Tailoring topological order and $\pi$-conjugation to engineer quasi-metallic polymers

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Topological band theory predicts that a topological electronic phase transition between two insulators must proceed via closure of the electronic gap. Here, we use this transition to circumvent the instability of metallic phases in $\pi$-conjugated one-dimensional (1D) polymers. By means of density functional theory, tight-binding and GW calculations, we predict polymers near the topological transition from a trivial to a non-trivial quantum phase. We then use on-surface synthesis with custom-designed precursors to make polymers consisting of 1D linearly bridged acene moieties, which feature narrow bandgaps and in-gap zero-energy edge states when in the topologically non-trivial phase close to the topological transition point. We also reveal the fundamental connection between topological classes and resonant forms of 1D $\pi$-conjugated polymers.

The $\pi$-conjugated polymers have received particular interest from scientists and industry alike, since the discovery of high conductivity in doped polyacetylene (PA) showed that it was possible to create organic synthetic metals. Such a finding opened the new field of what is known today as organic electronics and triggered intense research in understanding the fundamental chemistry and physics of $\pi$-conjugated macromolecules. Notably, the relation between topological band theory and conduction in doped PA was soon introduced by the Su–Schrieffer–Heeger (SSH) model. The rapid development of on-surface synthesis has emerged as a new paradigm for engineering nanomaterials, while it also circumvents the solubility limitations associated with synthetic wet chemistry. The might of this novel approach was recently exemplified by graphene nanoribbons, whereby robust topological SSH quantum phases were rationally engineered. Although on-surface synthesis, up until now, has been primarily concerned with graphene-derived nanostructures, in future applications it will be desirable to design long, defect-free and transferable 1D $\pi$-conjugated polymers.

Following this on-surface synthetic paradigm, we have just reported the pathway to engineer surface-confined ethynylene-bridged anthracene polymers featuring high $\pi$-conjugation. Inspired by this recent discovery and based on the roots of topological band theory, we introduce here the theoretical basis and an experimental demonstration of the rational engineering of 1D polymers that are located near the quantum phase transition from the topologically trivial to non-trivial class, thus featuring a narrow bandgap. Such polymers are topologically non-trivial and consequently exhibit in-gap zero-energy edge states.

Topological phase transition in acene polymers

The concept of a structure-related topological phase transition and the corresponding bandgap closure is exemplified in Fig. 1a for the structure family of linearly bridged acene polymers. Density functional theory (DFT) and GW calculations show a monotonic decrease of the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the acene monomer as a function of the acene size (where $n$ denotes the number of benzene rings of the acene species), as expected from the increasing delocalization of the frontier orbitals. However, the bandgap of the ethynylene-bridged polymers shows a distinctly non-monotonic behaviour, which is characterized by the closing of the bandgap for the ethynylene-bridged polymers...
the pentacene polymer \((n=5)\) and its reopening for larger acenes \((n>5)\). The topological analysis of the polymers, by determination of the Zak phase, reveals that the closure of the bandgap is associated with a transition of the topological class of the polymers from trivial \(Z_2=0\) to non-trivial \(Z_2=1\) (see Supplementary Notes 1–3 and Supplementary Figs. 3–5 for details of the topological analysis and definition of the topological invariant \(Z_2\) in this case). The sequence of the linearly bridged acene polymers can therefore be understood as representing a topological phase transition in the discrete variable \(n\) denoting the acene size. According to topological band theory, such a phase transition must come along with a metallic, that is zero, bandgap interface. Figure 1 shows that this transition happens near a specific structure (‘near’, because \(n\) cannot vary continuously), which is the ethynylene-bridged pentacene polymer \((n=5)\). As discussed in the following, experiments indeed show that the pentacene polymer has a narrow bandgap. Furthermore, it also features characteristic in-gap zero-energy edge states, evidencing that it is located just at the onset of the non-trivial topological phase region (Fig. 1a).

This topological transition in the polymer can be tentatively understood in terms of the dimerized atomic chain described by the SSH model\(^\text{28}\) (see Supplementary Note 4 and Supplementary Figs. 6–9). Here, the gap between valence band \(E_1(k)\) and conduction band \(E_2(k)\), with \(E_\pm(k) = \pm \sqrt{t_1^2 + t_2^2 + 2t_1t_2\cos(k)}\), vanishes when \(|t_1| = |t_2|\), that is when the intra-cell coupling strength \(t_2\) between the dimers. The situation \(|t_1| > |t_2|\) yields a topologically trivial insulator, and \(|t_1| < |t_2|\) a topologically non-trivial insulator.

Translating this situation to the acene polymer case means associating the HOMO and LUMO orbitals of an isolated acene unit to the bonding and antibonding SSH dimer states, respectively. The HOMO–LUMO gap is then directly related to the intra-cell coupling strength. The inter-cell coupling, given by a single atomic bond in the SSH model, is provided by the ethynylene bridge in our polymers (see Supplementary Note 4 and Supplementary Figs. 6–9 for details of this concept). For small acenes, the HOMO–LUMO gap is large and the intra-cell coupling \((t_1)\) exceeds the inter-cell coupling \((t_2)\), which results in a topologically trivial insulating phase \((n=1\) and \(n=3\) in Fig. 1). As the size of the acene unit increases, the HOMO–LUMO gap decreases, and the intra-cell coupling starts matching the inter-cell coupling, which results in the closure of the bandgap \((n=5)\). Further increase of the acene size makes the inter-cell coupling \((t_2)\) overcome the intra-cell coupling \((t_1)\), resulting in a change of the topological class and a reopening of the bandgap.

Remarkably, as we will justify later, the polymers described here may adopt two distinct arrangements of the \(\pi\)-conjugated structure (resonant forms): either the acene monomers are fully aromatic and linked through ethynylene bridges, or the acene blocks adopt a quinoid structure connected by cumulene linkers (see Fig. 1a). Our results reveal that the ground state of the polymers is composed of a distinct mixture of the two distinct resonant forms. For small acenes \((n<5)\) the dominant form is the aromatic–ethynylene structure, whereas for higher acenes \((n\geq5)\) the dominant structure is the quinoid–cumulene form. In this manuscript, we will demonstrate that the topological phase transition of the acene polymers is related to a change in the dominant resonant form, as illustrated in Fig. 1a.

### On-surface synthesis of topologically non-trivial 1D polymers

To experimentally implement the outlined strategy, we have used on-surface synthesis to produce two different polymers of the acene structural family. We synthesized the required molecular precursors 4BrAn (9,10-bis(dibromomethylene)-9,10-dihydroanthracene) and 4BrPn (6,13-bis(dibromomethylene)-6,13-dihydronpentacene) (see Methods section for synthetic details). These precursors bear the \(=\text{CBr}_2\) functionality. Such a terminal group has been used recently to steer skeletal rearrangements on NaCl by voltage pulses\(^\text{29}\) or to induce homocoupling through a set of chemical reactions on Au(111) (ref. \(^\text{30}\)), as recently shown by us for 4BrAn (ref. \(^\text{28}\)). The periodic homocoupling of the precursors gives rise to the formation of anthracene \((n=3)\) and pentacene \((n=5)\) polymers, whose structural and electronic characterization is summarized in Figs. 2 and 3.
The deposition of a submonolayer coverage of 4BrAn or 4BrPn on Au(111) and subsequent annealing at 500 K results in the emergence of long polymeric wires (see Supplementary Fig. 10). Residual bromine atoms detached from the precursors are fully removed from the substrate at this temperature. High-resolution non-contact-AFM (nc-AFM) imaging with a CO-functionalized tip reveals that polymers are planar and formed by intact anthracene (Fig. 2a,b) and pentacene (Fig. 3a,b) moieties, and linked by linear bridges (Figs. 2b and 3b). Defects within the polymer chains are scarce (see Supplementary Fig. 10 for long-range images of the different polymers). The polymerization eventually terminates once the entire =CBr3 group is lost and the acene backbone passivated by residual atomic hydrogen.

In the case of the anthracene polymer, as recently reported by us and others, the calculated electronic structure using DFT reveals the presence of dispersive valence bands (VBs) and conduction bands (CBs; Fig. 2c), where scanning tunnelling spectroscopy (STS) shows a sizable bandgap of ~1.5 eV (Fig. 2d). Calculated band structures and dI/dV maps (Fig. 2e) match very well with the experimental evidence. In addition, the DFT electronic structure of a finite anthracene chain reveals the absence of end states (Fig. 2f and Supplementary Fig. 11), and inspection of the hydrogen-terminated ends of the polymer shows no signatures of an in-gap topological edge state (Fig. 2g,h). These findings demonstrate that the anthracene polymer is in a topologically trivial electronic phase, as predicted in Fig. 1a.

In the case of the pentacene precursor (n = 5), the reaction proceeds as previously described, achieving planar polymers with linearly linked pentacene moieties (Fig. 3b). DFT calculations display the presence of dispersive VBs and CBs (Fig. 3c). STS shows two resonances at ~150 meV and 200 meV (Fig. 3d), which we assign to the edge of the VB and CB, respectively (Fig. 3e). This results in the narrow bandgap of ~0.35 eV. The bandgap value obtained from STS measurements is typically reduced by the additional electron screening imposed by the presence of an underlying metallic surface, with respect to the intrinsic bandgap of the polymer in the gas phase. The proximity to the topological transition within the structure family (Fig. 1) makes the polymer highly susceptible to strong relative bandgap renormalization. This can be induced for example by structural relaxations (by influencing the bond length) or by the environment, independently of screening effects (see details in Supplementary Note 5). Consequently, the bandgap of the polymer in the gas phase with respect to the one placed on a metallic surface can be further reduced if it is found closer to the topological phase transition. This scenario is supported by quasiparticle GW calculations of the free-standing pentacene polymer, which predict a nearly metallic bandgap E-gallery of ~0.05 eV and a reopening of the bandgap for polymers with larger acene units (see Supplementary Note 5).

Despite the fact that DFT simulations cannot correctly predict the magnitude of the intrinsic bandgap of the polymer, they describe the character of the frontier orbitals of the VB and CB edges of both polymers well. Indeed, the agreement between experimental and simulated dI/dV maps is excellent, validating the character of the frontier orbitals predicted by DFT calculations (see Figs. 2e and 3e). Interestingly, the character of the CB dI/dV maps of the pentacene polymer is similar to that of the VB dI/dV maps of the anthracene polymer, and vice versa. This electronic swap plays a critical role in the understanding of the topological phase and the...
electronic transformation of the π-conjugated polymers, as we will show in the next section.

Regarding the topological class of the pentacene polymer, the DFT calculation predicts the presence of in-gap zero-energy edge states at the H-terminated end of finite polymer chains (Fig. 3f and Supplementary Fig. 11), thus positioning it in the non-trivial region of the structural phase diagram. Experimentally, this end state is indeed readily observed as a strong resonance by STS at the Fermi level, at –75 meV (edge of VB) and 200 meV (edge of CB; Fig. 4c). Experimental STS spectra recorded over the polymers on the Au(111) surface show two frontier resonances close to the Fermi level, at –75 meV (edge of VB) and 200 meV (edge of CB; Fig. 4d) giving a narrow bandgap of ~0.3 eV. Interestingly, the dI/dV maps of the VB and CB edges have intensity maxima over the coupling bridges and on the voids adjacent to them.

The deposition of a submonolayer coverage of 4BrBiA (10,10′-bis(dibromomethylene)-10H,10′H-9,9′-bianthracenyldiene) precursor (Fig. 4a), which belongs to the family of fused acenes.

Next, we show that our concept of achieving narrow-bandgap polymers by tuning their structure to the topological phase boundary can be extended to other structure families. To this end, we adopted the same on-surface synthesis strategy as before to form bisanthenyl polymers on the Au(111) surface, this time using the bisanthenyl precursor (Fig. 4a), which belongs to the family of fused acenes.

The deposition of a submonolayer coverage of 4BrBiA on Au(111) and subsequent annealing at 500 K gives rise to the emergence of long polymeric wires (Fig. 4a,b and Supplementary Fig. 10). As illustrated by high-resolution nc-AFM imaging with a CO tip, the polymers are planar and formed by bisanthenyl moieties linked by linear bridges; that is, we keep the same bridge structure, but change to a larger repeating unit.

Again, the excellent agreement between experimental STS measurements and DFT calculations allows the unambiguous determination of the bulk electronic structure of the polymer (Fig. 4c). Experimental STS spectra recorded over the polymers on the Au(111) surface show two frontier resonances close to the Fermi level, at ~75 meV (edge of VB) and 200 meV (edge of CB; Fig. 4d) giving a narrow bandgap of ~0.3 eV. Interestingly, the dI/dV maps of the VB and CB edges have similar symmetry to the pentacene polymer.

Both tight-binding and GW calculations of the polymer family of fused acenes reveal that the topological phase transition, with a nearly vanishing gap (smaller than 0.05 eV), is expected at n = 3, that is, the bisanthenyl polymer (Supplementary Figs. 1, 16 and 17).
DFT calculations predict a larger bandgap (Supplementary Fig. 1) and the presence of edge states for the finite structures (Fig. 4g and Supplementary Fig. 11). The latter is in full correspondence with the observation of the zero-energy edge states in the experiment (Fig. 4h,i). In analogy to the pentacene case, the bisanthene polymer is located close to the topological transition in the non-trivial region.

Relation between resonant form and topological quantum phase of $\pi$-conjugated polymers

At this stage, it is important to realize that the polymers described here may adopt two extreme resonant forms: either the bridge being an alkyne (ethynylene) and the acene fully aromatic, or the bridge being a cumulene and the acene adopting a quinoid structure (see Fig. 1a and Supplementary Fig. 18). In combination with the small gap, this raises the question of a Jahn–Teller- or Peierls-type structural instability forcing an opening of the bandgap. Herein, it is important to highlight that the ground state of these polymers is composed of a different mixture of the two $\pi$-conjugated forms instead of their pure states depending on the acene moiety size, with only one global minimum along the variation of the resonant form from aromatic–ethynylene towards quinoid–cumulene, according to the DFT simulations (see Supplementary Note 7 and Supplementary Fig. 19). As a result, the existence of the single global minimum opens up a possibility to tune the system to achieve the metallic state.

The symmetry of the frontier orbitals seen in the $dI/dV$ maps is not the only similarity shared by the topologically non-trivial bisanthene and pentacene polymers. High-resolution AFM images acquired with a CO tip also show several similarities that are not present in the case of the anthracene polymers. Namely, the nc-AFM images of the anthracene polymer display the triple bond as a faint protrusion (see Fig. 2 and Supplementary Fig. 20), revealing the presence of the ethynylene $\text{Br}_2$ arrangement of the linear...
bridge, as recently illustrated for 1D molecular wires\textsuperscript{26,27}. However, in the case of the pentacene and bisanthene polymers, the triple-bond signature in the bridges is absent, as shown in Figs. 3 and 4 and Supplementary Fig. 20, indicating the increasing cumulene (=C≡C=) character of the bridge.

These findings highlight that the anthracene polymer adopts the ethynylene aromatic structure of the \( \pi \)-conjugation, while the two topologically non-trivial polymers prefer the cumulene-like quinoid form. Such results are also supported by a thorough analysis of the DFT simulations of the bond length variations (see explanation in Supplementary Note 8 and Supplementary Fig. 21) and of the charge density isosurfaces plotted with the high-resolution nc-AFM images (see details in Supplementary Note 9 and Supplementary Fig. 22).

The transition between aromatic/quinoid and ethynylene/cumulene character in \( \pi \)-conjugated polymers was rationalized by the level crossing, where HOMO/LUMO frontier orbitals of distinct symmetry swap\textsuperscript{39}. A detailed analysis of the character of the frontier orbitals of all three polymers confirms this scenario (see Supplementary Fig. 23). Namely, in the case of the anthracene polymer, the highest-occupied wave function at the K edge of the Brillouin zone shows \( \pi \)-bonding character between the two C atoms forming the triple bond, reinforcing the ethynylene \( \equiv \text{C} \equiv \text{C} \equiv \) character. However, in the case of the pentacene and bisanthene polymers, the wave function with this symmetry is found as the lowest unoccupied orbital. This rationalizes the weakening of the triple bond. This effect, together with a relatively small energy difference between the two \( \pi \)-conjugated forms, facilitates the promotion of the cumulene-like quinoid over the ethynylene aromatic form. The level crossing of the frontier orbitals accompanying the electronic \( \pi \)-conjugated transition changes the nodal character of the frontier wave functions forming the conduction band. Consequently, this gives rise to a change of the Zak phase identifying the transition of the topological phase (see underlying discussion in Supplementary Notes 2–4). Thus, we conclude that there is a direct relationship between the topological and the \( \pi \)-conjugated transitions.

It has been demonstrated that the aromatic character of acene monomers tends to \( \pi \)-electron confinement within the rings while the quinoid character promotes delocalization of \( \pi \)-electrons along the polymer. Therefore, polymers consisting of acene monomers linked by ethynylene/cumulene bridges open a playground for the competition between \( \pi \)-electron localization within acene rings and delocalization along the bridges\textsuperscript{39}. For small acene monomers with a large bandgap, the ground-state aromatic form has a much lower energy than the quinoid form. Under such circumstances, the polymers prefer to adopt the ethynylene aromatic \( \pi \)-conjugation form as the ground state. However, with increasing size of the acene monomers, the energy difference between the aromatic and quinoid structures becomes small, lowering the energy penalty for promoting the cumulene-like quinoid \( \pi \)-conjugation form along the polymer. At a certain size of the acene monomer, the enhanced contribution of the cumulene-like quinoid \( \pi \)-conjugation in the ground-state structure of the polymer causes the level crossing, and the polymers transform into the topologically non-trivial phase. The situation when two frontier orbitals involved in the crossing level mechanism become degenerated corresponds exactly to the topological phase transition featuring metallic character. In the topologically trivial phase, the enhancement of the cumulene-like quinoid \( \pi \)-conjugation leads to a decrease of the bandgap value, whereas in the topologically non-trivial phase, this causes its increase and the appearance of the zero-energy edge states within the gap. Thus, it is evident that the size of the bandgap is determined by the proximity to the topological phase transition, that is, the variation of the crossing level with degenerated frontier orbitals.

Conclusions

We establish the fundamental relationship between topological quantum phases and change of resonant forms in \( \pi \)-conjugated polymers. We predict a topological phase transition in the families of linearly bridged acene and fused acene polymers while increasing the size of the monomer. By exploiting on-surface chemical protocols we engineer \( \pi \)-conjugated polymers exhibiting unique electronic properties featuring narrow bandgaps and in-gap zero-energy edge states when in the topological non-trivial quantum phase close to the topological transition point. We envision that these polymers could find applications in a wide variety of areas including molecular electronics, optoelectronics, organic solar cells and quantum information technology\textsuperscript{40}.

Furthermore, we anticipate that from the conceptual framework described here, the bandgap could be tuned by a clever chemical design, targeting to position the polymer as close as possible to the topological transition point, with the final goal of synthesizing intrinsic metallic polymers, that is, achieving metallic character without chemical or electrochemical doping\textsuperscript{41}. In addition, intrinsic conducting polymers could revive efforts in condensed matter physics such as the quest for high-temperature organic superconductors\textsuperscript{42}, the expression of Tomonaga–Luttinger liquid behaviour in polymers or the deeper understanding of the metal-to-insulator Mott transition in organic nanomaterials\textsuperscript{43}.

Online content

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Methods

Synthesis of molecular precursors. The molecular precursors were synthesized following the general Ramirez–Corey–Fuchs protocol for synthesizing alkynes from carbononyls, with minor modifications. The general procedure was as follows: a solution of carbon tetrabromide (4 equiv.) and triphenylphosphine (8 equiv.) in dry toluene was stirred at room temperature for 30 min. Thereafter, corresponding quinone (1 equiv.) was added in one portion and the resulting mixture refluxed for a period of time between 24 and 48 h until the reaction was completed (monitored by TLC). Reaction products were purified by column chromatography (with silica gel as the stationary phase and hexane as the eluent). The characterization of all 4BrAn, 4BrPn (ref. 35) and 4BrBA (ref. 36) products is in agreement with their reported spectroscopic features.

Sample preparation and STM/STS/nc-AFM measurements. Experiments were performed in an ultrahigh vacuum system that hosts a low-temperature Omicron STM and in an ultrahigh vacuum system equipped with a Createc STM, both with a base pressure below 5 × 10−10 mbar. For the Omicron STM, images were acquired with electrochemically etched tungsten tips, whereas for the Createc STM, images were taken by Pt/Ir tips, cut and sharpened by focused ion beam. In both cases, a bias (Vz) was applied to the sample at a temperature of ~4 K. The Au(111) substrate was prepared by standard cycles of Ar+ sputtering (800 eV) and subsequent annealing at 723 K for 10 min. Molecular precursors were deposited by organic molecular-beam epitaxy from a quartz crucible maintained at 373 K (4BrAn), 423 K (4BrPn) or 443 K (4BrBA) on a clean Au(111) surface held at room temperature. Whenever necessary samples were annealed to the desired temperature and subsequently transferred to the STM stage, which was maintained at 4 K. In nc-AFM imaging, a Pt/Ir tip mounted on a qPlus sensor (resonant frequency of ~30 kHz, stiffness of ~1,800 N m−1) was oscillated with a constant amplitude of 50 pm. The tip apex was functionalized with a CO molecule, and all images were captured in constant-height mode.

DFT and GW calculations of electronic structure. DFT calculations for all DFT and GW calculations of electronic structure.

images were captured in constant-height mode. The tip apex was functionalized with a CO molecule, and all STM, images were taken by Pt/Ir tips, cut and sharpened by focused ion beam. In both cases, a bias (Vz) was applied to the sample at a temperature of ~4 K. The Au(111) substrate was prepared by standard cycles of Ar+ sputtering (800 eV) and subsequent annealing at 723 K for 10 min. Molecular precursors were deposited by organic molecular-beam epitaxy from a quartz crucible maintained at 373 K (4BrAn), 423 K (4BrPn) or 443 K (4BrBA) on a clean Au(111) surface held at room temperature. Whenever necessary samples were annealed to the desired temperature and subsequently transferred to the STM stage, which was maintained at 4 K. In nc-AFM imaging, a Pt/Ir tip mounted on a qPlus sensor (resonant frequency of ~30 kHz, stiffness of ~1,800 N m−1) was oscillated with a constant amplitude of 50 pm. The tip apex was functionalized with a CO molecule, and all images were captured in constant-height mode.

DFT and GW calculations of electronic structure. DFT calculations for all free-standing finite and infinite systems (anthracene, pentacene and bisanthene) were done using FHI-AIMS and Fireball packages. All geometry optimizations and electronic structure analyses were performed twice, using two different exchange–correlation functionals: BEEF (ref. 37) and B3LYP (ref. 38). Systems were allowed to relax until the remaining atomic forces reached below 10−2 eV Å−1. We also performed many-body non-self-consistent GW calculations to obtain quasiparticle spectra of infinite polymers implemented within the FHI-AIMS package with default values. In these G, W, calculations, the initial single-particle wave functions and the optimized geometries were obtained using the GGA–PBE exchange–correlation functional. For all infinite systems with a periodic boundary condition, a Monkhorst–Pack grid of 18 × 1 × 1 was used to sample the Brillouin zone. Theoretical d/dV maps were calculated by the DFT FireballII program and with Probe Particle Scanning probe Microscopy (PPSTM) code for an s-like orbital tip.

Data availability

The data for the tight-binding calculation as presented in Fig. 1, as well as data from DFT and DFT DOS data as presented in Figs. 2, 3 and 4 are available as source data. Other data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Code availability

The tight-binding calculations have been performed using a custom-made code written by B.C., O.G., P.J., N.M. and D.E., with contributions from all the authors.

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