, 2459 reflns measured, 2107 indep. reflns, 175 parameters, 0 restraints, $2.799^\circ < \theta < 66.017^\circ$, $R_1 [I > 2\sigma(I)] = 0.0354$ and $wR^2 [I > 2\sigma(I)] = 0.0935$.

Single-crystal XRD data for **1**: $\text{C}_{24}\text{H}_{22}\text{Cl}_4\text{Cu}_1\text{N}_2\text{O}_3$, $M_r = 575.78$, monoclinic, $P2_1/c$, $a = 23.499(4)$ Å, $b = 7.4335(12)$ Å, $c = 7.0455(10)$ Å, $\beta = 97.462(12)^\circ$, $V = 1220.28(34)$ Å³, $T = 296(2)$ K, $Z = 4$, $\rho_{\text{calcd}} = 1.567$ g cm⁻³, 2128 reflns measured, 1471 indep. reflns, 152 parameters, 0 restraints, $6.249^\circ < \theta < 66.637^\circ$, $R_1 [I > 2\sigma(I)] = 0.0986$ and $wR^2 [I > 2\sigma(I)] = 0.2641$.

CCDC Nos. for **L**, $[\text{H}_2\text{L}]\text{Cl}_2$, **1** are 1484918, 1484919 and 1484920, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. SI contains additional crystallographic data and photophysical characterization.

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Hybrid Metal-Organic Materials

Daniele Cortecchia,
Cesare Soci, Massimo
Cametti, Annamria
Petrozza,* Javier Martí-
Rujas* _____ **Page**

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Crystal Engineering of a
2D Lead-free Perovskite
with Functional Organic
Cation by Second
Sphere Coordination *

A new lead-free 2D Cu-perovskite has been synthesized using second sphere coordination interactions containing an optoelectronically active organic cation. The 2D-perovskite shows near-UV/blue photoluminescence and is stable under ambient conditions for months. The possibility to replace the organic ligand offers the opportunity to synthesize on-demand new functional hybrid metal-organic materials.

Supporting Information

Crystal Engineering of a 2D Lead-free Perovskite with Functional Organic Cation by Second Sphere Coordination**

Daniele Cortecchia, Cesare Soci, Massimo Cametti, Annamria Petrozza, Javier Martí-Rujas**

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Materials and methods

All the reagents were purchased from Sigma-Aldrich and used without further purification.

*Single crystal growth of **L** = 4,4'-(1,1'-biphenyl-4,4'-diylldioxy)dianiline:* Single crystals of **L** suitable for single crystal X-ray diffraction were obtained by slow evaporation (one week) of an ethanol solution (2 mg of **L** in 6 ml of ethanol) at room temperature.

*Synthesis of **[H₂L]Cl₂**,* 1 g of **L** was dissolved in 12 ml of DMSO, and 5 ml of HCl (37% wt) were added dropwise to the solution cooled with an ice-bath and under vigorous magnetic stirring. The reaction was left overnight, and the product recovered by precipitation and washed with ethanol. The resulting chlorinated salt **[H₂L]Cl₂** was recovered as powders with a yield of 55%. Single crystals were prepared by dissolving 100 mg of **[H₂L]Cl₂** in DMSO and exposing the solution to diethyl ether vapours inside a sealed container. Large single crystals of suitable size for X-ray diffraction were obtained after one week.

*Synthesis of **1** perovskite powders:* 100 mg of **[H₂L]Cl₂** were dissolved in about 10 ml of DMSO. Apart, 30.45 mg of CuCl₂ were dissolved in 2 ml of DMSO and then added dropwise to the 4,4'-(1,1'-biphenyl-4,4'-diylldioxy)dianilinium dichloride (**BPOA**)Cl₂ solution under vigorous magnetic stirring at room temperature. The solution was then acidified by adding 2 ml of HCl (37% wt). The addition causes the immediate formation of a yellow powder. After running the reaction for 12 h under vigorous magnetic stirring, the precipitate was recovered by washing with ethanol (x2) and diethyl ether (x2) and dried in vacuum at room temperature. The **1** yellow powder was collected with a yield of 74%.

Optical and morphological characterization: the synthesized powders were pressed and encapsulated within two fused silica windows and used for further characterization. Reflection spectra were measured on powders using a UV/VIS/NIR spectrophotometer (Lambda 1050, Perkin Elmer) equipped with integrating sphere (module 150mm InGaAs Int. Sphere), while the

photoluminescence emission and excitation spectra were measured with a NanoLog (Horiba Jobin Yvon) using 5 nm entrance and exit slits and 0.5s of integration time. CIE coordinates of the luminescence were calculated using the software LED ColorCalculator, OSRAM SYLVANIA. Morphological characterization was performed using a JEOL Scanning Electron Microscope JSM 6010LV equipped with tungsten filament source.

Single crystal X-ray diffraction data collection was carried out with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with a microfocusing mirror (Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$) and low temperature device (Oxford Cryosystems; 700 Series Cryostream Cooler). The crystal structures were plotted using the software Diamond.

High quality powder XRD data were recorded at ambient temperature on a Bruker D8 Advance diffractometer (reflection mode; CuK α ; $\lambda = 1.5406 \text{ \AA}$). The samples were mounted by loading them onto the sample holder without using any tape. The sample holder was spinning throughout all the experiment.

X-Ray Crystallographic Analysis

Figure S1 | Crystal structure of **L** = 4,4'-(1,1'-biphenyl-4,4'-diyl)diethanolamine viewed along the *a* axis (a) and *c* axis (b) showing the π - π stacking and CH- π interactions of the aromatic units. The crystals were isolated in hydrated form, and the structure shows the inclusion of water molecules interacting with the amino groups.

Figure S2 | Crystal structure of $[H_2L]Cl_2$ viewed along the a axis showing the packing of the L^{2+} cations through π - π stacking. The salt co-crystallized with the presence of dimethyl sulfoxide (DMSO), shown in the picture.

Figure S3 | XRPD of powders of **1** immediately after synthesis (a) and after one month of exposure in ambient condition (b). The perovskite preserved its crystallinity without decomposition, confirming the improved moisture resistance.

Photophysical Characterization

Figure S4 | Diffuse reflectance analysis of the powders of organic precursor $[H_2L]Cl_2$ (a, b) and hybrid perovskite **1** (c, d). Diffuse reflectance spectra (a, c) and transformed Kubelka-Munk function for band-gap determination (b, d).

The remission function $F(R)$ proportional to the absorption coefficient was determined from the powder reflectance spectra (Fig. S1a, c) using the Kubelka-Munk equation $F(R) = (1-R)^2/2R$. The direct band-gap of the semiconductors (E_g) were then identified from the transformed Kubelka-Munk function vs incident photon energy ($h\nu$) using the relation $(F(R)h\nu)^2 = A(h\nu - E_g)$ (Fig. S1b, d). The direct band-gaps resulted 3.80 eV (326 nm) for $[H_2L]Cl_2$ and 2.67 eV (464 nm) for the perovskite **1**.

Figure S6 | Blue photoluminescence from the perovskite **[H₂L][CuCl₄]** under excitation wavelength $\lambda_{\text{exc}}=280$ nm.