



**EXPLORATION OF THE 2-DIMENSIONAL π -d CONJUGATED COORDINATE
POLYMER Cu-BENZENEHEXATHIOL**

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1. Background

In the field of materials science, coordination polymers comprise a promising subdiscipline. With applications in energy storage, catalysis, photovoltaics, computing, and more, many scientists are conducting cutting-edge research on these materials. Research into coordination polymers only began in fervor a few decades ago – compared to centuries for many other scientific disciplines. To better understand my thesis work, I will first delve into the history of my field of coordination polymer development and research.

Coordination polymers are a class of materials composed of repeating coordination entities extending in one, two or three dimensions¹. When a molecule is “coordinated”, it has a central node (often a metal ion or cluster-shaped molecule) which is surrounded by many tightly bound molecules or ions, called ligands. Interest in this diverse class of molecules took off from a groundbreaking paper written in 1990 that has now been cited over 2000 times. The paper entitled: “Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods...” by B. F. Hoskins and R. Robson² was the seminal text for what is now a thriving and branched field within materials science.

Conceptually, this paper lays the groundwork for the decades of research that came after. Through their writing, Hoskins and Robson describe their thought process while devising and then synthesizing these frameworks. Within the brainstorm, the authors suggest multiple potential ligand (linker) molecules but ultimately settle on a simple cyanide (CN) ligand. Because of its propensity to bind metals on either end, this ligand creates the “...metal-ligand-metal-ligand...” chain required for these theoretically infinite chains. They also propose much of the basis theory for why these polymers can form infinite, ordered, three dimensional frameworks (limited by molecule availability and kinetics) with very few defects. This includes the authors elaborating on how the bonding between metal center and linking ligand is reversible; the forming material can “backtrack” to remove any incorrect links, then reform the correct bond. This mechanism is the heart of how coordination polymers remain nearly defect-free and can exhibit all the exotic phenomena mentioned later in this paper. Without their detailed work, the field of coordination polymer chemistry either would not exist or would be pushed back decades.

Since the publication of Hoskins and Robson’s paper, the coordination polymer field has come far. From its 1990 publication, their work has been directly cited 2000 times and built upon much more. For this new era, the textbook Coordination Polymers: Design, Analysis and Application³, published in 2008, is a useful compilation of information in this field. Detailed syntheses, characterizations, and applications are described for a plethora of coordination polymers throughout its 400 pages. The authors of this text synthesized the most impactful works that built upon Hoskins and Robson’s research across the many subdisciplines of coordination polymers—including metal organic frameworks (MOFs), molecular nets, two-dimensional coordination

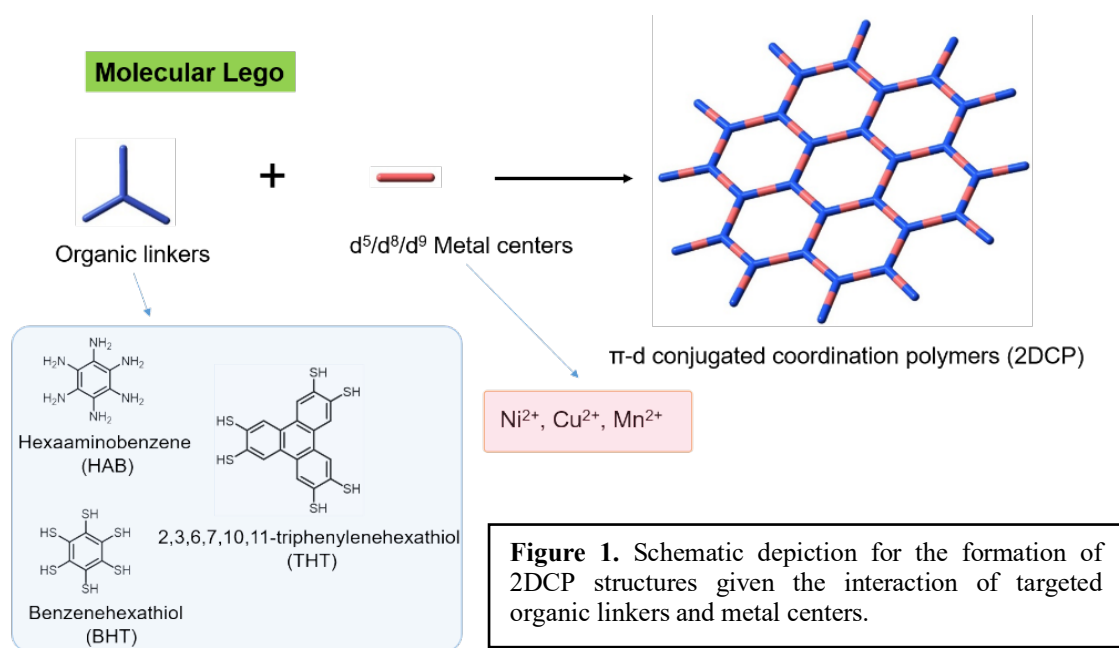
polymers, and reactive coordination polymers—and all with a wide variety of metallic and ligand compositions.

At the field's inception, Hoskins and Robson propose that scaffold-like coordination polymers could only be formed from tetrahedral or octahedral metal centers, but in the 2008 textbook, authors highlight many newly discovered geometries beyond what Hoskins and Robson originally predicted. They also envision the synthesis of new frameworks with larger pores and cavities with applications in storage. This is the basis for the exploding field of (MOFs) today. The framework that Hoskins and Robson synthesized was more demonstrative than application based, but this demonstration prompted other researchers to begin designing coordination polymers with specific applications. The genesis of the coordination polymer research field directly leads back to Hoskins and Robson's exploratory work making this paper seminal.

2. Two-Dimensional Coordination Polymers

One emergent area in the field of coordination polymers focuses on two-dimensional coordination polymers (2DCPs). Two-dimensional materials are comprised of single-layer sheets stacked on top of each other, like a ream of printer paper, and held together by weak non-covalent Van der Waal forces. The stacks can then be exfoliated down to single atom thick layers via various methods if the researcher decides; otherwise, they are left in a thin stack (20-50 nm), usually as a thin film. These delicate materials feature a wide range of electronic, optical, and structural properties arising from the tunable atomic composition and varied crystal structure of their layers. These allow for the synthesis of layered 2DCPs with precisely controlled electronic, optical, and structural properties. Application of these materials in devices is ultimately constrained by the fact that only a small number of 2DCPs have been discovered thus far that can be synthesized, and researchers lack control over the morphology of those materials that do have synthetic schemes. 2DCPs are typically obtained as nano- or microcrystalline powders, and few experimental procedures have been identified that furnish 2DCPs as highly oriented thin films which are required for further characterization and application in devices.

A class of 2DCPs with promising electronic properties have electron orbital overlap between the d orbital on the ionic transition metal center and a π bond on the ligand [Figure 1].



This so called π -d conjugation creates unique electronic character since the conjugation delocalizes the electron density allowing for easy electronic conduction. To take advantage of this long-range charge delocalization, π -d conjugated 2DCPs are made up of planar organic ligands, such as benzenehexathiol (BHT), and first-row transition metal ions including Mn, Co, Ni, and Cu. It is possible to achieve 2D structures with high electrical conductivity ($> 10^3 \text{ S cm}^{-1}$), high-temperature magnetic ordering ($T_c = 105 \text{ K}$), and enhanced catalytic activity⁴. These properties allow the 2DCPs to be utilized as active layers and electrodes in a wide range of applications such as electrocatalysis⁵, energy storage⁶, transistors⁷, and sensors⁸. Additionally, computational researchers have predicted these conjugated CPs to exhibit optoelectronic phenomena as the quantum anomalous Hall effect⁹, superfluid transport¹⁰, and high-temperature surface superconductivity¹¹.

Recently, Cu-BHT has attracted much research attention due to its planar and metallic nature and its potential for conducting behavior driven by oxidation and additional theorized properties that remain unproven experimentally. For example, metal-BHT-based 2DCPs are predicted topological insulators, giving them great potential for applications in quantum computing and spintronics.

3. Topological Insulating Properties

Topological insulators are best understood from the viewpoint of electron conduction—electricity—and superconduction. Electricity is created when electrons, negatively charged particles, move through a material. The mechanism of their transmission is termed *conduction* by scientists. The conduction of electricity is crucial in everyday life to operate electronic devices that the world is now dependent on. To be usable, electricity needs to be transported from a power plant to individual homes, but normal methods of conduction lead to major losses of electricity each year of around 5%¹². To solve this problem, scientists are exploring applications of superconducting materials, or those that have infinite conductivity and no resistance.

The biggest drawback is that superconduction in the past has only existed at very cold temperatures. This makes applications of superconduction materials very costly and impractical. To get around this problem, researchers have attempted adjusting material parameters, including material thickness, to create high-temperature superconductors. Until the 1980s, scientists believed that superconduction could only occur in the thick area inside of a material, or the bulk, in opposed to on the surface. That theory is now obsolete because of the work done by David J. Thouless, F. Duncan M. Haldane, and J. Michael Kosterlitz on 2-dimensional materials exhibiting superconductivity which ultimately culminated in the 2016 Nobel Prize in Physics¹³.

In a metal, “free” electrons make up an *electron cloud* that can flow inside of to conduct electricity. This is like a sea of negatively charged particles floating through the metal’s crystalline lattice. Issues occur when those electrons bump into each other or the positively charged nuclei that make up the lattice. The frequency of these collisions dictates the resistance of a certain material; the more resistive, the more collisions occur within a given time. These collisions convert any electricity the colliding electrons held into heat which then disseminates through the crystal lattice. This electricity to heat conversion causes the 5% loss of energy during long-distance electricity transmission¹². This problem leads directly to the biggest benefit of superconductors which is their property of having no resistance.

Superconductivity was first discovered by Karmarlingh Onnes who was awarded the Nobel Prize in Physics in 1913¹⁴. His superconductor was simply a piece of solid mercury supercooled to 4.2K by liquid helium in which he measured no electronic resistance¹⁵. Onnes believed superconductivity could occur in other bulk metals, but never in very thin layers of a material now known as 2-dimensional materials. Over the next few decades, scientists discovered the mechanism by which superconductivity occurs. When two electrons “bond” together to form a

particle known as a Cooper Pair, they distort the crystalline lattice as they pass through which allows for the measured zero resistance. As with Onnes' work, following researchers said this always occurred at temperatures just above absolute zero which made superconductors very impractical to use despite their world changing properties. In the search for high-temperature superconductors, the 2016 Physics Nobel Laureates unintentionally overturned Onnes' theory of exclusive bulk superconducting by showing materials that could be superconductive in thin layers. This was made possible due the material exhibiting *topological phases* which were previously unknown phenomenon in conductive materials.

Topological phases have replaced the bulk superconducting theory. They arise from the branch of mathematics called topology which deals with shapes and their surfaces and allows for their deformation within space. Famously, this field focuses on the number of holes in an object and therefore allows researchers to think of a coffee mug and a donut as the same shape—both have one hole. When applied to the 2016 Physics Nobel Prize research, topological phenomena are those that occur on the surface of a material. The topological states form in a very thin sheet on the surface of a given material. This thin layer acts much differently than the material's bulk and therefore is referred to as a 2-dimensional material, which Onnes previously theorized could not become superconductive.

In regard to conduction, these surface states act like ice on top of a road; a car can easily slide over the icy road, but the road by itself does not have the slippery properties of ice. In terms of conduction, the car (an electron) moves along the road (a conductive material) with friction between its tires and the road (resistance). When the car drives down a hill, there is enough friction between the tires and the road to brake and slow down the car. If a thin layer of ice formed over this hill (a new topological state), there would no longer be the resistance necessary to slow the car and it will slide very quickly down the hill with no resistance. Here, the normal asphalt is analogous to the "bulk" inside of the material while the slippery ice would be the superconducting "surface". Materials whose bulk is insulating—very resistive—but have a nearly superconductive—little to no resistance—surface are termed topological insulators.

Topological materials are the next generation of superconductive materials and will replace Onnes' original supercooled gas contraptions which are costly and hard to maintain. Luckily, researchers have found that the desired intrinsic topological states can exist in crystalline materials at much higher temperatures. From this odd conduction mechanism, topological insulators exhibit unique electron spin and charge/ion transport phenomena that may lead to entirely new device paradigms for spintronics and quantum computing. Notably, conducting surfaces can exhibit helical Dirac bands with strong spin-polarized linear dispersions, quantum spin Hall effects¹⁶, giant magneto-electric effects¹⁷, giant magneto-optical effects¹⁸, and the appearance of Majorana fermions¹⁹. Intrinsic topological states could exist in crystalline materials, such as topological insulators with strong spin-orbit coupling (SOC). Their special π -d electron conjugation elicits topological phenomena and therefore superconduction. These materials are usually made of inorganic atoms which have many drawbacks. One is that they do not easily lend themselves to chemical functionalization or tunability. Since they must be made from specific inorganic atoms, researchers struggle to adjust the characteristics of each material. Also, these materials do not readily form large area and uniform thin films which are necessary for further applications.

To solve this problem, researchers, including myself, are exploring topological insulators made of organic materials which are much more tunable. My research explores thin layer (topological) superconduction and other quantum phenomena within a Cu-BHT 2DCP. Without the work from the 2016 Nobel Prize in Physics, my research would not exist.

4. Cu-Benzenehexathiol Coordination Polymer

Until recently, all topological insulating materials that were theoretically predicted and experimentally confirmed are purely inorganic based on metal-chalcogenides; this includes HgTe quantum wells²⁰, binary metal chalcogenides such as Bi₂Te₃²¹, ternary metal chalcogenides such as TlBiTe₂²², and several Heusler compounds²³. Although the topological insulating nature of these inorganic materials has been experimentally observed for very size constrained flakes (2-5 nm), they do not easily lend themselves to chemical functionalization or tunability, and do not readily form large area and uniform thin films. To address these challenges, various organic materials have been predicted to exhibit topological insulating states since they have well-established synthetic protocols, and a variety of ligands. For example, Prof. Feng Liu in the Department of Materials Science and Engineering here at the University of Utah reported the first theoretical prediction for the possible existence of organic topological insulators in 2D π -d conjugated coordination polymers (2DCPs) based on copper benzenehexathiol (Cu-BHT) structures²⁴. While a good number of theory groups have followed to predict different forms of organic topological insulating materials, the experimental realization of organic topological phases with confirmed topological properties remains underexplored.

In general, 2DCPs can be produced in a more flexible, scalable, and inexpensive way than their inorganic counterparts, putting forth a new promising platform to investigate various topological effects. More importantly, the organic nature of 2DCPs provides a versatile platform wherein molecular structure, intermolecular packing, and mesoscale morphology can be systematically and predictably tuned. This fine control will allow for in-depth multiscale correlations between structure and properties, thereby enabling the development of rational and predictive design principles for tuning topological, thermal, and electronic properties. Cu-BHT thin films are a very promising material for this purpose and my work will detail preliminary experiments done.

5. Previous Work

Previously, the scientific challenge to overcome was to develop a synthetic approach that would yield large area, highly ordered, and defects-controlled 2DCPs with specific magnetic and electronic properties that can be incorporated into functional devices. While several synthetic routes have been reported for the fabrication of 2DCPs thin films⁸, these assembly strategies typically yield thin films that are too thick (> 300 nm) or have limited crystalline quality (i.e., domain sizes of a few hundred nanometers or smaller). These characteristics make them unsuitable for the fabrication of large area devices that require single (or few) layered 2DCPs with large surface area (mm² or cm²) and exquisite crystalline quality. Recently, Galeotti *et al.* proved that 2DCPs can achieve dimensions greater than 100 x 100 nm², but they used an expensive Au (111) substrate²⁵. The next goal is to achieve large area and highly ordered thin films of 2DCPs that exhibit desirable quantum phenomena with cheaper metal centers such as Ni and Cu on inexpensive substrates such as glass. Previously, synthesis of these films involved coordinating the transition metal center and ligand at the interface between two substances, one containing metal ions and the other ligands. The two substances were either both liquids with an aqueous and organic layer (liquid-liquid growth), or one vapor and one liquid (vapor-liquid growth). During these two synthetic schemes, the 2DCPs often aggregate and do not form the desired long-range ordering. These aggregates can be characterized, but with unreliable results. To overcome this challenge, as part of my first experiment, I utilized a chemical vapor deposition (CVD) synthetic route to successfully investigate the formation of single crystalline 2DCP thin films. With that challenge overcome, I moved to conducting a rigorous exploration of the magnetic and exotic electronic properties that Cu-BHT 2DCP thin films are theorized to exhibit.

So far, I have worked to develop synthetic protocols that allow for the fabrication of large area, highly oriented 2DCP thin films with controlled defect states for the experimental realization

of topological and spin states. Thus, I performed an iterative closed-loop (theory-synthesis-characterization) search for new 2DCPs with higher energy scales and novel topological ground states.

The second goal of my research aims to explore new phenomena within Cu-BHT organic-based 2DCPs. Since synthetic procedures are now standardized, atomic composition and defects can be precisely tuned to elicit topological phenomena related to the evolution of Dirac cones, magnetism, and spin-thermal transfer. I will achieve this by magnetically doping the Cu-BHT films with Fe to create a paramagnetic sample.

Work Cited

- (1) Batten, S. R.; Champness, N. R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Öhrström, L.; O’Keeffe, M.; Suh, M. P.; Reedijk, J. Terminology of metal–organic frameworks and coordination polymers (IUPAC Recommendations 2013). *Pure Appl. Chem.* **2013**, *85* (8), 1715–1724. <https://doi.org/10.1351/PAC-REC-12-11-20>.
- (2) Hoskins, B. F.; Robson, R. Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods. A Reappraisal of the Zinc Cyanide and Cadmium Cyanide Structures and the Synthesis and Structure of the Diamond-Related Frameworks $[\text{N}(\text{CH}_3)_4][\text{CuI}\text{ZnII}(\text{CN})_4]$ and $\text{CuI}[4,4',4'',4''']\text{-Tetracyanotetraphenylmethane}\text{BF}_4\cdot\text{XC}_6\text{H}_5\text{NO}_2$. *J. Am. Chem. Soc.* **1990**, *112* (4), 1546–1554. <https://doi.org/10.1021/ja00160a038>.
- (3) Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers: Design, Analysis and Application*; Royal Society of Chemistry, 2008.
- (4) Stassen, I.; Burtch, N.; Talin, A.; Falcaro, P.; Allendorf, M.; Ameloot, R. An Updated Roadmap for the Integration of Metal–Organic Frameworks with Electronic Devices and Chemical Sensors. *Chem. Soc. Rev.* **2017**, *46* (11), 3185–3241. <https://doi.org/10.1039/C7CS00122C>.
- (5) Dong, R.; Pfeiffermann, M.; Liang, H.; Zheng, Z.; Zhu, X.; Zhang, J.; Feng, X. Large-Area, Free-Standing, Two-Dimensional Supramolecular Polymer Single-Layer Sheets for Highly Efficient Electrocatalytic Hydrogen Evolution. *Angew. Chem. Int. Ed.* **2015**, *54* (41), 12058–12063. <https://doi.org/10.1002/anie.201506048>.
- (6) Sheberla, D.; Bachman, J. C.; Elias, J. S.; Sun, C.-J.; Shao-Horn, Y.; Dincă, M. Conductive MOF Electrodes for Stable Supercapacitors with High Areal Capacitance. *Nat. Mater.* **2017**, *16* (2), 220–224. <https://doi.org/10.1038/nmat4766>.
- (7) Wu, G.; Huang, J.; Zang, Y.; He, J.; Xu, G. Porous Field-Effect Transistors Based on a Semiconductive Metal–Organic Framework. *J. Am. Chem. Soc.* **2017**, *139* (4), 1360–1363. <https://doi.org/10.1021/jacs.6b08511>.
- (8) Campbell, M. G.; Sheberla, D.; Liu, S. F.; Swager, T. M.; Dincă, M. $\text{Cu}_3(\text{Hexaiminotriphenylene})_2$: An Electrically Conductive 2D Metal–Organic Framework for Chemiresistive Sensing. *Angew. Chem. Int. Ed.* **2015**, *54* (14), 4349–4352. <https://doi.org/10.1002/anie.201411854>.
- (9) Zhao, A.; Shen, S.-Q. Quantum Anomalous Hall Effect in a Flat Band Ferromagnet. *Phys. Rev. B* **2012**, *85* (8), 085209. <https://doi.org/10.1103/PhysRevB.85.085209>.

- (10) Julku, A.; Peotta, S.; Vanhala, T. I.; Kim, D.-H.; Törmä, P. Geometric Origin of Superfluidity in the Lieb-Lattice Flat Band. *Phys. Rev. Lett.* **2016**, *117* (4), 045303. <https://doi.org/10.1103/PhysRevLett.117.045303>.
- (11) Kopnin, N. B.; Heikkilä, T. T.; Volovik, G. E. High-Temperature Surface Superconductivity in Topological Flat-Band Systems. *Phys. Rev. B* **2011**, *83* (22), 220503. <https://doi.org/10.1103/PhysRevB.83.220503>.
- (12) Wirfs-Brock, J. Lost In Transmission: How Much Electricity Disappears Between A Power Plant And Your Plug? <http://insideenergy.org/2015/11/06/lost-in-transmission-how-much-electricity-disappears-between-a-power-plant-and-your-plug/> (accessed 2021 -11 -11).
- (13) Class for Physics of the Royal Swedish Academy of Sciences. The Nobel Prize in Physics 2016: Topological Phase Transitions and Topological Phases of Matter. The Nobel Prize 2016.
- (14) Onnes, H. K. Nobel Lecture: Investigations into the Properties of Substances at Low Temperatures, Which Have Led, amongst Other Things, to the Preparation of Liquid Helium. The Nobel Prize 1913.
- (15) Onnes, H. K. *Research Notebooks 56, 57*; Kamerlingh Onnes Archive: Leiden, the Netherlands.
- (16) Qi, X.-L.; Wu, Y.-S.; Zhang, S.-C. Topological Quantization of the Spin Hall Effect in Two-Dimensional Paramagnetic Semiconductors. *Phys. Rev. B* **2006**, *74* (8), 085308. <https://doi.org/10.1103/PhysRevB.74.085308>.
- (17) Essin, A. M.; Moore, J. E.; Vanderbilt, D. Magnetoelectric Polarizability and Axion Electrodynamics in Crystalline Insulators. *Phys. Rev. Lett.* **2009**, *102* (14), 146805. <https://doi.org/10.1103/PhysRevLett.102.146805>.
- (18) Tse, W.-K.; MacDonald, A. H. Giant Magneto-Optical Kerr Effect and Universal Faraday Effect in Thin-Film Topological Insulators. *Phys. Rev. Lett.* **2010**, *105* (5), 057401. <https://doi.org/10.1103/PhysRevLett.105.057401>.
- (19) Fu, L.; Kane, C. L. Superconducting Proximity Effect and Majorana Fermions at the Surface of a Topological Insulator. *Phys. Rev. Lett.* **2008**, *100* (9), 096407. <https://doi.org/10.1103/PhysRevLett.100.096407>.
- (20) König, M.; Wiedmann, S.; Brüne, C.; Roth, A.; Buhmann, H.; Molenkamp, L. W.; Qi, X.-L.; Zhang, S.-C. Quantum Spin Hall Insulator State in HgTe Quantum Wells. *Science* **2007**, *318* (5851), 766–770. <https://doi.org/10.1126/science.1148047>.
- (21) Xia, Y.; Qian, D.; Hsieh, D.; Wray, L.; Pal, A.; Lin, H.; Bansil, A.; Grauer, D.; Hor, Y. S.; Cava, R. J.; Hasan, M. Z. Observation of a Large-Gap Topological-Insulator Class with a Single Dirac Cone on the Surface. *Nat. Phys.* **2009**, *5* (6), 398–402. <https://doi.org/10.1038/nphys1274>.
- (22) Chen, Y. L.; Liu, Z. K.; Analytis, J. G.; Chu, J.-H.; Zhang, H. J.; Yan, B. H.; Mo, S.-K.; Moore, R. G.; Lu, D. H.; Fisher, I. R.; Zhang, S. C.; Hussain, Z.; Shen, Z.-X. Single Dirac Cone Topological Surface State and Unusual Thermoelectric Property of Compounds from a New Topological Insulator Family. *Phys. Rev. Lett.* **2010**, *105* (26), 266401. <https://doi.org/10.1103/PhysRevLett.105.266401>.

- (23) Chadov, S.; Qi, X.; Kübler, J.; Fecher, G. H.; Felser, C.; Zhang, S. C. Tunable Multifunctional Topological Insulators in Ternary Heusler Compounds. *Nat. Mater.* **2010**, *9* (7), 541–545. <https://doi.org/10.1038/nmat2770>.
- (24) Wang, Z. F.; Su, N.; Liu, F. Prediction of a Two-Dimensional Organic Topological Insulator. *Nano Lett.* **2013**, *13* (6), 2842–2845. <https://doi.org/10.1021/nl401147u>.
- (25) Galeotti, G.; De Marchi, F.; Hamzehpoor, E.; MacLean, O.; Rajeswara Rao, M.; Chen, Y.; Besteiro, L. V.; Dettmann, D.; Ferrari, L.; Frezza, F.; Sheverdyaeva, P. M.; Liu, R.; Kundu, A. K.; Moras, P.; Ebrahimi, M.; Gallagher, M. C.; Rosei, F.; Perepichka, D. F.; Contini, G. Synthesis of Mesoscale Ordered Two-Dimensional π -Conjugated Polymers with Semiconducting Properties. *Nat. Mater.* **2020**, *19* (8), 874–880. <https://doi.org/10.1038/s41563-020-0682-z>.