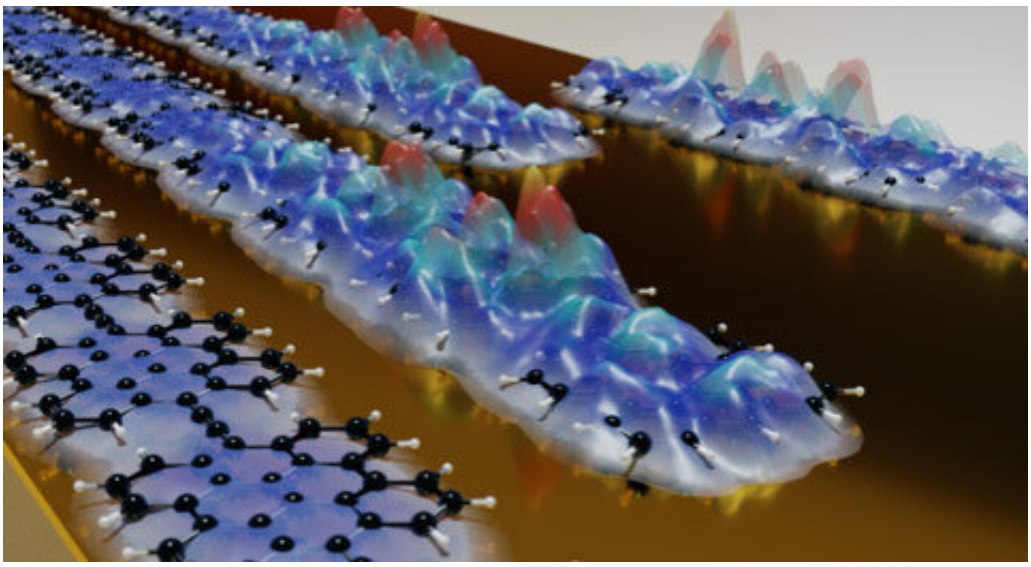
Researchers developing metallic polymers by exploiting topological order and π-conjugation

May 5 2020, by Imdea Nanociencia



Artistic representation of non-trivial topological polymers exhibiting the characteristic end-state. Credit: M. Pykal.

Researchers at IMDEA Nanociencia, Universidad Autónoma de Madrid and Universidad Complutense de Madrid have presented a new strategy to fabricate quasi-metallic 1-D polymers with atomic precision, in collaboration with The Czech Academy of Science, EMPA (Zürich, Switzerland) and RCATM (Olomouc, Czech Republic). This investigation advances the possibility of designing stable organic polymers with vanishing electronic bandgaps with applications that

include molecular optoelectronics and quantum information technology.

Organic (synthetic) metals attracted much attention in the final decades of the last century due to their envisioned futuristic applications and affordable costs. This field was boosted by the early advances in polyacetylene polymers, which exhibited high conductivity upon doping and opened a new route toward organic electronics and the Nobel Prize to their discoverers. However, scientists found that dopants compromised the stability of the polymers, thus reducing their applications as synthetic metals in real devices.

From a theoretical point of view, early efforts to understand the fundamental processes in the model trans-polyacetyene system resulted in the Su-Shrieffer-Heeger (SSH) model. The theory revealed that the resonant form adopted by the polymer, which emanates from the conjugation of pi electrons (pi conjugation), can alter the electronic class of the material in an unexpected way.

Topological band theory classifies gapped materials by mathematically studying their band structure in insulators and topological nontrivial insulators. In the SSH model, one resonant form behaves as a normal insulator, whereas the other resonant form is a topological nontrivial 1-D insulator, i.e., a gapped material featuring in-gap edge states. Thus, a crossover of resonant form can change the topological class of a polymer. But polyacetylene, in any of its resonant forms, is a gapped material. As a result, this polymer can only increase its conductivity by being chemically or electrochemically doped.

Thus, the question is whether scientists can engineer 1-D organic intrinsic metals. To answer this question, scientists need to come back to the roots of topological band theory, which states that the transition between two gapped materials must proceed through closure of the bandgap, i.e., through a metallic state. Thus, if researchers could

engineer a family of chemical materials and tailor the topology of its bands by tuning the chemical structure, it could become feasible to approximate or even locate the material at the topological transition point.

In the current study reported in the journal *Nature Nanotechnology*, the scientists devised a combined experimental-theoretical investigation bridging the fields of topological band theory (solid state physics) and pi-electron conjugation (organic chemistry) in order to give rise to quasi-metallic organic polymers.

"For the first time, we can observe with scanning probe microscopy the connection between the topological class and the resonant form of a polymer, paving avenues to engineer novel electronic classes of materials, including intrinsic organic metals and one-dimensional topological nontrivial insulators," Prof. Ecija says.

"To illustrate such concepts, we relied on the power of organic synthesis to prepare suitable molecular precursors, and we trusted in on-surface chemistry to drive the engineering of the polymers through an unprecedented reaction" Prof. Martín says.

First, a new family of acene polymers, classified by the number of benzene units in their backbone (n=1, 2, 3…), is identified to undergo a discrete topological transition. For small n (n5) are nontrivial, identifying the boundary close to n=5 (pentacene polymer).

The different polymers are fabricated with atomic precision on top of gold substrates implementing ultimate on-surface synthesis approaches, tuning the topology and the electronic properties of the resulting polymers at will. "According to our theoretical prediction, the pentacene polymer is located in nontrivial topological phase very close to the topological boundary with very small gap," says Jelinek. Indeed,

experimental measurements revealed their quasi-metallic behavior with 0.35 eV experimental band gap and the presence of in-gap topological edge states.

Authors generalize the concept by extending it to the polymer family of periacenes, achieving band gaps as low as 0.3 eV for bisanthene polymers, which are located close to the topological transition. Additionally, the different resonant forms of the pi-system can be identified, demonstrating an ethynylene-bridged aromatic nature for the trivial polymers, whereas locating a cumulene-linked p-quinoid resonant form for the nontrivial wires. Thus, there is a crossover between the resonant forms, which corresponds to the topological band transition.

In summary, this work serves both as a proof of the intimate relation between resonant form and topological class, while offering a new tool to produce stable organic intrinsic metals by designing polymers at the exact topological boundary.

More information: Borja Cirera et al. Tailoring topological order and π-conjugation to engineer quasi-metallic polymers, *Nature Nanotechnology* (2020). DOI: 10.1038/s41565-020-0668-7

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