

Intrinsic glassy-metallic transport in an amorphous coordination polymer

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Conducting organic materials, such as doped organic polymers¹, molecular conductors^{2,3} and emerging coordination polymers⁴, underpin technologies ranging from displays to flexible electronics⁵. Realizing high electrical conductivity in traditionally insulating organic materials necessitates tuning their electronic structure through chemical doping⁶. Furthermore, even organic materials that are intrinsically conductive, such as single-component molecular conductors^{7,8}, require crystallinity for metallic behaviour. However, conducting polymers are often amorphous to aid durability and processability⁹. Using molecular design to produce high conductivity in undoped amorphous materials would enable tunable and robust conductivity in many applications¹⁰, but there are no intrinsically conducting organic materials that maintain high conductivity when disordered. Here we report an amorphous coordination polymer, Ni tetrathiafulvalene tetrathiolate, which displays markedly high electronic conductivity (up to 1,200 S cm⁻¹) and intrinsic glassy-metallic behaviour. Theory shows that these properties are enabled by molecular overlap that is robust to structural perturbations. This unusual set of features results in high conductivity that is stable to humid air for weeks, pH 0–14 and temperatures up to 140 °C. These findings demonstrate that molecular design can enable metallic conductivity even in heavily disordered materials, raising fundamental questions about how metallic transport can exist without periodic structure and indicating exciting new applications for these materials.

Using molecular design to engender high conductivity in undoped amorphous materials would enable tunable and robust conductivity in many applications, but there are no intrinsically conducting organic materials that maintain high conductivity when completely disordered. Inorganic glassy metals have been discovered but require careful fabrication¹¹. Furthermore, the relationship between metallic behaviour, which classically requires periodicity giving rise to a well-defined band structure, and geometric disorder in glassy metals is still unclear¹². Electron-rich and redox-active tetrathiafulvalene (TTF) motifs feature prominently as molecular building blocks in conducting materials⁸. Appending thiolate groups to TTF to generate tetrathiafulvalene tetrathiolate (TTFtt) enables the formation of extended coordination polymers that combine TTF motifs with electronically complex transition metal dithiolenes¹³. Although the promise of these materials has been recognized, their structure, purity, composition and hence properties are not well-defined because of synthetic challenges¹⁴.

We recently discovered syntheses for a series of redox congeners of capped TTFtt compounds and their facile transmetalation to group 10 metals¹⁵. Here we report that this synthetic strategy enables the isolation of the material NiTTFtt in high purity as an amorphous powder.

Despite its disordered structure, NiTTFtt exhibits notable conductivity, as high as 1,200 S cm⁻¹ at room temperature, and glassy-metallic electronic behaviour. Theory shows that these properties are enabled by strong molecular overlap that is robust to structural perturbations. This unusual set of structural and electronic features results in conductivity that is robust to air, water, acid/base and temperatures up to 140 °C. These results demonstrate that molecular design can enable metallic conductivity even in completely disordered materials, raising fundamental questions about charge transport mechanisms in disordered materials and indicating exciting new applications for intrinsically metallic organic materials.

Synthesis and structure

NiTTFtt is synthesized by mixing [TTFtt(SnBu₂)₂][BAR^F₄]₂ (BAR^F₄ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, Bu = *n*-butyl) with excess [TEA]₂[NiCl₄] (Fig. 1a; TEA, tetraethylammonium). Composition analyses support a Ni:S ratio of 1:8 and confirm the proposed formula of NiTTFtt with [Bu₂Sn][BAR^F] chain terminations (Supplementary Tables 5 and 6). The absence of ammonium counterions implies that the TTF

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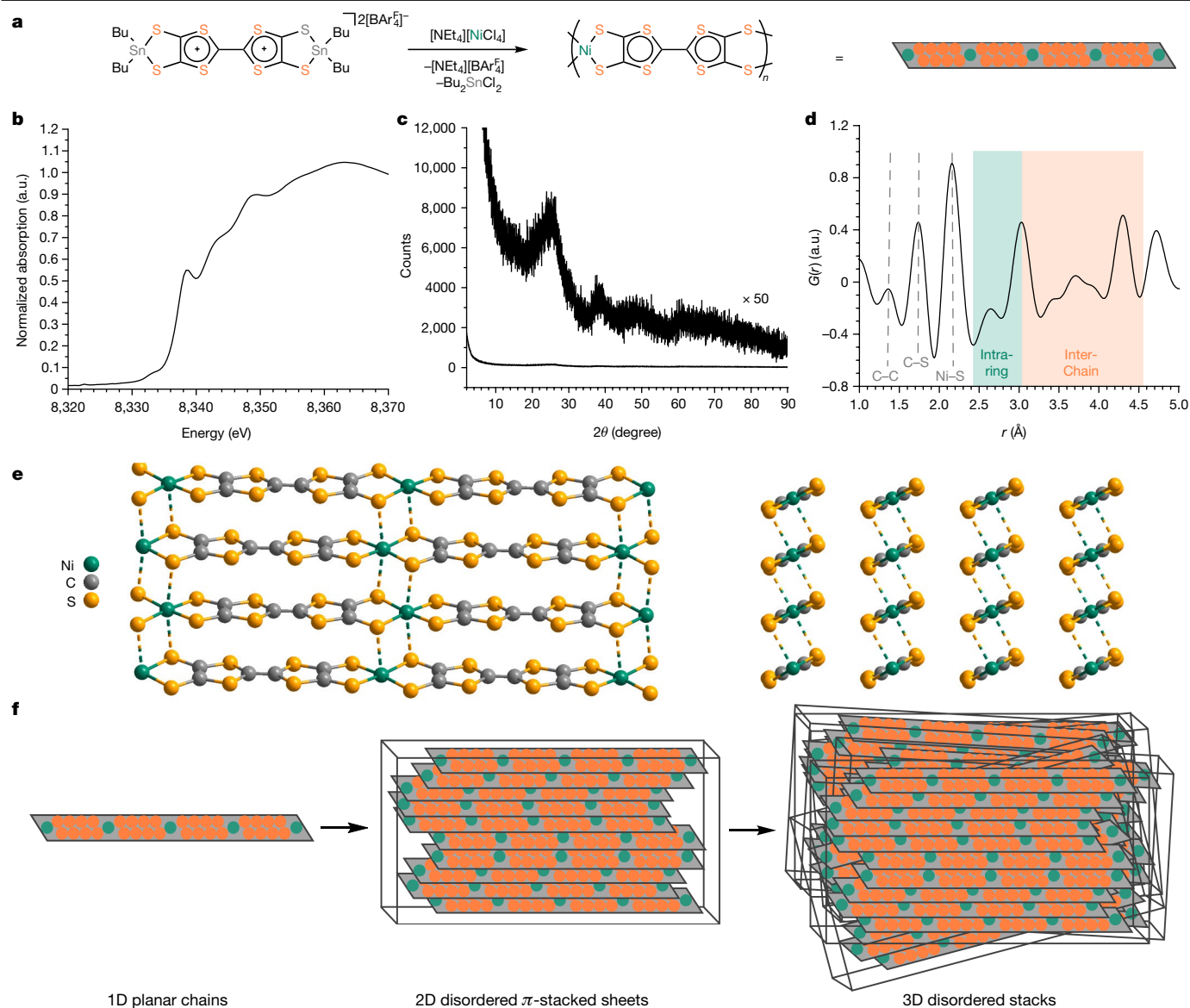


Fig. 1 | Synthesis and structure of NiTTfTt. **a**, Synthetic scheme. **b**, Ni K-edge X-ray absorption near-edge structure spectrum of amorphous NiTTfTt powder. **c**, PXRD pattern of amorphous NiTTfTt powder. **d**, Pair distribution function of amorphous NiTTfTt powder. **e**, Proposed idealized structure based on

structural characterization of semicrystalline NiTTfTt. **f**, Hierarchical structure showing coplanar chains but disordered packing in sheets and stacks.

cores have formal 2+ charges, which is also supported by the absence of electron paramagnetic resonance (EPR) signals⁸ (Supplementary Fig. 44). X-ray photoelectron spectroscopy (Supplementary Fig. 24) reveals features at 871 and 854 eV, assigned as Ni 2 $p_{1/2}$ and 2 $p_{3/2}$ peaks respectively, and a satellite at 860 eV associated with a plasmon loss, all of which are consistent with low-spin ($S = 0$) square planar Ni(II) centres. The S 2 p spectra appear with a head and shoulder pattern spanning 161–166 eV, indicating multiple sulfur sites in NiTTfTt, and are similar to spectra of TTF[Ni(dmit)₂] (dmit, 1,3-dithiole-2-thione-4,5-dithiolate)¹⁶. Ni K-edge X-ray absorption spectroscopy shows a rising edge at 8,338.6(4) eV, which also supports the assignment of pseudo- D_{4h} Ni(II) centres (Fig. 1b)¹⁷.

There are only broad features in the powder X-ray diffraction (PXRD) pattern for NiTTfTt, which indicate an amorphous material with domain sizes of around 1 nm, similar to amorphous silica¹⁸ (Fig. 1c and Supplementary Fig. 8). Variable-temperature X-ray scattering and differential scanning calorimetry confirm that this amorphous structure persists from –90 to 210 °C with no phase changes (Supplementary Figs. 10 and 63).

We have also investigated the structure of NiTTfTt with X-ray pair distribution function (PDF) analysis (Fig. 1d). The peaks below 3 Å can be assigned to C–C, C–S and Ni–S bonds, and intraring distances. The peaks between 3 and 4.5 Å represent additional interchain distances and are consistent with typical intermolecular S–S distances in TTF systems⁸.

Despite the amorphous nature of NiTTfTt, we have built a structural model based on experimental data (Fig. 1e). This model is supported by attempts to grow more crystalline NiTTfTt by slow diffusion, which show a PXRD pattern that can be indexed to a monoclinic unit cell (Supplementary Figs. 9 and 21). This unit cell indicates staggered coplanar chain packings with S–S distances of around 3.4–3.7 Å along the π -stack and around 3 and 4 Å side-to-side between chains. These values are similar to those observed in the single-component molecular metal, Ni(tmdt)₂ (tmdt, trimethylene-tetrathiafulvalene-dithiolate)¹⁹, and also support tight packing as previously proposed²⁰. This model indicates that the disordered structure of NiTTfTt arises from one-dimensional (1D) chains that pack face-to-face into disordered two-dimensional

Table 1 | Summary of electronic, thermal, magnetic and optical properties

Physical properties	NiTTft
Electrical conductivity (S cm^{-1})	470–1,200
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	6.3(1)
Lorenz number ($\text{W } \Omega \text{K}^{-2}$)	1.7×10^{-7}
Arrhenius fit, E_a (meV)	0.08–2.1
Mott 3D VRH fit, T_0 (K)	13
Efros–Shklovskii fit, T_{ES} (K)	1.4
Seebeck coefficient ($\mu\text{V K}^{-1}$)	–3.6(1)
Pauli paramagnetic susceptibility, χ_{Pauli} ($\text{cm}^3 \text{mol}^{-1}$)	6.0×10^{-4}
Plasma frequency (cm^{-1})	~12,000
Carrier concentration (cm^{-3})	~ 10^{21}

(2D) sheets that then pack side-to-side into a three-dimensional (3D) structure (Fig. 1f). Scanning electron microscopy (SEM) confirms the presence of 2D flakes (Supplementary Figs. 19 and 20). Importantly, this structure mandates planar NiTTft chains that can π -stack strongly; both features should facilitate electronic delocalization.

Physical properties

Four-probe conductivity measurements on pressed pellets of NiTTft at room temperature reveal a conductivity of $470 \pm 30 \text{ S cm}^{-1}$. Pellets hot-pressed at 200°C provide values as high as $1,200 \text{ S cm}^{-1}$ (Table 1 and Supplementary Fig. 48). These values make NiTTft among the most conductive organic materials. The thermal conductivity of NiTTft was measured by Raman thermometry as $6.3(1) \text{ W m}^{-1} \text{K}^{-1}$ (ref. 21; Supplementary Fig. 51), a value similar to inorganic glassy metals²², but higher than typical coordination polymers (lower

than $0.4 \text{ W m}^{-1} \text{K}^{-1}$)²³. The resulting Lorenz number at 300 K, $1.7 \times 10^{-7} \text{ W } \Omega \text{K}^{-2}$, is roughly one order magnitude higher than that for most metals, $2.44 \times 10^{-8} \text{ W } \Omega \text{K}^{-2}$. This deviation may arise from limited measurement accuracy but may also be related to weak localization as seen in molecular conductors²⁴.

Variable-temperature conductivity experiments on pressed pellets of amorphous NiTTft show an almost temperature-independent electrical resistivity with only a slight increase at low temperatures (Fig. 2a). Arrhenius fitting gives an activation energy of 2.1 meV above 60 K and 0.08 meV below 20 K (Supplementary Fig. 54). These extremely small barriers may arise for two reasons. Macroscopic interparticle transport may provide a barrier to charge flow as is frequently observed in pressed pellets of conducting organic materials^{2,25}. Alternatively, a flat variable-temperature conductivity profile has been observed for glassy metals with resistivities greater than $150 \mu\Omega \text{ cm}$ (ref. 26). The increase of resistivity as temperature (T) decreases has been ascribed to ‘weak localization’ with a characteristic $T^{1/2}$ upturn in resistivity due to electron–electron interactions. We observe this same $T^{1/2}$ dependence at low temperature, indicating similar behaviour in NiTTft. This observation, combined with a finite zero-temperature extrapolation of the resistivity, indicates that NiTTft is best thought of as having metallic character²⁶.

Charge transport in disordered systems is typically analysed with variable-range hopping (VRH) models. Application of a 3D Mott VRH model to the resistivity data of NiTTft gives $T_0 = 13 \text{ K}$, which indicates a high density of states at the Fermi level (Supplementary Fig. 55). Ultraviolet photoelectron spectroscopy of a pellet of NiTTft also supports a non-zero density of states at the Fermi level (Fig. 2b). Values of T_0 between 1 and 10^4 K are commonly observed in granular metals in which hopping between metallic islands is assumed²⁷. The observed $T^{1/2}$ upturn in resistivity led us to apply the Efros–Shklovskii VRH model in this region (Supplementary Fig. 56). The observed linear relationship indicates the presence of a Coulomb gap, which further indicates electron–electron interactions as discussed above. Interestingly, the T_{ES} value obtained from this fit is extremely small, 1.4 K, indicating

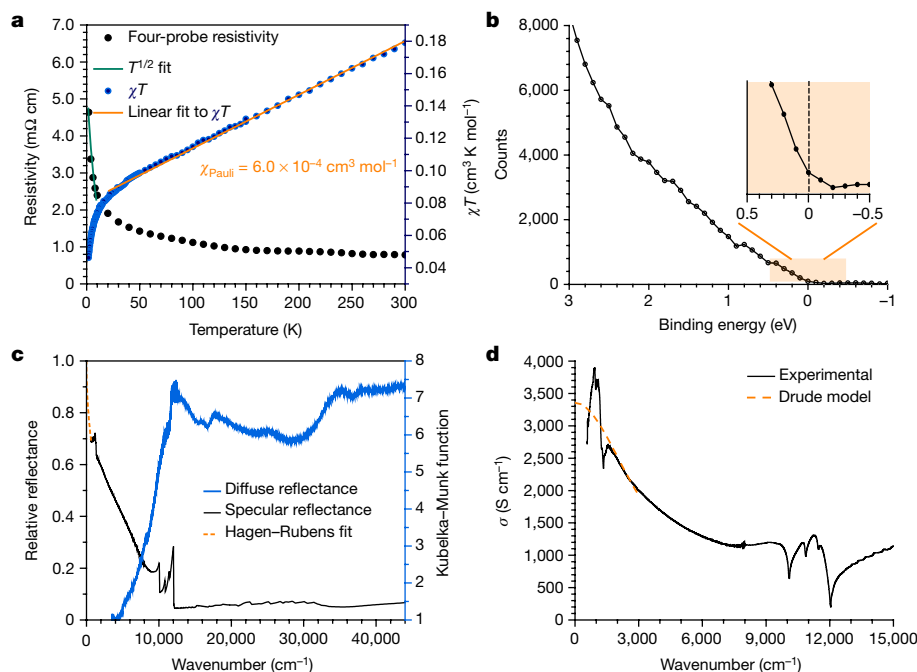


Fig. 2 | Physical properties of amorphous NiTTft. **a**, Variable-temperature resistivity (black) and magnetic susceptibility (blue) data. The green line indicates a $T^{1/2}$ fit to the resistivity data at low temperature accounting for weak localization and the orange line indicates a linear fit to the magnetic susceptibility data with the shown Pauli paramagnetic contribution.

b, Ultraviolet photoelectron spectrum showing a non-zero density of states at the Fermi level. **c**, Specular (black) and diffuse (blue) reflectance data. A Hagen–Rubens fit at low energy is shown by an orange dashed line (see Supplementary Fig. 59 for an enlarged view). **d**, Optical conductivity at the low energy limit with a Drude model fit shown by an orange dashed line.

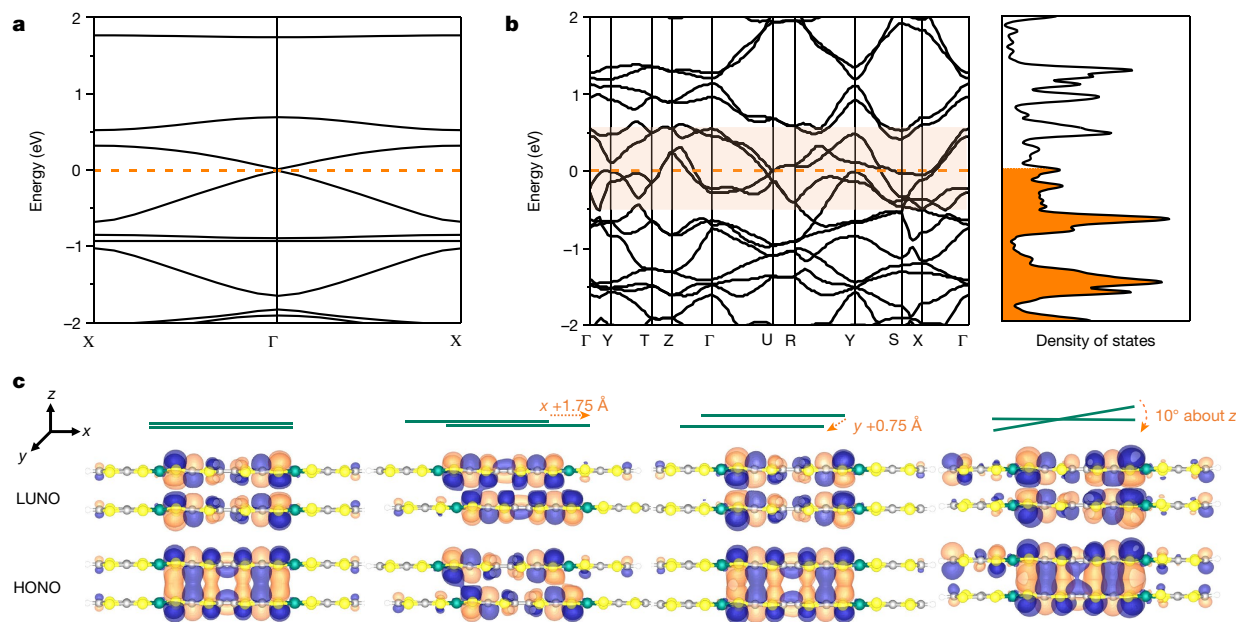


Fig. 3 | Theoretical analysis of NiTTFtt. **a**, Computed band structure of an isolated chain. **b**, Computed band structure of the idealized 3D structure determined from experimental data. **c**, Orbital diagrams of a molecular dimer

of NiTTFtt building blocks showing that substantial overlap is maintained regardless of structural distortions. HONO, highest occupied natural orbital; LUNO, lowest unoccupied natural orbital.

large delocalization lengths²⁸. All these data support glassy-metallic conductivity in NiTTFtt.

The Seebeck coefficient of NiTTFtt is $-3.6(1) \mu\text{V K}^{-1}$ and its magnitude increases linearly with temperature (Supplementary Fig. S7). The negative Seebeck coefficient indicates that electrons are the charge carriers and the small magnitude and linearity with temperature are commonly observed in metallic inorganic conductors²⁹. The magnetic susceptibility, χ , of NiTTFtt is only weakly temperature dependent, implying a paramagnetic contribution from charge carriers, namely Pauli paramagnetism (Fig. 2a). The value of χ_{Pauli} , $6 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$, is consistent with reported values in organic metals^{7,8}. Finally, we note a deviation from linearity in χT at low temperatures, which coincides with the increase in resistivity and putative weak localization.

We wanted to obtain more detailed quantification of the metallic nature of NiTTFtt and so we used both diffuse and specular reflectance spectroscopies^{30,31} (Fig. 2c). NiTTFtt has a broad absorption over the ultraviolet (UV)–visible (vis)–near-infrared (NIR) region up to around $12,000 \text{ cm}^{-1}$. At the low frequency limit, the Hagen–Rubens relation can be used to extrapolate the specular reflectance to zero frequency and thereby estimate the d.c. conductivity as approximately $4,200 \text{ S cm}^{-1}$, a value which is consistent with four-probe measurements on pressed pellets ($1,200 \text{ S cm}^{-1}$). The observed plasma frequency of approximately $12,000 \text{ cm}^{-1}$ provides a carrier density of 10^{21} cm^{-3} , which is similar to values in crystalline metallic polymers^{1,26}.

We have further analysed the reflectivity data by applying the Kramers–Kronig transformation (Fig. 2d). Surprisingly, the optical conductivity from this analysis continuously increases as the frequency goes to zero. This behaviour, particularly in the far-IR region below $3,000 \text{ cm}^{-1}$, is suggestive of Drude behaviour for a classic metal³². Although the data range and quality limit fitting reliability, analysis of these data with a Drude model ($\sigma_{\text{D}}(\omega) = (\omega_p^2 \tau / 4\pi) (1 + \omega^2 \tau^2)^{-1}$; ω , wave-number) gives a plasma frequency (ω_p) of $12,000 \text{ cm}^{-1}$, a relaxation time (τ) of $9.0 \times 10^{-15} \text{ s}$, a d.c. conductivity of $3,300 \text{ S cm}^{-1}$, a carrier density of $3.4 \times 10^{21} \text{ cm}^{-3}$ (assuming effective mass $m^* = 2m_0$)³², and a mean free path of around 2.4 nm (Supplementary Information). Thus, all fitted and measured values for NiTTFtt across different techniques are consistent and support metallic behaviour. The Drude-like behaviour and small T_{ES} values furthermore raise the possibility of metallic

charge transport limited by macroscopic interparticle hopping transport.

Conducting organic polymers and coordination polymers also exhibit high conductivity, but the mechanism of charge transport in these materials is typically not metallic or intrinsic and relies on doped charge carriers⁶. In intrinsic molecular conductors, metallic character is always accompanied by crystalline order. The properties of NiTTFtt, which exhibits intrinsic metallic charge transport with a disordered structure, are thus highly unusual. We have therefore undertaken detailed theoretical analyses of NiTTFtt.

Theoretical analysis

Density functional theory (DFT) calculations were performed on 1D chains and 3D stacks of NiTTFtt on the basis of our structural model. Interestingly, isolated 1D chains of NiTTFtt show semi-metallic behaviour but metallic band structure forms on 3D assembly (Fig. 3a,b respectively). Analysis of the band structure shows that metallic character arises from both π -stacking interactions within the 2D sheets (Γ to Z), as well as side-to-side S–S interactions between sheets (Γ to X). Similar interactions have been invoked in single-component molecular conductors⁷. We have also analysed why the metallic character of NiTTFtt is maintained with disorder by examining molecular models that can be systematically distorted (Fig. 3c). Two molecular fragments of NiTTFtt were fixed at positions that vary the slip, π -stacking and side-to-side distances as well as the interchain twist angle. The electronic structures of these models were analysed by variational two-electron reduced density matrix complete active space self-consistent field³³ and DFT calculations. This analysis demonstrates that the molecular fragments of NiTTFtt have substantial electronic overlap that is notably robust to disorder. This is illustrated by the fact that the highest occupied natural orbital–lowest unoccupied natural orbital gaps have little to no change with structural distortions (Supplementary Tables 7 and 8 and Supplementary Figs. 81 and 83). These computations explain how metallic character is preserved in amorphous NiTTFtt: periodicity is disrupted by small-scale structural disorder, but this disorder is not large enough to disrupt overlap and delocalization.

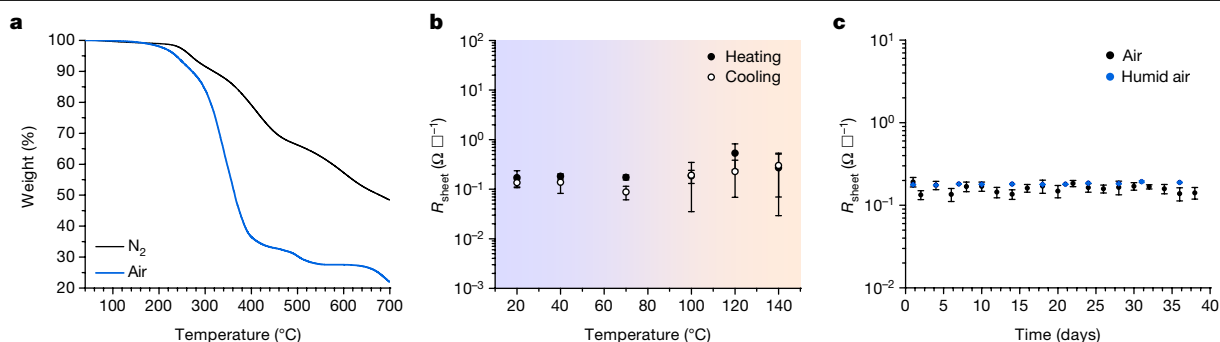


Fig. 4 | Thermal and aerobic stability of NiTTFt. **a**, Thermogravimetric analysis under N_2 and air. **b**, Sheet resistance in air on heating and cooling. **c**, Long-term stability of the resistance in air. Black symbols show the resistance

in ambient air and blue symbols show the resistance in 100% humid air. The data points in **b** and **c** represent the average and error bars represent standard deviations.

Thermal, aerobic and acid/base stability

The combination of structural disorder and intrinsic metallic character in NiTTFt suggests some advantageous properties. Organic conductors, including n-type conducting polymers³⁴, coordination polymers such as Cu_3 (benzenhexathiolate)³⁵ and molecular conductors, typically suffer from fast degradation when exposed to air, acid/base or heat²⁶. Metallic character in these systems arises from their crystalline structure, which can be disrupted with sufficient thermal energy (that is melting or decomposition), and exposure to air and heat leads to chemical reactions that remove charge carriers and reduce conductivity⁹. Although these are issues for most conducting organic materials, the disordered structure and intrinsic electronic properties of NiTTFt suggest that it should be more robust.

Thermal stability measurements show that NiTTFt is stable both under N_2 gas (up to 270 °C) and, notably, in air (up to 235 °C, Fig. 4a, Supplementary Fig. 62). Inspired by the stability of NiTTFt, we monitored its sheet resistance (R_{sheet}) in air while heating and cooling between 20 and 140 °C (Fig. 4b). The high electrical conductivity of NiTTFt is preserved even under these comparatively harsh conditions. Interestingly, pellets left in air (ambient or 100% humidity) over a month also show no conductivity loss (Fig. 4c and Supplementary Fig. 67). More remarkably, tests with acid/base demonstrate that the conductivity of NiTTFt is relatively stable over pH 0–14 (Supplementary Figs. 70 and 71). Inspired by these observations, we generated light-emitting diode light bulb circuits with NiTTFt, Cu foil and commercial poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (Supplementary Figs. 68 and 69). The light-emitting diode brightness with NiTTFt is similar to or better than these common conductors. These data demonstrate that the unusual combination of intrinsic metallic character with an amorphous structure in NiTTFt imparts substantial stability for conductivity with heat, air and acid/base.

Conclusion

Organic conductors are an enormously important class of materials. Realizing conductivity in normally insulating organic materials typically requires optimization of their electronic structure through doping and their geometric structure through crystallinity. However, the requirement for doping and crystallinity imposes restrictions on composition and stability. Here we report an unusual new material, NiTTFt, that is structurally amorphous, precluding a classical band structure. Nevertheless, detailed characterization of NiTTFt reveals high conductivity and a metallic character. Theory shows that the presence of this metallic behaviour is enabled by overlap between the molecular units of NiTTFt that is insensitive to structural distortions. Although an in-depth understanding of the microscopic details of charge transport in NiTTFt requires further studies, we propose

that the metallic character arises from the conjugated NiTTFt chains that generate an infinite π system and a negligible bandgap combined with efficient interchain orbital overlap that is robust to structural disorder. The robustness of NiTTFt to structural disorder may be understood in the Anderson localization framework in which sufficiently wide bandwidths maintain a delocalized metallic state around the Fermi level even as structural disorder is introduced⁸ (Supplementary Fig. 88). Regardless of the exact mechanism, the juxtaposition of metallic character and disorder in NiTTFt provides notable thermally and aerobically stable conductivity. These results demonstrate that the use of molecular units that have strong overlap, and subsequently strong electronic delocalization, can lead to metallic character even in amorphous materials.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-022-05261-4>.

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Methods

Synthesis

Unless otherwise noted, all synthetic manipulations were performed under an inert atmosphere of dry N_2 using a Schlenk line or a N_2 -filled MBraun UNILab glovebox. Dichloromethane (DCM) was initially dried and sparged with Ar on a solvent purification system from Pure Process Technologies and stored over 4 Å molecular sieves. Methanol (MeOH) was dried with NaOH, distilled before being transferred and then passed through activated alumina and stored over 4 Å molecular sieves in the glovebox. TTFtt($SnBu_2$)₂, $Fc^{BzO}BAR_4^F$ and $[TEA]_2[NiCl_4]$ were synthesized following previously reported procedures^{15,36}.

NiTTFTt. TTFtt($SnBu_2$)₂ (0.667 mmol, 266 mg) in 5 ml DCM was mixed with $Fc^{BzO}BAR_4^F$ (1.33 mmol, 1.54 g) in 5 ml DCM resulting in a homogenous dark purple solution. The resulting solution was added into a 10 ml MeOH solution of $[TEA]_2[NiCl_4]$ (2.00 mmol, 920 mg) with vigorous stirring. The mixture was stirred at 40 °C overnight. The solid product was isolated by centrifugation and washing with DCM (3 × 12 ml), MeOH (1 × 12 ml) and DCM (1 × 12 ml) sequentially. After being dried under vacuum at 100 °C overnight, 235 mg of NiTTFTt was isolated as a black powder (91%).

Semicrystalline NiTTFTt. TTFtt($SnBu_2$)₂ (0.040 mmol, 43 mg) in 0.4 ml DCM was mixed with $Fc^{BzO}BAR_4^F$ (0.080 mmol, 93 mg) in 0.4 ml DCM to form a homogenous dark purple solution. After mixing, 0.8 ml of this dark purple solution was added into a clean 5 ml shell vial and 2.4 ml of a 1:1 DCM:MeOH solution (by volume) and then 0.8 ml of pure MeOH were slowly layered on the DCM layer sequentially, forming three distinct layers. Finally, a 0.8 ml MeOH solution of $[TEA]_2[NiCl_4]$ (0.12 mmol, 55 mg) and LiCl (0.40 mmol, 17 mg, as an optional modulator) was layered on top. The shell vial was carefully capped and placed in a secondary 24 ml vial that was allowed to sit and diffuse for 5 days. The resulting black powders were collected and washed identically to the procedure for amorphous NiTTFTt described above yielding 13 mg (85%).

Pressed pellets. Pressed pellets were prepared at 800 MPa in the glovebox by using a hydraulic pellet press (TMAX-15T) and dies with different sizes (7, 8 and 12 mm round dies and 6 mm square dies). Hot pressing was carried out with an additional heated die (13 mm Across International heated die with digital controller). Before pressing, powders were ground to particle sizes below 20 μm. For hot-pressed samples, 240 mg of powder was ground with a ball mill (Spex SamplePrep 5100 Mixer miller, 440C steel balls) for 15 min (in air) and loaded into 13 mm round dies that were preheated to 150–200 °C (under N_2). During pressing the pressure was maintained for 5–20 min after stabilizing at 800 MPa. The thickness of the pressed pellets is around 100–300 μm.

Structural characterization

X-ray powder diffraction. PXRD for screening reaction conditions was performed on a SAXSLAB Ganesha equipped with a Xenocs GeniX3D Cu Kα source. Samples were loaded into 0.8–1.1 mm internal diameter, 0.25 mm wall borosilicate capillaries and sealed with wax. Data reduction and integration was performed using the SaxsGui software. In addition, a Rigaku SmartLab X-ray diffractometer equipped with a HyPix3000 detector was used for measurements in either transmission or reflection modes. For transmission, both samples of amorphous and semicrystalline NiTTFTt were loaded into 1.0 mm outer diameter, 0.01 mm wall borosilicate capillaries as fine powders and sealed with wax. All measurements were carried out with Cu Kα radiation (1.54186 Å). Scans were measured using a parallel beam mode selected through the attached Cross Beam Optics. The tube was energized at 44 mA and 40 kV. The data collection was completed in the SmartLab Studio II software package (v.4.4.241.0).

Synchrotron X-ray powder diffraction. Synchrotron PXRD was collected at beamline 11-BM at the Advanced Photon Source (APS) at Argonne National Laboratory. The sample of semicrystalline NiTTFTt was loaded into Cole Parmer Polyimide tubing provided by the beamline and capped with clay. The powders were rotated during the measurement at around 50 Hz. The powder patterns were measured at 295 K using a wavelength of $\lambda = 0.458126$ Å, from 0.5 to 50° 2θ with a step size of 0.001° and a counting time of 0.1 s per step.

X-ray absorption spectroscopy. Powder samples were prepared by grinding finely with polypropylene as a binder. A Teflon washer (5.3 mm internal diameter) was sealed on one side with Kapton tape and the ground powder was then transferred to the inside of this ring before compacting with a Teflon rod and sealing the remaining face with Kapton tape. X-ray absorption near-edge spectra of Ni K-edge (8,333 eV) data were acquired at the MRCAT 10-BM beamline in transmission at APS at Argonne National Laboratory with a bending magnet source with ring energy at 7.00 GeV. Data collected were processed using the Demeter software suite³⁷ by extracting the extended X-ray absorption fine-structure oscillations $\chi(k)$ as a function of photoelectron wave-number k . The theoretical paths were generated using FEFF6 (ref. ³⁸) and the models were done in the conventional way using the fitting program Artemis.

X-ray total scattering and paired distribution function analysis. Samples were loaded into Cole Parmer Polyimide tubing provided by the beamline and capped with clay. High-energy X-ray total scattering experiments were performed at 11-ID-B at the APS, using an X-ray wavelength of 0.2115 Å. The raw 2D data were azimuthally integrated and reduced to 1D intensity versus 2θ in GSAS-II³⁹ using CeO₂ powder for the calibration to determine sample to detector distance. The xPDFsuite program⁴⁰ was used to correct and normalize the diffraction data and then Fourier transform the reduced structure factor to obtain the PDF, $G(r)$.

Scanning electron microscope. SEM images were taken on a Carl Zeiss Merlin using the In-Lens detector in the Materials Research Science and Engineering Center at the University of Chicago. The accelerating voltage is 5.00 kV.

Composition and vibrational characterization

X-ray photoelectron spectra. X-ray photoelectron spectra were collected with the AXIS Nova spectrometer (Kratos Analytical) equipped with a monochromatic Al Kα X-ray source. The Al anode was powered at 10 mA and 15 kV. The instrument work function was calibrated to give a Au 4f_{7/2} metallic gold binding energy of 83.95 eV. The instrument base pressure was around 1×10^{-10} Torr. The analysis area size was 0.3×0.7 mm². For calibration purposes, the binding energies were referenced to the C 1s peak at 284.8 eV. Survey spectra were collected with a step size of 1 and 160 eV pass energy.

Ultraviolet photoelectron spectra. Ultraviolet photoelectron spectroscopy were collected with the AXIS Nova spectrometer using a UV-radiation source. The high-resolution spectra were collected with a pass energy of 40 and a 0.1 eV step size. Then 7 mm cold pressed pellets were affixed to conductive carbon tape under N_2 before loading into the spectrometer.

Inductively coupled plasma-mass spectrometry/optical emission spectroscopy. Inductively coupled plasma (ICP)–mass spectrometry (MS) data was obtained with an Agilent 7700x ICP mass spectrometer and analysed using Mass Hunter v.B01.03. Solutions for ICP–MS were prepared by digesting 2 mg of material in 1 ml HNO₃ (trace metal grade) solution in a fume hood overnight and diluting with ultrafiltered deionized water. An Agilent 700 series spectrometer was used for ICP–optical

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emission spectroscopy (ICP–OES). The sample preparation was referred to the reported procedure⁴¹ to improve the accuracy of sulfur determination. Solutions for ICP–OES were prepared by digesting 2 mg of materials in 0.5 ml HNO₃ and 0.5 ml H₂O₂ (trace metal grade) solutions in tight-sealed high-density polyethylene centrifuge tubes overnight and then diluting with ultrafiltered deionized water.

X-ray fluorescence. X-ray fluorescence measurements were performed on pressed pellets with a Rigaku NEX DE VS spectrometer under a He atmosphere.

Combustion elemental analyses. Combustion elemental analyses (C, H, N) were performed by Midwest Microlabs.

Electron paramagnetic resonance. EPR spectra were recorded on a Bruker Elexsys E500 spectrometer with a quartz finger dewar at 77 K. NiTTFtt was mixed and ground with dry KBr powder into a uniform mixture (of concentration around 0.5 mg per 1 g KBr). This ‘solid matrix’ was loaded into the EPR tube to fill about 0.1 ml volume.

Infrared spectra. Infrared spectra were recorded on a Bruker Tensor II Fourier transform infrared spectrometer with a mercury–cadmium–telluride detector operated at 77 K. Data were processed and background corrected with OPUS software (v.7.5). Samples were prepared under N₂ by grinding solid sample with dry KBr powder, pressed as pellets and measured in air under ambient conditions.

Raman spectra. were obtained with a Horiba LabRamHR Evolution confocal microscope. A Si(111) wafer was used for calibration. The sample of a 7 mm round pressed pellet of NiTTFtt powder was excited using a 532 nm light source operating at 5% of its power and using 100× long path objective and a 600 mm^{−1} grating.

Physical characterization

Room-temperature electrical conductivity and Seebeck measurements. Room-temperature electrical conductivity and Seebeck measurements are based on a previously reported setup⁴². Gold electrical contacts (75 nm thick) were deposited onto 8 mm pressed pellets by thermal evaporation through home-made shadow masks. Four-probe conductivity measurements were performed using a custom-designed probe station in an argon-filled glovebox. Voltage and current measurements were performed using a Keithley 2400 source meter and a Keithley 6221 precision current source. The Seebeck coefficient measurements were performed on the same probe station. Two Peltier elements were placed 5 mm apart to provide the temperature difference ($\Delta T = T_H - T_C$). Two thermocouples were used to collect the hot (T_H) and cold (T_C) side temperatures, and two probes were used to measure the corresponding voltage value. A minimal amount of thermally conductive silicone paste was applied to the tips of the thermocouple to ensure good thermal contact between the thermocouple and the gold pads. A delay of 200 s was used for voltage measurements to ensure that a steady-state temperature gradient and voltage (V) were reached. The Seebeck coefficient was calculated from the slope of a linear fit for the ΔV versus ΔT plot. The measurements were taken within an approximate ΔT of ± 3 K around 300 K.

Thermal conductivities. Thermal conductivities of the samples were determined through single-laser Raman thermometry using the same confocal Raman microscope discussed above on the basis of a reported method²¹. In Raman thermometry, a focused laser beam is used as a heat source whereas the temperature-dependent Raman spectra are used as a thermometer. First, the spectral positions of the Raman peaks around 495 cm^{−1} were measured as a function of the incident absorbed laser power ($\lambda = 532$ nm). The laser power was varied by using 0.1, 1, 2.5 and 5% of the maximum power of the 532 nm light source. The individual

powers were examined with a Si power detector. The operational setup also includes a 100× long path objective and an 1,800 mm^{−1} grating. Second, the shift in the spectral position of the Raman peaks is recorded as a function of temperature, which is controlled externally by a Linkam cryostat in air.

The temperature rise in the laser spot region for the case of a semi-infinite medium can be written as $\Delta T = P_{\text{abs}}/\pi Rk$, where P_{abs} is the laser power absorbed by the sample, R is the Gaussian spot radius and k is the thermal conductivity of the specimen. R is calculated by using the ToptiCalc program and based on the technical information of the laser source and the lens.

Variable-temperature electrical resistance. A strip of double-sided polyimide tape was placed on a d.c. resistivity/Electrical Transport Option (ETO) sample puck (Quantum Design P102), which serves as an electrical insulator, and then pressed pellets with 75-nm-thick deposited gold contacts were put on the top of the tape. Then 0.015 inch outer diameter indium wires were used to bond to the gold nodes of the samples. The puck was then loaded into a physical property measurement system (Quantum Design) under a He-filled inert atmosphere. The four-point probe resistivity measurements on a 13 mm hot pressed pellet and two-point probe resistivity measurements on 8 mm cold pressed pellets were carried out in an a.c. mode with a d.c. excitation of 1 mA. The temperature-dependent resistivity and/or resistance measurements were performed from 300 K to 2 K.

Variable-temperature Seebeck coefficients. Variable-temperature Seebeck coefficients were measured with a MMR Technologies Inc. K-20 Programmable Temperature Controller and a P-100 Programmable Seebeck Controller. A 1 mm × 4 mm piece of a pressed pellet was gently put between the electrodes of the sample chip. Ag epoxy (Epoxy Technology H20E) was used for the connection between the sample and the electrodes. The sample chip was heated in a muffle furnace at 175 °C for 0.5 h for complete curing, before loading the chip into the sample device.

Solid-state magnetic measurements. Solid-state magnetic measurements were performed on a Quantum Design MPMS3 SQUID magnetometer. The bulk powder of the sample (36.0 mg) was suspended in an eicosane matrix in a polycarbonate capsule to prevent movement. Diamagnetic corrections for the capsule and eicosane were made by measuring temperature versus moment in triplicate for each to determine a moment per gram correction. Diamagnetic corrections for the sample itself were applied using Pascal’s constants of each atom on the basis of the formula of NiC₆S₈.

Hall effect measurements. A 6 × 6 mm² pressed pellet (264 μm) and a double-sided polyimide tape was put on the sample puck (P102). Hall effect experiments were carried out on a physical property measurement system at 300 K. The maximum current of 5 mA was used during the test. While the magnetic field (H) was scanned between 0 and 7 T, the Hall resistance (R_{xy}) was measured from the Hall voltage (V_{Hall}) over the current (I) ($R_{xy} = V_{\text{Hall}}/I$). The Hall coefficient ($R_H = dR_{xy}/dH$) was calculated on the basis of a linear fit of the R_{xy} – H plot.

UV–vis–NIR diffuse reflectance spectra. UV–vis–NIR diffuse reflectance spectra were collected on a Varian Cary 5000 spectrophotometer with powder samples loaded in a Praying Mantis air-free diffuse reflectance cell with KCl powder as the non-adsorbing matrix. The Kubelka–Munk conversion of the raw diffuse reflectance spectrum was obtained by applying the formula $F(R) = (1 - R)^2/2R$, where $F(R)$ is the Kubelka–Munk function and R is the diffuse reflectance.

UV–vis–NIR specular reflectance spectra. UV–vis–NIR specular reflectance spectra (200–2000 nm) were collected on a Shimadzu

UV-3600 Plus UV-vis-NIR spectrophotometer with a 5-degree relative specular reflectance accessory. IR specular reflectance spectra (570–8,000 cm^{-1}) were collected with 64 scans at a spectral resolution of 4 cm^{-1} on an IR microscope (Hyperion 2000, Bruker Optics Inc.) coupled to a Fourier transform infrared spectrometer (Vertex 70, Bruker Optics Inc.) with a mid-IR glowbar source. As the rough surface of the pressed pellet causes non-specular reflectance light loss compared with mirror standards, the experiments were conducted following a reported method³¹ based on pressed pellets with a metal coating. First, a 12 mm pressed pellet of NiTTFt was coated with a 100-nm-thick aluminium layer covering half of one of the faces and on the other face a 100-nm-thick gold layer was applied in the same way. Second, for UV-NIR reflectance spectra, we measured the relative reflectance of both the sample surface and the aluminium-coated surface separately with respect to the aluminium mirror. Finally, the absolute reflectance spectrum of NiTTFt was obtained by dividing the sample's reflectance with that of the aluminium-coated surface. For the IR spectrum, the method is similar but, instead of aluminium, gold was used as the reference.

Stability tests

Thermogravimetric analysis. Thermogravimetric analysis was performed using a TA Instruments Discovery analyser. Approximately 2 mg of sample was loaded into a pre-tared Pt pan and measured under N_2 or air. Samples were measured from 35 °C to 700 °C using a linear temperature ramp of 10 °C min^{-1} . The decomposition temperature was defined to be the temperature at which less than 95% mass was left.

Differential scanning calorimetry. Differential scanning calorimetry analysis was performed using a TA Instruments Discovery analyser. Approximately 5 mg of sample was loaded into a pre-weighted Tzero aluminium pan and sealed with a Tzero hermetic lid with a TA Instruments press in an N_2 -filled glovebox. Samples were measured in the ranges of –90–150 °C and 20–210 °C using a linear temperature ramp of 10 °C min^{-1} .

High-temperature variable-temperature resistance. A 7 mm pressed pellet (thickness, 162 μm) was symmetrically deposited with four gold nodes on the edges. The heated resistance measurements were carried out in air with a home-made setup. A polyimide flexible heater (PLM-106/10-P) was used as the heat source, and its temperature was read and controlled by a temperature controller (Digi-Sense Advanced Temperature Controller, Cole Parmer). The sample temperature was read by a thermometer (Traceable Thermocouple). The sheet resistances were measured by a Semiconductor Device Analyser (Keysight B1500A) using the van der Pauw method.

Long-term in-air resistance measurements. After the high-temperature varied-temperature resistance measurements were done, the same setup and sample were maintained in air and the resistance at room temperature was examined every 2 days. For humid air tests, another gold-deposited pellet was loaded in a water-filled zip bag and its conductivity was examined every 3–4 days.

Theoretical calculations

Band structure calculations. In these calculations, we determined the band structure and density of states for the 3D dimer, 3D monomer and 1D monomer models using DFT in Quantum espresso^{43,44}. The kinetic energy cutoff of basis plane-wave functions (100 Ry), Marzari-Vanderbilt-DeVita-Payne cold smearing⁴⁵ temperature (0.001 Ry), energy convergence threshold (1×10^{-8} Ry) and k -point sampling were optimized to reduce error in the band structure. All calculations used a projector-augmented-wave pseudopotential with a Perdew-Burke-Ernzerhof functional and a nonlinear core correction from PSLibrary^{46,47}.

Band paths and Brillouin zone images were generated using the XCrySDen tool⁴⁸.

Molecular calculations. A bimolecular model was constructed from the NiTTFt structure to emulate some possible interlayer interactions present in the amorphous extended structure, with the individual unit displayed in Supplementary Fig. 79. B3LYP/6-31G* DFT calculations with the GD3BJ dispersion correction were performed to find the potential energy surface of the bimolecular model, aiming to investigate the stability of the NiTTFt coordination polymer solid with respect to structural distortions.

Data availability

All relevant data is included in the supplementary information. The raw datasets are available from the corresponding author upon request.

Code availability

The codes used in this study are available in the repository at <https://github.com/damazz/NiTTFt>.

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Author contributions J.X. synthesized samples and performed their physical characterization. S.E. conducted band structure calculations. J.-N.B. performed the molecular calculations. A.S.F. performed and refined the structural determination. B.C. performed electrical measurements and gold depositions. T.M. and G.L.G. carried out the room-temperature

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Seebeck and four-probe conductivity measurements. N.Z. and R.I. collected Raman and specular reflectance IR spectra, respectively. X.S. performed the Kramers–Kronig analysis. H.C. measured variable-temperature Seebeck coefficients. Z.C. and K.W.C. collected and analysed the PDF data. J.X. and J.S.A. conceived and wrote the manuscript. B.C., S.N.P., D.V.T., J.P. and D.A.M interpreted the data and wrote the manuscript.

Competing interests J.S.A and J.X. are inventors on patent application no. 17771266 submitted by the University of Chicago that covers TTFTt-based coordination complexes and materials.

Additional information

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