

# Crystalline solids with intrinsic quantum confinement

D. B. Mitzi, K. Chondroudis, C. R. Kagan, *Organic-inorganic electronics, IBM J. Res. Develop.* 45 (2001) 29.

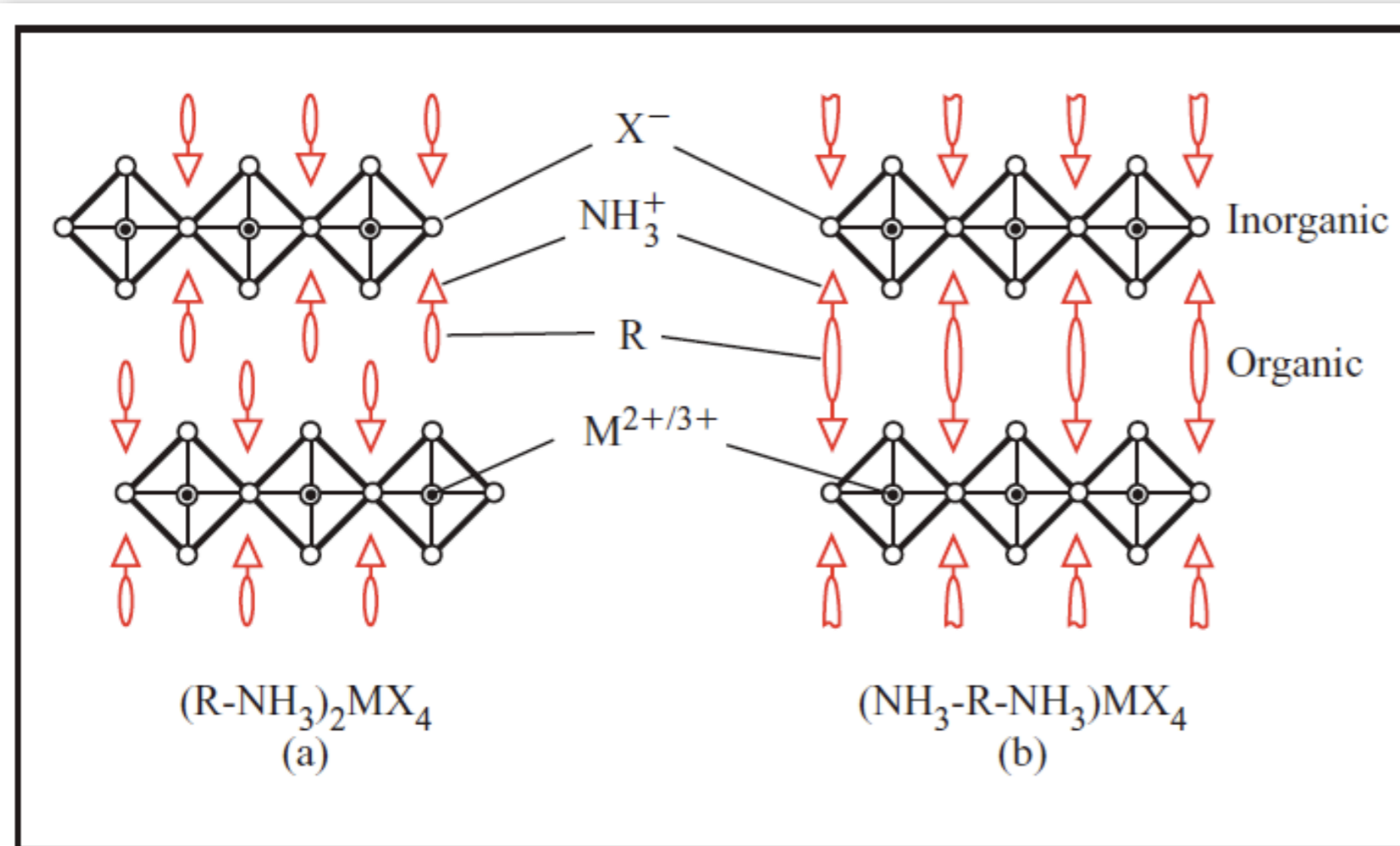
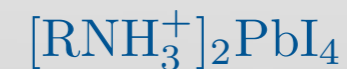


Figure 1

Schematic representation of single-layer ( $n = 1$ )  $\langle 100 \rangle$ -oriented perovskites with (a) monoammonium ( $\text{R-NH}_3^+$ ) or (b) diammonium ( $^+\text{NH}_3-\text{R}-\text{NH}_3^+$ ) organic cations. Note that divalent ( $\text{M}^{2+}$ ) metals generally occupy the metal site. For certain systems, however, a mixture of trivalent ( $\text{M}^{3+}$ ) cations and vacancies can occupy the metal site, yielding  $\text{M}_{2/3}\text{X}_4^{2-}$  layers.

Organic-inorganic hybrid materials can be prepared with inorganic slabs that are semiconducting separated by organic groups that act as wide band-gap dielectrics. The architecture of these crystals results, naturally, in quantum confinement of excitons within the inorganic slab.

Examples of such materials are the alkylammonium salts such as those of alkylammonium iodides with lead iodide.

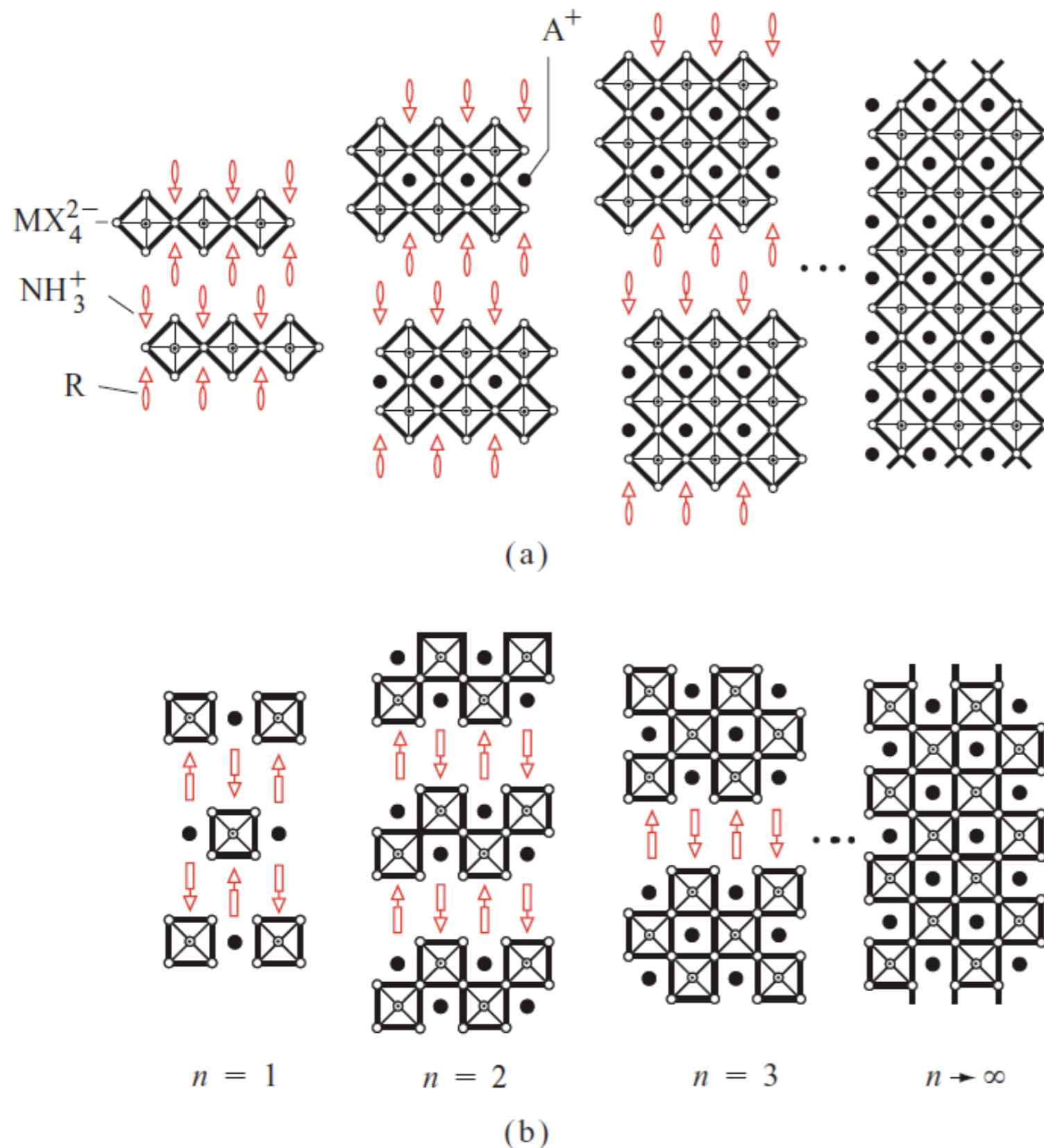


Compounds such as these are easily formed by mixing the alkylamine and lead iodide in excess HI.

The structures of many of these compounds are related the perovskites and the Ruddlesden-Popper phases.

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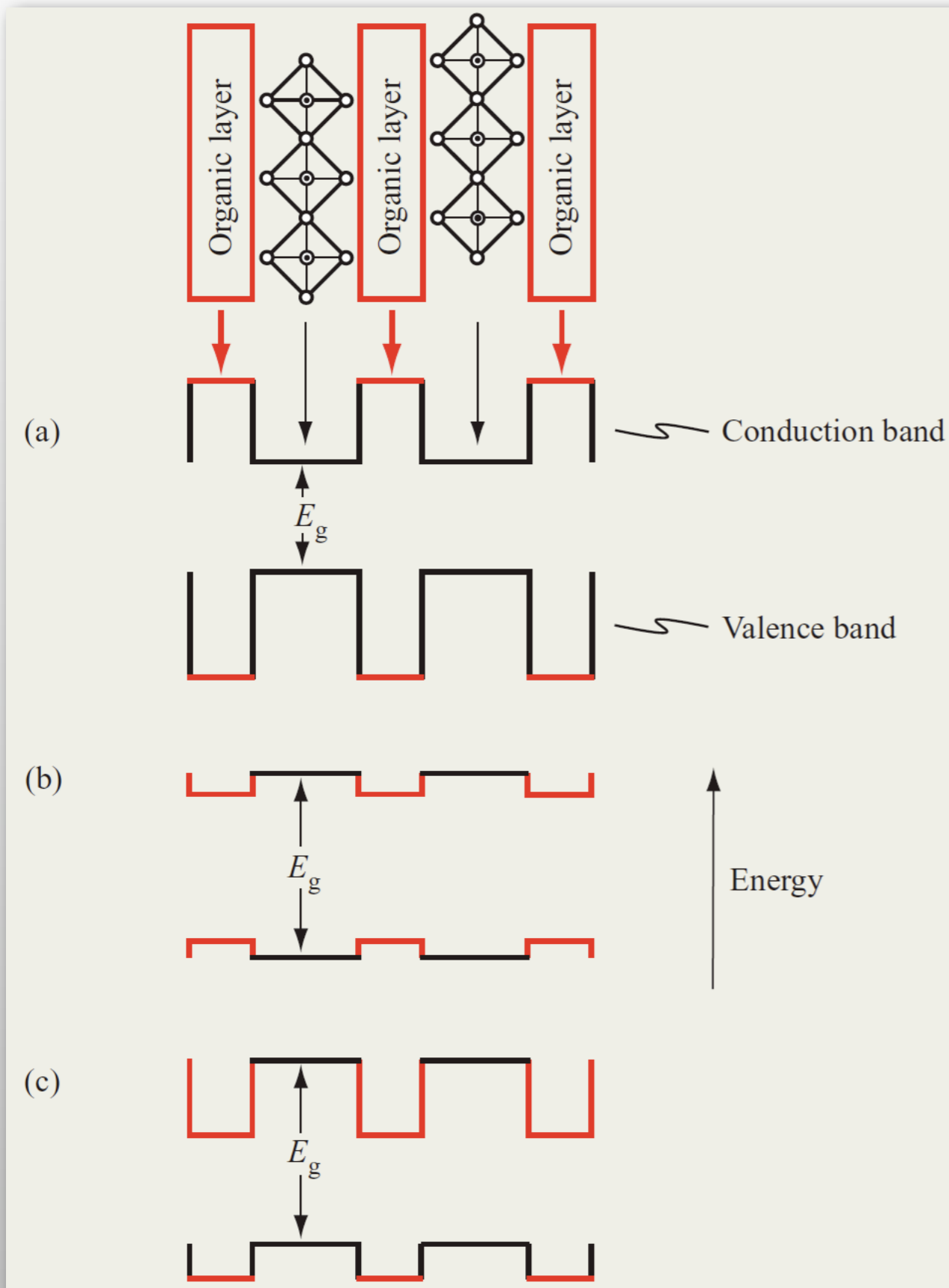
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The types of hybrid structures that form are a function of the metal halide and the alkylamine [sometimes a mix of alkylamines], and the infinite perovskite  $\text{ABX}_3$  can be cut in many ways to form hybrids: with 0D, 1D, 2D inorganic/semiconducting slabs.

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The schematic on the left explains the natural “multiple quantum well” nature of some of these materials. Because the materials are crystalline, the degree of perfection of these heterostructures is unmatched by artificial superlattices. (a) and (b) are so-called type I heterostructures, with the roles of organic and inorganic reversed. (c) is a so-called type II heterostructure.

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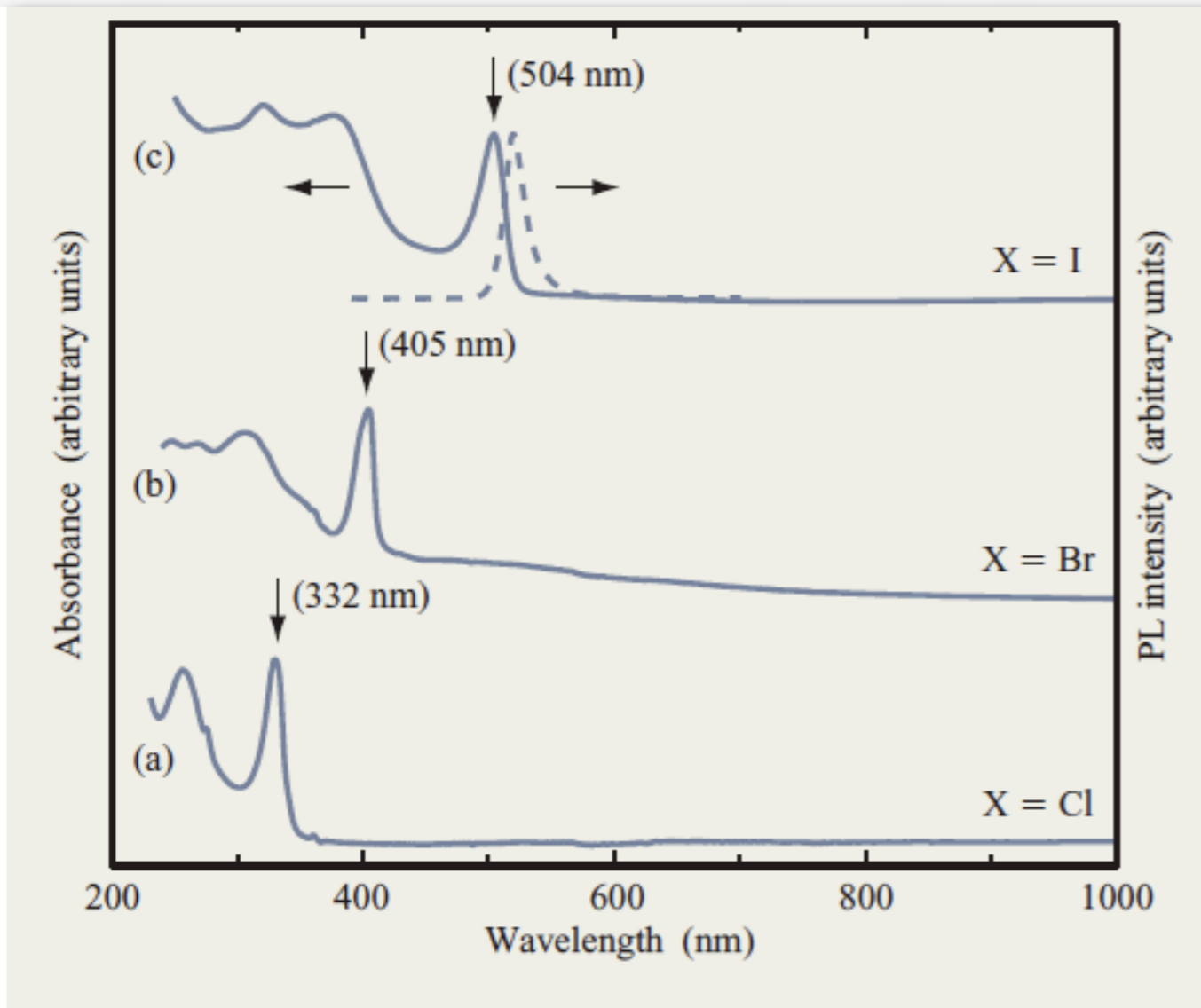


Figure 4

Room-temperature UV-vis absorption spectra for thin films of  $(C_4H_9NH_3)_2PbX_4$  with (a) X = Cl, (b) X = Br, (c) X = I. In each spectrum, the arrow indicates the position of the exciton absorption peak (with the wavelength in parentheses). In (c), the corresponding photoluminescence (PL) spectrum ( $\lambda_{ex} = 370$  nm) is indicated by the dashed curve. Note the small ( $\sim 15$  nm) Stokes shift between the absorption and emission peaks for the excitonic transition.

Typically of systems with exciton confinement, very sharp emission peaks are seen, and these peaks are nearly overlapped with the absorption peaks [very small Stokes shift].

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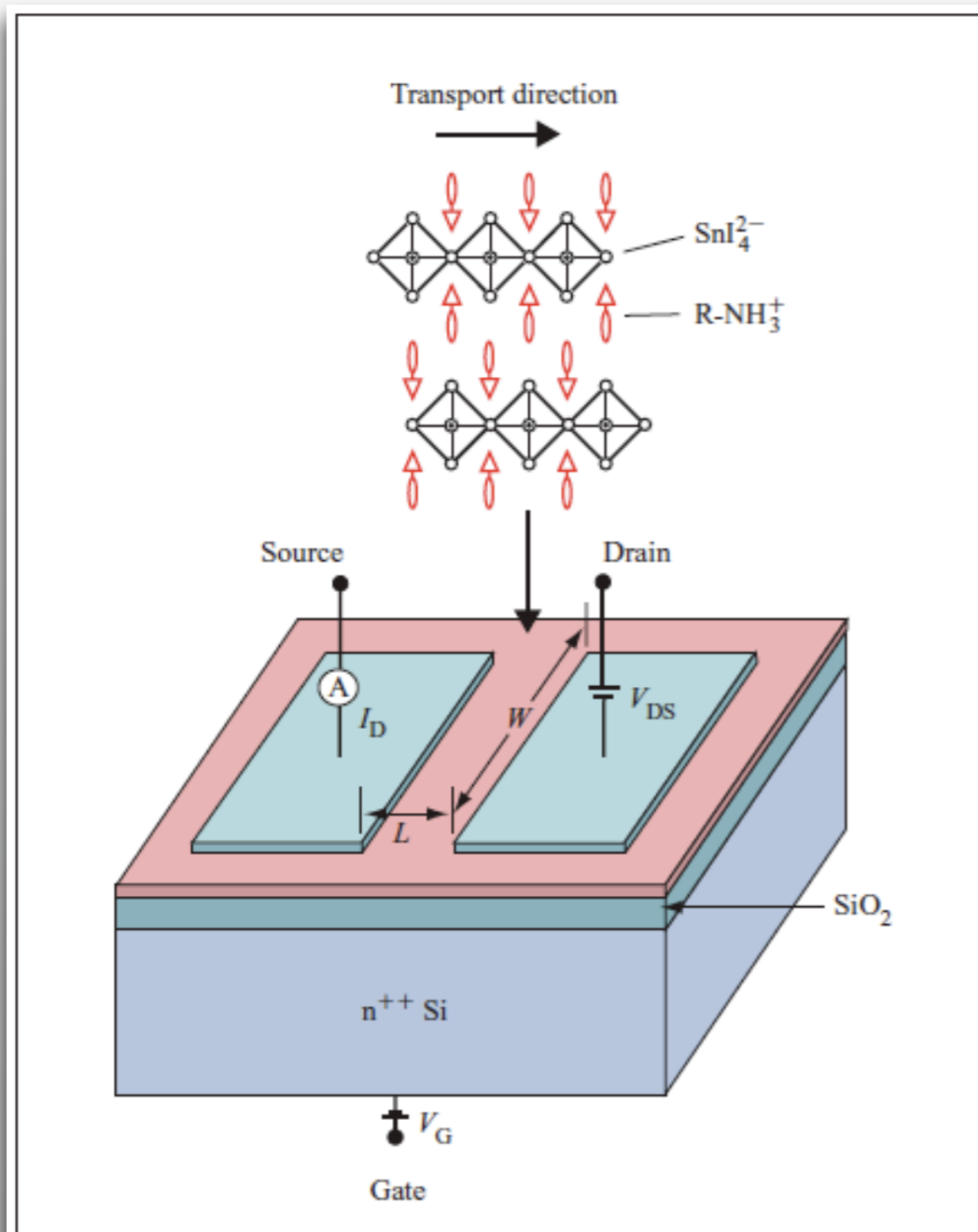


Figure 15

Schematic diagram of a TFT device structure employing a layered organic-inorganic perovskite as the semiconductor channel.

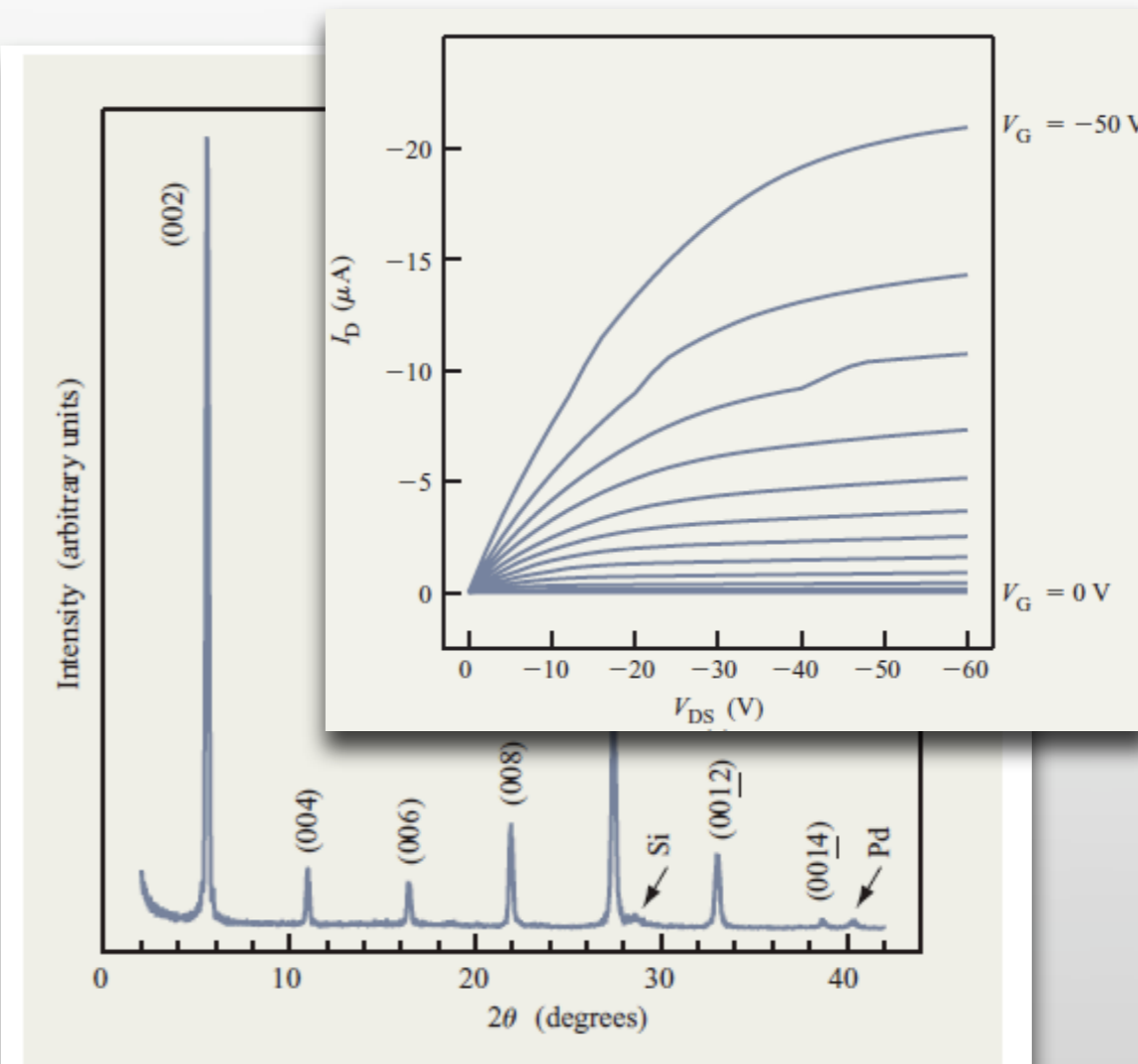


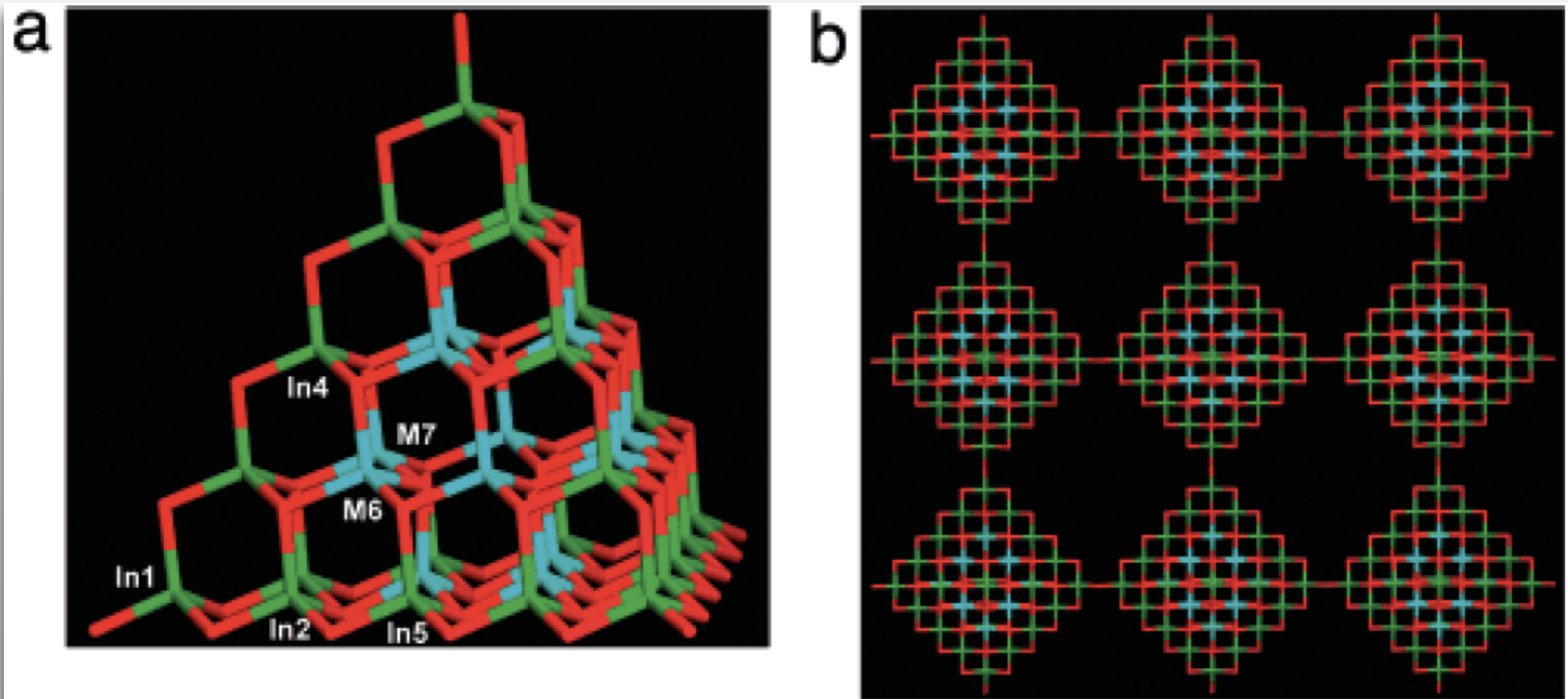
Figure 16

X-ray diffraction pattern for a completed TFT with  $(C_6H_5C_2H_4NH_3)_2SnI_4$  as the semiconducting channel and Pd source and drain electrodes. Inset is an SEM image of the hybrid perovskite film.

Thin film field-effect transistors where the active layers are organic-inorganic hybrids have been prepared by spin-coating and other methods.

# Crystalline solids with intrinsic quantum confinement

W. Su, X. Huang, J. Li, and H. Fu, Crystal of Semiconducting Quantum Dots Built on Covalently Bonded T5 [In<sub>28</sub>Cd<sub>6</sub>S<sub>54</sub>]-12: The Largest Supertetrahedral Cluster in Solid State, *J. Am. Chem. Soc.* 124 (2002) 12944.



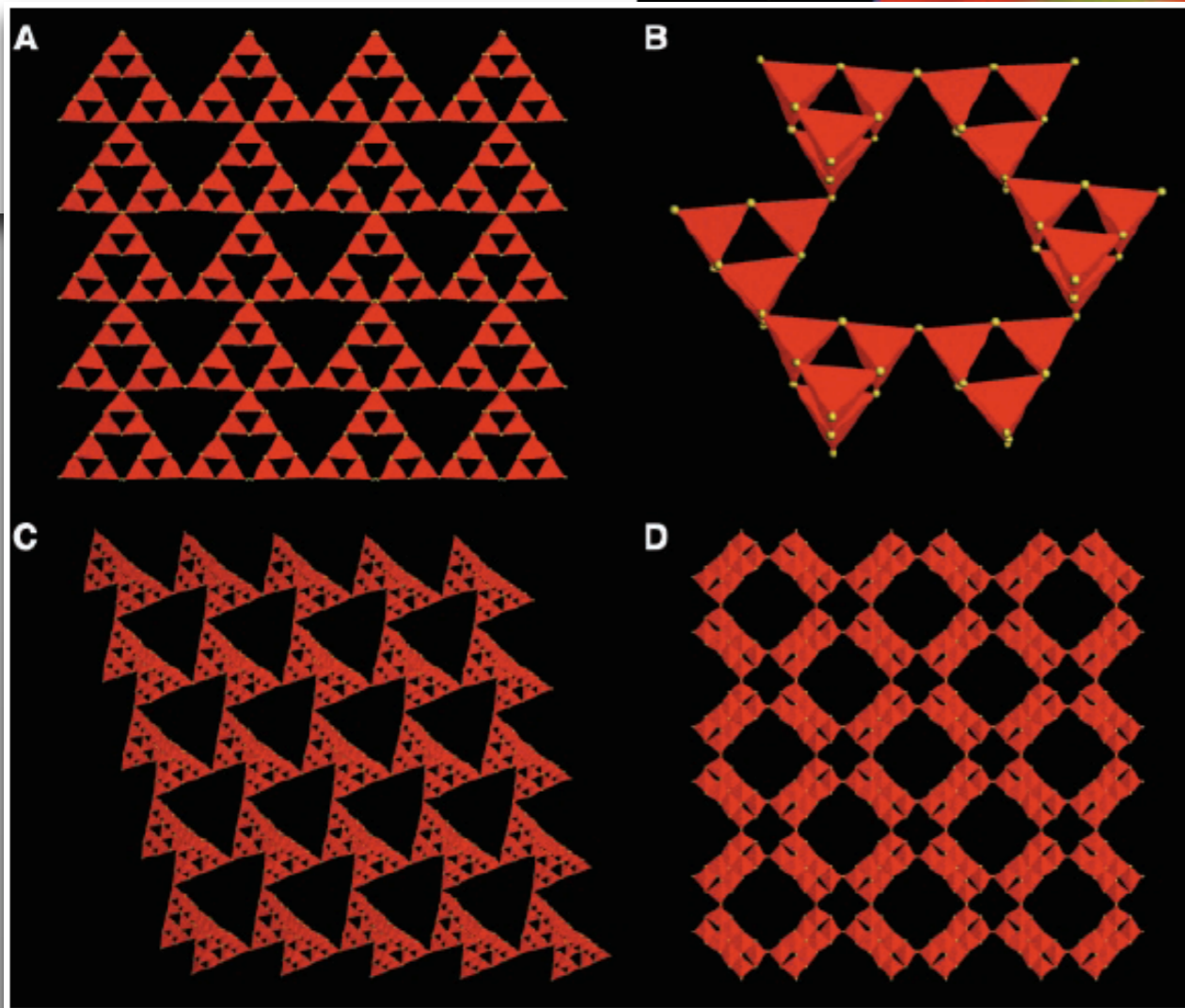
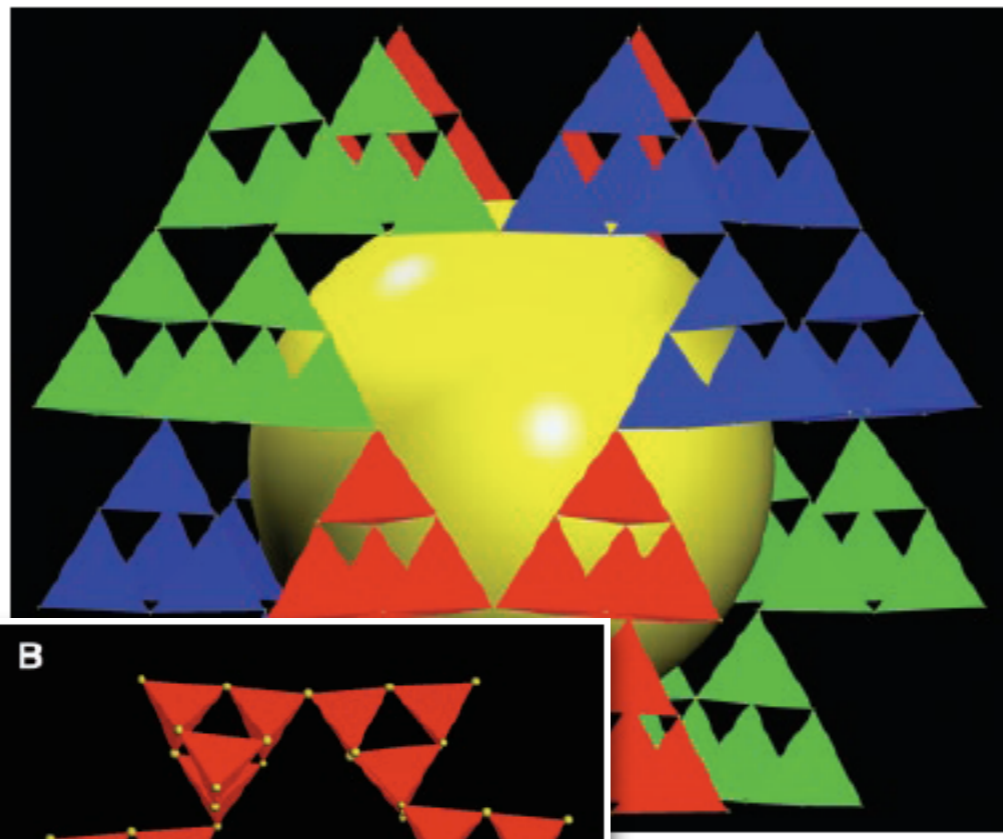
**Figure 1.** (a) View of a “defected” [In<sub>28</sub>Cd<sub>6</sub>S<sub>56</sub>]<sup>-12</sup> cluster in **1**. In (green), In/Cd (blue), S (red). (b) View of the two-dimensional network of the [In<sub>28</sub>Cd<sub>6</sub>S<sub>56</sub>]<sup>-12</sup> clusters along the *c*-axis.

Small clusters incised from the zinc blende (tetrahedral 4-4 lattice) are assembled together using organic groups.

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N. Zheng, X. Bu, B. Wang, and P. Feng, Microporous and photoluminescent chalcogenide zeolite analogs, *Science*, **298** (2002) 2366.

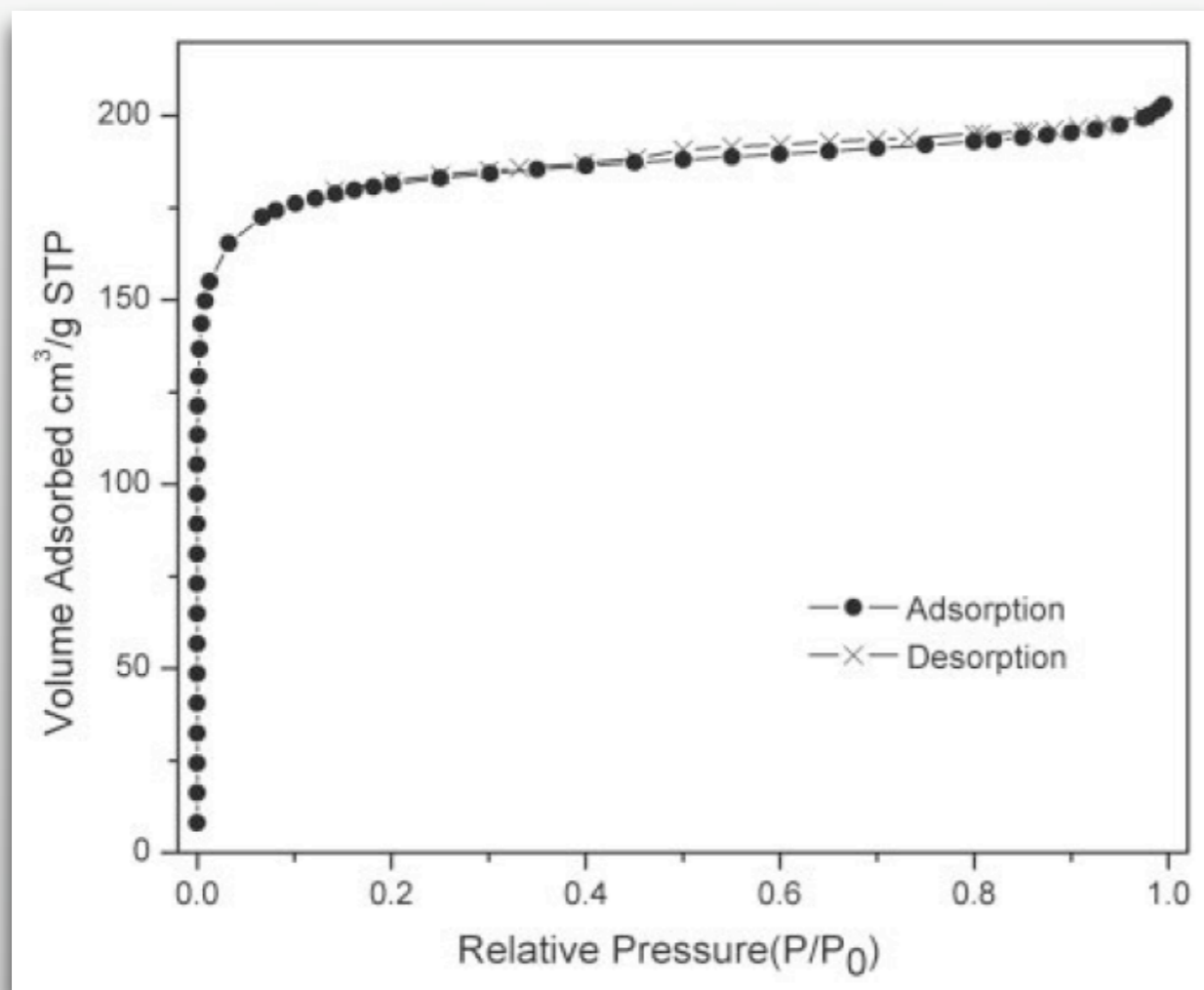
Fig. 1. A sodalite cage decorated with  $M_4X_{10}$  ( $M = \text{Ga/Ge, Ga/Sn, In/Ge, and In/Sn}$ ;  $X = \text{S and Se}$ ) clusters in UCR-20. Colors are arbitrary and represent different chemical units.



Supertetrahedral cages assembled hydrothermally using amine templates. The compounds are aluminosilicate analogs.

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The compounds can be made to show the sorption properties of zeolites.

Unlike zeolites, the compounds show visible photoluminescence.

