Highlights

RESEARCH AREA 2 – Functional and Complex Materials for Innovative Electronics and Sensing - 2024

Giant piezoelectricity driven by Thouless pump in conjugated polymers

S.P. Villani[1], M. Campetella[2], P. Barone[2], F. Mauri[1]

[1]Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 5, 00185 Roma, Italy
[2]CNR-SPIN Institute of Superconductors, Innovative Materials and Devices, UOS-Roma, Via del Fosso del Cavaliere 100, 00133 Roma, Italy

npj Comput. Mater. 10, 81 (2024)

Piezoelectricity of organic polymers has attracted increasing interest because of several advantages they exhibit over traditional inorganic ceramics. While most organic piezoelectrics rely on the presence of intrinsic local dipoles, a highly nonlocal electronic polarisation can be foreseen in conjugated polymers, characterised by delocalised and highly responsive π-electrons. These 1D systems represent a physical realisation of a Thouless pump, a mechanism of adiabatic charge transport of a topological nature which results, as shown in this work, in anomalously large dynamical effective charges, inversely proportional to the bandgap energy. A structural ferroelectric (FE) phase transition further contributes to an enhancement of the piezoelectric response reminiscent of that observed in piezoelectric perovskites close to morphotropic phase boundaries. First-principles density functional theory calculations performed in two representative conjugated polymers - monofluorinated polyacethylene (MFPA) and polymethineimine (PMI) – using range-separated hybrid functionals, show that state-of-the-art organic piezoelectrics such as polyvinylidene fluoride (PVDF) can be outperformed by piezoelectric conjugated polymers, mostly thanks to strongly anomalous effective charges of carbon, larger than 5e—ordinary values being of the order of 1e—and reaching the giant value of 30e for band gaps of the order of 1 eV.

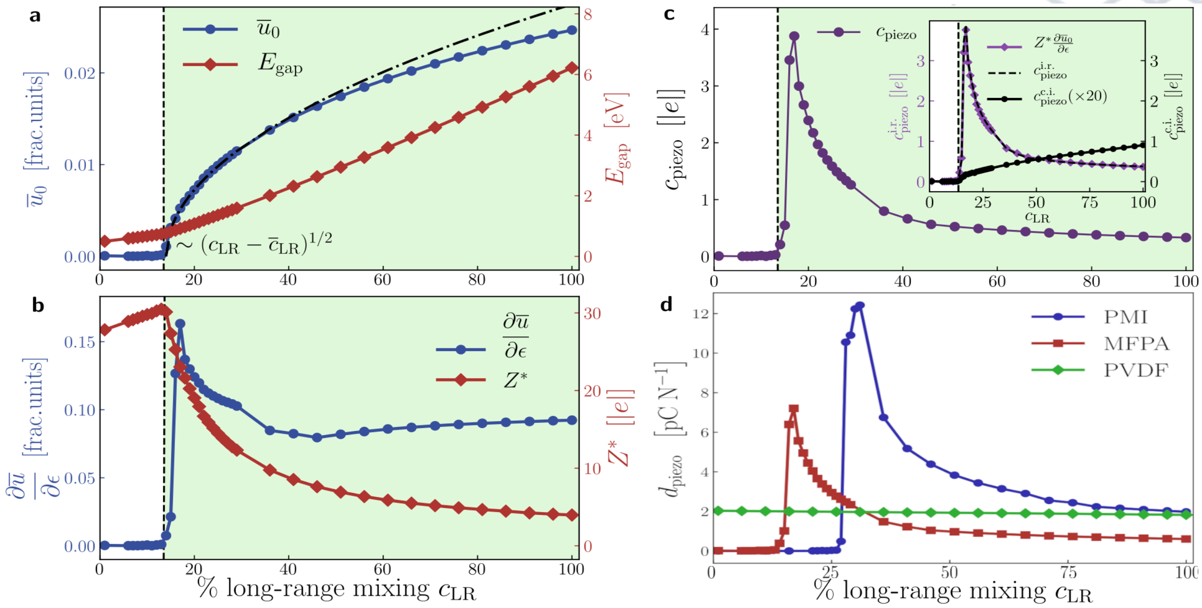

Figure a Band-gap and bond-length alternation ū₀ (order parameter of the FE transition) of MFPA as a function of the fraction c_{LR} of long-range exact exchange included in the range-separated hybrid functional, that accounts for the reduced screening of the dielectric environment. An increasing c_{LR} is responsible for enhanced electron-lattice interaction, driving the structural phase transition to a FE dimerized phase (coloured area). **b** Corresponding evolution of internal strain and dynamical effective charges of MFPA, both quantifying the internal-relaxation (i.r.) contribution to the piezoelectric response. **c** Longitudinal piezoelectric coefficient of MFPA; its decomposition in i.r. and clamped-ion (c.i.) contributions is shown in the inset. **d** Comparison of converse piezoelectric response of conjugated polymers PMI and MFPA with the best-performing organic piezoelectric PVDF, a non-conjugated polymers not realizing the Thouless adiabatic charge pumping.