Identification of strongly interacting organic semimetals

R. Matthias Geilhufe,1 Bart Olsthoorn1

1 Nordita, KTH Royal Institute of Technology and Stockholm University, Roslagstullsbacken 23, 10691 Stockholm, Sweden

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Semimetals have attracted huge attention due to their striking transport properties, analogies to high energy physics phenomena, and potential for functionalization. Their realization relies on a delicate combination of symmetry, electron-filling, and band ordering enforcing the existence of the nodes in the band structure at the chemical potential while having a vanishing density of states (DOS) at the crossing point. It has been shown extensively for the case of Dirac semimetals, that under a sufficiently high interaction strength a dynamical mass term can be generated leading to a quantum phase transition into a gapped phase. This quantum phase transition strongly depends on: i) the effective fine structure constant $\alpha_{\text{eff}}$; ii) the dimension of the system; iii) the number of fermionic flavors. Similar phenomena where also discussed in the case of Weyl semimetals and line-node semimetals and organic crystals.

With the goal of identifying experimentally feasible materials to investigate interaction effects in nodal semimetals we focus on organic crystals. Organic crystals typically exhibit strong intramolecular forces and weak intermolecular forces, leading to tiny hopping amplitudes for electrons between molecules and resulting flat electronic bands. The flatness corresponds to a tiny quasiparticle kinetic energy and dominant interaction effects. We focus on the excitonic insulator state occurring when a weakly screened Coulomb interaction between a hole and an electron leads to an electron-hole bound state. Due to generically flat bands, organic crystals represent a promising materials class in this regard. We combine machine learning, density functional theory, and effective models to identify specific example materials. Without taking into account the effect of many-body interactions, we found the organic charge transfer salts (EDT-TTF-I$_2$)$_2$(DDQ)$\cdot$(CH$_3$CN) and TSeF-TCNQ and a bis-1,2,3-dithiazolyl radical conductor to exhibit a semimetallic phase in our ab initio calculations. Adding the effect of strong particle-hole interactions for (EDT-TTF-I$_2$)$_2$(DDQ)$\cdot$(CH$_3$CN) and TSeF-TCNQ opens an excitonic gap in the order of 60 meV and 100 meV, which is in good agreement with previous experiments on these materials.

INTRODUCTION

Dirac- and Weyl point- and line-node semimetals are characterized by a zero band gap with simultaneously vanishing density of states. Given a sufficient interaction strength, such materials can undergo an interaction instability, e.g., into an excitonic insulator phase. Due to generically flat bands, organic crystals represent a promising materials class in this regard. We combine machine learning, density functional theory, and effective models to identify specific example materials. Without taking into account the effect of many-body interactions, we found the organic charge transfer salts (EDT-TTF-I$_2$)$_2$(DDQ)$\cdot$(CH$_3$CN) and TSeF-TCNQ and a bis-1,2,3-dithiazolyl radical conductor to exhibit a semimetallic phase in our ab initio calculations. Adding the effect of strong particle-hole interactions for (EDT-TTF-I$_2$)$_2$(DDQ)$\cdot$(CH$_3$CN) and TSeF-TCNQ opens an excitonic gap in the order of 60 meV and 100 meV, which is in good agreement with previous experiments on these materials.

RESULTS

The general workflow of our study can be summarized as follows.

1. **Machine learning.** We trained a neural network (the continuous-filter convolutional neural network scheme - SchNet) on 24,134 band gaps of nonmagnetic materials taken from the Organic Materials Database - OMDB. We applied the model to 202,117 materials containing carbon and hydrogen stored in the crystallographic open database - COD.

2. **Band structure calculations.** We select 414 materials where the band gap is predicted small, but nonzero ($0.01 \text{ eV} \leq \Delta \leq 0.4 \text{ eV}$) and perform medium accuracy ab initio calculations using VASP incorporating the effect of spin-orbit interaction (SOI). Note that all calculations stored within the OMDB were performed without SOI. Out of the 414 materials we found promising features in the band structures for 9 materials. For these 9 materials we performed high-accuracy VASP calculations taking into account structural optimization and SOI. We found the organic charge transfer salts (EDT-TTF-I$_2$)$_2$(DDQ)$\cdot$(CH$_3$CN) and TSeF-TCNQ and a bis-1,2,3-dithiazolyl radical conductor which exhibit a semimetallic phase. Based on
symmetry and chemistry we determine the relevant mechanisms to protect the nodal features.

3. Effective models and excitonic gap. We construct an effective model for (EDT-TTF-1$_2$)$_2$(DDQ)·(CH$_3$CN) and TSeF-TCNQ using qsymm \cite{21} and GTPack \cite{22,24}. We solve a self-consistent excitonic gap equation, assuming a \textit{s}-wave gap.

We will discuss the outcome of the three steps in more detail in the following.

\section*{Machine Learning}

According to the OMDB, organic crystals show a mean \textit{ab initio} band gap of \( \approx 3 \text{ eV} \) with a standard deviation of 1 eV \cite{18}. Fig. 1(a) shows a comparison of the band gap distribution of the training set with the band gap distribution obtained using machine learning (ML). While the amount of data is much bigger for the materials taken from the COD, the general shape of the histogram of calculated and predicted gaps agrees well, i.e., the ML model successfully reproduced the band gap statistics. Due to the highly complex structures of organic crystals and the relatively small data set, we trained ML model has a large mean absolute error (MAE) of 0.406 eV. Compared to the average band gap of \( \approx 3 \text{ eV} \), this value represents a sufficient accuracy. However, as we are interested in the tiny gap regime, the order of the MAE value represents a sufficient accuracy. However, as we are interested in the tiny gap regime, the order of the MAE value is similar to our acceptance range 0.01 eV \( \leq \Delta \leq 0.4 \text{ eV} \). Nevertheless, the general guidance of our model was sufficient to identify a few final example materials. We note that a more sophisticated prediction scheme reaching a significantly advance the outcome of our approach in the future.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Machine learning predictions of electronic band gaps using the continuous-filter convolutional neural network scheme – SchNet. (a) band gap statistics of the initial OMDB data (\( \approx 2 \times 10^4 \) materials, count on the left) and the predicted gaps (\( \approx 2 \times 10^5 \) materials, count on the right); (b) performance of SchNet on the test set.}
\end{figure}

\textbf{Band Structure Calculations}

We verified the effect of SOI on the 414 predicted tiny gap materials. Our calculations revealed nine materials which exhibit nodes in their electronic band structure close to the Fermi level (respective COD-IDs \cite{20} are 1508451, 2100065, 2101483, 4114836, 4324376, 4334234, 4506562, 7014584, 7106265; see supplementary material). After performing a structural optimization, only 3 materials remain candidates for organic molecular semimetals: the organic charge transfer salts (EDT-TTF-I$_2$)$_2$(DDQ)·(CH$_3$CN) (1508451) and TSeF-TCNQ (2101483) and the bis-1,2,3-dithiazolyl radical (7106265) (COD-IDs given in brackets). The crystal and electronic structures are shown in Fig. 2.

(EDT-TTF-I$_2$)$_2$(DDQ)·(CH$_3$CN) (bis(3,4-diiodo-3’,4’-ethylenedithio-tetrathiafulvalene), 2,3-dichloro-5,6-dicyanobenzoquinone,acetenitrile) crystallizes in a triclinic lattice with space group P\(\bar{1}\) (2). The synthesis and characterization is described in Ref. \cite{21}, where indications towards (EDT-TTF-I$_2$)$_2$(DDQ)·(CH$_3$CN) being a semiconductor with a conductivity gap of 1220 K \( (\approx 105 \text{ meV}) \) were reported.

Synthesis and characterization of the organic charge transfer salt 2,2’,5,5’-tetracenealufavulene–7,8,8-tetracyano-p-quinodimethane (TSeF-TCNQ) can be found in Refs. \cite{25,26}. The material crystallizes in the monoclinic space group P2\(_1\)/c (14), where TSeF and TCNQ molecules arrange in a segregated stack structure, known to mediate conductivity in organic salts \cite{27}. The material exhibits a metallic high-temperature phase with a metal to insulator transition at temperatures of \( \approx 40 \text{ K} \) \cite{28}.

The ABABAB \( \pi \)-stacked bis-1,2,3-dithiazolyl radical was synthesized by Yu \textit{et al.} \cite{29}. It crystallizes in the non-centrosymmetric space group P2\(_1\)/c (19) and orders in a canted antiferromagnetic structure with \( T_N \approx 4.5 \text{ K} \). It was reported to undergo a spin-flop transition to a field-induced ferromagnetic state at 2 K and a magnetic field strength of \( H \approx 20 \text{ kOe} \).

For all materials the calculated crossing points occur at the Fermi level with simultaneously vanishing DOS. The selected \( \vec{k} \)-path follows the convention of pymatgen \cite{30}. (EDT-TTF-I$_2$)$_2$(DDQ)·(CH$_3$CN) shows a crossing of 4 bands at the Brillouin zone center (\( \Gamma \); Fig. 2(d)) exhibiting a tiny splitting of two fold-band degeneracies away from \( \Gamma \) due to a small magnetization of two central carbon atoms with \( \approx 0.65 \mu_B \). For (TSeF-TCNQ) we observe 8-fold degenerate Dirac nodes along the paths \( \vec{M} \) (M = (0.5, 0.44, 0.6), D = (0.5, 0.0, 0.5)); in units of the reciprocal basis vectors) and \( \vec{D} \) (D = (0.5, 0.0, 0.5), R = (0.5, 0.5, 0.5)) as well as at the corresponding symmetry partners. These nodes belong to line nodes passing through the Brillouin zone as shown in the density plot of Fig. 2(e). Our DFT calculations give a zero magne-
phase along the path \( \Gamma X \). For the corresponding symmetry partners for the ferromagnetic phase.

For the \( \pi \)-stacked bis-1,2,3-dithiazolyl radical we find a four-fold degenerate Dirac node at the Brillouin zone center \( \Gamma \). (e) (TSeF-TCNQ) shows pairs of line nodes passing through the Brillouin zone. (f) bis-1,2,3-dithiazolyl has a Weyl node along the path \( \Gamma X \) and corresponding symmetry partners for the ferromagnetic phase.

Protection of the nodes

To understand the nature of the crossings observed in the electronic band structures we are going to discuss the symmetry protection of the nodes. In Fig. 2 we show the molecule resolved partial DOS of (EDT-TTF-I\(_2\))(DDQ)-(CH\(_3\)CN). While there are in total four (EDT-TTF-I\(_2\)) and two DDQ and CH\(_3\)CN molecules in the unit cell, the inversion symmetry present in the crystal enforces pairwise degenerate contributions to the DOS. As can be verified, the main contribution to the DOS around the Fermi energy stems from (EDT-TTF-I\(_2\)). Due to the specific stacking structure, molecules in charge transfer salts are known to undergo a transition into a dimerized electronic state, where molecular orbitals of pairs of molecules bind significantly stronger to each other than to other molecules in the crystal [24, 31, 32]. In other words, we can introduce three energy scales: i) the hopping \( \tau_{\alpha\beta} \) of electrons between atoms \( \alpha, \beta \) within a molecule; ii) the hopping \( t_{\mu\nu} \) of electrons between molecules \( \mu, \nu \) within a molecular dimer; iii) the hopping \( s_{ij} \) of electrons between different dimers \( \mu, \nu \) within a unit cell. Hence, the two eigenstates are given by \( \phi_{\pm} = \frac{1}{\sqrt{2}} (\hat{c}_1 \pm \hat{c}_2) \) with the respective energies \( E_{\pm} \). In the crystalline unit cell these dimer states can be used to construct a basis where the Hamiltonian describing the dimerization can be written as

\[
H = \tau \hat{\Psi}^\dagger \sigma_x \hat{\Psi}
\]

with \( \hat{\Psi} = (\hat{c}_1, \hat{c}_2) \), where \( \hat{c}_i^\dagger (\hat{c}_i) \) creates (annihilates) an electron in molecule \( i \). The Hamiltonian reveals a symmetry protected four-fold degenerate Dirac node at the center of the Brillouin zone.

\[
H_{\text{eff}} \approx \sum_{i=1}^{3} \left[ a_i \tau_1 \sigma_1 k_i + b_i \tau_1 \sigma_2 k_i \right].
\]  

The Hamiltonian reveals a symmetry protected four-fold degenerate Dirac node at the center of the Brillouin zone.
By lattice symmetry this node does not carry any topological charge according to the Nielsen-Ninomiya theorem \cite{nielsen1983topological, ninomiya1983topological}.

In general, the underlying space group symmetry for (TSeF-TCNQ) (P2\textsubscript{1}c) does not allow for the high degeneracy of the nodal line observed. The nature of the crossing stems from the quasi one-dimensional nature of the charge transfer salt due to the specific molecular stacking. In Fig. 3 (a) we show the center of mass coordinates of the involved molecules which form weakly interacting one-dimensional chains. Each chain can be approximated to have a dispersion relation of \( E_{\mu \sigma} = \frac{s_0^{(\mu)}}{2} + 2s_1^{(\mu)} \cos \tilde{a}_\mu \cdot \tilde{k} \), with \( \mu \) being the molecule index distinguishing between TSeF and TCNQ and \( \sigma \) denoting the spin (note that the dispersion relation itself is independent of the spin). As there are two TSeF chains as well as two TCNQ chains present in the crystal, we observe two fourfold degenerate bands (2 chains \( \times \) 2 spins per molecule) which are allowed to cross in a plane if no hybridization is taken into account (see Fig. 4 (d)). From the tilted stacking of molecules in the different chains (shown in Fig. 4(b)+(c)) it becomes apparent that the involved hopping of electrons between different chains (interchain coupling) has to be weaker by several order of magnitude than the intrachain coupling (see also fitted parameters in methods section). In the basis \( \hat{\Psi} = (\hat{c}_{\text{TSeF},1\sigma}, \hat{c}_{\text{TSeF},2\sigma}, \hat{c}_{\text{TCNQ},1\sigma}, \hat{c}_{\text{TCNQ},2\sigma})^T \) and allowing for a hopping between chains we formulate an effective Hamiltonian of the form

\[
H_\sigma(\tilde{k}) = \begin{pmatrix}
E_{\text{TSeF}\sigma} & \Delta_1 & \Delta_2 & 0 \\
\Delta_1 & E_{\text{TCNQ}\sigma} & 0 & \Delta_4 \\
\Delta_2 & 0 & E_{\text{TSeF}\sigma} & \Delta_1 \\
0 & \Delta_3 & \Delta_4 & E_{\text{TCNQ}\sigma}
\end{pmatrix},
\]

where we use \( \Delta_1 = t_1 \cos \left( \frac{1}{2} \tilde{a}_1 \cdot \tilde{k} \right) \), \( \Delta_{2,3} = t_{2,3} \cos \left( \frac{1}{2} (\tilde{a}_2 + \tilde{a}_3) \cdot \tilde{k} \right) \).

The radical bis-1,2,3-dithiazoyl exhibits Weyl nodes for the low-temperature high-field ferromagnetic phase. Hence, time-reversal symmetry is broken and the crystal reflects a magnetic space group symmetry, depending on the magnetization direction. Assume we choose the magnetization in \( x \)-direction then the corresponding group is given by \( P2_12_1' \) (\# 19.27). To verify that the observed nodes are Weyl nodes we calculated the atom and orbital resolved weights to the band structure. We observe that the two bands forming the node belong to different atoms in the molecules within the unit cell. The main contributions stem from either the unsaturated nitrogen and the oxygen atom or the saturated nitrogen and one sulfur atom as shown in Fig. 5. Hence, we conclude that the bands belong to different orbital subspaces allowing for a crossing. In symmetry terms the two orbitals correspond to bands with different eigenvalues to the only unitary symmetry element present, \((C_{2z}, 1/2, 1/2, 0)\), along the invariant line \( k_x \). Hence, a 2-band \( \tilde{k} \cdot \tilde{p} \) Hamiltonian at a crossing point has to be invariant under the Pauli matrix \( \tau_x \), \( H(k_x, k_y, k_z) = \tau_x H(k_x, -k_y, -k_z) \tau_x \). This results in an allowed low energy Hamiltonian \( H(\tilde{K}^\pm + \tilde{k}) \approx \pm t_x k_x \tau_x + t_y k_y \tau_y + t_z k_z \tau_z \), at two points \( \tilde{K}^\pm \) along the \( x \)-axis. Both points reveal a monopole charge of \( \nu^\pm = \text{sign} [\pm t_x t_y t_z] \).
Effective Models and Excitonic Gap

To explain the discrepancy between DFT semimetallic phases and experimentally observed semiconductivity in (EDT-TTF-I₂)₂(DDQ):(CH₃CN) and (TSeF-TCNQ) we argue that both systems are likely to undergo an excitonic instability. Compared to known inorganic Dirac or Weyl semimetals, the bandwidth of all three materials discussed here is smaller by at least one order of magnitude. As the decreased band width induces a small Dirac velocity (small kinetic energy) of the elementary excitations of the system, we verify that a quasiparticle interaction term becomes dominant. We estimate the size of the effect using effective band structure models. For (EDT-TTF-I₂)₂(DDQ):(CH₃CN) we extended the model given in (1) to a lattice periodic version \((x \rightarrow \sin(x))\). For (TSeF-TCNQ) we construct an eight band model incorporating two spin and four orbital degrees of freedom (two belonging to molecular orbitals from TSeF and two belonging to TCNQ). The allowed dispersion relation of the model is restricted by the symmetry generators: parity, two-fold rotation about \(x\)-axis, time-reversal symmetry (details given in the methods section).

To approximate the size of the instability, we solve a BCS-like excitonic gap equation, similar to Refs [36–38]. Note that given the numerous degrees of freedom, multiple excitonic gap symmetries might occur, such as inter- or intranode instabilities with or without breaking of time-reversal or other lattice symmetries [38, 39]. We focus on an \(s\)-wave gap. Details on the calculation are given in the methods section.

We obtained an excitonic gap of \(\approx 60\) meV for (EDT-TTF-I₂)₂(DDQ):(CH₃CN) at \(T \rightarrow 0\) K. This value agrees with the experimentally determined gap of \(\approx 105\) meV. We argue that despite (EDT-TTF-I₂)₂(DDQ):(CH₃CN) being a regular semiconductor, it is an excitonic insulator with an electronic structure shown in Fig. 6(a). We repeat the approach for (TSeF-TCNQ) and obtain a slightly higher value of \(\approx 150\) meV (Fig. 6(b)). In contrast to the Dirac semimetal (EDT-TTF-I₂)₂(DDQ):(CH₃CN), (TSeF-TCNQ) has two degenerate line nodes which gap out while the excitonic gap is formed. To verify the experimentally observed metal-insulator transition at 40 K would require a full temperature-dependent screening which is beyond our present study.

METHODS

Machine Learning

The ML model is trained on a dataset of 24,134 ab initio band gaps of non-magnetic organic crystals stored in the organic materials database - OMDB [18, 40]. The dataset is divided into a training, validation and test set of 15000, 3000 and 6134 materials, respectively. We used the continuous-filter convolutional neural network scheme - SchNet [19] with a batch size of 32, a cutoff radius of 5.0 Å, 32 features, 3 interaction blocks, a learning rate of \(10^{-4}\), and 50 Gaussians to expand atomic distances (see Ref. 40 for parameter choice). The initial band gap data exhibits a Wigner-Dyson like shape as shown in Fig. 1(a), having a mean of \(\approx 2.9\) eV and a standard deviation of \(\approx 1.1\) eV. Our trained ML model shows a mean absolute error (MAE) of 0.406 eV and a RMSE of 0.602 eV which is interpreted as an accuracy of \(\approx 90\%\). Note that the underlying data is rather small (\(\approx 2 \times 10^4\) materials) and highly complex (average of 85 atoms per unit cell). The trained ML model is able to reproduce the band gap statistics on a set of 202,117 organic crystals (\(\approx 2 \times 10^4\) materials) taken from the COD [20], as shown in Fig. 1(a). These predictions also fit a Wigner-Dyson distribution \(\sim x^{5.62}e^{-0.45x^2}\). The performance of our model on the test set is shown in Fig. 1(b).

ab initio Calculations

We performed ab initio calculations in the framework of the density functional theory (DFT) using a projector augmented-wave method as implemented in the Vienna
ab initio simulation package VASP. Structures are taken from the COD and transformed into VASP input using pymatgen. During the self-consistent calculation of the electron density and the DOS we used a Γ-centered mesh with a \( k \)-mesh density of 800 points per \( A^{-3} \) for the quick materials scan of 414 candidate materials and a \( k \)-mesh density of 1500 points per \( A^{-3} \) for the refined calculations of 9 prospective semimetals. For the latter we performed an optimization of the atomic positions using a conjugate gradient algorithm. All calculations were performed with SOI and the exchange correlation functional was approximated by the strongly constrained and appropriately normed semilocal exchange correlation functional was approximated by the Tkatchenko-Scheffler method with iterative Hirshfeld partitioning. The cut-off energy of the plane wave expansion was chosen to be 600 eV.

Effective Hamiltonians

We generated effective Hamiltonians for (EDT-TTF-I)\(_2\)(DDQ)-(CH\(_3\)CN) and TSeF-TCNQ. To describe the four-fold degeneracy at the \( \Gamma \) point observed for (EDT-TTF-I)\(_2\)(DDQ)-(CH\(_3\)CN), we construct a model with two orbital (\( \tau \)) and two spin (\( \sigma \)) degrees of freedom,

\[
H_{\text{eff}} = \sum_{i=0}^{3} \sum_{j=0}^{3} f_{ij}(k_x, k_y, k_z) \tau_i \sigma_j.
\]

Here, each molecule in the unit cell contributes one molecular orbital. Neglecting higher and lower energy bands, a four-fold degeneracy is obtained assuming an even- and an odd-parity molecular orbital, and add respective lattice symmetries (space group PT): parity \( \hat{P} = \tau_3 \sigma_0 \) (\( \hat{k} \rightarrow -\hat{k} \)), time-reversal \(-i\sigma_2 \hat{K} \) (\( \hat{k} \rightarrow -\hat{k} \); \( \hat{K} \) being the complex conjugation), and an emergent particle-hole symmetry \( \hat{C} = \sigma_2 \). Up to linear order we obtain

\[
H_{\text{eff}} \approx \sum_{i=1}^{3} [a_i \tau_1 \sigma_1 k_i + b_i \tau_2 \sigma_2 k_i].
\]

The best fit to the ab initio calculated band structure resulted in the parameters \( a_1 = 0.47 \text{ eV} \), \( a_2 = -0.33 \text{ eV} \), \( a_3 = 0.11 \text{ eV} \), \( b_1 = 0.16 \text{ eV} \), \( b_2 = -0.38 \text{ eV} \), \( b_3 = 0.15 \text{ eV} \).

The nodes for TSeF-TCNQ occur in the interior of the Brillouin zone. Therefore, we construct a lattice-periodic model with 8 bands (4 orbital-, 2 spin degrees of freedom). The orbital degrees of freedom are obtained from respective permutations of the two TSeF and two TCNQ molecules within the primitive unit cell. We represent the generators of the factor group \( \mathcal{G}/\mathcal{T} \simeq C_{2h} \) (\( \mathcal{G} \) is the space group P2\(_1\)/c, \( \mathcal{T} \) is the corresponding group of pure lattice translations) as follows, \( \hat{P} = P(1, 2, 3, 4) \times \sigma_0 \) (\( \hat{k} \rightarrow -\hat{k} \)), \( \hat{C}_{2x} = P(2, 1, 4, 3) \times i\sigma_1 \) (\( k_x \rightarrow -k_x \), \( k_y \rightarrow -k_y \), \( k_z \rightarrow -k_z \)) and add time-reversal symmetry as before. Here \( P(\text{permutation}) \) denotes a \( 4 \times 4 \)-dimensional permutation matrix. Note that each symmetry element comes with a corresponding double group partner. The total Hamiltonian is written as \( H = H_{\text{orbital}} \times H_{\text{spin}} \). We generate \( H_{\text{orbital}} \) in the basis \( |\Psi_{\text{TSeF1}}\rangle, |\Psi_{\text{TSeF2}}\rangle, |\Psi_{\text{TCNQ1}}\rangle, |\Psi_{\text{TCNQ2}}\rangle \) using

\[
\begin{align*}
H_{mn}^{\text{orbital}} &= t_{mn} \exp(i\vec{k} \cdot \vec{\delta}_{mn}), \\
H_{mm}^{\text{orbital}} &= \sum_i s_i^m \exp(i\vec{k} \cdot \vec{a}_i), \quad (5)
\end{align*}
\]

with \( m, n = \text{TSeF1, TSeF2, TCNQ1, TCNQ2} \), \( \vec{\delta}_{mn} \) being the vector connecting molecules \( m \) and \( n \) and \( \vec{a}_i \) being the real space basis vectors. The full Hamiltonian is obtained by applying all symmetry operations and dividing by the total number of symmetry elements, i.e., twice the order of the factor group when all combinations incorporating time-reversal symmetry are taken into account. We implemented a Monte-Carlo scheme to fit the model to our ab initio band structure with the best fit being \( t_{\text{TSeF1, TSeF2}} = 0.008 \text{ eV}, t_{\text{TCNQ1, TCNQ2}} = -0.025 \text{ eV}, t_{\text{TSeF1, TCNQ1}} = 0.023 \text{ eV}, t_{\text{TSeF1, TCNQ2}} = 0.047 \text{ eV}, s_1^{\text{TSeF1}} = -0.033 \text{ eV}, s_2^{\text{TSeF1}} = -0.023 \text{ eV}, s_3^{\text{TSeF1}} = 1.057 \text{ eV}, s_1^{\text{TCNQ1}} = -0.704 \text{ eV}, s_2^{\text{TCNQ1}} = 0.080 \text{ eV}, s_3^{\text{TCNQ1}} = -0.093 \text{ eV} \).

Excitonic Instability

We model quasiparticle-quasihole excitations of the material in terms of the following interaction process, where incoming (outgoing) solid lines belong to fermionic material in terms of the following interaction process,

\[
\begin{align*}
\text{Incoming} & \quad \begin{array}{c}
\text{Outgoing}
\end{array}
\end{align*}
\]

The Hamiltonian is given by

\[
\hat{H} = \hat{H}_0 + \frac{1}{2} \sum_{\nu\nu'} \sum_{\vec{k}\vec{k}'\vec{q}} V(\vec{q}) \hat{\Psi}_{\nu,\vec{k}+\vec{q}}^\dagger \hat{\Psi}_{\nu',\vec{k}'}^\dagger \hat{\Psi}_{\nu',\vec{k}'} \hat{\Psi}_{\nu,\vec{k}+\vec{q}}.
\]

Here, \( \nu \) is a corresponding quantum number and \( a = \pm (\vec{a} = -a) \) denotes electron and hole states. \( \hat{H}_0 \) denotes the non-interacting effective Hamiltonian of the system. We derive an excitonic gap equation using a Green function approach similar to Refs 33–38 and define \( G_{\nu,\pm}(\vec{p}, \tau - \tau') = -\left\langle \hat{T} \hat{\Psi}_{\nu,\vec{p}+\vec{q}}(\tau) \hat{\Psi}_{\nu,\vec{p}+\vec{q}}^\dagger(\tau') \right\rangle \) and
\[ F_{\nu, \pm}(\vec{p}, \tau - \tau') = \left\langle \hat{T} \hat{\Psi}_{\nu, \vec{p} \pm}^\dagger(\tau) \hat{\Psi}_{\nu, \vec{p} \mp}(\tau') \right\rangle. \]

We proceed by calculating the equations of motion for \( G \) and \( F \) using the Heisenberg formalism and decomposing the four-point functions in terms of \( G \) and \( F \). We impose particle-hole symmetry of the electronic band structure \( \xi^+ (\vec{k}) = \xi^- (\vec{k}) \) as well as a real excitonic gap function \( \Delta_\nu \) and derive the BCS-like gap equation

\[
\Delta_\nu(\vec{p}) = - \sum_{\vec{q}} V(\vec{q} - \vec{p}) \frac{\Delta_\nu(\vec{q})}{2E_{\nu, \vec{q}}} \tanh \left( \frac{\beta E_{\nu, \vec{q}}}{2} \right),
\]

which is in agreement with Ref. [36]. Here, \( E_{\nu, \vec{q}} = \sqrt{\xi^2(\vec{p}) + \Delta^2(\vec{p})} \). We construct the exact Brillouin zone using the algorithm of Finney [17] and solve \([7]\) using a Liouville-Neumann series, where the integration is performed using a quasi-Monte-Carlo integration scheme [48]. We calculate the zero temperature excitonic gap \( \Delta_\nu \) determined with respect to the identification of novel examples. We note that the choice of the \( s \)-wave excitonic instability due to strong interactions is only the simplest scenario and was chosen to estimate the size of the effect. However, other forms of gap openings and richer phase diagrams are imaginable.

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**Appendix A: Materials Candidates**

Out of the 202,117 materials in the crystallographic open database COD [20], a subset of 414 organic materials were predicted to have a small band gap (0.01 ≤ \( \Delta \) ≤ 0.4 eV) by our trained machine learning model. We performed ab initio calculations to scan for potential organic semimetals (details on the calculations can be found in the methods section) and find 9 materials candidates which exhibit nodes close to the Fermi level (\( E = 0 \) eV). The band structures of the nine materials are shown in Fig. [7]. Materials are denoted with their COD-IDs. The labeling of the high symmetry points was generated automatically using pymatgen [30]. Respective space group symmetries are PT: 1508451, 2100065, 4334234, 4506562; \( P2_1/c: 2101483, 4324376, 7015484; 1T_2m: 4114836; P2_12_12_2: 7106265 \). Of the nine materials only the three materials with COD-IDs 1508451, 2101483, and 7106265 still exhibit their nodes after a full structural optimization was performed.
FIG. 7. Promising materials candidates. Out of 414 band structure calculations of organic molecular crystals and metal organic frameworks, 9 materials exhibited nodes close to the Fermi level and were selected for revision using a more sophisticated computational approach. The number indicates the COD ID of the material.

Appendix B: Magnetic phases of bis-1,2,3-dithiazolyl

The ABABAB $\pi$-stacked bis-1,2,3-dithiazolyl radical was reported to undergo a transition into a canted antiferromagnet below a critical temperature of 4.5 K and to undergo a spin-flop transition to a field-induced ferromagnetic state at a temperature of 2 K and a magnetic field strength of $H \approx 20$ kOe $^{29}$. Our calculations revealed Weyl nodes along the path $\Gamma X$ in the Brillouin zone for the ferromagnetic phase. To better understand the emergence of the phase and its correspondence to the underlying magnetic ordering we performed similar band structure calculations incorporating full structural optimization for an antiferromagnetic and a non-magnetic ordering (details on the ab initio calculation can be found in the methods section). Even though the nonmagnetic phase exhibits topological nodes along the path $\Gamma Y$ the overall behavior is metallic as there is no vanishing density of states at the Fermi level. The topological protection of the nodes for the nonmagnetic phase is a consequence of the underlying orthorhombic symmetry with space group $P2_12_12_1$ where the mechanism is described in Ref. $^{55}$. The antiferromagnetic phase exhibits a clear band gap of the size of $\approx 0.15$ eV. The comparison of the electronic structure for all three magnetic phases is shown in Fig. 8.
Appendix C: Nodes in (EDT-TTF-I)$_2$(TCNQ), COD-ID 4506562

The material (EDT-TTF-I)$_2$(TCNQ) with COD-ID 4506562 exhibits topological nodes within the Brillouin zone close to the Fermi level as shown in Fig. 9. However, the material is not a semimetal as it exhibits a large density of states at the Fermi level.

![Topological nodes in the fully optimized band structure of (EDT-TTF-I)$_2$(TCNQ), COD-ID 4506562.](image)

FIG. 9. Topological nodes in the fully optimized band structure of (EDT-TTF-I)$_2$(TCNQ), COD-ID 4506562.

Appendix D: List of predictions

We trained a machine learning model based on the continuous-filter convolutional neural network scheme SchNet [19] on 24,134 ab initio calculated band gaps stored within the organic materials database - OMDB [18] (details can be found in the method section). We applied the successfully trained model on 202,117 crystal structures stored within the crystallographic open database - COD [20]. All crystal structures considered belong to organic molecular crystals or metal organic frameworks which were synthesized before. Organic materials tend to be large band gap insulators and only 414 materials were predicted to have a band gap of $0.01 \leq \Delta \leq 0.4$ eV, where we explicitly tried to exclude organic metals. The list of predicted band gaps for the 414 materials denoted with their COD-ID is given in Table I.

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TABLE I. COD-IDs, band gap $\Delta$, and number of atoms in the primitive unit cell $N_a$ for the subset of 414 COD materials where the band gap was predicted to be small (0.01 $\leq \Delta \leq$ 0.4 eV).

| COD ID | $\Delta$ (eV) | $N_a$ | COD ID | $\Delta$ (eV) | $N_a$ | COD ID | $\Delta$ (eV) | $N_a$ | COD ID | $\Delta$ (eV) | $N_a$ | COD ID | $\Delta$ (eV) | $N_a$ |
|--------|-------------|------|--------|-------------|------|--------|-------------|------|--------|-------------|------|--------|-------------|------|--------|-------------|------|
| 4109852| 0.25        | 104  | 4113773| 0.02        | 312  | 4113682| 0.33        | 236  | 7057131| 0.06        | 178  | 4000867| 0.35        | 212  | 8100483| 0.09        | 148  |
| 4102191| 0.10        | 68   | 4313682| 0.33        | 156  | 4313682| 0.33        | 236  | 7047891| 0.31        | 328  | 7006006| 0.10        | 174  | 4344542| 0.36        | 116  |
| 4316167| 0.25        | 52   | 4337453| 0.22        | 396  | 4060716| 0.12        | 110  | 2219623| 0.21        | 232  | 4333919| 0.13        | 106  | 4311621| 0.40        | 45   |
| 7205290| 0.25        | 172  | 7202871| 0.27        | 56   | 7204124| 0.21        | 100  | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   |
| 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   |
| 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   |
| 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   | 7203123| 0.03        | 82   |