Highly Planarized Naphthalene Diimide–Bifuran Copolymers with Unexpected Charge Transport Performance

Rukiya Matsidik,†,‡ Alessandro Luzio,‡ Öze Askin,‡ Daniele Fazzi,§ Alessandro Sepe,◊ Ullrich Steiner,◊ Hartmut Komber,⊥ Mario Caironi,∥ Alessandro Sepe,§ Hartmut Komber,⊥ Mario Caironi,∥ and Michael Sommer,†

†Universität Freiburg, Institut für Makromolekulare Chemie, Stefan- Meier-Str. 31, 79104 Freiburg, Germany
‡Freiburger Materialforschungszentrum, Stefan- Meier-Str. 21, 79104 Freiburg, Germany
§Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy
¶Max-Planck-Institut für Kohlenforschung (MPI-KOFO), Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany
◊Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland
⊥Leibniz Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany
∥FIT Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien, Georges-Köhler-Allee 105, 79110 Freiburg, Germany

ABSTRACT: The synthesis, characterization, and charge transport performance of novel copolymers PNDIFu2 made from alternating naphthalene diimide (NDI) and bifuran (Fu2) units are reported. Usage of potentially biomass-derived Fu2 as alternating repeat unit enables flattened polymer backbones due to reduced steric interactions between the imide oxygens and Fu2 units, as seen by density functional theory (DFT) calculations and UV–vis spectroscopy. Aggregation of PNDIFu2 in solution is enhanced if compared to the analogous NDI–bithiophene (T2) copolymers PNDIT2, occurring in all solvents and temperatures probed. PNDIFu2 features a smaller π–π stacking distance of 0.35 nm compared to 0.39 nm seen for PNDIT2. Alignment of aggregates in films is achieved by using off-center spin coating, whereby PNDIFu2 exhibits a stronger dichroic ratio and transport anisotropy in field-effect transistors (FET) compared to PNDIT2, with an overall good electron mobility of 0.21 cm2/(V s). Despite an enhanced backbone planarity, the smaller π–π stacking and the enhanced charge transport anisotropy, the electron mobility of PNDIFu2 is about three times lower compared to PNDIT2. Density functional theory calculations suggest that charge transport in PNDIFu2 is limited by enhanced polaron localization compared to PNDIT2.

1. INTRODUCTION

In the exploration of polymer semiconductors for organic electronics, good hole conducting conjugated polymers have been extensively studied making high-performance p-type devices available in manifold variations. Good electron conducting or electron accepting conjugated polymers have been less explored, and extremely versatile building block used in n-channel devices. In 2009, Yan et al. reported high electron-mobilities for NDI bithiophene (T2) copolymers known as PNDI2OD-T2 and herein referred to as PNDIT2, which triggered tremendous interest in NDI-based polymers for use in n-type devices. Since then, PNDIT2 has been the subject of many fundamental investigations regarding electronic structure, morphology and device performance. Meanwhile, many derivatives of PNDIT2 have been synthesized. Interestingly, only a few isolated examples outperformed PNDIT2 while other comonomer structures did not lead to enhanced device performance. Indeed, thiophene (T) is a simple, cost-effective, well-explored, and extremely versatile building block used in conjugated polymers. Compared to the overwhelming presence

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of thiophene in conjugated materials, its oxygen analogue furan (Fu) has received much less attention despite its advantageous properties.\textsuperscript{27,28} For example, Fu is available from biomass\textsuperscript{29} and gives materials with improved solubility.\textsuperscript{23,30} In cases in which sterical hindrance between thiophene and adjacent aromatic units lowers conjugation by increased torsion, the smaller size of furan can lead to enhanced planarization, which is thought to allow smaller π−π stacking distances and eventually improved charge transport performance.\textsuperscript{23,34} A drawback of furan-based copolymers is their reduced thermal stability that arises from the decreased aromatic character of furan, which might have contributed to the limited deployment of furan-based (co-)polymers in material science.\textsuperscript{29} We have recently reported that the incorporation of FuNDIFu, which is a π-extended monomer of NDI unit flanked with furan, into conjugated polymers with tetrafluorobenzene F$_4$ leading to PNDIFu$_2$F$_4$ allowed for a reduced π−π stacking distance compared to the thiophene analogue PNDIT$_2$F$_4$.\textsuperscript{35} However, contrary to the general assumption that smaller π−π stacking distances are beneficial for enhanced electron transport, the thiophene analogue PNDIT$_2$F$_4$ showed higher electron mobilities as a result of beneficial long-range ordering.\textsuperscript{36} Further investigations have compared furan-based structures with their thiophene analogues with mixed outcomes. While some furan-derived structures showed enhanced performance,\textsuperscript{32,33} others showed adverse results with furan-based small molecules and DPP copolymers exhibiting reduced mobilities.\textsuperscript{34−36} Thus, the impact of replacing thiophene with furan can vary greatly depending on the system and structure under scrutiny. In order to investigate structure−function relationships resulting upon replacing thiophene by furan in main chain NDI copolymers, we synthesized the bifuran analogue of PNDIT$_2$ with two different side chains, namely, 2-hexyloctyl (PNDIFu$_2$-C16) and 2-octyldodecyl (PNDIFu$_2$-C20), using a nickel-catalyzed activation with Rieke zinc to generate radical anions followed by the subsequent addition of NidpppCl$_2$ (Scheme 1).\textsuperscript{38} However, contrary to the previously reported mechanism including partial chain-growth character, low catalyst loadings led to low molecular weights in the case of PNDIFu$_2$. A similar issue was also reported for KCTP of poly(3-hexylfuran) due to strong aggregation.\textsuperscript{39} Increasing the catalyst loading to 10 mol %, molecular weights of $M_n$ ≈ 17 kDa were readily achieved after 1 h with high conversion and yield (~90%). However, early precipitation of PNDIFu$_2$ occurred as well as a result of significant aggregation. Monitoring the reaction kinetics by taking aliquots during polymerization and analyzing them by size exclusion chromatography (SEC) showed that the starting monomer was completely consumed after 30 min (Figure S1). Most likely, subsequent coupling of prepolymerized Br(FuNDI-Fu)Br segments may have led to high molecular weight and precipitation, whereby the yield of soluble product can be maximized by reducing the reaction time, thus limiting precipitation.\textsuperscript{40} To enable high yields and overcome issues with precipitation, target molecular weights for this comparative study were set to $M_n,SEC$ ≈ 17 kg/mol. Thus, a set of three samples, referred to as PNDIFu$_2$-C16, PNDIFu$_2$-C20, PNDIT$_2$-C16, with $M_n,SEC$ ≈ 16, 17, 18, kDa, respectively, and dispersities around 2.4 were prepared using NidpppCl$_2$.

A fourth sample PNDIT$_2$-C20, albeit synthesized by direct arylation polycondensation,\textsuperscript{14} exhibits the same structural integrity as PNDIT$_2$-C16, based on high-temperature $^1$H NMR spectroscopy and SEC, and can thus be used for comparison (Table 1).

### 2.2. Intramolecular Structure: Insights into Neutral and Charged States from DFT Calculations

Gas-phase DFT calculations were first carried out to get insight into the geometric and electronic structure of PNDIFu$_2$ to highlight the differences that arise from the replacement of T with Fu. Both the repeat units (i.e., monomer, $n = 1$) and the oligomers (i.e., five repeat units, $n = 5$) of PNDIFu$_2$ and PNDIT$_2$ were...
considered. Relaxed DFT potential energy profile calculations (\(\omega\)B97X-D/6-311++G\(^*\)) along the dihedral coordinate (\(\tau\)) connecting the NDI unit with Fu or T rings were computed for the monomers, revealing an asymmetric double well potential\(^1\) with stable conformations around \(\tau = 28^\circ\) (or \(152^\circ\)) for NDI-Fu and \(\tau = 42^\circ\) (or \(138^\circ\)) for NDI-T. At the monomer level, FuNDIFu features a more planar structure than TNDIT. To model the structure of the polymers’ backbone, we built up conformationally regular oligomer chains (NDIFu\(_2\))\(^5\) and (NDIT\(_2\))\(^5\) with five repeat units. The ground state (neutral) DFT equilibrium molecular structures are reported in Figure 1a. (NDIFu\(_2\))\(^5\) features a planar and flat structure. On the contrary, (NDIT\(_2\))\(^5\) shows tilted conformations that lead to out-of-plane distortions between the NDI and T2. We believe the more planar structure of (NDIFu\(_2\))\(^5\) and the distorted one of (NDIT\(_2\))\(^5\) are intrinsic structural properties of the polymers, as calculations were intentionally carried out without the presence of any other interacting molecules or chains. In general care needs to be taken when comparing gas-phase calculations with experimental data. However, previous studies on PNDIT\(_2\)\(^4\)\(^1\)\(^4\)\(^2\) have already shown that this polymer can give coiled conformations in solution. The planar structure of PNDIFu\(_2\) would allow for a strong tendency to aggregate via stabilized \(\pi−\pi\) and van der Waals interactions. This feature is actually observed and will be discussed in the following paragraphs. A more planar polymer backbone leads to a red-shifted absorption band in the electronic transitions and UV−vis spectra, as computed and observed for PNDIFu\(_2\) with respect to PNDIT\(_2\) (see Figure 3 and Supporting Information). From the analysis of the molecular orbitals involved in the S\(_0\)−S\(_1\) transition, we can deduce that the substitution of bithiophene with bifuran does not alter the character of Table 1. Summary of Physical, Thermal, Optical, Electrical, and Structural Properties of PNDI\(_{X2}\)-R (X = Fu, T; R = C\(_{16}\), C\(_{20}\))

| polymer      | \(M_{\text{SEC}}\) \([\text{kDa}]\) | \(\rho\) | \(T_m\) \([\text{°C}]\) | \(T_c\) \([\text{°C}]\) | \(T_{\text{onset}}\) \([\text{°C}]\) | \(E_{\text{LUMO}}/E_{\text{HOMO}}\) \([\text{eV}]\) | \(E_{\text{HOMO}}\) \([\text{eV}]\) | \(E_{\text{LUMO}}\) \([\text{eV}]\) | \(E_{\text{g,elec}}\) \([\text{eV}]\) | \(E_{\text{g,opt}}\) \([\text{eV}]\) | \(E_{\text{g,opt}}\) \([\text{eV}]\) | \(E_{\text{g,opt}}\) \([\text{eV}]\) | \(\text{π−π}\) distance \([\text{Å}]\) |
|--------------|---------------------------------------|--------|-----------------------------|-----------------------------|-----------------------------|---------------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| PNDIFu2-C\(_{16}\) | 17/2.24                               | n.d.   | n.d.                        | 390                         | -3.77/-5.59                 | 1.82                            | 1.66                         | 1.48                         | 1.46                       | 2.12                       | 10.28                       | 3.94                        |                               |
| PNDIT2-C\(_{16}\) | 18/3.28                               | 341    | 318                         | 445                         | -3.82/-5.67                 | 1.97                            | 1.75                         | 1.46                         | 1.46                       | 2.52                       | 8.08                        | 3.55                        |                               |
| PNDIFu2-C\(_{20}\) | 16/2.38                               | n.d.   | n.d.                        | 390                         | -3.76/-5.79                 | 1.91                            | 1.68                         | 1.49                         | 1.47                       | 2.90                       | 14.50                       | 3.55                        |                               |
| PNDIT2-C\(_{20}\) | 17/2.35                               | 298    | 288                         | 445                         | -3.78/-5.81                 | 2.03                            | 1.75                         | 1.61                         | 1.47                       | 2.52                       | 8.08                        | 3.86                        |                               |

*From size exclusion chromatography (SEC) in chloroform at room temperature. bFrom CV of thin films, average value from three measurements. cFrom the onset of absorption: in CN at room temperature for PNDIT2 and at 170 °C for PNDIFu2. dFrom the onset of absorption in toluene at room temperature. eFrom the onset of absorption in film. fGIWAXS data from PNDIFu2 and PNDITh2 films annealed at 250 and 100 °C, respectively. gCoherence length (CL) for the 100 reflection (face-on orientation).
excited state, prevalently involving the HOMO → LUMO and
the HOMO−1 → LUMO+1 contributions for both PNDIFu2
and PNDIT2. Frontier occupied molecular orbitals (e.g.,
HOMO−1, HOMO) are mainly localized on the donor units
(i.e., bifuran and bithiophene), whereas the unoccupied (e.g.,
LUMO, LUMO+1) are on the acceptor NDI unit (see the
isosurfaces reported in the Supporting Information). Due to the
change in the electron density during the S0–S1 excitation,
as suggested by the analysis of the molecular orbitals, the
first absorption band can be assigned to a charge-transfer excitation
for both polymers, with the transition dipole moment
oscillating along the polymer axis.43

To get insights in the charged electronic state, we computed
the molecular structures for the charged species (here referred
to as polarons) of (NDIFu2)₅ and (NDIT2)₅. In the charged
states (i.e., anion) structural polaron relaxations occur,16
as reported in Figure 1b for (NDIFu2)₅ and (NDIT2)₅. The
structural relaxations are computed as bond length differences
(BLD) between the structures in the charged and in the neutral
state. In (NDIFu2)₅, the polaron is prevalently localized over
a single polymer unit, while in (NDIT2)₅, it is more delocalized,
covering almost two polymer repeat units. A different polaron
extension is also reflected by the polaron spin density, as
reported in Figure 1b for both polymers. As a consequence of a
different polaron extension, the computed electron intra-
molecular reorganization energy (λelectric) is higher for
(NDIFu2)₅ than for (NDIT2)₅, namely, 0.52 and 0.40 eV,
respectively. This is due to the fact that the overall structural
reorganizations (i.e., bond length and bond angle variations)
are occurring over the single unit for the furan-based oligomers,
while over a more extended segment length for PNDIT2.
Although this is not the aim of the current study and more
detailed investigations will be pursued in this direction, a
different polaron extension might lead to a different transport
regime, according to the small polaron and large polaron
descriptions.44,45

In a first and qualitative approximation (i.e., homogeneous
electron reaction transfer and similar electronic coupling
integrals), the calculation of the intramolecular reorganization
energy can suggest a lower electron mobility for PNDIFu2
compared to PNDIT2, despite the more planar ground state
conformation of the former. Regardless of the kind of charge
transport regime (e.g., Marcus, variable-range-hopping, small/
large polaron, coherent/incoherent transport),46 the calculation
of the intramolecular reorganization energy suggests a slower
intrachain electron transfer process for PNDIFu2 compared to
PNDIT2. This conclusion might be correlated with the measured
electron mobility, which is lower for PNDIFu2
than PNDIT2 (see section 2.6); however, more appropriate
multiscale computational investigations should be carried out
before addressing the correct charge transport regime.47,48

2.3. Aggregation in Solution and Optical Properties.

To further investigate aggregation behavior in detail, we
measured temperature-dependent NMR spectroscopy of
PNDIT2 and PNDIFu2 at different temperatures. PNDIT2 is
known to give very narrow signals in tetrachloroethane at 120
°C, suggesting molecularly dissolved chains.14

Figure 2 shows ¹H NMR spectra of PNDIFu2-C16 and
PNDIT2-C16 at different temperatures but at the same
concentration of 10 mg/mL. Marked qualitative differences
are spotted between PNDIFu2-C16 and PNDIT2-C16. At 30
°C both polymers showed broadened signals indicating aggregation.42
While for PNDIT2-C16 the additional signals
arising from aggregation vanished already at T > 75 °C and
narrow signals were observed at 120 °C suggesting molecularly
dissolved chains,14 this effect is much less pronounced for
PNDIFu2-C16. Here, a strong aggregation was observed in
tetrachloroethane even at 120 °C. This hampers signal
assignment; however, the three narrow signals at 9.23, 7.64,
and 7.11 ppm are characteristic of the PNDIFu2 backbone.
Additionally, signals of 2-bromofuran end groups appeared
(Figure 2b). Cooling solutions of PNDIFu2-C16 from 120 °C
reproduced the ¹H NMR spectra, suggesting that the various
signals arise from aggregation and not from temperature-
induced decomposition of PNDIFu2.

Temperature-dependent UV–vis spectroscopy is an effective
method to investigate aggregation in solution. Aggregation
behavior of PNDIT2 was previously investigated by Steyr-
leuthner et al. showing strong aggregation in toluene and
molecularly dissolved chains in 1-chloronaphthalene (CN).14

Figure 3 shows solution absorption spectra of PNDIFu2 and
PNDIT2 in CN and in toluene at room temperature and in
film, which display marked differences between PNDIFu2 and
PNDIT2. In CN (Figure 3a), the low energy absorption charge
transfer (CT) band of PNDIFu2 is red-shifted by 66 nm
compared to PNDIT2, and the intensity ratio between the CT
and the high-energy band is much higher for PNDIFu2 than
PNDIT2. Additionally, PNDIFu2-C20 displays a shoulder in
the lower energy band, while in PNDIFu2-C16 it turns into a
marked absorption band, pointing to strong aggregation even in
CN, a solvent in which PNDIT2-C20 does not aggregate.42
PNDIT2-C16 has an absorption spectrum very similar to
PNDIT2-C20 in CN, with a slightly higher intensity ratio
between the CT and the high-energy band than PNDIT2-C20.
In the preaggregating solvent toluene (Figure 3b, solid line),
However, the absorption bands of PNDIT2 are clearly red-shifted. Moreover, in toluene, the difference between the two different side chains is more obvious for PNDIT2 than for PNDIFu2. Both PNDIFu2 polymers give same onset in toluene as in CN, while the shape of absorption is completely different. Further solvents are also investigated, which show similar behavior as in toluene (Figure S2). In thin films, all four polymers exhibit almost the same absorption onset regardless of heteroatoms and side chains, while the absorption intensity and the shape of the absorption band vary with respect to the type of heteroatom. PNDIT2-C20 is known to have similar absorption features in solid state and in preaggregating solvents. This is found to be also the case for PNDIFu2. Further warming of the films eliminates the red-shifted features that disappeared at 90 °C, while PNDIFu2-C16 again required a much higher temperature of 190 °C to reach a molecularly dissolved state, confirming that aggregation of PNDIFu2 is much stronger than that of PNDIT2. The extracted optical energy gaps \( E_{g,opt} \) from molecularly dissolved, preaggregated solutions and from the film state mirror the absorption changes between PNDIFu2 and PNDIT2 in different conditions, as collected in Table 1. Molecularity dissolved PNDIFu2 has a smaller \( E_{g,opt} \) than PNDIT2, indicating enhanced NDI-Fu intramolecular coupling compared to NDI-T. However, the difference between PNDIFu2 and PNDIT2 in terms of optical absorption onset obtained from preaggregating solutions and in film is reduced, leading to similar energy values. The electrical band gaps (\( E_{\text{el,calc}} \), calculated from cyclic voltammetry, were smaller for PNDIFu2 than PNDIT2, while the shape of oxidation and reduction peaks was similar in all polymers (Figure S3). The Fu2 or T2 comonomer mostly affects the HOMO energy level, with PNDIFu2 having a higher HOMO energy level than PNDIT2 (Table 1).

2.4. Thermal Properties. To study thermal stability, we measured thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1 and Figure S4). From TGA, regardless of the side chain length, PNDIT2 polymers showed a higher thermal stability than PNDIFu2, giving decomposition temperatures at around 445 and 390 °C, respectively. Thus, the degradation temperature of PNDIFu2 is lower but still appreciably high. We found PNDIFu2 to be stable in air when stored as solid film with no degradation being observed within two years. However, in solution, PNDIFu2 is sensitive to light and starts to degrade within 2 weeks (if stored under dry light). Replacing T2 by Fu2 again showed marked differences in the melting (\( T_m \)) and crystallization temperatures (\( T_c \) (Figure S4). PNDIT2 owns clear \( T_m \) and \( T_c \) with distinct differences between two different side chains. Usage of the shorter side chains increases \( T_m \) of PNDIT2-C16 significantly from 298 °C commonly found for PNDIT2-C20 to 341 °C. PNDIFu2 polymers did not show \( T_m \) and \( T_c \) within the temperature range tested, with temperatures higher than 380 °C not being accessible because of potential decomposition. It is likely that the increased aggregation in PNDIFu2 leads to much higher \( T_m \) values that cannot be probed by conventional DSC experiments.

2.5. Thin Film Morphology. To obtain more insights into the structural properties, we investigated all samples by grazing incidence wide-angle X-ray scattering (GIWAXS), giving access to information about molecular packing. Structural changes upon thermal annealing were also examined. Figure 5 represents GIWAXS scattering pattern of as-spun and annealed films with different annealing conditions consistent with later FET preparation temperatures are found in Figures S5 and S6. The vertical integration shows the \( a \)-axis (100) reflections being edge-on and \( \pi-\pi \) stacking directions (010) being face-on oriented.

Horizontal integration represents the evolution of the \( a \)-axis face-on and \( \pi-\pi \) stacking edge-on oriented. As it can be seen from Figure 5, as-spun films (solid lines) of all four polymers showed short-range order with mixed orientations including edge-on, face-on, and random orientations with respect to the substrate, with PNDIT2 films showing more oriented crystallites than PNDIFu2 ones. Thermal treatment was not effective for PNDIFu2 films, while PNDIT2 showed the known transition from face-on to edge-on with increasing temperature, with both C16 and C20 side chains giving comparable effects. Up to five orders of (h00) reflections are observed in the vertical direction when PNDIT2 films are subjected to 300 °C annealing, indicating significant order of edge-on oriented conjugated segments along the \( a \)-axis. However, the effect of furan and side chain length is more predominantly reflected by
the (100) spacing and π–π stacking distance. For both PNDIFu2 and PNDIT2, in agreement with the side chain length, a larger (100) spacing was observed for the larger side chain 2-octyldecyl (C20) compared to C16 chain. Additionally, this side chain effect on the (100) spacing is more predominant for PNDIFu2 than PNDIT2 as listed in Table 1. Clear π–π stacking peaks are also observed for all polymers, with a significantly smaller π–π stacking distance for PNDIFu2 (0.35 nm for C16, and 0.37 nm for C20), compared to PNDIT2 (0.39 nm for C16 and C20). The former is in agreement with the enhanced coplanar structure of PNDIFu2 that if persisting in the solid state can be caused by the smaller torsional angle between NDI and Fu2.

2.6. Charge Transport in Field-Effect Transistors. The charge transport properties of the copolymers were investigated using top-gate bottom-contact (TGBC) field effect transistors (FETs) (Figure 6a). In light of recent observations of charge transport anisotropy in polymeric films simply controlled using directional flow during film deposition (negligibly affecting crystallographic parameters), the thin films were deposited using off-center spin coating, as sketched in Figure 6b. Transport anisotropy can then be evaluated comparing transport properties parallel (Figure 6c, channel configuration A) and perpendicular (Figure 6c, channel configuration B) to the flow of the solution. In order to confidently establish the effect of the two donor moieties on performance, preliminary investigations were carried out aimed at optimizing solution formulation and annealing temperatures independently (Figures S7 and S8). It is worth noting that given the intrinsic anisotropic nature of the thin films processed from preaggregated solutions, probing transport on uniaxially aligned films is more representative than in films with random distributed orientational domains, as obtained by a common, centered spin-coating deposition. In agreement with previous reports on PNDIT2-C20, negligible dependence of FET behavior on annealing temperature was found. Diifferently, FET transport in PNDIFu2 is maximized upon annealing at 250 °C for 30 min, while a drop of field effect mobility is observed by using annealing temperatures $T \geq 300$ °C, which might be related to thermal degradation even though thermal decomposition occurred at 390 °C according to TGA measurements. Concerning solution formulation, both PNDIT2-C20 and PNDIFu2-C20 gave best FET results using toluene (in terms of mobility and transport anisotropy). Diifferently, the best performance for PNDIT2-C16 and PNDIFu2-C16 was obtained using chlorobenzene (CB) and 1,2-dichlorobenzene (o-DCB) solutions, respectively (Figure S8). Typical electron accumulation $n$-type channel behavior is observed in all FETs of this work, each polymer displaying superior source to drain currents ($I_{DS}$) in A channel configuration than in B, as expected in case of flow-directed orientational alignment. In Figure 6 the transfer curves (d)
and the corresponding extracted mobility values ($\mu$), obtained after a thorough process optimization, are reported and compared. It can be observed that for equal side chains PNDIFu2 displays a stronger anisotropy than PNDIT2 (molecular alignment investigation carried out through polarized UV–vis measurements is also reported in Figure S9).

This is in agreement with PNDIFu2 showing superior aggregation in solution, which seeds the long-range directional alignment in flow aligned films.19,51 $I_{DS,A}/I_{DS,B}$ values ($V_{GS} = 60$ V) of 8.7 and 18.3 were extracted for PNDIFu2-C16 and PNDIFu2-C20, respectively, and 2.69 and 4.9 for PNDIT2-C16 and PNDIT2-C20, respectively. It is noteworthy that C20 side chains result in stronger transport anisotropy both for PNDIFu2 and PNDIT2, potentially due to a stronger nematic liquid-crystalline character of the lyotropic solutions induced using bulkier side chains.54 In terms of absolute electron mobilities, the best PNDIT2 FETs displayed an approximately three times higher mobility than the best PNDIFu2 devices: we extracted similar $\mu_{sat,max}$ of 0.6 and 0.7 cm$^2/(V \cdot s)$ for PNDIT2-C20 and PNDIT2-C16, and $\mu_{sat,max}$ = 0.21 and 0.1 cm$^2/(V \cdot s)$ for PNDFu2-C20 and PNDIFu2-C16, respectively.

As a result of the strong aggregation of PNDIFu2 in solution, directional alignment of films, driven by the orientation of fibrillar domains under flow-induced shear fields, can be readily achieved during the fast off-center spin-coating deposition, in analogy with the thiophene based analogous PNDIT2.51 Figure 7 shows AFM height (a,c) and phase (b,d) images of PNDIT2-C20 (a,b) and PNDIFu2-C20 (c,d) films made from toluene followed by optimal thermal annealing processes (120 and 250 °C, respectively). Both films exhibit typical fibrillar-like morphologies with elongated domains mostly aligned along the flow direction as indicated by the red arrows. The small roughness of PNDIT2-C20 ($R_{rms} = 0.4$ nm) allows to distinguish fibrillar domains within the topography of the films (Figure 7a). A larger $R_{rms}$ of 1.1 nm is measured on PNDIFu2-C20, mostly hiding fibrillar microstructure in the height image (Figure 7c), but clearly visible in the phase image (Figure 7d). Moreover, the superior aggregation of PNDIFu2 in solution, eventually induced by its more planar backbone, leads to stronger transport anisotropy of the resulting films.

Whether this is caused by larger aggregates or a larger amount of aggregates poses an unsolved yet interesting question, which opens up possibilities for enhanced alignment of conjugated backbones in thin films. Regardless of this, our observations on PNDIFu2 films further confirm that alignment efficiency under shear fields depends on an intermediate step during the deposition, where preformed aggregates in solution form the seed for the film growth.19,51

Despite the enhanced alignment of PNDIFu2 chains in films, electron transport of PNDIFu2 is good but lower by a factor of ~3 compared to the extensively studied PNDIT2. This may appear surprising since the combination of a more effective alignment and a more planarized backbone of PNDIFu2 are typically correlated with improved intrachain transport properties.9,11 Moreover, the closer $\pi–\pi$ stacking distance observed in the ordered phase of PNDIFu2, which is also characterized by a higher coherence length in the (100) direction, should improve charge carrier mobility through enhanced interchain charge hopping if the interchain step was the bottleneck.

Apparently, these potentially beneficial parameters are counterbalanced by electronic effects induced by furan. In PNDIFu2, the polaron mainly relaxes over a single NDI unit, resulting in a higher electron reorganization energy with respect to PNDIT2, where polaron relaxation occurs at least over two
repeat units. We speculate that the more electron-rich sulfur, having d-electrons, is at the origin of this behavior. The different polaron extension should lead to a higher energetic barrier for charge transfer in PNDIFu2 films, both at the interchain level, frustrating the effect of a closer π−π stacking, and at the intrachain level, therefore limiting the benefit of structural alignment. While further studies are required to fully explain the transport differences between the two copolymers on more quantitative basis, our findings show that higher backbone planarity coupled with smaller π−π stacking distances does not lead to improved transport properties per se. In this context, it appears interesting to investigate PNDISe2, which is the known analogous material with biselenophene as comonomer.37

3. CONCLUSION
Conjugated copolymers made of alternating naphthalene diimide and bifuran units PNDIFu2 can be synthesized using Ni(dppp)Cl2 catalyzed polymerization of radical anions. The effects of incorporating the bifuran unit into the copolymer backbone was thoroughly investigated for the two different side chains 2-hexyldecyl (C16) and 2-octyldodecyl (C20), and compared to the well-known analogue PNDIT2. PNDIFu2 showed a much more coplanar backbone due to reduced steric hindrance between the imide oxygen and the furan ring compared to thiophene. The oscillator strength of the low energy absorption band of PNDIFu2 is also enhanced...
compared to PNDIT2, making PNDIFu2 an interesting electron transporting material for usage also in all polymer solar cells with complementary absorbing donor polymers. The backbone planarization of PNDIFu2 can explain the observed stronger aggregation in solution with respect to PNDIT2, which eases directional alignment of polymer chains within aggregates using off-center spin-coating. As a consequence, optimized PNDIFu2 films show a markedly stronger transport anisotropy when tested in FETs, achieving a ratio of 18.3 for PNDIFu2-C20 for backbones aligned perpendicular and parallel to the electrodes. Overall, optimized FETs made from PNDIFu2 show a maximum electron field-effect mobility of 0.21 cm²/(V s), which is approximately three-times lower compared to the mobility of PNDIT2 under the same conditions. Thus, the greater backbone planarity, closer π−π stacking distance, and stronger aggregation leading to enhanced anisotropy for PNDIFu2 do not result in superior charge transport properties compared to PNDIT2. A possible molecular-based reason for this unexpected behavior is a higher intramolecular reorganization energy of PNDIFu2 than in PNDIT2 owing to an enhanced polaron localization, which counterbalances the otherwise beneficial properties of PNDIFu2. This scenario offers clear directions for further improvement of charge transport in specifically designed and orientationally aligned donor–acceptor copolymers, in which, besides a planar ground state conformation, delocalization of charge excited states is required to benefit from uniaxial alignment thanks to improved intrachain transport.

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■ ASSOCIATED CONTENT

 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-

Synthesis procedures, general information, additional UV–vis spectroscopy, polarized UV–vis spectroscopy, cyclic voltammetry, thermal analysis, additional GIWAXS data, additional electrical characterization, additional AFM images, and additional DFT calculations (PDF)

■ AUTHOR INFORMATION
Corresponding Authors
*E-mail: michael.sommer@chemie.uni-chemnitz.de.
*E-mail: mario.caironi@iit.it.

ORCID
Ulrich Steiner: 0000-0001-5936-339X
Mario Caironi: 0000-0002-0442-4439
Michael Sommer: 0000-0002-2377-5998

Present Address
Technische Universität Chemnitz, Polymerchemie, Straße der Nationen 62, 09111 Chemnitz, Germany.

Notes
The authors declare no competing financial interest.

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