

ESI Figure Captions:

Figure S 1: (a) Packing structure of 4-BAPC including the hydrogen bonds viewed along the b direction, (b) Hydrogen bonds type one, and (c) Hydrogen bonds type two.

Figure S 2: π ...Br interactions within the hybrid structure with the C...Br short contacts mapped on the Hirshfeld surfaces.

Figure S 3: (a): Hirshfeld surfaces of the different organic molecules mapped with shap index (black circles indicate C...H short contacts) and (b): C-H... π interactions between the organic moieties.

Figure S 4: Infrared spectrum of 4-BAPC in the range of 450-4000 cm^{-1} .

Figure S 5: Simultaneous thermogravimetric analysis and differential thermal analysis scan for $(\text{C}_6\text{H}_7\text{NBr})_3[\text{CdBr}_5]$.

Figure S 6: Zoomed band structure.

Figure S 7: Visualization of C...Br (a) and C...H (b) contacts, within the pur organic compound $\text{C}_6\text{H}_6\text{BrN}$, on the Hirshfeld surface and (c): different C-H... π and N-H... π interactions within the organic crystal $\text{C}_6\text{H}_6\text{BrN}$.

Figure S 8: Multi-peaks fitting of the PL spectra of $(\text{C}_6\text{H}_7\text{BrN})^+\cdot\text{Br}^-$ salt ($\lambda_{\text{exc}}=200$ nm)