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Hydrogen Bonding and Broad-Band Emission in Hybrid Zinc Halide Phosphors

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ABSTRACT. In Solid-State Lighting (SSL) applications, hybrid zinc halide phosphors is a promising family as they meet specific criteria such as high color rendering, low-cost and non toxicity. However, contrary to hybrid lead halide phosphors, the quantum efficiencies are low and the origin of this luminescence remains unclear. To unravel this origin and provide new insights on the enhancement of this emission, four hybrid zinc halides have been investigated. These four compounds exhibit similar crystal structures but different photoluminescence properties. We show that the photoemission requires the formation of V_k centers which can be promoted by specific hydrogen bonding. We anticipate that the selection of specific environment for the zinc halide units could lead to a promising family of low-cost and environmentally friendly phosphor for SSL.

In Solid-State Lighting (SSL), the demand for new phosphors has been rising strongly in the past years owing to their important role in Light-Emitting Diodes (LEDs). By replacing inefficient incandescent and fluorescent lighting sources, this technology is expected to greatly reduce electrical consumptions for lighting.^{1,2} The most common approach of creating white light consists in using broad-band phosphor to convert blue or UV light generated by a LED. In addition of being efficient (high quantum yield, high color rendering, ...), such phosphor should be non toxic and environmentally friendly. Recently, low-dimensional hybrid lead halide perovskites have shown to be promising intrinsic white phosphor. However, the presence of lead leads to important toxicity and environmental issues. For this reason, we investigated hybrid zinc halides to analyze the origin of the luminescence and give new insights on its possible enhancement. Photoluminescence from hybrid zinc halides has previously been reported but its origin remains under debate.³⁻⁸ Thus, Bushuev et al. reported the luminescence to originate from intra-ligands transitions,⁵ while Yangui et al. reported a luminescence from excitons localized in the organic molecules and self-trapped excitons.⁸ The latter assignment of the white emission is similar as the ones commonly reported in hybrid lead halide perovskites.^{9,10} Thus, not only hybrid zinc halides are interesting as lead-free white phosphor for SSL applications, but a better understanding of the mechanism of broad-band emission is important to optimize the white emission of hybrid halides including the hybrid perovskites.

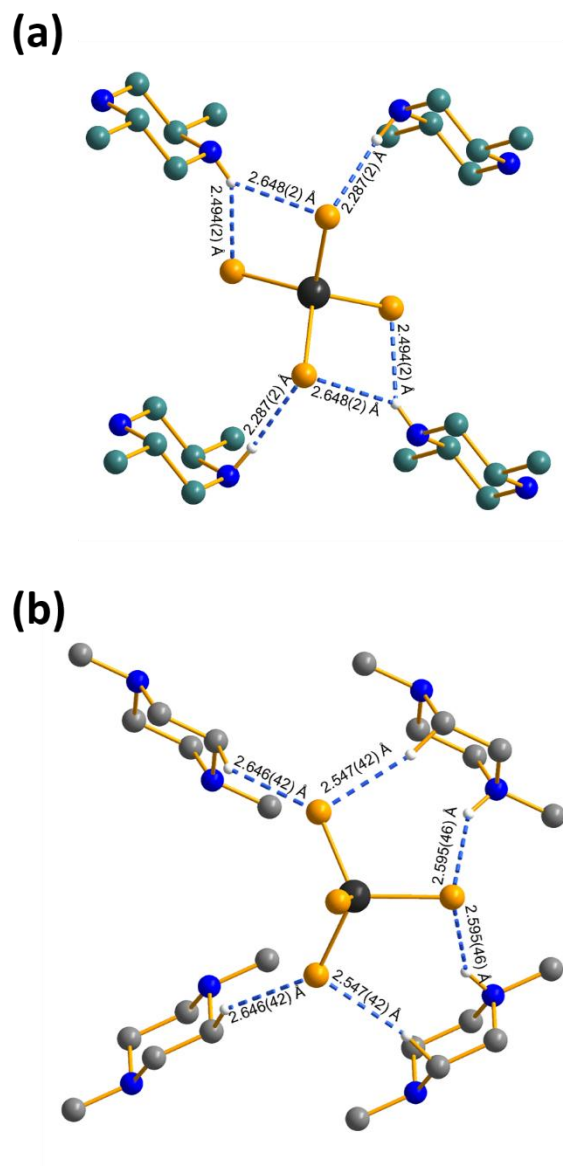


Figure 1. Analysis of estimated hydrogen bonding ($d_{\text{Cl-H}} < 2.8 \text{ \AA}$) for (a) $(2,5\text{-DMP})\text{ZnCl}_4$ and (b) compound $(1,4\text{-DMP})\text{ZnCl}_4$. Hydrogen atoms were included in the refinement model as riding atoms in idealized positions.

In this context, we synthesized two new hybrid zinc halide compounds (chloride and bromide) with trans-2,5-dimethylpiperazine (2,5-DMP). This organic molecule was previously used to synthesize 1D hybrid post-perovskite with record quantum yields of white photoluminescence among the hybrid lead halides.^{11–13} The synthesis is carried out under hydrothermal conditions from a mixture of zinc metal, HX (X= Cl or Br) and 2,5-DMP (see experimental section in SI).

Hybrid zinc iodides are rare in comparison to chloride and bromide analogues. Thus, the synthesis was focused on chlorides and bromides to better compare with previously reported zinc halides. The crystal structures of the resulting materials were determined by single-crystal X-ray diffraction (Table S1 and Figure S1). Both compounds are isostructural and crystallize in the space-group *C2/c*. The halide compounds are built of anionic $[\text{ZnX}_4]^{2-}$ tetrahedral units and cationic trans-2,5-dimethylpiperazinediium with a ratio 1:1. The presence of trans-2,5-dimethylpiperazinediium cations is also confirmed by FTIR spectroscopy (Figure S2). The bond lengths in the tetrahedral anionic units are $2.2546(12) \text{ \AA} < d_{\text{Zn-Cl}} < 2.2837(11) \text{ \AA}$ for (2,5-DMP)ZnCl₄ and $2.3965(6) \text{ \AA} < d_{\text{Zn-Br}} < 2.4248(6) \text{ \AA}$ for (2,5-DMP)ZnBr₄ (Table S2). The Cl-Zn-Cl angles range from $103.99(2)^\circ$ to $116.24(2)^\circ$ for (2,5-DMP)ZnCl₄ and $105.69(1)^\circ$ to $114.25(1)^\circ$ for (2,5-DMP)ZnBr₄. The crystal structures of these two isostructural compounds can be compared to the ones of zinc halides with 1,4-dimethylpiperazinediium cations (1,4-DMP) (Figure 1).^{14,15} Among the different organic molecules (e.g. piperazine, methylpiperazine, DABCO, ...) crystallizing with zinc halide tetrahedral units,¹⁶⁻¹⁸ compounds with 1,4-DMP have been selected because 1,4-DMP and 2,5-DMP have the same formula and differ only by the localization of the two -methyl groups on the piperazine. Secondary and tertiary ammonium groups are both strong N-H donors whereas C-H groups are relatively weak donors.¹⁹ This agrees well with the hydrogen bond lengths of our compounds estimated from single crystal X-ray diffraction (X--H shorter for N-H than C-H groups). In addition, the Zn-X bond lengths and X-Zn-X angles are similar when comparing (2,5-DMP)ZnCl₄ vs. (1,4-DMP)ZnCl₄ (chloride compounds) and (2,5-DMP)ZnBr₄ vs. (1,4-DMP)ZnBr₄ (bromide compounds). Thus, comparing the two series of compounds enables a direct comparison of the secondary and tertiary amines on the hydrogen bonding networks around the metal halide anions.

Concerning the photoluminescence properties, the compounds exhibit strong absorptions below 400 nm (Figure S3) and similar broad-band emissions with maxima between 470 nm and 520 nm (Figure 2) and large pseudo-Stokes shift as shown in the excitation vs. emission mappings (Figures S4-S7). However, despite the similar crystal structures, the photoluminescence quantum yields (PLQY) differ : 4%, 5%, 1% and < 1% for (2,5-DMP)ZnCl₄, (2,5-DMP)ZnBr₄, (1,4-DMP)ZnCl₄, and (1,4-DMP)ZnBr₄, respectively. Such values of PLQYs for broad-band emissions and the quenching of the luminescence with temperature (Figure S8) are similar to the ones previously reported for lead halide perovskites.^{20,21,10} As the emission wavelength depends on the nature of the halogen, and as the corresponding chloride and bromide salts of trans-2,5-dimethylpiperazine do not show any luminescence, one can deduce that the photoemissions do not arise from the organic molecules but from the zinc halide tetrahedral anions. In addition, time resolved photoluminescence performed for the chloride compounds shows decay times in the same time range ($\tau_{\text{mean}} = 1.5$ ns for (2,5-DMP)ZnCl₄, and $\tau_{\text{mean}} = 1.1$ ns for (1,4-DMP)ZnCl₄).

To unravel the origin of the luminescence from the inorganic [ZnX₄]²⁻ tetrahedral units, TD-DFT calculations were performed. After geometry optimization at the ground state, units with $d_{\text{Zn-Cl}} = 2.37$ Å and $d_{\text{Zn-Br}} = 2.54$ Å were obtained. The geometry optimization at the excited state leads to the deformation of the tetrahedral units with the lengthening of the four Zn-X bonds (Figure 3 and Figure S9). This deformation includes the formation of X₂⁻ molecular ion (V_k center) as the consequence of the charge transfer from a halogen to zinc. This is associated with a considerable shortening of X-X internuclear distances (From $d_{\text{Cl-Cl}} = 3.874$ Å in the ground state to $d_{\text{Cl-Cl}} = 2.693$ Å in the excited state for [ZnCl₄]²⁻ and from $d_{\text{Br-Br}} = 4.100$ Å in the ground state to $d_{\text{Br-Br}} = 2.919$ Å in the excited state for [ZnBr₄]²⁻). Interestingly, Martin et al. suggested

V_k -type centers to be responsible of the broad band emission in Rb_2ZnCl_4 and K_2ZnCl_4 but were not able to confirm their hypothesis.²² V_k centers have also been identified in other metal halides such as Cs_2HfCl_6 .²³

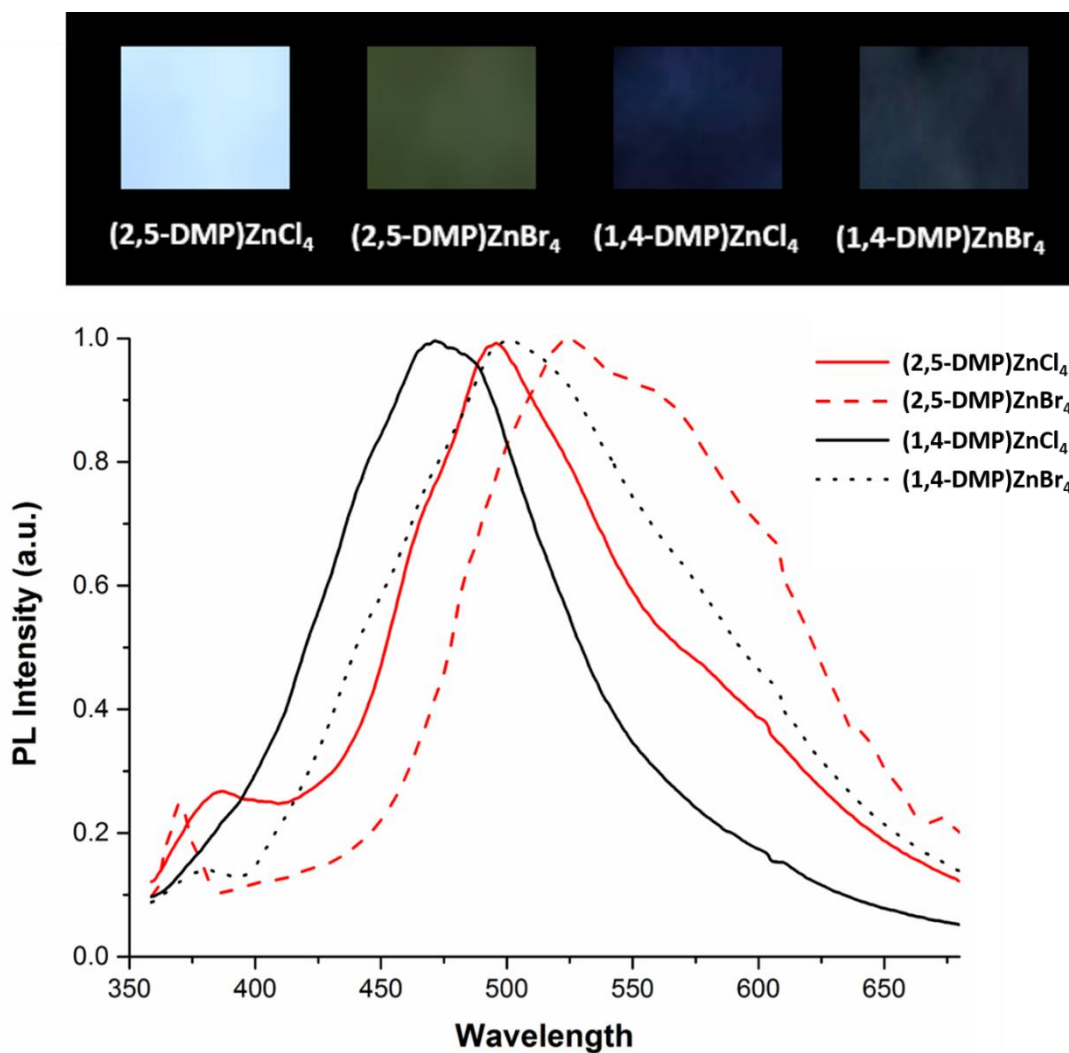


Figure 2. View of the luminescent compounds under excitation at 365 nm (top) and Photoluminescence emission spectra at 77K for compounds $(2,5\text{-DMP})ZnCl_4$ ($\lambda_{exc} = 320$ nm), $(2,5\text{-DMP})ZnBr_4$ ($\lambda_{exc} = 345$ nm), $(1,4\text{-DMP})ZnCl_4$ ($\lambda_{exc} = 290$ nm), and $(1,4\text{-DMP})ZnBr_4$ ($\lambda_{exc} = 310$ nm) (bottom).

$[\text{ZnX}_4]^{2-}$ interacts with its environment through hydrogen bonding. Such network has been reported to influence the optical and electronic properties of hybrid metal halides including hybrid perovskites.²⁴⁻²⁷ To investigate the hydrogen bonding network, we used a mechanically embedded two-layers Quantum Mechanics/Molecular Mechanics (QM/MM) hybrid approach called ONIOM, as implemented in Gaussian 16.²⁸ To limit excessive computation time, the eight nearest organic molecules embedding the $[\text{ZnCl}_4]^{2-}$ anion (localized according to the crystal structures) are optimized at a low level of theory (MM region) while the metal halide units are optimized at a high level of theory using a DFT approach for ground state and a TD-DFT approach for excited state (QM approach) (see Computational details). These optimizations were performed freezing the organic molecules (except the hydrogen atoms) and the Zn atom. The excited state systems were calculated for both organic molecules but only the 2,5-DMP- ZnCl_4 was successful. In the ground state, the four shortest (N-H)...Cl bond lengths range from 2.29 Å to 3.16 Å with a mean value of 2.66 Å. We can observe in Figure 3(c) that the V_k center, previously observed in our calculations for isolated $[\text{ZnX}_4]^{2-}$ units, occurs where the (N-H)...Cl bonds are the shortest. One can notice that the two chlorides involved in the V_k center are symmetrically equivalent as each of them interact with one proton of ammonium groups. Thus, the symmetry of the ground state is similar to the one of the excited state. Upon excitation, the short hydrogen bonds are weakened and the corresponding bond lengths increase significantly (Table S3 and Figure 3(c)) because the chlorides become weaker hydrogen bond acceptors (decrease of the electron density on chloride upon excitation as observed on Figure 3(a)). This increase of hydrogen bond lengths will promote the formation of the V_k centers. Thus, the shorter/stronger the hydrogen bonds are in the ground state, the more promoted the formation of V_k centers will be in the excited state. The results of the DFT calculation is also confirmed by an

analysis of the structures of previously reported hybrid zinc chloride phosphors as all of them exhibit short H...Cl bonds similar to the ones of compounds (2,5-DMP)ZnCl₄ ($d(\text{H}\dots\text{Cl})_{\text{min}} = 2.28 \text{ \AA}$) and (2,5-DMP)ZnBr₄ ($d(\text{H}\dots\text{Br})_{\text{min}} = 2.45 \text{ \AA}$). For example, $d(\text{H}\dots\text{Cl})_{\text{min}} = 2.28 \text{ \AA}$ has been reported for 2-(1-hydroxy-4,5-dimethyl-1H-imidazol-2-yl)pyridinium zinc chloride,⁵ $d(\text{H}\dots\text{Cl})_{\text{min}} = 2.35 \text{ \AA}$ for pyridoxalaminoguanidinium zinc chloride,⁶ and $d(\text{H}\dots\text{Br})_{\text{min}} = 2.61 \text{ \AA}$ for 4-aminopyridinium zinc bromide.⁸

By comparing the different structures of isostructural (2,5-DMP)ZnCl₄ / (2,5-DMP)ZnBr₄ vs. (1,4-DMP)ZnCl₄ or (1,4-DMP)ZnBr₄ and based on these DFT calculations, one can rationalize the differences of intensity of luminescence observed for the two series of compounds. In all crystal structures, the [ZnX₄]²⁻ anions interact with the organic cations through the network of hydrogen bonding. However, these hydrogen bondings differ for different organic molecules. With 1,4-dimethylpiperazinediium cations (Figure 1(b)), hydrogen atoms are localized in between halides and no short hydrogen bonds are observed. Such interactions would, consequently prevent the formation of X₂⁻ species. With trans-2,5-dimethylpiperazinediium cations, short hydrogen bondings tend to promote the creation of the V_k centers (Figure 1(a)). In addition, upon photoexcitation, the charge transfer from halogen to zinc (Figure 3 and Figure S9) leads the halides to lose their ability of being hydrogen acceptor. The shortest hydrogen bondings would also lengthen and, consequently, promote the formation of X₂⁻ species. As such hydrogen bonding enables a strong deformation at the excited states, a large pseudo-Stokes shift in photoluminescence spectra could be observed.²⁹

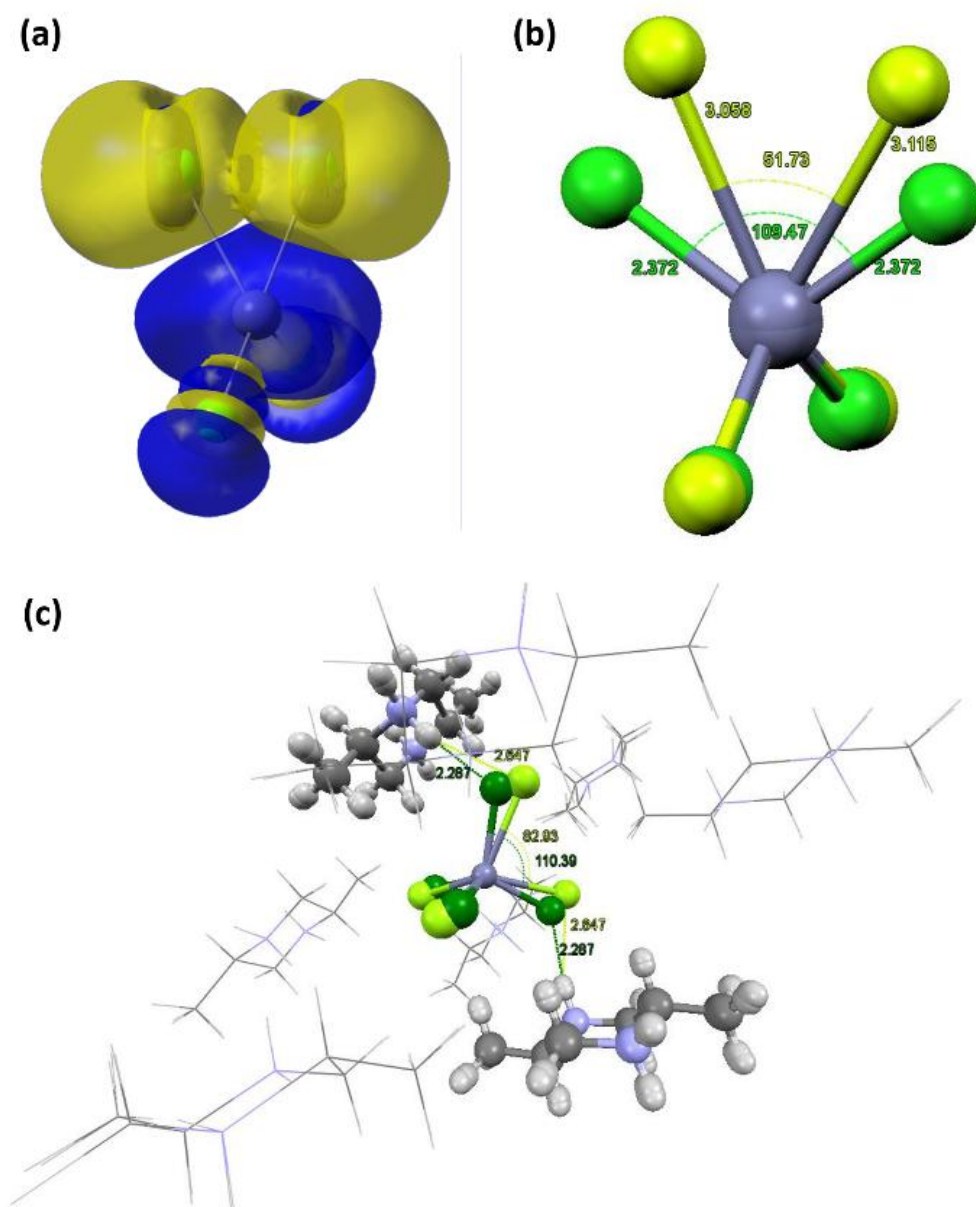


Figure 3. DFT and TD-DFT calculations of $[\text{ZnCl}_4]^{2-}$: (a) Change of electron density from the ground state to the excited state (decrease/increase of electron density in yellow/blue), (b) Optimized geometry in its ground state (green) and excited state (yellow) from TD-DFT calculations of the isolated anion, and (c) of the anion in environment of (2,5-DMP)ZnCl₄.

To confirm the role of the hydrogen bond strength on the formation of V_k centers, ^1H - ^{13}C CP-MAS NMR spectra were acquired. As one can observe on Figure 4, the NMR spectra depend on the halogen and on the organic molecule. For the *trans*-2,5-dimethylpiperazine molecule, in contrast to the bromide compound $(2,5\text{-DMP})\text{ZnBr}_4$, the spectrum of the chloride compound $(2,5\text{-DMP})\text{ZnCl}_4$ shows narrow lines exhibiting broadening at the bottom (wing). Such wings, easily visible for CH and CH_2 resonances (at ~ 50 and ~ 45 ppm, resp.), suggest higher mobility of the *trans*-2,5-dimethylpiperazine in $(2,5\text{-DMP})\text{ZnCl}_4$ than in $(2,5\text{-DMP})\text{ZnBr}_4$. For the 1,4-dimethylpiperazine molecule, the wing is even more pronounced (CH_2 resonance at ~ 52 ppm) in $(1,4\text{-DMP})\text{ZnCl}_4$. Finally, the organic is much more mobile in $(1,4\text{-DMP})\text{ZnBr}_4$ since no ^1H - ^{13}C CP-MAS signal was obtained. Thus, the mobility of the organic molecule follows the trend $(2,5\text{-DMP})\text{ZnBr}_4 < (2,5\text{-DMP})\text{ZnCl}_4 < (1,4\text{-DMP})\text{ZnCl}_4 < (1,4\text{-DMP})\text{ZnBr}_4$. The rigidity of the environment of the organic molecules is directly related to the hydrogen bond strength. Hence, the hydrogen bonding network is stronger following the trend $(2,5\text{-DMP})\text{ZnBr}_4 > (2,5\text{-DMP})\text{ZnCl}_4 > (1,4\text{-DMP})\text{ZnCl}_4 > (1,4\text{-DMP})\text{ZnBr}_4$. One can notice that this trend is the same as the one of measured PLQYs, confirming the link between the hydrogen bond strength and the resulting luminescence intensity.

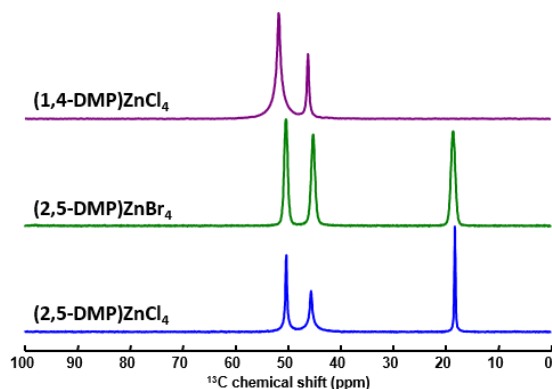


Figure 4. ^1H - ^{13}C CP-MAS NMR spectra of compounds $(2,5\text{-DMP})\text{ZnCl}_4$, $(2,5\text{-DMP})\text{ZnBr}_4$ and $(1,4\text{-DMP})\text{ZnCl}_4$. No signal is obtained for $(1,4\text{-DMP})\text{ZnBr}_4$.

In summary, the experimental and theoretical investigations of the ZnX_4 units provide new insights on the origin of the white luminescence by creation of V_k centers. Such mechanism might also be at the origin of broad-band emission in other metal halides compounds such as hybrid lead halide perovskites. Modifying the hydrogen bond network in the environment of zinc halide units enable for the enhancement of these optical properties. Thus, a future approach could consist in reinvestigating the physical properties of chemical systems in which the V_k centers could be favorably formed by specific hydrogen bonding.

ASSOCIATED CONTENT

Supporting Information. Experimental details, Tables S1-S2, Figures S1-S9 and details on the calculation of the activation energies.

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TOC SYNOPSIS

Four compounds exhibiting similar crystal structures with $[\text{ZnX}_4]^{2-}$ units but different photoluminescence properties have been investigated to unravel the mechanisms of photoemission of hybrid zinc halides. We show that the photoemission requires the formation of V_k centers which can be promoted by specific hydrogen bonding.

