Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information: Colloidal nanocrystals as LEGO bricks for building electronic band structure models

Athmane Tadjine and Christophe Delerue*

Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 - IEMN, F-59000 Lille, France

E-mail: christophe.delerue@iemn.univ-lille1.fr

We present in this document additional figures of the comparison between atomistic tight-binding results and the LEGO model for other investigated structures of CdSe and PbSe compounds. In all cases, we only present the lowest conduction bands for CdSe, and both valence (negative energies) and conduction (positive energies) bands for PbSe. We also show examples of valence bands for square and silicene-like lattices of CdSe nanocrystals (NCs).

*To whom correspondence should be addressed

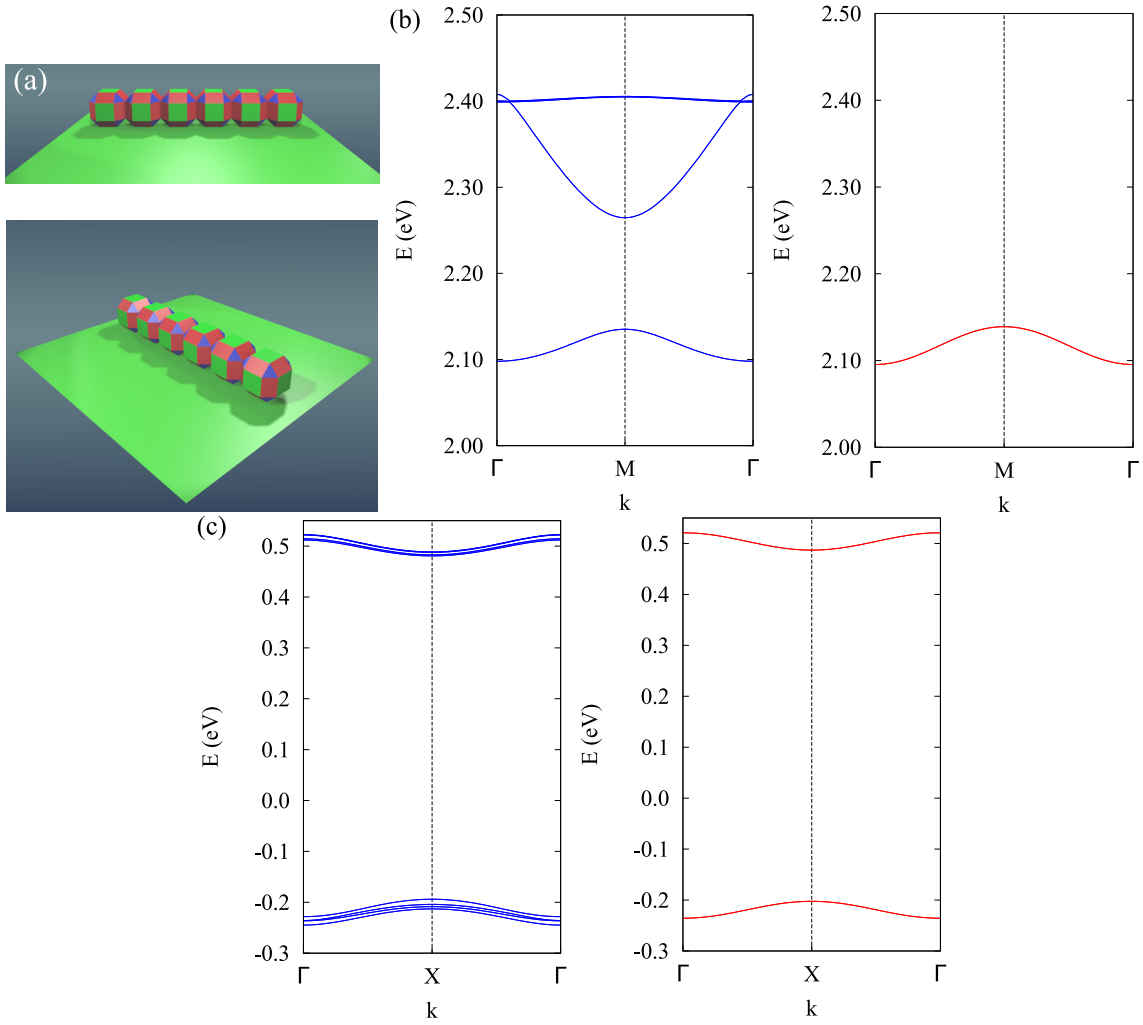

Figure 1: Experimentally synthesized 1D systems with their corresponding band structures. (a) Linear chain of NCs along a ⟨100⟩ direction. (b) The electronic band structure of the linear chain of CdSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line). (c) Same as (b) but for PbSe.

One-dimensional systems

In 1D, it is possible to obtain linear and zigzag chains (Fig 1a and Fig 2a). Both of those structures were reported experimentally.[1]

The analytic band dispersion for the linear and zigzag chains is given in the main document (Table 2). For the linear and zigzag chain, the LEGO model gives good agreement with the atomistic calculations for both CdSe (Fig 1b and Fig 2b) and PbSe (Fig 1c and Fig 2c).

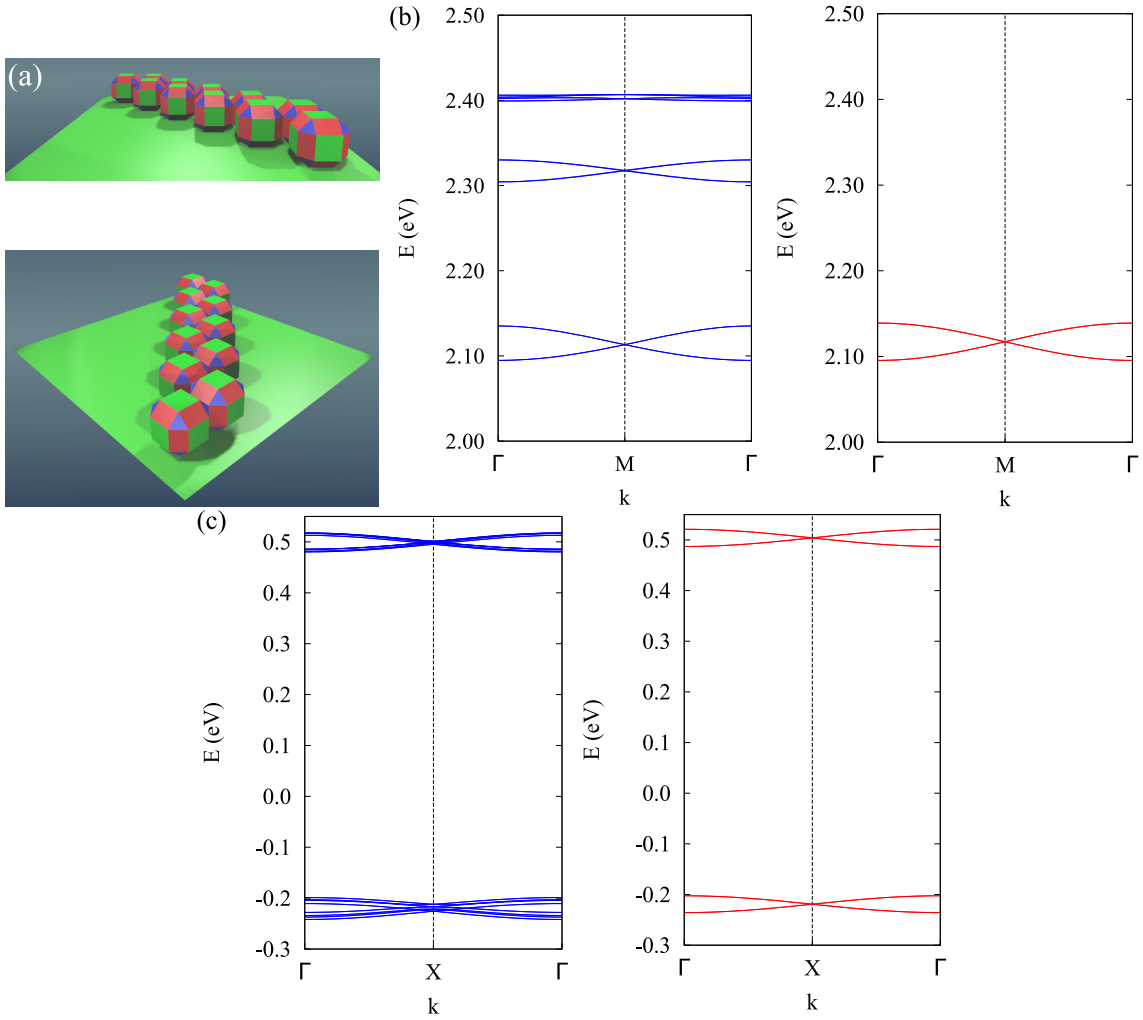

Figure 2: Experimentally synthesized 1D systems with their corresponding band structures. (a) Zigzag chain of NCs along a ⟨110⟩ direction. (b) The electronic band structure of the zigzag chain of CdSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line). (c) Same as (b) but for PbSe.

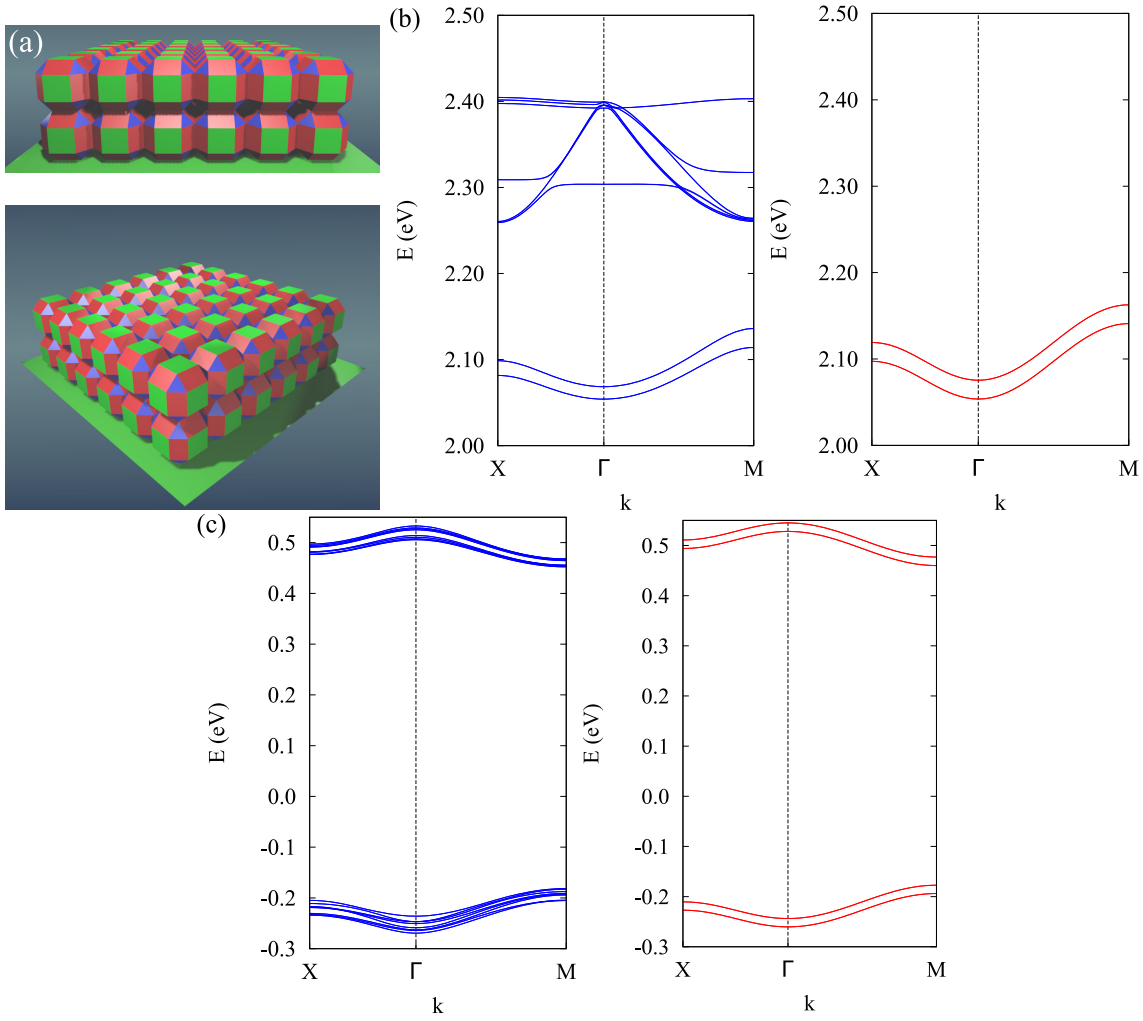

Figure 3: Experimentally synthesized multilayer systems with their corresponding band structures. (a) Bilayer square lattice of NCs that consist of two layers following (100) direction. (b) The electronic band structure of the bilayer square lattice of CdSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line). (c) Same as (b) but for PbSe.

Multilayers of square lattices

Multilayers of square lattices were also observed experimentally.[2] Here, we present the results for bilayer and trilayer systems (Fig 3a and Fig 4a). For both, the LEGO model gives once again a good agreement with the atomistic calculations for both CdSe (Fig 3b and Fig 4b) and PbSe (Fig 3c and Fig 4c).

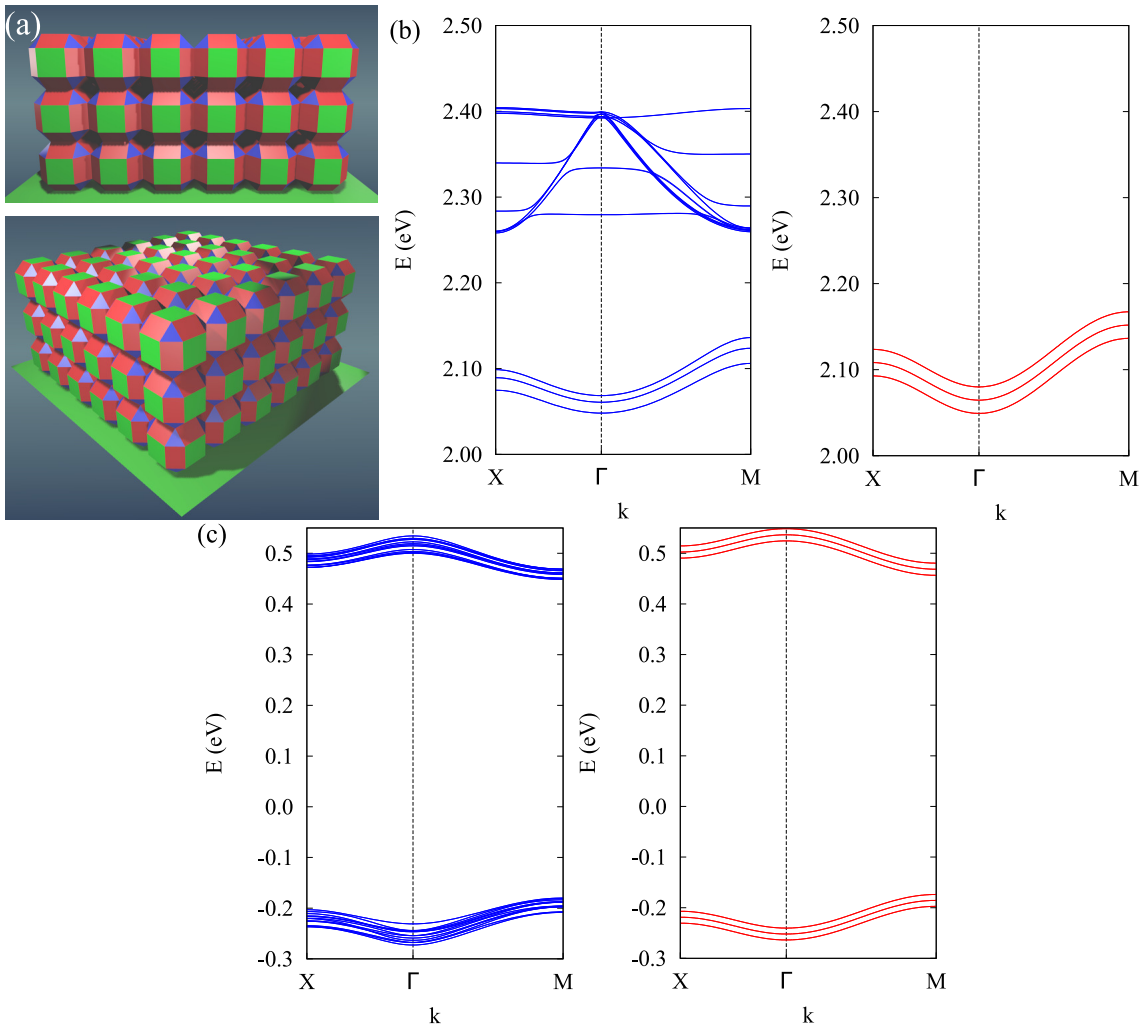

Figure 4: Experimentally synthesized multilayer systems with their corresponding band structures. (a) Trilayer square lattice of NCs that consist of three layers following (100) direction. (b) The electronic band structure of the trilayer square lattice of CdSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line). (c) Same as (b) but for PbSe.

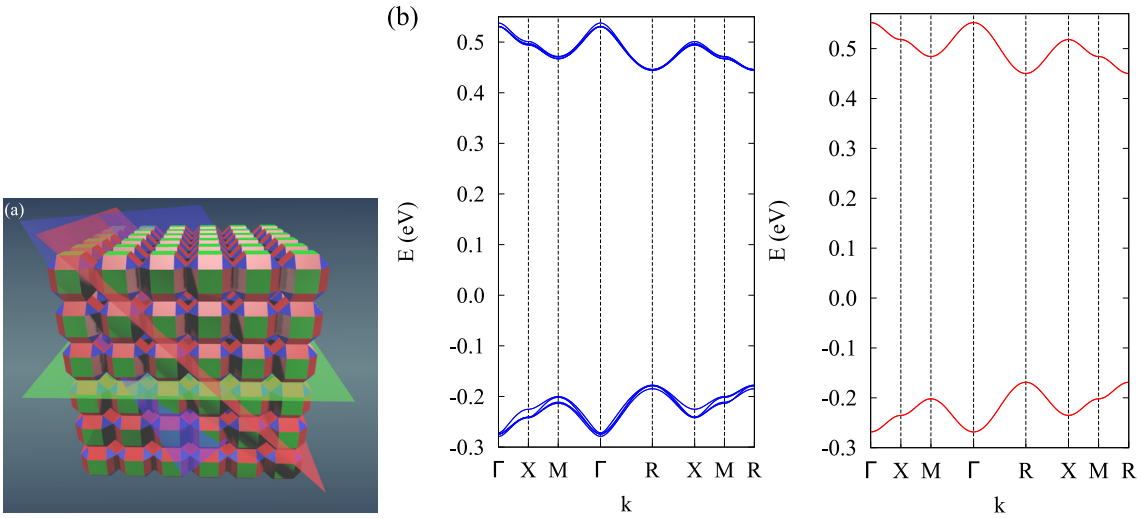

Figure 5: Basis of the LEGO model. (a) Simple cubic lattice of NCs connected through (100) facets. The (100), (110) and (111) facets of the truncated nanocubes are shown in green, red and blue colors, respectively. Crystallographic planes that share the same colors are shown following these directions. (b) The electronic band structure (lowest conduction bands) of the simple cubic lattice of PbSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line).

LEGO model for other PbSe structures

We provide in this section the band structures in the case of PbSe for the systems considered in the main paper. The analytical energy band dispersions are the same as in the case of CdSe, and are given in the main document.

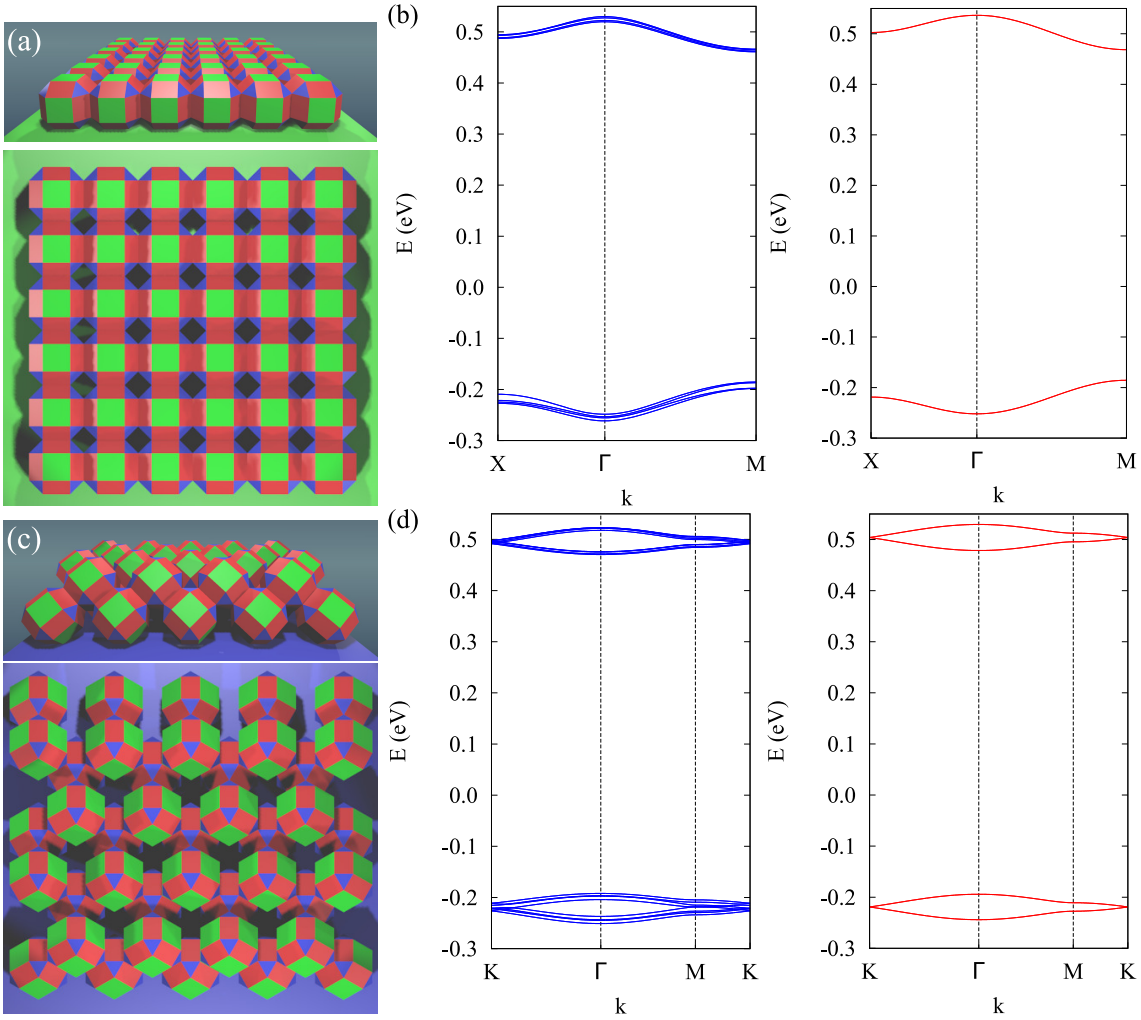

Figure 6: Experimentally synthesized systems with their corresponding band structures. (a) Square lattice of NCs that consist of a monolayer following (100) direction. (b) The electronic band structure of the square lattice of PbSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line). (c) Silicene-like lattice of NCs that consist of two layers following (111) direction. (d) The electronic band structure of the silicene-like lattice of PbSe NCs obtained with the atomistic tight-binding calculations (blue solid line) and with the LEGO Hamiltonian (red solid line).

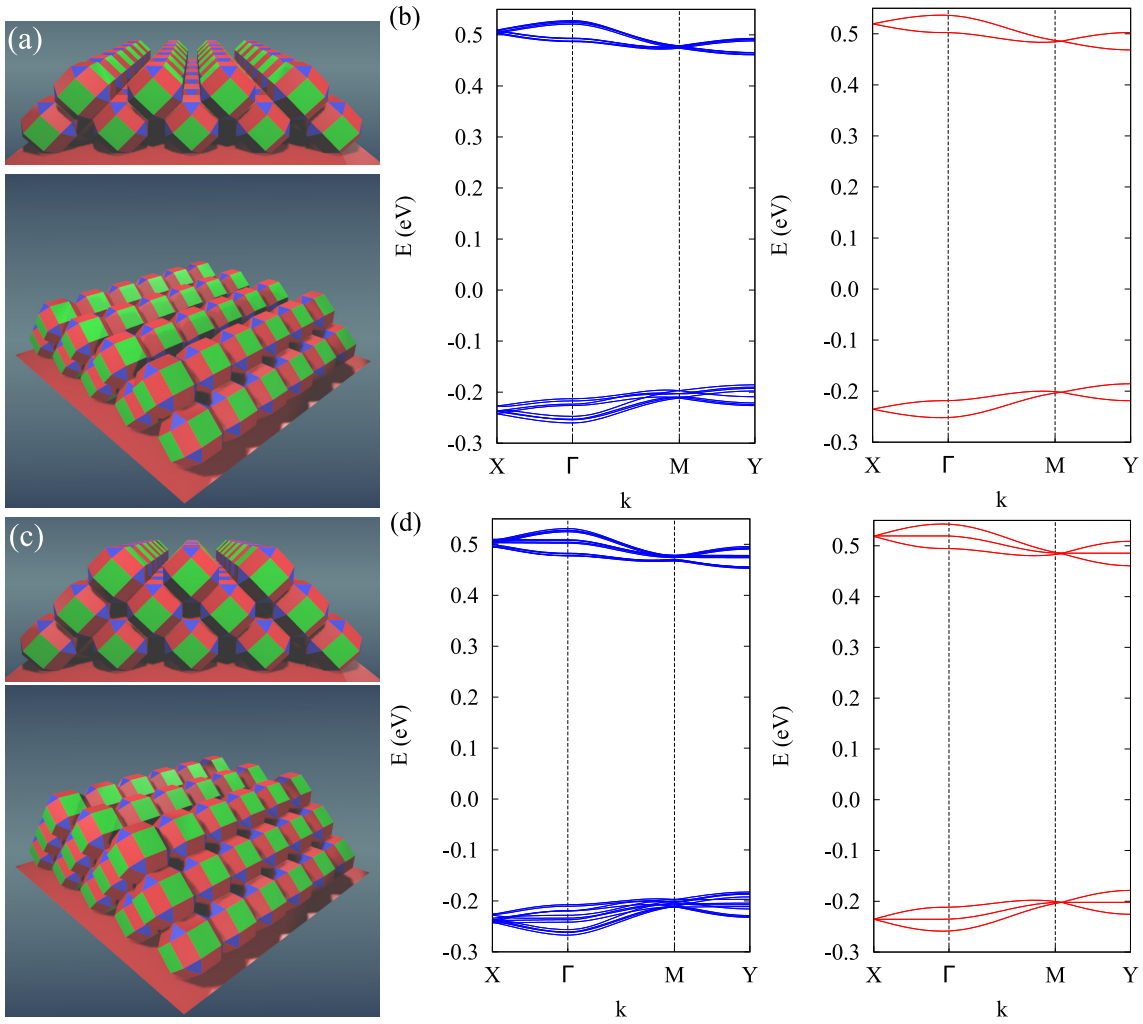

Figure 7: Complex systems that could be synthesized with their corresponding band structures. (a) 2D (110) lattice of NCs that consist of two layers following (110) direction. (c) The three-layer (110) lattice. (b) (d) The electronic band structures for the systems shown in (a),(c), respectively. The calculations are for PbSe and obtained with the atomistic tight-binding method (blue solid line) and with the LEGO Hamiltonian (red solid line).

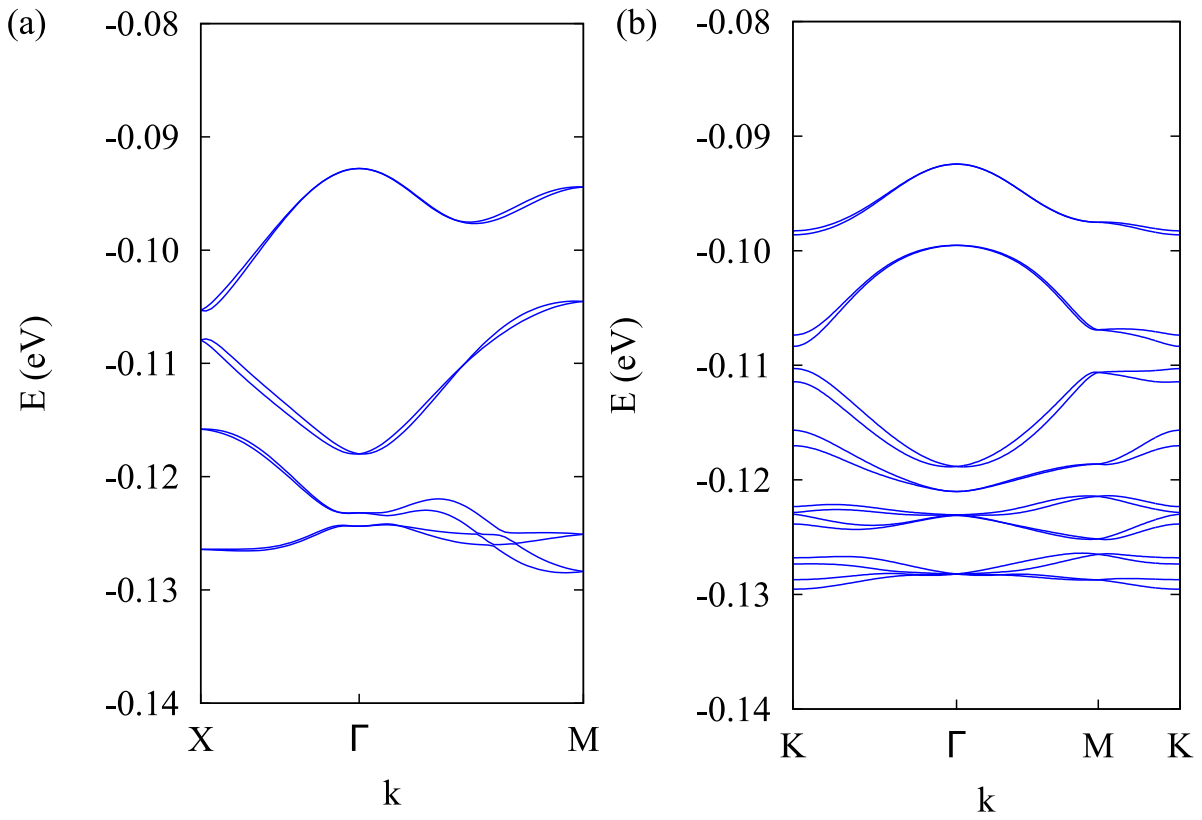

Figure 8: Highest valence bands in square (a) and silicene-like (b) lattices of CdSe NCs.

Valence bands of lattices of CdSe NCs

Valence band structures for square and silicene-like lattices of CdSe NCs are presented in Fig. 8. These examples reveal the much higher complexity of the energy dispersion of the valence bands compared to conduction bands. Such a complex behavior is found for all CdX and HgX compounds. The reason is that, in the bulk semiconductors, the Bloch states at the top of the valence band are made of p atomic orbitals. At $k = 0$ (Γ), the sixfold degeneracy of the p-like bands is lifted by the spin-orbit coupling. At $k \neq 0$, the bands are further split by anisotropic k-dependent couplings. In the NC lattices, the quantum confinement induces additional shape-dependent couplings between the states derived from the different bands. As a consequence, the valence bands cannot be described by a simple LEGO model in which the electronic structure is directly connected to the spatial arrangement of the NCs.

References

1. van Overbeek, C.; Peters, J. L.; van Rossum, S. A. P.; Smits, M.; van Huis, M. A.; Vanmaekelbergh, D. Interfacial self-assembly and oriented attachment in the family of PbX (X=S, Se, Te) nanocrystals. **2017**, Private communication.

2. Savitzky, B. H.; Hovden, R.; Whitham, K.; Yang, J.; Wise, F.; Hanrath, T.; Kourkoutis, L. F. Propagation of Structural Disorder in Epitaxially Connected Quantum Dot Solids from Atomic to Micron Scale. *Nano Lett.* **2016**, *16*, 5714–5718.