

# Polymer and Colloid Highlights

Division of Polymers, Colloids and Interfaces

A Division of the Swiss Chemical Society

## Emerging Semiconductive Properties in Dynamically-Diverse Ion-Nanoparticle Superlattices

Chiara Lionello<sup>b</sup>, Claudio Perego<sup>a</sup>, and Giovanni M. Pavan<sup>\*ab</sup>

\*Correspondence: Prof. G. M. Pavan, E-mail: giovanni.pavan@polito.it  
<sup>a</sup>Department of Innovative Technologies, SUPSI, Manno (CH); <sup>b</sup>Department of Applied Science and Technology, Politecnico di Torino, Turin (IT)

**Keywords:** Colloids · Molecular Dynamics · Self-assembly · Superlattices

The engineering of colloidal materials via self-assembly of functionalized nanoparticles (NPs) is attracting increasing interest in material science.<sup>[1,2]</sup> Hierarchical colloidal superlattices have been assembled using, *e.g.* the action of mediating species that promote NP aggregation *via* electrostatics or complementary DNA strands.<sup>[3–5]</sup> As a relevant example, NP superlattices have been recently obtained via the assembly in water of positively charged, TMA-functionalized gold NPs, mediated by multivalent negatively-charged citrate (CIT) ions.<sup>[6]</sup> By means of coarse-grained (CG) molecular dynamics we have shown that the CIT population exhibits a diverse behavior, with some ions ‘gluing’ the NPs (Fig. 1a, blue), and other ones remaining mobile across the NP surfaces (Fig. 1a, red and green), thus enabling charge-mobility.<sup>[6]</sup> This sparked the idea that CITs could impart conductivity to the system, in which an electric current transported by the fraction of mobile ions propagates through the superlattice. *In silico* experiments allowed this idea to be explored.

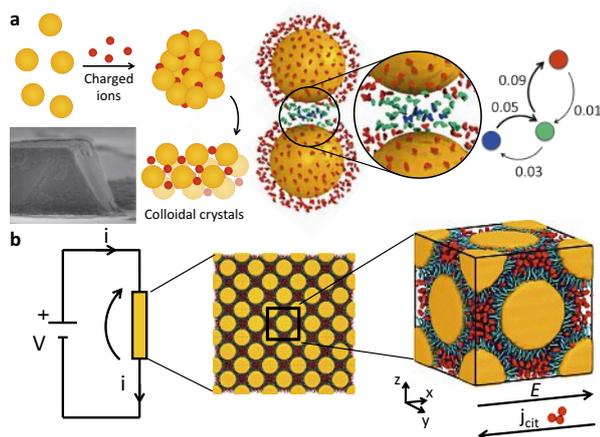


Fig. 1. (a) Self-assembly of TMA-NPs mediated by CIT ions (left) and CG model of two assembled NPs with CITs colored based on their mobility (diagram: transition rates between the ionic states). (b) Ohmic in silico experiment. CG model of the FCC lattice, with NP cores in yellow, TMAs in cyan and CIT ions in red. Adapted from ref. [7].

We designed a CG model of an FCC superlattice of TMA-NPs co-assembled with CITs, where a directional electrostatic field

$E$  is applied during MD simulations (Fig. 1b). The MD demonstrated a supramolecular semiconductive-like behavior, in which the field  $E$  generates a CIT current only when the intensity of  $E$  overcomes a threshold intensity, thus switching from an insulating to a conductive response. A data-driven analysis of the local environments<sup>[8]</sup> of the CIT ions under the application of  $E$  identified three ionic domains, differing in terms of structure and dynamics. While part of the ions are involved in the lattice binding (as in Fig. 1), the CIT ions located in the octahedral and tetrahedral cavities of the FCC lattice (Fig. 2c) transport the charge. Conductivity emerges as ‘ionic gates’ emerge in the superlattice that dynamically connect the FCC cavities. This fascinating example shows how a concerted dynamics of molecular units can determine emergent features in such hierarchical self-assembled materials, reminiscent of those typical of atomic crystals properties.

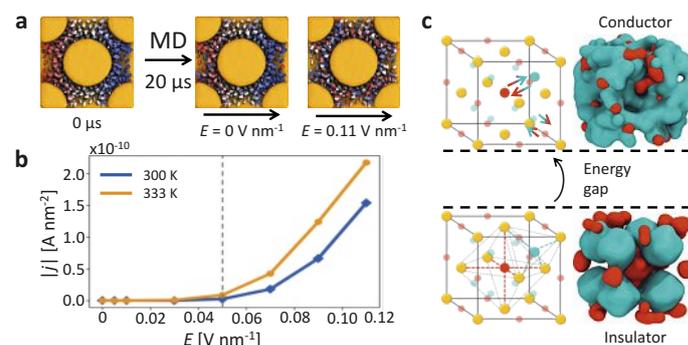


Fig. 2. (a) Starting and final configurations of the system with and without  $E$  field. The coloring shows the CITs reshuffling at high  $E$ . (b) CIT current density  $j$  as a function of  $E$ . (c) CIT population of in the FCC cavities in conductive vs. insulating regimes. Adapted from ref. [7].

Received: February 28, 2023

- [1] M. A. Boles, M. Engel, D. V. Talapin, *Chem. Rev.* **2016**, *116*, 11220, <https://doi.org/10.1021/acs.chemrev.6b00196>.
- [2] M. Grzelczak, L. Liz-Marzán, R. Klajn, *Chem. Soc. Rev.* **2019**, *48*, 1342, <https://doi.org/10.1039/C8CS00787J>.
- [3] M. Girard, S. Wang, J. S. Du, A. Das, Z. Huang, V. P. Dravid, B. Lee, C. A. Mirkin, M. Olvera de la Cruz, *Science* **2019**, *364*, 1174, <https://doi.org/10.1126/science.aaw8237>.
- [4] S. Wang, S. Lee, J. S. Du, B. E. Partridge, H. F. Cheng, W. Zhou, V. P. Dravid, B. Lee, S. C. Glotzer, C. A. Mirkin, *Nat. Mater.* **2022**, *21*, 580, <https://doi.org/10.1038/s41563-021-01170-5>.
- [5] X. Zhao, L. Yang, J. Guo, T. Xiao, Y. Zhou, Y. Zhang, B. Tu, T. Li, B. A. Grzybowski, Y. Yan, *Nat. Electron.* **2021**, *4*, 109, <https://doi.org/10.1038/s41928-020-00527-z>.
- [6] T. Bian, A. Gardin, J. Gemen, L. Houben, C. Perego, B. Lee, N. Elad, Z. Chu, G. M. Pavan, R. Klajn, *Nat. Chem.* **2021**, *13*, 940, <https://doi.org/10.1038/s41557-021-00752-9>.
- [7] C. Lionello, C. Perego, A. Gardin, R. Klajn, G. M. Pavan, *ACS Nano* **2023**, *17*, 275, <https://doi.org/10.1021/acsnano.2c07558>.
- [8] A. P. Bartók, R. Kondor, G. Csányi, *Phys. Rev. B* **2013**, *87*, 184115, <https://doi.org/10.1103/PhysRevB.87.184115>.

If you are interested in submitting a new highlight, please contact:

Prof. Dr. Christoph Weder, Adolphe Merkle Institute, University of Fribourg  
 E-mail: christoph.weder@unifr.ch, Tel.: +41 26 300 94 65