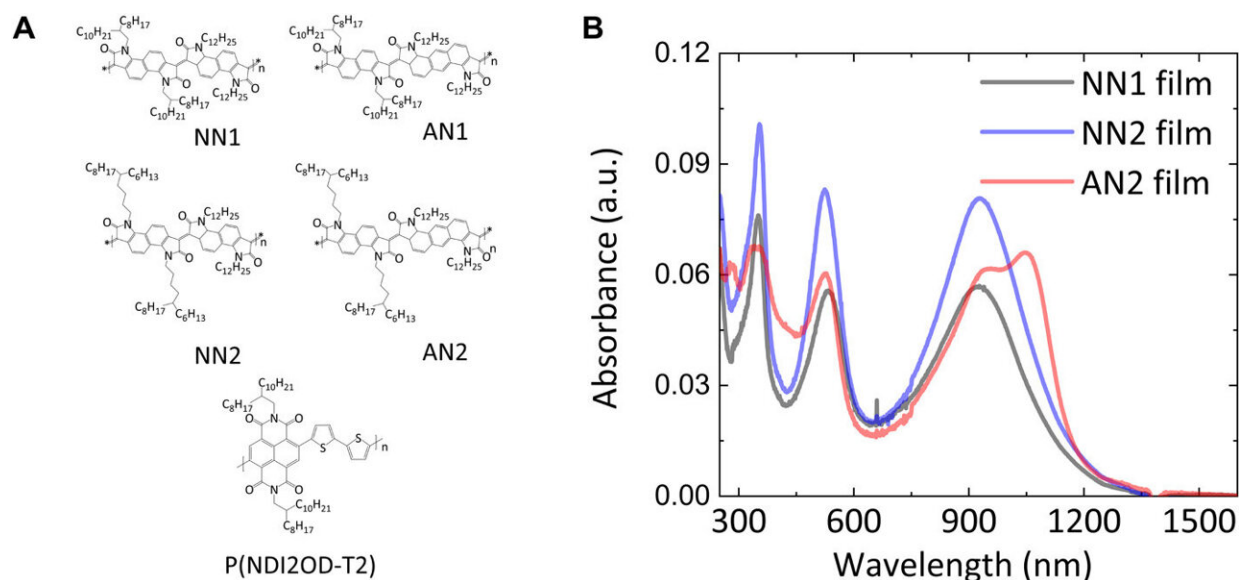


Charge transport physics of a unique class of rigid-rod conjugated polymers

June 1 2021, by Thamarasee Jeewandara



Chemical structures and thin-film UV-Vis-NIR absorption spectra. (A) Chemical structure of NN1, NN2, AN1, AN2, and P(NDI2OD-T2) polymers. (B) Thin-film UV-Vis-NIR absorption spectra of the polymers. The films were spun from hot 1,2,4-trichlorobenzene solution. Credit: Science Advances, doi: 10.1126/sciadv.abe5280

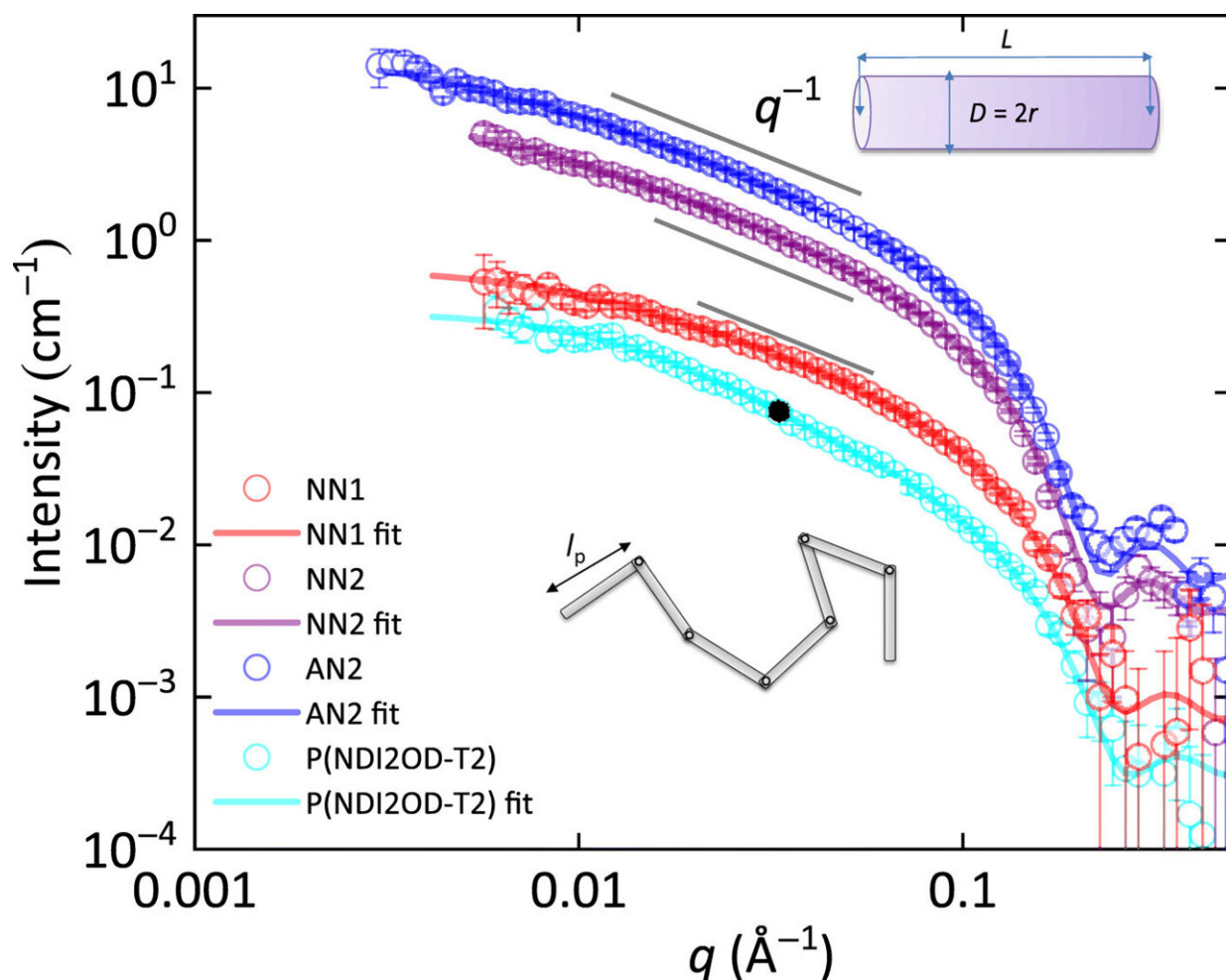
In a new report now published on *Science Advances*, Mingfei Xiao and a team of interdisciplinary and international scientists in the U.K., Saudi Arabia, Australia, India, China and Belgium, investigated the charge transport physics of a previously unidentified class of conjugated

polymers. Such polymers are expected to behave as rigid rods, however, not much is known of their actual chain conformation and electronic structure. In this work, Xiao et al. detailed a study of the structural and charge transport properties of a family of four such polymers based on anthracene-derived (AN1 and AN2) and naphthalene-derived (NN1 and NN2) systems. By adopting copolymer designs, the team achieved high electron mobilities of up to $0.5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$. This work provides important insights into the factor limiting charge transport in this unique class of polymers to allow the identification of molecular strategies to achieve higher levels of performance.

Conjugated polymers

Conjugated polymers are attractive for [a range of applications](#) across displays, bioelectronics and large-area electronics due to their large-area, low-temperature, solution-based manufacturing deposition with [solubilizing side chains](#). By understanding the molecular-level chain conformations, researchers aim to detect structure-property relationships in conjugated polymer systems. In a new report, Xiao et al. systematically investigated the chain conformations, persistence lengths, microstructure, energetic disorder and charge transport properties in four such polymers labelled NN1, NN2, AN1 and AN2. They compared the air stability of these four polymers to the widely investigated electron-deficient polymer known as [P\(ND120D-T2\)](#). The strategy can improve charge transport properties in other rigid-rod polymers and will promote crystallinity and mobility. The researchers then characterized the molecular weight dependence of charge transport properties using [grazing-incidence wide-angle X-ray scattering](#) (GIWAXS), to understand the film microstructure, while quantifying the energetic disorder via [photothermal deflection spectroscopy](#) (PDS) and [quantum-chemical modelling](#). Xiao et al. used [small-angle neutron scattering](#) (SANS) to quantify persistence lengths and field-induced [electron](#)

[spin resonance](#) to quantify charge hopping times and hopping lengths in working [organic field-effect transistors](#) (OFETS) to show how a long persistence length facilitated good charge transport properties. The work aims to identify further strategies to enhance charge transport properties of a unique class of conjugated polymers.

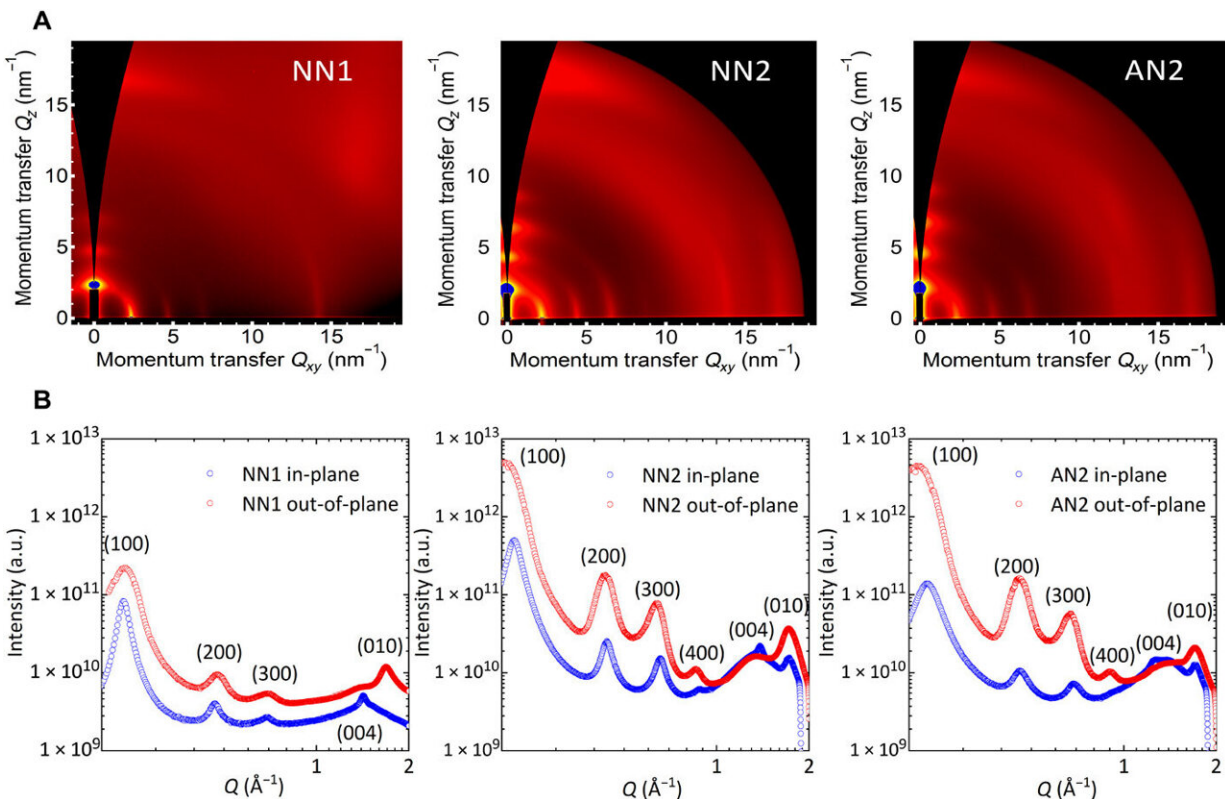


SANS of NN1, NN2, AN2, and P(NDI2OD-T2) in hot, dichlorobenzene solution. The NN1, NN2, and AN2 fused polymers adopt a rigid-rod shape with a scaling of $I \approx q^{-1}$ over a large region, while the semiflexible P(NDI2OD-T2) polymer shows a characteristic worm-like chain behavior.

The curves have been shifted vertically for clarity. The incoherent scattering background was subtracted. Credit: Science Advances, doi: 10.1126/sciadv.abe5280

The experiments—small angle neutron scattering (SANS)

During the experiments, Xiao et al. noted that the AN1 polymer caused synthetic problems due to limited solubility. They also noted well-resolved vibronic absorption in the near-infrared region with the AN2 polymer suggests a smaller degree of energetic disorder. The electron affinity among the polymers were in the range between -4.1 and -4.2 eV and high electron affinity allowed good air-stable electron transport in these polymers. The scientists performed SANS ([small-angle neutron scattering](#)) experiments on solutions of NN1, NN2 and AN2 fused polymers to understand their properties. The results confirmed the AN2 polymer to maintain the largest molecular weight. The general SANS features were similar for the NN1, NN2, and AN2 polymers where a rapid decrease in scattering intensity was visible for large scattering vectors. The outcomes highlighted the three polymers to be significantly more rigid and less flexible than the test polymer P(ND120D-T2). The materials architecture with a rigid rod-like nature clearly distinguished these materials from other more traditional conjugated polymers.

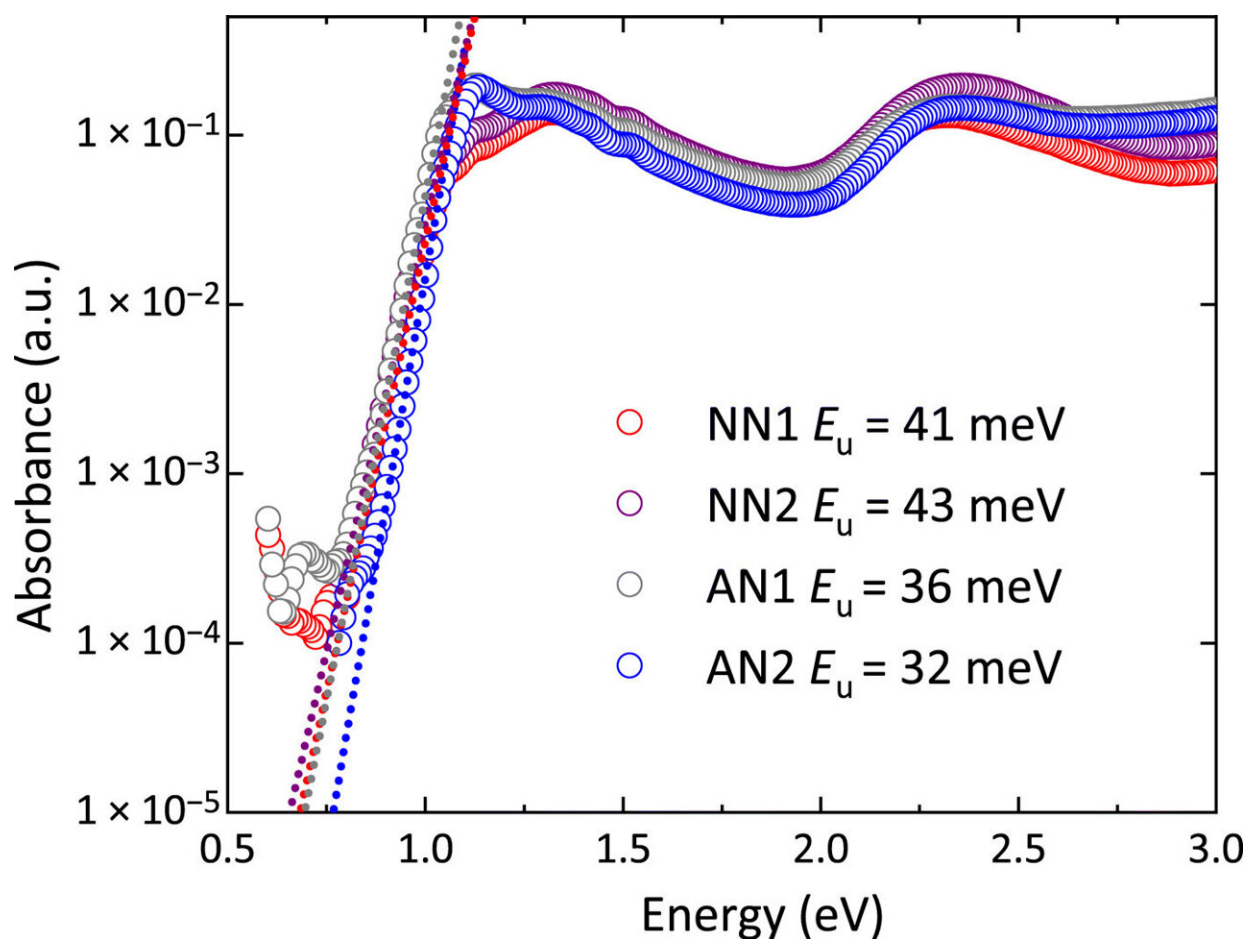


Structural characterization of the representative rigid-rod polymer thin films. (A) 2D GIWAXS patterns of NN1, NN2, and AN2 thin-film samples. (B) In-plane and out-of-plane 1D linecuts of NN1, NN2, and AN2's 2D GIWAXS patterns. Credit: Science Advances, doi: 10.1126/sciadv.abe5280

Grazing-incidence wide-angle X-ray scattering (GIWAXS) and photothermal deflection spectroscopy (PDS)

The GIWAXS patterns for the three fused polymers also showed bimodal textures with face-on and edge-on crystallites co-existent within the samples. The team noted differences between the three polymers, where the NN1 samples showed a face-on texture and NN2 and AN2 indicated a significant edge-on population. The GIWAXS results provided evidence for a highly ordered semicrystalline thin-film

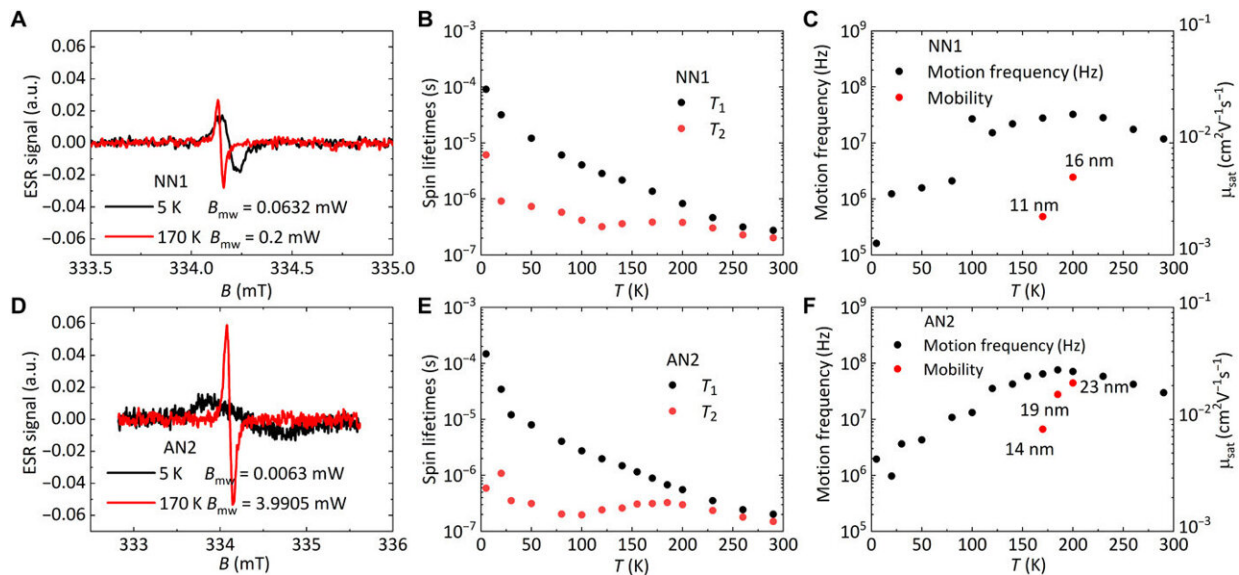
microstructure with pronounced interchain interactions and close π - π stacking. To then investigate energetic disorder in the solid state of the materials, Xiao et al. used photothermal deflection spectroscopy (PDS) and measured the broadening of the tail of optical absorption below the band edge. Both AN1 and AN2 (anthracene-derived) polymers showed lower energetic disorder compared to the naphthalene-derived systems NN1 and NN2. To understand the origin of low energetic disorder in the polymers, Xiao et al. simulated the conformational potential energy surface of the representative systems. The scientists credited the smaller thermal energetic disorder for AN versus NN to the spreading of the π system in anthracene vs naphthalene polymers.



PDS of rigid-rod polymer thin films. Absorbance of the NN1, NN2, AN1, and AN2 thin films measured by PDS. Dotted lines represent exponential tail fits for extraction of the Urbach energies E_u (inset). Credit: Science Advances, doi: 10.1126/sciadv.abe5280

Investigating the charge transport properties

To then understand charge [transport](#) properties of different polymers, Xiao et al. developed spin-coated, top-gate, bottom-contact OFETs ([organic field-effect transistors](#)) using a [polymethyl methacrylate](#) (PMMA) dielectric material. The devices showed [ambipolar transport](#) characteristics, where the scientists noted the highest mobilities in AN2 with corresponding large changes in the [lowest unoccupied molecular orbital](#) (LUMO) energy with chain length. They credited the additional results to residual energetic disorder, trap filling or electron-electron interactions of the semicrystalline [polymer](#) OFETs. At fixed molecular weights, both AN2 and NN2 showed higher carrier mobilities compared to AN1 and NN1 polymers. The activation energies of all four polymers reached approximately 100 meV: comparable to other high-performance semicrystalline polymeric OFETs. The team credited the high activation energy to the reorganization energy of the materials. They also conducted [continuous-wave, field-induced electron spin resonance](#) (FI-ESR) to study polaron spin dynamics and gain insight into the corresponding charge dynamics of the materials. The outcomes provided information on the coupling between electron spins and vibrational modes.



FI-ESR characterization of rigid-rod polymers. FI-ESR spectra of the top-gate, bottom-contact sample ($L = 100 \mu\text{m}$, $W = 243 \mu\text{m}$) fabricated from spin-coated (A) NN1 and (D) AN2 film at 5 and 170 K. Spin lifetimes T_1 and T_2 for electron polarons in (B) NN1 and (E) AN2 FI-ESR sample at $V_G = 60 \text{ V}$. Motion frequency of charges determined from T_2 (left axis) and saturation mobilities from FET measurements at $V_G = 60 \text{ V}$ (right axis) of (C) NN1 and (F) AN2 FI-ESR samples. Labels show the calculated hopping distances in the motional narrowing regime by relating the motion frequency and saturation electron mobility with the Einstein relation for charge transport. Credit: Science Advances, doi: 10.1126/sciadv.abe5280

In this way, Mingfei Xiao and colleagues gathered direct evidence to realize rigid-rod behavior in conjugated polymers containing only double-bond linkages between the fused ring conjugated units. Such systems can retain the unique rigid-rod nature of these polymers to achieve lower energies of disorder and reorganization energies to facilitate the potential to reach even higher charge carrier mobilities that exceed the existing state-of-the-art systems.

More information: Xiao M. et al. Charge transport physics of a unique class of rigid-rod conjugated polymers with fused-ring conjugated units linked by double carbon-carbon bonds, *Science Advances*, [DOI: 10.1126/sciadv.abe5280](https://doi.org/10.1126/sciadv.abe5280)

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