Journal of Materials Chemistry C

ROYAL SOCIETY OF CHEMISTRY

PAPER

Published on 24 June 2026

Cite this: DOI: 10.1039/d6tc01447j

Enabling mixed ionic-electronic conduction in thienoisoindigo-based polymers *via* side chain engineering

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Organic mixed ionic–electronic conductors (OMIECs) are becoming increasingly important for electrochemical applications, particularly bioelectronic devices. Multiple strategies have been investigated to achieve mixed conduction in organic conductors, notably side chain engineering which introduces hydrophilic units onto conjugated backbones. Although this approach has been extensively explored in well-studied conjugated systems, thienoisoindigo (TIG)-based systems remain comparatively underexplored. Here, we focus on TIG as a promising building block and systematically investigate a series of side chain-engineered polymers in aqueous environments. By tuning the ratio of glycolated side chains, we not only establish a structure–property relationship between glycol side chain composition and electrochemical performance, but also demonstrate significantly enhanced ionic conductivity, gravimetric capacitance, and redox activity in resulting devices. Solid state and electrochemical characterizations reveal that these improvements arise from changes in both side-chain-induced morphology and chain reordering. Particularly, the fully glycolated TIG polymer adopts a predominantly edge-on orientation, in contrast to the face-on orientation observed in alkylated analogues, and displays reduced long-range aggregation. These structural features improve ion accessibility and facilitate efficient ion-electron coupling. Device-level characterization using organic electrochemical transistors (OECTs) demonstrates substantial performance gains, with drain current and the figure of merit (μC*) increasing by approximately two orders of magnitude upon intermediate glycolation. However, this enhanced electrochemical performance is accompanied by reduced structural stability, likely due to increased disruption of polymer packing by mobile ions. This study shows that side chain engineering in TIG-based polymers is a promising platform for mixed ionic–electronic conduction, while underscoring the critical balance between performance and stability in OMIEC design, especially in underexplored building blocks.

Received 6th May 2026,
Accepted 24th June 2026

DOI: 10.1039/d6tc01447j

rsc.li/materials-c

Introduction

Organic mixed ionic–electronic conductors (OMIECs) are an emerging class of materials for advanced bioelectronic devices, including organic electrochemical transistors (OECTs) and energy storage components.[1–4] By leveraging the ability to conduct ions and electrons simultaneously, OMIECs are able to interact with biological (aqueous) environments and convert ionic signals into electronic signals for sensing and data processing applications. Numerous strategies have been developed and are well documented to achieve this mixed conduction phenomenon. The three main strategies that are commonly utilized include grafting ionic or hydrophilic side chains onto conjugated backbones, copolymerization to form block copolymers with polyelectrolytes, and blending of conjugated polymers with polyelectrolytes.[2,5–7]

The main challenge in designing novel OMIECs is attaining balanced electronic and ionic conduction in a single material. A common approach for achieving mixed conduction is backbone and side chain engineering.[8–11] The intrachain electronic conduction relies on the chemical structure of the conjugated polymer backbone, and many structures leverage the donor–acceptor design, thereby alternating electron-rich and electron-poor units to achieve efficient charge transport.[12–15] The interchain electronic conduction relies on the ability for the polymer chains to achieve extended conjugation and stack efficiently through π–π stacking to allow electrons to flow between the polymer chains.

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However, the introduction of side chains, especially polar units, into the polymer structure hinders packing and reduces interchain electronic conduction. It has also been well established that ion insertion into the microstructure disrupts packing and reduces electronic conduction.[16] These competing requirements make it fundamentally and practically difficult to balance electronic conduction and ionic insertion.

One of the more commonly studied conjugated cores is isoindigo, an isomer of the indigo dye, for its relatively simple and tunable synthesis and good backbone planarity, and hence favorable electronic conduction properties.[17–22] Recently, isoindigo derivatives have been investigated to further improve planarity and electronic conduction properties. Of those, thienoisoindigo (TIG) is of particular interest due to its unique structure which replaces the benzene rings in the backbone with thiophene rings.[23–26] This substitution reduces the aromatic character and improves the planarity with backbone dihedrals nearing 0 degrees.[17] Despite its merits, TIG remains an understudied material with applications mainly in dry state devices such as organic field effect transistors (OFETs) and organic photovoltaics.[27,28] To date, there have been only a few studies on TIG polymers for OECT devices and electrochemical applications, all of which require efficient ion insertion.[17,29]

In this work, we use TIG as a model system and explore how varying the ratio of alkyl to glycol side chains from 0% to 100% (P-0, P-50, P-100, where the number represents the percentage of glycol side chains) enables mixed ionic–electronic conduction. This design leverages the strong inter- and intra-chain charge transfer, leading to high electronic conductivity, in TIG backbones and the use of polar side chains to impart ionic transport. We find that by systematically increasing the content of glycol side chains, we can retain the quinoidal features of TIG while tuning its electrochemical response. As a result, we observe significant enhancement in OECT device performance, specifically in terms of ON current, transconductance, as well as switching kinetics. Combined solid-state and electrochemical characterizations reveal that these performance enhancements arise from modulated surface energies, reduced chain aggregation as well as side-chain-dependent reorientation of π–π stacks, factors which contribute to enhanced ionic insertion into an otherwise efficient electron-transporting system.

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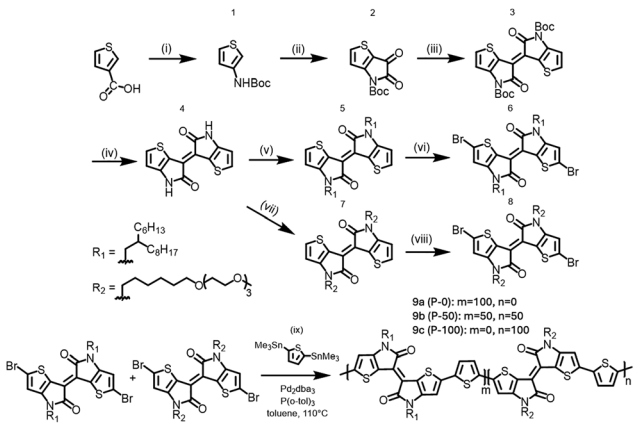
Professor Gumyusenge received a BS in chemistry from Wofford College and a PhD in chemistry from Purdue University. Before joining the department of materials science and engineering at MIT, he was a postdoctoral fellow of the Geballe Lab for Advanced Materials at Stanford University. Professor Gumyusenge's research background and interests are in semiconducting polymers, their processing and characterization, and their role in the future of electronics. Particularly, he has tackled long-standing challenges in operation stability of semiconducting polymers under harsh environments. At MIT, Professor Gumyusenge's research group, OMSE Lab, focuses on (i) developing new mixed conductive materials, (ii) relating structure to property, and (iii) developing new device designs for applications in health, environmental monitoring, and energy-efficient computing.

Results and discussion

As shown in Scheme 1, a TIG system with a branched alkyl side chain and a thiophene donor unit (P-0) was synthesized as the parent polymer. Using the same Stille coupling reaction, polymers with varying amounts of triethylene glycol (TEG) terminated hybrid side chains were synthesized. In the scheme, compounds **9a**, **9b** and **9c** correspond to P-0, P-50 and P-100 respectively. Full synthetic procedures and physical characterizations are detailed in the (SI). This copolymerization approach, inspired by our previous works on donor–acceptor OMIECs,[11,30] was chosen to investigate the push–pull effect in donor–acceptor polymers, which can maximize electronic conduction, especially in highly planar systems.

We investigate the thienoisoindigo unit because, relative to the isoindigo parent structure, it reduces the aromatic character, promotes the quinoidal conformation, and thus chain planarity (as confirmed by our density functional theory, DFT, calculations, Fig. S1).[13] We select a single thiophene unit as the donor molecule as it yields a high-lying HOMO and thus p-type character to the overall copolymer. At the same time, the two monomers readily yield polymers bearing polar side chains (Scheme 1). For the fully alkylated polymer, we use the commonly studied branched side chains (R_1) to preserve the solubility and processability of TIG and promote backbone packing in solid-state. In the P-50 and P-100 structures, we select a



Scheme 1 Synthetic scheme from monomer to TIG-T polymer (i) Et_3N, t-butanol, DPPA, 80 °C (ii) Et_3N, oxalyl chloride, DCM, −15 °C (iii) Lawesson's reagent, toluene, 60 °C (iv) TFA, RT (v) $BrC_{16}H_{33}$, K_2CO_3, DMF, 120 °C (vi) NBS, 0 °C (vii) $C_{16}H_{33}Br$, K_2CO_3, TBAF, DMF, 120 °C (vi) NBS, 0 °C (ix) Pd_2dba_3, P(*o*-tol)$_3$, toluene, 110 °C.

hybrid side chain (R_2) with a six-carbon spacer and a TEG terminus. By placing the polar groups six carbons away from the conjugated backbone, we hypothesize that the TIG main chains can retain their inherent ordering while incorporating ion-transporting side units. We also expect that the oxygen-containing groups would have minimal effect on the electronic charge distribution along the backbone as supported by the DFT calculations (Fig. S1) and literature precedents.[31,32]

The three polymers were synthesized in high yield and purified following previous reports.[33–35] The weight-average molecular weights (M_w) were extracted to be 11.2, 17.1, 11.9 kDA, respectively, using high temperature gel permeation chromatography (HT GPC). These values were comparable to those previously reported in analogous TIG systems.[33–35] As the ratio of TEG-terminated side chains increased, the solubility decreased, making both polymerization and accurate molecular-weight determination using conventional standards and eluents challenging. Nonetheless, all polymers could be processed into thin films from chloroform solutions allowing us to probe the effects of side chain composition on mixed ionic–electronic behaviors and device performance.

To analyze the impact of glycolated side chains on topological and solid-state properties of the TIG polymers, we used atomic force microscopy (AFM), grazing-incidence wide-angle X-ray scattering (GIWAXS) and UV-Vis absorption spectroscopy. Fig. 1A shows AFM height images from annealed thin films of P-0, P-50, and P-100 revealing smooth surface morphologies, especially for P-100 films. Film roughness was quantified using the root mean squared roughness, r_q, and was found to be 1.01 ± 0.19 nm, 0.62 ± 0.13 nm, and 0.86 ± 0.06 nm for P-0, P-50 and P-100 respectively. 2D GIWAXS diffraction patterns further revealed that the incorporation of glycol side chains induces a change in packing orientation. That is, P-0 shows a predominantly face-on orientation which is retained in P-50 and shifts fully to an edge-on orientation in P-100 films (Fig. 1B and C). This change in packing orientation has been recently observed in planar MIEC polymers based on isoindigo, when bulky and polar side chains are introduced.[30]

It is worth noting that the extracted π–π stacking distance was around 3.55 Å and the lamellar spacing of 20.94 Å in the case of P-0 and P-50 (Fig. 1C and Table S2). These structural features, particularly in the case of P-50, are of interest for mixed ionic–electronic conduction as the crystalline domains are retained despite 50% of the backbone bearing polar side-chain termini. Upon full glycolation, in addition to the reorientation, a slight decrease in the π–π stacking distance was detected (down to 3.49 Å) at the expense of the lamellar spacing that increased to 22.44 Å in P-100 (Fig. 1C and Table S2). Although it remains unclear whether this chain reorientation benefits charge transport upon bulk doping, the side-chain-induced lamellar expansion, while preserving the π–π stacking distance, would facilitate ion insertion and subsequent mixed conduction.

UV-vis absorption spectra from the annealed films further supported the change in packing and aggregation behavior with a noticeable blue shift in the maximum absorption peak.

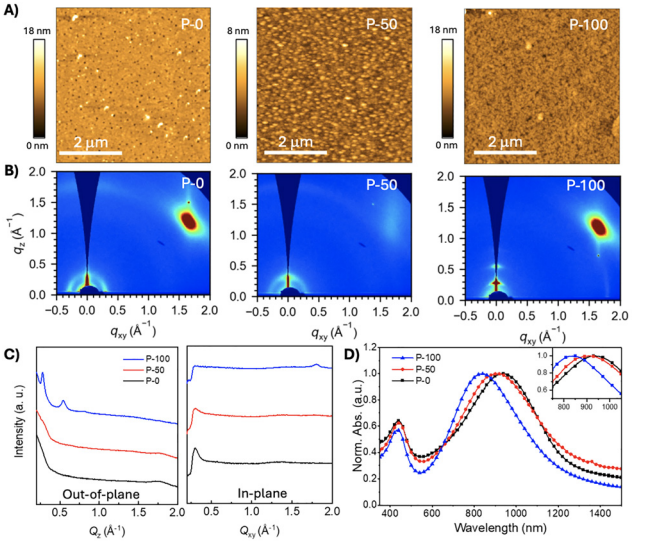


Fig. 1 Solid-state properties of synthesized TIG polymers. (A) AFM height images, (B) and (C) 2D GIWAXS patterns and corresponding 1D linecuts, and (D) thin-film UV-vis absorption spectra with increasing content of glycol side chains.

That is, from the parent polymer (P-0), we observe a blue shift up to 60 nm in the intermolecular charge transfer (ICT) band, signature of TIG polymers (Fig. 1D). Introducing glycol side chains into the polymer structure blue-shifts the peak maxima from 936 nm for P-0 to 910 nm for P-50 and 848 nm for P-100. This reduced aggregation, especially when achievable independent of the molecular weight, is desirable for electrochemical performance, particularly in terms of ion accessibility to the de-aggregated main chains. However, for balanced ionic–electronic transport this comes with a trade-off, as electronic charge transport typically relies on long-range coupling.

In terms of electrochemical performance, the introduction of EG side chains in P-50 and P-100 showed increased interfacial hydrophilicity of the resulting annealed thin films, as revealed by the contact angle measurements (Fig. 2A). Notably, compared to P-0, decreases of 17° and 19° in the contact angle was observed in films of P-50 and P-100, respectively. We anticipate this change in the surface energy to translate into improved ability of the newly synthesized polymers to uptake hydrated ions.[31,36,37] In fact, electrochemical impedance spectroscopy (EIS) measurements showed that increasing the fraction of glycol side chains boosts the ionic conductivity by up to a factor of two in the case of P-100 (Fig. 2B and Fig. S2). In terms of the gravimetric capacitance, we found that P-50 and P-100 showed 21-fold and 35-fold increases, respectively, as shown in Fig. 2C and D. As shown by the cyclic voltammograms in NaCl electrolyte and corresponding capacitance, P-0 exhibits low charge-storage capacity as a working electrode. We attribute this inefficient charging to the hydrophobicity, aggregation, and low ionic conductivity discussed above. With increasing content of TEG-terminated side chains, the capacity increased systematically as a result of tuned solid-state and molecular-level properties.

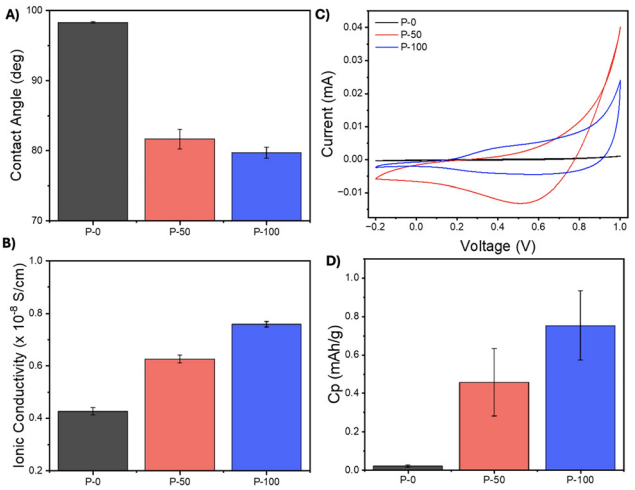


Fig. 2 Electrochemical performance analyzed through electrochemical impedance spectroscopy (A) and extracted ionic conductivity (B). Cyclic voltammetry (C) and extracted gravimetric capacitance (D) for the polymer series.

Though it is generally understood that tuning the alkyl to glycol side chain ratio in OMIEC polymers modulates ion insertion and conductivity,[32,42] it remains unclear whether the optimal ratio can be generalized, especially when investigating new building blocks. In previous investigations, the optimal ratios have typically been reported to be around 1 : 1 or lower, and structures often target to minimize packing disruption caused by the glycol side chains. For the first time in TIG polymers, we show that the redox activity continues to increase with increasing glycol side chain content. We hypothesize that the planar nature of TIG renders the resulting polymers less permissive to ion insertion compared to more open and less aggregating OMIECs reported to date,[38–41] thus requiring complete glycolation in order to attain optimal charge capacity. Notably, here we employ hybrid side chains with the spacer unit, which may keep ions further from the newly investigated backbone than intended.[16] In fact, even with 100% of side chains being TEG-terminated, the measured contact angle remains as high as 80 degrees, suggesting persistent hydrophobicity in the TIG polymers. This behavior suggests that perhaps future iterations of these OMIECs may therefore require higher glycol content through side-chain elongation, branching, or both.[29]

To further probe the ionic–electronic coupling capability of the TIG polymers, we evaluated the polymer series in OECT devices. Fig. 3A illustrates the investigated device architecture with NaCl as the electrolyte. All TIG polymers (P-0, P-50 and P-100) showed a p-type turn-on behavior in 0.1 M NaCl with a V_{DS} of −0.6 V. As the ratio of glycolated side chains increases, the transistor devices exhibited increased source-drain current (over 30× compared to the fully alkylated polymer) (Fig. 3B and Fig. S3). Note the differences in the hysteresis (as well as the maximum current in the output curves where successive gate voltages are employed, Fig. S3) behavior between P-50 and P-100. That is, with a moderate amount of TEG side chains, the devices exhibit slower reversibility, likely due to greater charge coupling and slower doping kinetics during the channel gating (Fig. 3B and Fig. S3). In the case of devices based on P-100, the ions are able to rapidly dope and de-dope the channel and hence the reduced channel hysteresis. Note that once P-50 is doped, the slope of the transfer curve, and hence the extracted g_m value (Fig. 3B, inset) is much greater than in other polymers. We attribute the increased transconductance in P-50 (despite its greater hysteresis) to a balance between electrolyte uptake and electronic charge transport. In other words, while P-0 is unable to effectively uptake ions, P-100 exhibits enhanced capacitance and ionic transport but more limited electronic transport (attributed to the presence of the polar side chains, and likely the above-discussed changes in inter-chain packing and chain aggregation); P-50 offers a balance between the two modes.

Fig. 4 shows the recorded channel current from the TIG polymers in response to a series of gate voltage pulses. P-0 exhibits a maximum current no greater than 3.0 μA which remains stable even after hundreds of pulses. At the same time, transistor devices based on P-0 show slow turn-on kinetics with the maximum failing to plateau within the 1s pulses. Devices based on P-50 exhibit a similar behavior, but with current levels up to 20× higher (Fig. 4C and D). As the backbone becomes fully glycolated, the current response reaches as high as 40 μA and the device channels exhibit much faster response times. However, the current degrades rather quickly upon long-term cycling (Fig. 4E and F). We attribute the faster response times in the case of P-100 to the enhanced polarity as well as the lowered aggregation as discussed above. Both factors promote more efficient ion penetration into the bulk of the film, as supported by the electrochemical characterizations, but also make the

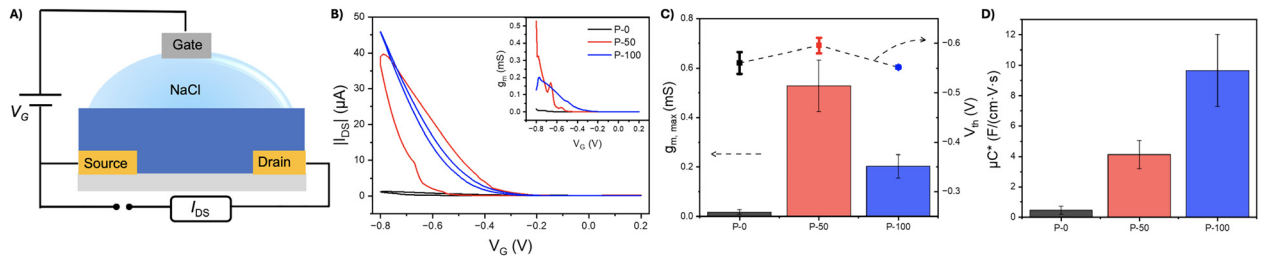


Fig. 3 OECT device performance of TIG polymers (W/L = 400/5 μm). (A) Schematic illustration of the transistor device, (B) representative transfer curves with extracted transconductance values (inset), (C) maximum transconductance values and threshold voltages, and (D) and extracted μC* parameters.

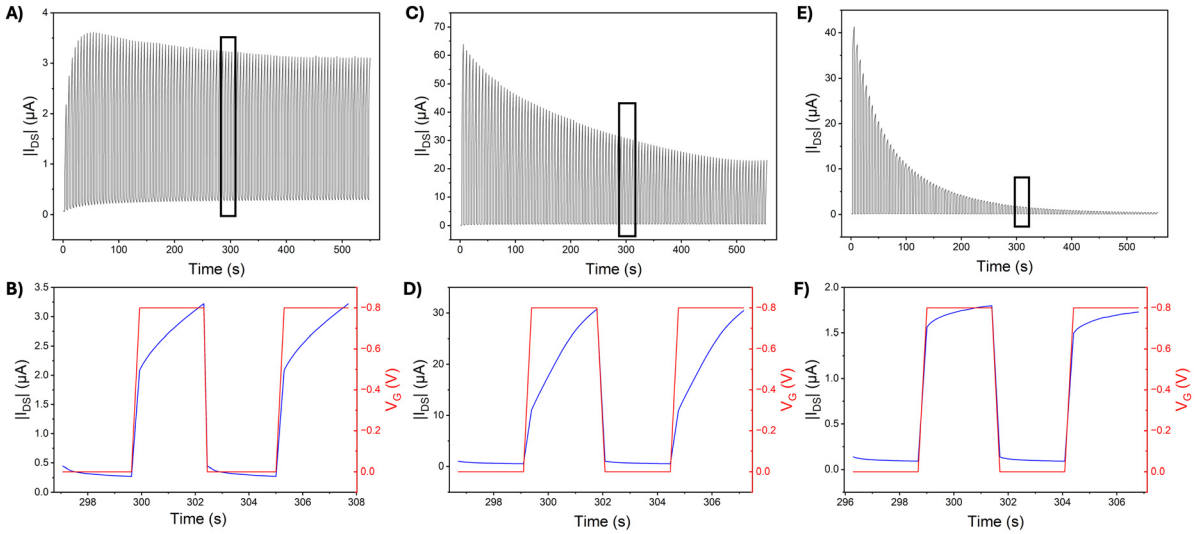


Fig. 4 Cycling stability of TIG polymers in OECT devices. Current response to gate voltage pulses over 8 minutes for P-0 (A) and (B), P-50 (C) and (D), and P-100 (E) and (F).

channel less stable under repeated cycling. These cycling and stability tests further demonstrate that, in these TIG polymers, striking a balance with TEG-terminated side chains is critical for performance optimization. P-50 achieves greater transconductance alongside improved device stability.

Conclusions

In summary, we developed a novel series of thienoisoindigo (TIG)-based polymers and systematically investigated their mixed ionic–electronic conduction behavior through side-chain engineering. By tuning the ratio of alkyl to glycol side chains, we established structure–property relationships linking side-chain composition to morphology, ion transport, and device performance. In particular, polymers with intermediate glycolation exhibit an optimal balance between ionic accessibility and electronic charge transport, resulting in substantial enhancements in ionic conductivity, gravimetric capacitance, redox activity, and overall OECT performance. Our combined structural and electrochemical analyses reveal that these changes in performance arise from glycol-induced modulation of polymer packing, reduced aggregation, and reorientation of π–π stacking. These findings highlight TIG as a promising yet underexplored building block for mixed ionic–electronic conductors and demonstrate the critical role of side-chain engineering in governing multifunctional transport properties. Looking forward, further optimization of TIG-based systems may benefit from more dedicated side-chain designs, such as varying spacer length, branching, or incorporating more hydrophilic functionalities to better control ion–polymer interactions without excessively disrupting electronic pathways.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data to support the findings of this study are available in the main text and/or the supplementary information (SI). Supplementary information: experimental details and supporting figures. See DOI: https://doi.org/10.1039/d6tc01447j.

Acknowledgements

E. R. L. and A. G. acknowledge support from the Natural Sciences and Engineering Research Council of Canada (NSERC). Part of this work was carried out in the shared experimental facilities at MIT supported by the National Science Foundation (grant no. DMR-14-19807), the MIT Department of Chemistry Instrumentation Facility (DCIF), and MIT.nano facilities.

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