SUPPORTING INFORMATION

Role of Specific Distorted Metal Complexes in the Exciton Self-Trapping for Hybrid Metal Halides

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Synthesis

The metal halide materials have been synthesized by hydrothermal methods from mixtures of the chosen metal Cu (Merck, 99.7%) or Cd (Tougart and Matignon, 99%), *trans*-2,5-dimethylpiperazine (Alfa Aesar, 98%) and HCl (Alfa Aesar, 37%). The two compounds were synthesized by mixing 500 mg of cadmium (4.4 mmol) or copper (7.9 mmol), 500 mg of *trans*-2,5-dimethylpiperazine (4.4 mmol), and 3 ml of HCl 37%. The reactants were placed in a 23 mL Teflon-lined stainless-steel autoclave, heated to 180°C during 24 hours and slowly cooled down to room temperature at the rate of 10°C/h. Single crystals or/and powders were recovered by vacuum filtration.

Structure determination

Structure determinations were carried out from single-crystal X-ray diffraction with a Bruker-Nonius Kappa CCD diffractometer with monochromated Mo K α radiation and a crystal to detector distance of 60 mm. Absorption corrections were carried out with SADABS.¹ Direct methods were used to determine the crystal structures and were completed by Fourier difference syntheses with SIR2004.² The refinement of the crystal structures with anisotropic displacement parameters was carried out using SHELXL-2013.³ The CIFs were compiled with Olex2.12.⁴ Additional symmetry elements were checked with the program PLATON.⁵ Crystallographic data for these compounds are summarized in table S1.

NMR spectroscopy

¹¹³Cd NMR experiment was conducted on a 300 MHz (7 T) Bruker NEO spectrometer. The powder sample was packed in a 4 mm o.d. rotor. ¹H-¹¹³Cd CP-MAS (Cross-Polarization Magic Angle Spinning) spectrum was acquired with a contact time of 2 ms. MAS frequency was set to 2.5 kHz and the recycle delay to 1 s. ¹¹³Cd chemical shift is referenced to $Cd(ClO_4)_2$ at 0 ppm. 'dmfit' program was used for spectral simulation.⁶

¹³C and ¹⁵N NMR experiments were conducted on a 500 MHz (11.7 T) Bruker Avance III spectrometer. Powdered samples were packed in a 4 mm o.d. rotor. ¹H-¹³C and ¹H-¹⁵N CP-MAS spectra were acquired with a contact time of 3 ms. The recycle delay was set to 3 s for both ¹³C and ¹⁵N experiments. MAS frequency was set to 10 and 5 kHz for ¹³C and ¹⁵N spectra, respectively. ¹³C and ¹⁵N chemical shifts are referenced to TMS and NH₃, respectively.

Magnetic susceptibility measurements

The magnetic susceptibility measurements were performed on a Quantum Design SQUID MPMS-XL magnetometer housed at the Centre de Recherche Paul Pascal at temperatures between 1.8 and 400 K and *dc* magnetic fields ranging from -7 to +7 T. The measurements were carried out on polycrystalline samples (20.50 mg) introduced in a sealed polyethylene bag (typically $3 \times 0.5 \times 0.02$ cm; 23.02 mg). Prior to the experiments, the field-dependent magnetization was measured at 100 K in order to detect the presence of any bulk ferromagnetic impurities. Paramagnetic or diamagnetic materials should exhibit a perfectly linear dependence of the magnetization that extrapolates to zero at zero *dc* field which is the case for the present sample confirming the absence of any ferromagnetic impurities. The magnetic susceptibilities were corrected for the sample holder and the intrinsic diamagnetic contributions.

The magnetic susceptibility of (TDMP)CuCl₄ follows a Curie-Weiss law with an average *g* factor of 2.11(5) and a Weiss constant of -0.74(2)K indicating weak antiferromagnetic interactions between S = 1/2 Cu centers through the chloride bridges. A quantum S = 1/2 spin chain model (H = -2J $\Sigma(\mathbf{S}_i \cdot \mathbf{S}_{i+1})$) was used considering only the dichloride bridges as a magnetic pathway. This model gives a remarkably good theory/experience agreement with $J/k_{\rm B} = -0.56(1)$ K (and g = 2.11(5)) (Figure S14). Even if our model is slightly different than the one previously reported by Kersen et al.,⁷ the paramagnetic properties of (TDMP)CuCl₄ and the *g* (2.17) and $J/k_{\rm B}$ (-0.84 K) parameters are in good agreement.

UV/Visible and FTIR Spectroscopy

UV/Visible Spectroscopy. Diffuse reflectance spectra from 250 to 2500 nm were recorded on a Varian Cary 5G spectrophotometer using a 60 mm integrating sphere. Kubelka Munk function $(a/S = (1-R)^2/2R$ where *a* is the absorption coefficient, *S* the scattering coefficient and *R* the reflectance) was used to calculate absorbance from reflectance spectra.

FT-IR Spectroscopy. The materials were mixed with KBr and pressed into pellets. FT-IR spectra (100 scans) were collected with a Vertex 70 Instrument from 400 to 4000 cm⁻¹ and a resolution of 4 cm⁻¹. A background spectrum was subtracted from the collected spectra.

Photoluminescence

Photoluminescence spectra were collected using a Spex Fluorolog-3 spectrofluorometer from Instruments Jobin Yvon. 450W Xe light was used as excitation source. The variations of incident lamp flux and of the response of the photomultiplier were corrected for excitation and emission spectra, respectively. Photoluminescence Quantum Yields (PLQY) measurements are relative to the PLQY of SGA 550 100 isiphor® from Sigma Aldrich (exhibiting a PLQY near 95%). Time-resolved photoluminescence (TRPL) measurements were obtained with an excitation of 267 nm provided by a regenerative amplified femtosecond Ti:Sapphire laser system (Spectra Physics Hurricane X) frequency-tripled. Transient signals were recorded by means of a streak camera Hamamatsu C7700 coupled with a SP2300 imaging Acton spectrograph from Princeton Instruments.

DFT calculations

Molecular structures were optimized using Gaussian 16 Rev. A.03 suite of programs.⁸ Isolated octahedral units were optimized using DFT calculation for ground state and TD-DFT for excited state, immersed in pyridine and *n*-methylformamide-mixture respectively, by means of the Polarizable Continuum Model (PCM). The initial geometry (bond lengths and angles) of the octahedral units was the ideal one, with all bond Cd-Cl equal to 2.868 Å. Relaxed ground and excited states geometries were obtained without any imaginary frequency. The long-range corrected CAM-B3LYP functional⁹ was employed with the LANLDZ basis including a pseudopotential for inner electron for Cd and the 6-31+G** basis for Cl and Br.^{10–13}

Table S1. Crystallographic data for compounds (TDMP)MCl₄ (M = Cu or Cd).

	(TDMP)CuCl ₄	(TDMP)CdCl ₄
Space group	C2/c	C2/c
a/Å	14.5625(5)	15.2462(10)
b/Å	14.5977(5)	15.1744(9)
$c/\text{\AA}$	5.9349(1)	5.7267(2)
α/°	90	90
$\beta/^{\circ}$	107.284(2)	105.733(4)
$\gamma/^{\circ}$	90	90
Radiation	Μο Κα	Μο Κα
2Θ range for data collection/°	13 to 57.18	12.84 to 54.18
Reflections collected	12984	11969
Data/restraints/parameters	1519/0/61	1393/0/60
Goodness-of-fit on F^2	1.042	1.033
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0305$ $wR_2 = 0.0998$	$R_1 = 0.0265$ $wR_2 = 0.0757$
Largest diff. peak/hole / e Å ⁻³	0.85/-0.40	0.88/-0.47

Table S2. Comparison of bond lengths (Å) of TDMP in the salt (TDMP)Cl₂,¹⁴ and (TDMP)CdCl₄.

	(TDMP)Cl ₂	(TDMP)CdCl ₄	
C _{methyl} -C _{cycle1}	1.5151(9)	1.5087(27)	
C _{cycle1} -C _{cycle2}	1.5346(17)	1.5105(24)	
C _{cycle1-} N _{cycle}	1.5026(8)	1.5000(24)	
C _{cycle2-} N _{cycle}	1.5063(9)	1.4857(23)	

Table S3. Atomic positions for (TDMP)CuCl₄.

Atoms	x/a	у/b	z/c
C2	0.34885(9)	0.25157(10)	0.6387(2)
C3	0.36523(13)	0.40903(11)	0.4962(4)
C4	0.31071(9)	0.32021(9)	0.4429(2)
Cl1	0.33014(2)	0.08833(2)	0.11949(5)
Cl2	0.5	-0.06741(3)	0.25
C13	0.5	0.24315(3)	0.25
Cu1	0.5	0.08853(2)	0.25
H1A	0.3169	0.12609	0.71207
H1B	0.30152	0.13809	0.46277
H2A	0.41599	0.23925	0.65523
H2B	0.34496	0.27736	0.78622
H3A	0.33411	0.45412	0.38106
H3B	0.36653	0.42988	0.65055
H3C	0.42984	0.3998	0.49105
H4	0.31852	0.29491	0.29678
N1	0.29384(7)	0.16421(8)	0.59146(19)

Atoms	x/a	y/b	z/c
C2	0.15803(12)	0.25154(12)	-0.1503(3)
C3	0.31017(12)	0.18150(12)	-0.0500(3)
C4	0.36035(16)	0.09537(13)	0.0142(5)
Cd1	0	0.09457(2)	0.25
Cl1	0	0.07748(3)	-0.25
Cl2	0.17741(3)	0.08773(3)	0.38394(7)
Cl3	0	0.25817(4)	0.25
H1A	0.19008	0.13035	-0.21749
H1B	0.19882	0.14331	0.03679
H2A	0.16568	0.27553	-0.30056
H2B	0.09368	0.23993	-0.17335
H3	0.32185	0.2046	-0.19849
H4A	0.35577	0.07588	0.16994
H4B	0.42332	0.10349	0.01967
H4C	0.33389	0.05193	-0.10618
N1	0.20958(10)	0.16758(9)	-0.0942(3)

Table S4. Atomic positions for (TDMP)CuCl₄.



Figure S1. Powder X-ray diffraction patterns of (a) (TDMP)CuCl₄ (red asterisk: unknown impurity phase) and (b) (TDMP)CdCl₄ at room temperature.



Figure S2. FTIR spectra of (a) (TDMP)CuCl₄ and (b) (TDMP)CdCl₄ at room temperature.



Figure S3. EDX analysis of (a) (TDMP)CuCl₄ (Ratio 1/4.3 for Cu /Cl) and (b) (TDMP)CdCl₄ (Ratio 1/4.0 for Cd/Cl).



Figure S4. Representations of the metal chloride ladders in the crystal structures of (TDMP)CuCl₄ and (TDMP)CdCl₄.



Figure S5. Comparison of the ladders structure of cadmium/copper vs. lead chloride compounds.



Figure S6. ¹H-¹¹³Cd CP-MAS (2.5 kHz) NMR spectrum of (TDMP)CdCl₄ and its simulation by a single line at 181 ppm. The chemical shift anisotropy is 157 ppm and the asymmetry parameter is 0.79. The weak and broad line at ~200 ppm is attributed to a low amount of cadmium chloride impurity.



Figure S7. Temperature dependent photoluminescence mapping of (TDMP)CdCl₄.



Figure S8. Evolution of PL intensity integrated between 348 and 600 nm with temperature for (TDMP)CdCl₄.



Figure S9. Thermal analysis of (a) (TDMP)CuCl₄ and (b) (TDMP)CdCl₄ under air.



Figure S10. Evolution of the yellow emission of (TDMP)CdCl₄ with temperature ($\lambda_{exc} = 346$ nm).



Figure S11. Local environments of the TDMP²⁺ cations for (a) (TDMP)CdCl₄, and (b) (TDMP)PbCl₄ (For this compound, TDMP²⁺ cannot be localized by X-ray diffraction but solid-state NMR suggest a localization between the ten halide ions highlighted in black).



Figure S12. Kubelka-Munk spectra of (TDMP)CuCl₄ at room temperature.



Figure S13. ¹H-¹⁵N CP-MAS NMR spectra of (TDMP)CdCl₄ and (TDMP)PbCl₄. (TDMP)CdCl₄ exhibits a single line at 54 ppm whereas (TDMP)PbCl₄ exhibits two lines. This difference could originate from small differences in the hydrogen bond networks. In (TDMP)CdCl₄, the two hydrogen atoms of the NH_2^+ group bond with two bromine atoms belonging to the same crystallographic site. In contrast, in the case of (TDMP)PbCl₄, the two bromine atoms belong to two different crystallographic sites.



Figure S14. Temperature dependence of the χT product (where χ is the molar magnetic susceptibility that equals *M/H* per mole of (TDMP)CuCl₄) collected in an applied dc magnetic field of 0.1 T. The solid line is the best fit considering a quantum $S = \frac{1}{2}$ spin chain model (see text),

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