† Electronic Supplementary Information (ESI)

Covalent Organic-Inorganic Layered 2D $CdCl_2$(n-hexylamine)$_2$ and Not Cd_2S_2(n-hexylamine)

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Table S1: Attempts to synthesize Cd_2S_2(n-hexylamine) lead to formation of Product 1-6. Detailed synthesis of Product-1 is discussed in the manuscript. Product 2-6 are prepared with the same precursor concentrations as in Product-1, but with difference either in reaction apparatus, or in heating time, or in cooling rate, as tabulated below.

Name	Apparatus	Heating time	Cooling rate
Product-1	Glass vessel in oil bath	30 minute	natural cooling
Product-2	Glass vessel in oil bath	30 minute	slow cooling ~ 2 ˚C/ hr
Product-3	Glass vessel in oil bath	6 hour	natural cooling
Product-4	Glass vessel in oil bath	48 hour	natural cooling
Product-5	Acid-digestion bomb in oven	48 hour	natural cooling
Product-6	Acid-digestion bomb in oven	48 hour	slow cooling ~ 2 ˚C/ hr

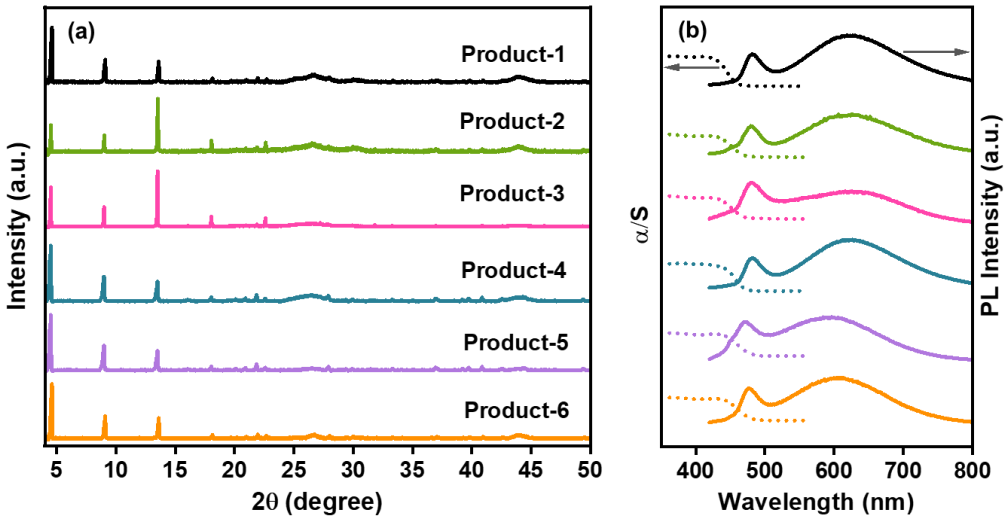

Fig. S1: Characterization of synthesized products 1-5 (see Table S1) by (a) Powder XRD and (b) optical absorption and PL spectra (λ_{ex} = 405 nm laser diode).

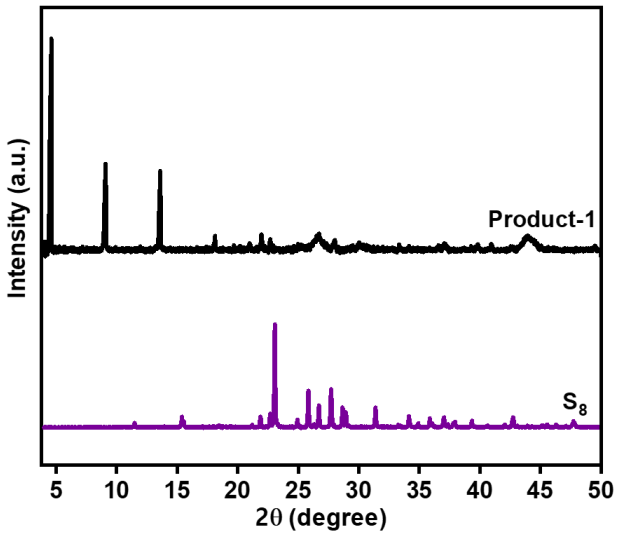

Fig. S2: Powder XRD of the Product-1 compared with that of the sulphur precursor.

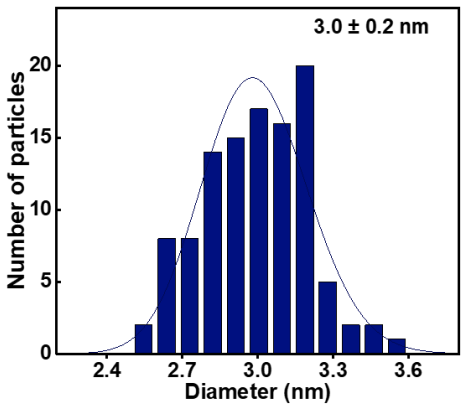

Fig. S3: Size distribution plot of CdS NCs separated from Product-1

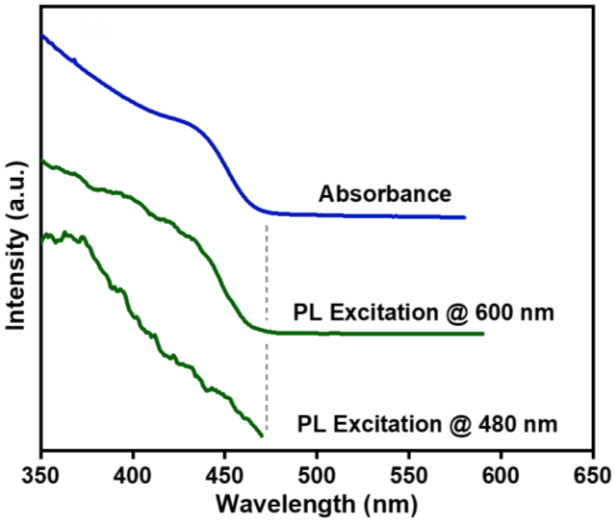

Fig. S4: UV-visible absorption spectrum of colloidal CdS NCs is compared with its PL excitation spectra measured at 480 nm (excitonic) and 600 nm (defect-related) emissions.

Table S2: Crystallographic data for $CdCl_2$(n-hexylamine)$_2$ obtained from single crystal XRD data collected at 100 K.

Empirical formula	$(C_6H_{13}NH_2)_2CdCl_2$
Formula weight (g/mol)	385.68
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal System	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 19.6125(16) Å, b= 5.5243(4) Å, c= 8.0101(7) Å, β= 90.068(3)º
Volume (Å^3)	867.86(12)
Z	2
Calculated density (g/cm^3)	1.476
F(000)	396
Crystal size	0.157× 0.136× 0.104 mm^3
$\theta_{min,max}$	2.077, 28.384
$h_{min,max}$ $k_{min,max}$ $l_{min,max}$	-26, 26 -7, 5 -10, 10
Absorption coefficient (mm^{-1})	1.551
Reflections collected	17561
Unique reflections/ No. parameters	2170/81
Goodness-of-fit	1.047
Final R indices (I>2σ (I))	R_{obs} = 0.0417, wR_{obs} = 0.0939
CCDC Number	2356630

Table S3: Bond lengths and angles involved in the hydrogen-bonding network of $CdCl_2$(n-hexylamine)$_2$.

Sl. No.	D-H -A	D – H(Å)	H...A(Å)	D...A(Å)	∠D - H...A/º
1	N1-H1A-Cl1	0.910	2.512	3.315	147.37
2	N1-H1B-Cl1	0.910	2.460	3.351	166.39

Covalent organic-inorganic PbI_2(4,4'-bipyridyl). The synthesis protocol is adapted based on ref 41 of the manuscript, after minor modifications. A solution of PbI_2 was made by adding 230 mg (0.5 mmol) PbI_2 in 1 mL dimethylformamide followed by sonication for 10 minutes. In a different vial, 78 mg (0.5 mmol) 4,4'-bipyridine was dissolved in 1 mL methanol. Then, the methanol solution of 4,4`-bipyridine was slowly injected to the PbI_2 solution along the walls

of the vial. A light yellow colored product precipitated out immediately, which was washed with ethanol three times and then with acetone.

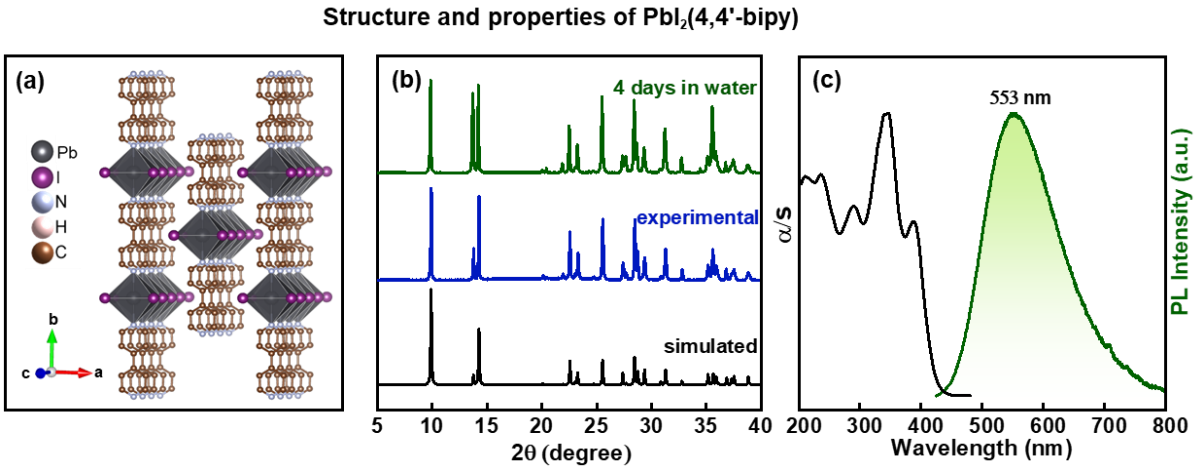

Fig. S5: (a) Packing diagram of PbI_2(4,4'-bipyridyl) as shown by single crystal XRD data reported in ref 41 of the manuscript. (b) Comparison of experimental powder XRD data of PbI_2(4,4'-bipyridyl) with the simulated pattern from reference data (ICSD 154548). Also, the powder XRD pattern of the sample remains unchanged after immersing the sample under water for 4 days. (c) UV-visible absorption and PL spectra of PbI_2(4,4'-bipyridyl) in the powder form. The absorption spectrum is obtained from the measured diffused reflectance spectrum by using Kubelka-Munk equation (see Experimental Section), where α is the absorption coefficient, and S is the scattering factor.

Synthesis of PbI_2(ethylenediamine)$_2$. Lead iodide (0.9 mmol, 414.9 mg,) was dissolved in 1.5 mL of ethylenediamine (solvent as well as reactant) by heating to ~70 ˚C rendering a transparent solution. The reaction mixture was then left to cool naturally to room temperature, resulting into the formation of a white precipitate. The precipitate was washed with ethanol and acetone, followed by drying in vacuum. The synthesized compound is confirmed to be PbI_2(ethylenediamine)$_2$ on comparison of the powder XRD pattern (Fig. S5) with that in prior literature (Ref. 43 of manuscript).

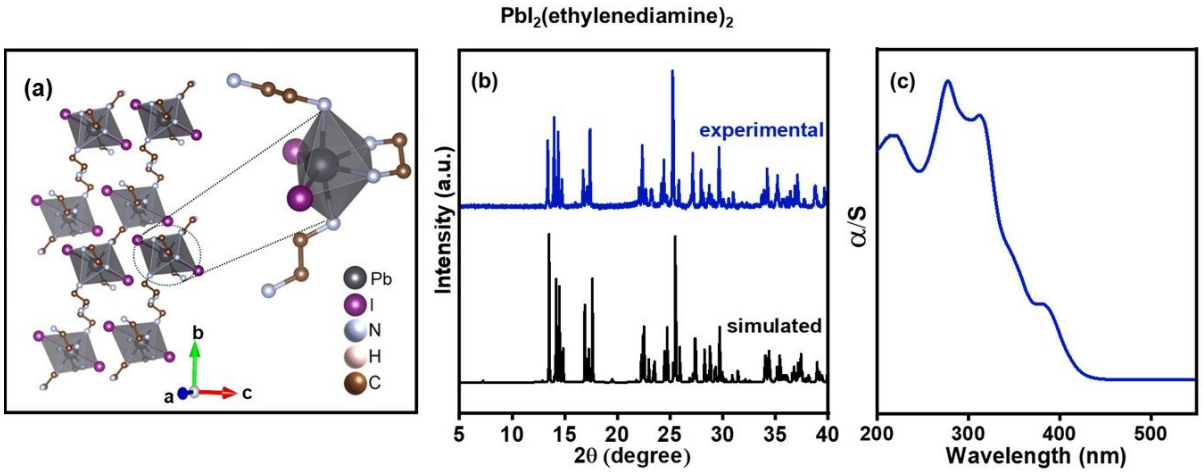

Fig. S6: (a) Packing diagram of PbI_2(ethylenediamine)$_2$ obtained from the single crystal XRD data reported in ref 43 of the manuscript. Pb is coordinated with two I and four N atoms. (b) Powder XRD patterns of PbI_2(ethylenediamine)$_2$ measured at room temperature compared to the simulated reference (ICSD 673646) pattern of the same compound at 123 K. (b) Optical absorption spectrum of PbI_2(ethylenediamine)$_2$ at room temperature. Experimentally measured diffused reflectance spectrum was converted to the absorption spectrum by using the Kubelka-Munk equation, where α is the absorption coefficient, and S is the scattering factor.