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C−H Arylation of Unsubstituted Furan and Thiophene with Acceptor Bromides: Access to Donor−Acceptor−Donor-Type Building Blocks for Organic Electronics

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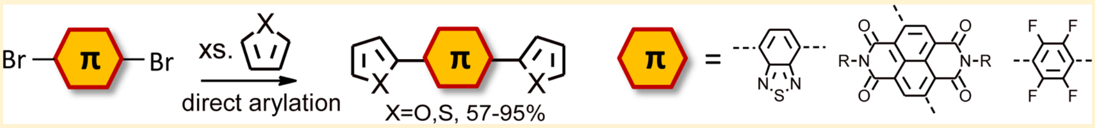

ABSTRACT: Pd-catalyzed direct arylation (DA) reaction conditions have been established for unsubstituted furan (Fu) and thiophene (Th) with three popular acceptor building blocks to be used in materials for organic electronics, namely 4,7-dibromo-2,1,3-benzothiadiazole ($BTBr_2$), N,N′-dialkylated 2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) ($NDIBr_2$), and 1,4-dibromotetrafluorobenzene (F_4Br_2). Reactions with $BTBr_2$, F_4Br_2, and $NDIBr_2$ require different solvents to obtain high yields. The use of dimethylacetamide (DMAc) is essential for the successful coupling of $BTBr_2$ and F_4Br_2, but detrimental for $NDIBr_2$, as the electron-deficient NDI core is prone to nucleophilic core substitution in DMAc as solvent but not in toluene. $NDIFu_2$ is much more planar compared to $NDITh_2$, resulting in an enhanced charge-transfer character, which makes it an interesting building block for conjugated systems designed for organic electronics. This study highlights direct arylation as a simple and inexpensive method to construct a series of important donor−acceptor−donor building blocks to be further used for the preparation of a variety of conjugated materials.

INTRODUCTION

Conjugated materials with a donor−acceptor−donor (D−A−D) structure are important electroactive and photoactive building blocks for applications in biochemical fluorescent technology,[1,2] nonlinear optics,[3] organic light emitting diodes (OLEDs),[4,5] organic field-effect transistors (OFETs),[6] and photovoltaic cells.[7] Alternating electron-rich and -poor moieties are very often incorporated into so-called “push−pull systems” via Suzuki or Stille cross couplings involving organometallic derivatives of the donor unit.[8,9] Although most frequently employed organometallic derivatives of donor units are commercially available or relatively easy to prepare, they are expensive as they require cryogenic or catalytic conditions and are additionally highly toxic in the case of organotin compounds.[10] Consequently, the development of alternative coupling methodologies is needed, given the importance of push−pull systems in organic optoelectronic materials and the drawbacks of especially Stille cross couplings. The concept of using the C−H bond of a hetereoarene as a functional group through transition-metal-catalyzed direct arylation (DA) has generated tremendous interest among synthetic chemists.[11−16] C−H activation has been applied to thiophene (Th)[17−29]and furan (Fu),[30−36] to name some examples, but the rigorous application to straightforward and simple syntheses of organic electronic materials is still in its infancy.[16,37−41] In many cases, a certain C−H bond of five-membered heterocycles is selectively addressed by the use of blocking or directing groups. However, for conjugated polymer synthesis, general design principles rely on the use of mostly unsubstituted building blocks to prepare π-conjugated backbones with small dihedral angles.[7] Therefore, the use of cheap pristine Th and Fu for the preparation of D−A−D building blocks, which can be further used as monomers in direct arylation polycondensation,[38−41] constitutes a major step toward cheap, simple, and nontoxic syntheses of conjugated materials.

Herein, we report simple direct arylation schemes of unsubstituted Fu and Th with alkylated 2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) ($NDIBr_2$), 4,7-dibromo-2,1,3-benzothiadiazole ($BTBr_2$), and 1,4-dibromotetrafluorobenzene (F_4Br_2) to give six different D−A−D building blocks in isolated yields up to 95% (Schemes 1−4). NDI and BT are among the most interesting and widely studied electron-deficient building blocks for small band gap conjugated

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Table 1. Optimization of Reaction Parameters for D−A−D Synthesis Starting from $BTBr_2$, $NDIBr_2$, or F_4Br_2 and Furan (Fu) or Thiophene (Th)

entry	reaction system	ratio A:D	catalyst (mol %)	base	additive	solvent	time (h)	T (°C)	yield[a] (%)
1	BT/Fu	1:15	$Pd(OAc)_2$/5	PivOK		DMAc	60	60	35
2	BT/Fu	1:15	$Pd(OAc)_2$/5	K_2CO_3	PivOH	DMAc	60	60	35
3	BT/Fu	1:15	$Pd(OAc)_2$/5	K_2CO_3	PivOH	DMAc/Tol 1:1	60	60	42
4	BT/Fu	1:15	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	DMAc/Tol 1:1	46	70	75
5	BT/Fu	1:15	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	toluene	60	60	0
6	BT/Fu	1:15	$Pd(OAc)_2$/5	K_2CO_3	PivOH	toluene	60	90	0
7	BT/Th	1:15	$Pd(OAc)_2$/5	PivOK		DMAc	47	70	72
8	BT/Th	1:20	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	DMAc	88	80	71
9	BT/Th	1:20	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	DMAc/Tol 1:1	90	70	42
10	BT/Th	1:20	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	toluene	88	70	0
11	NDI/Fu	1:20	$Pd(OAc)_2$/5	PivOK		DMAc	30	70	81[b]
12	NDI		$Pd_2(dba)_3$/5	PivOK		DMAc	30	70	60[b]
13	NDI			PivOK		DMAc	30	70	62[b]
14	NDI			AcOK		DMAc	30	70	10[b]
15	NDI			K_2CO_3		DMAc	30	70	12[b]
16	NDI			K_2CO_3	PivOH	DMAc	30	70	12[b]
17	NDI/Fu	1:15	$Pd(OAc)_2$/5	PivOK		toluene	30	70	10
18	NDI/Fu	1:15	$Pd_2(dba)_3$/2	PivOK		toluene	30	70	23
19	NDI/Fu	1:15	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	toluene	30	70	90
20	NDI/Fu	1:20	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	toluene	30	70	95
21	NDI/Fu	1:15	$Pd_2(dba)_3$/3	K_2CO_3	PivOH	toluene	30	70	72
22	NDI/Fu	1:15	$Pd_2(dba)_3$/2	K_2CO_3	PivOH	toluene	30	70	62
23	NDI/Fu	1:15	$Pd_2(dba)_3$/1	K_2CO_3	PivOH	toluene	30	70	45
24	NDI/Th	1:10	$Pd(OAc)_2$/5	PivOK		DMAc	30	70	0
25	NDI/Th	1:15	$Pd_2(dba)_3$/5	K_2CO_3	PivOH	toluene	30	70	80
26	F_4/Th	1:15	$Pd_2(dba)_3$/2.5	PivOK		toluene	30	70	0
27	F_4/Th	1:15	$Pd(OAc)_2$/5	PivOK		DMAc	72	80	58
28	F_4/Th	1:15	$Pd(OAc)_2$/5	PivOK		DMAc/Tol 1:1	80	80	52
30	F_4/Th	1:15	$Pd(OAc)_2$/5	Cs_2CO_3	PivOH	DMAc	72	70	24
31	F_4/Th	1:15	$Pd(OAc)_2$/5	Cs_2CO_3	PivOH	DMAc	72	80	31
32	F_4/Th	1:20	$Pd(OAc)_2$/5	PivOK		DMAc	97	80	43
33	F_4/Th	1:20	$Pd(OAc)_2$/5	PivOK		DMAc	97	80	52[c]
34	F_4/Fu	1:15	$Pd(OAc)_2$/5	PivOK		DMAc	72	70	45
35	F_4/Fu	1:20	$Pd(OAc)_2$/5	PivOK		DMAc	97	75	53
36	F_4/Fu	1:20	$Pd(OAc)_2$/5	PivOK		DMAc	97	75	57[c]

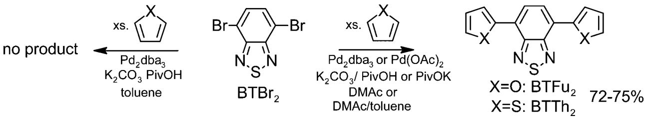
[a] Isolated yields after recrystallization or column chromatography. [b] Yields of side products HONDIFu and HONDIBr, respectively. [c] Another addition of the same portion of catalyst after 2 d.

copolymers as active materials in organic electronics.[7,42] Moreover, the F_4 unit is an interesting building block for conjugated polymers with enhanced planarity due to additional noncovalent S−F interactions.[43−45] $BTTh_2$,[46] $NDITh_2$,[47,48] F_4Th_2,[49] $BTFu_2$,[50] and $NDIFu_2$[51] are known and usually made by Stille coupling with yields between 60 and 80%. For F_4Th_2, a transition-metal-free route is additionally known to give similar yields compared to Stille coupling.[43] The herein presented protocols entail a major simplification, reduction in costs, and environmental friendliness for all compounds compared to the commonly used reagents for Stille-based cross couplings. The optical and structural properties of the most interesting building block $NDIFu_2$ are compared to its thiophene analogue, confirming a much higher planarity as a result of reduced steric hindrance, which results from the structural geometry of the NDI skeleton.

■ RESULTS AND DISCUSSION

During our investigations on the synthesis of copolymers via direct arylation polycondensation,[51,52] we established direct arylation conditions for the preparation of D−A−D-type monomers as well. A starting point was the reaction of pristine Fu with $BTBr_2$ using a simple procedure with $Pd(OAc)_2$ and potassium pivalate (PivOK) in pure DMAc, furnishing a low yield of 35% (Table 1, entry 1, Scheme 1). Exchanging PivOK with pivalic acid (PivOH) and potassium carbonate did not further increase the yield (entry 2); however, the use of DMAc/toluene gave 42% of $BTFu_2$ (entry 3). Maintaining the solvent mixture and exchanging $Pd(OAc)_2$ by Pd_2dba_3 further increased the isolated yield of $BTFu_2$ to a satisfying 75% (entry 4). Interestingly, when toluene was used as pure solvent, in the reactions with both $Pd(OAc)_2$ or Pd_2dba_3 $BTFu_2$ could not be detected (entries 5 and 6). The reason for this behavior

Scheme 1. Direct Arylation of Unsubstituted Furan and Thiophene with $BTBr_2$ (Entries 1−10)

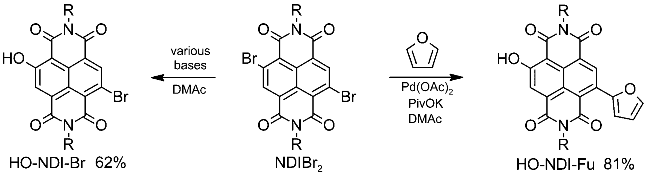


is not entirely clear, but it may be speculated that DMAc acts as a ligand[53] and is therefore needed to catalyze the reaction efficiently. However, this explanation alone is not sufficient, as a substrate dependence is also likely. As will be described below, the conditions of entry 5, which did not furnish $BTFu_2$, are in fact the most efficient ones for the DA of $NDIBr_2$ and Fu.

The reaction of Th and $BTBr_2$ was approached similarly. The conditions in analogy of entry 1 gave 72% isolated yield (entry 7). The replacement of catalyst and base could not increase this result (entry 8), and when toluene was added as cosolvent the yield decreased to 42% (entry 9). Toluene as pure solvent did not furnish $BTTh_2$; instead, Pd black precipitated from the mixture. The obtained yields of the reactions of $BTBr_2$ with Fu and Th are comparable to those obtained by conventional Stille couplings[46,50] and additionally benefit from the cheap and environmentally more friendly Fu and Th.

Having optimized the DA conditions leading to good yields of $BTFu_2$ and $BTTh_2$, we focused our attention to $NDIFu_2$. Our interest in $NDIFu_2$ is based on smaller dihedral angles compared to $NDITh_2$[51,54,55] as a result of reduced steric hindrance between the C−H bond of furan and the imide oxygen of the NDI core. However, the use of the optimized reaction conditions for the synthesis of $BTFu_2$ or $BTTh_2$ (entries 4 and 7) could not be successfully transferred to $NDIFu_2$ (entry 11). Instead, hydroxylated NDI derivatives were obtained as major products (Scheme 2).

Scheme 2. Base-Induced Hydroxylation of $NDIBr_2$ Resulting from Nucleophilic Core Substitution as a Side Reaction in DMAc[a]

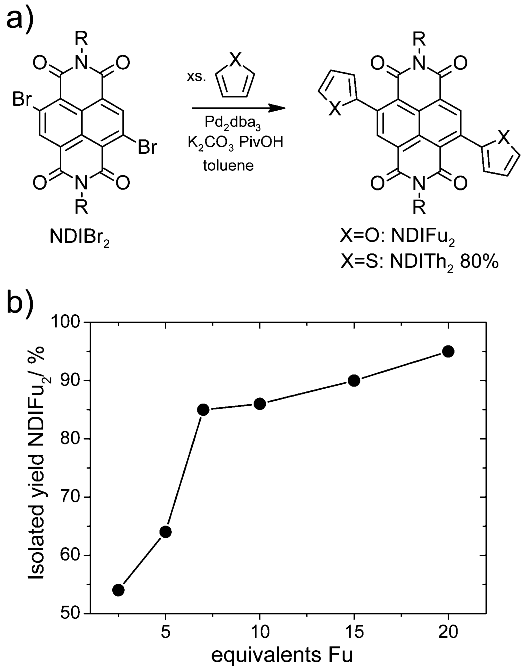


[a]Left: reaction in DMAc in the absence of furan; see entries 12−16, R = 2-hexyldecyl. Right: reaction in DMAc in the presence of furan; see entry 11, R = 2-octyldodecyl.

Identification of these compounds was convenient as the hydroxyl group shows up as a sharp singlet at 12.9 ppm in the ^1H NMR spectrum as a result of intramolecular H-bonding to the neighboring imide oxygen (see Supporting Information). The side product HO-NDI-Fu formed with 81% yield in pure DMAc as solvent (entry 11). The same reaction was conducted in the absence of furan (entries 12−16), where HO-NDI-Br was obtained as the main product, suggesting the base as the origin of hydroxylation. Upon screening different bases, PivOK was found to be most effective in installing the OH group at the NDI core (entries 13−16) and K_2CO_3 in combination with PivOH caused the smallest amount of HO-NDI-Br. However, none of the bases could eliminate the side reaction entirely. One possibility is that the OH group is installed by a nucleophilic substitution reaction with OH^- resulting from the base and water impurities,[56] which is possible here as the NDI core is strongly electron-deficient. Alternatively or additionally, nucleophilic attack of pivalate might generate an NDI-pivalic acid ester derivative, which in turn could transform into NDI−OH. A related nucleophilic side reaction occurs during the synthesis of $NDIBr_2$ where partial core amination takes place.[57]

A recently reported procedure with $NDIBr_2$ and 3,4-ethylenedioxythiophene, $Pd(OAc)_2$, K_2CO_3, and PivOH in DMAc at 80 °C gave 51% $NDIEDOT_2$.[58] However, this protocol was unsuccessful in our hands with both Fu or Th, which might be a result of the different times used and potentially also of the different reactivity of EDOT in comparison to Fu or Th. As nucleophilic substitution reactions are usually performed in polar solvents, we exchanged DMAc by toluene, even though the use of pure toluene as solvent did not lead to success in the DA of Fu/Th with $BTBr_2$. Surprisingly, $NDIFu_2$ was detected in varying yields between 10 and 95% as a function of catalyst precursor, base, and Fu equivalents (entries 17−20, Scheme 3a), and hydroxylated products were no longer observed. Reducing the relatively large amount of 5 mol % of Pd_2dba_3 to 1 mol % also reduced the yield strongly (entries 21−23). At this point, it is interesting to investigate to what extent the equivalents of furan can be reduced while maintaining a high yield of $NDIFu_2$. Although furan is very cheap compared to 2-(tributylstannyl)furan used in conventional Stille couplings, minimizing the equivalents of Fu is desirable from an atom-economical point of view. Using 2.5 equiv of Fu only, a respectable yield of 54% could be isolated under the reaction conditions of entry 20, and in order to obtain yields above 80% at least 7−10 equiv of Fu need to be used (Scheme 3b).

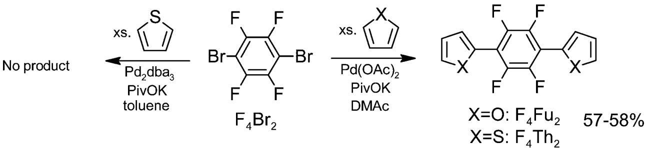
Scheme 3. (a) Direct Arylation of Unsubstituted Furan and Thiophene with $NDIBr_2$ in Toluene (Entries 17−25, R = 2-Hexyldecyl for $NDIFu_2$ and 2-Octyldodecyl for $NDITh_2$). (b) Isolated Yield of $NDIFu_2$ versus the Equivalents of Furan Used



This dependence can be used to estimate economic suitability of the presented DA protocol in comparison to Stille or Suzuki couplings, which is given for Fu and Th but not for, e.g., selenophene. The fact that DMAc is not needed to obtain high yields of $NDIFu_2$ is promising, as other solvents greener than toluene might work as well.[59,60] While this study has focused on the synthesis of symmetric D−A−D building blocks, the preparation of asymmetric ones[37d] is possible as well due to the long reaction times. Monosubstituted products are observed by TLC control during all reactions reported, and due to the low boiling points of Fu and Th all reactions can easily be trapped at the stage of monosubstitution. While DMAc was also found to be a detrimental solvent for the analogous reaction between $NDIBr_2$ and Th (entry 24), the optimized conditions of entry 19 could be transferred successfully, furnishing $NDITh_2$ in 80% yield (entry 25). The suppression of NDI hydroxylation in toluene as nonpolar solvent entails a promising possibility for polycondensation reactions of $NDIBr_2$, where such critical side reactions need to be avoided to maintain stoichiometry and end group fidelity. Our study also shines light on solvent effects that have been observed by other groups as well.[37d]

The case of F_4Br_2 is similar to that of $BTBr_2$ (Scheme 4). Using toluene as pure solvent did not furnish detectable amounts of product (entry 26). Again, DMAc is needed to obtain yields of 57−58% (entries 27−36) with some monosubstituted products still being visible even after long reaction times of up to 5 days. The slow reactions open up the possibility of preparing asymmetric D−A−D structures by controlling the equivalents of Th and Fu and the subsequent addition of a second C−H substrate. Further changes of reaction parameters (base, temperature, time, or equivalents of Fu/Th) (entries 30 and 31) did not help to improve the reaction yield much. In a consistent experiment with the additional addition of another portion of 5 mol % of $Pd(OAc)_2$ after 48 h, the yields slightly increased by ∼5−10% (entries 32, 33, 35, and 36). Taken together, the reduced yields of F_4Th_2 and F_4Fu_2 are caused by the formation of monosubstituted products and oligomers, and by a possible degradation of the catalytic system. While these values still require further optimization, they are similar to those obtained from alternative methods.[43,49,50] However, in combination with the general advantages of DA, the herein presented protocols toward F_4Th_2 and F_4Fu_2 are certainly competitive with conventional techniques and could additionally be improved toward higher yields by using catalytic systems with higher activities.

Scheme 4. Direct Arylation of Unsubstituted Furan and Thiophene with F_4Br_2 (Entries 26−36)



Next, the optical properties and structural differences of $NDIFu_2$ and $NDITh_2$ were investigated. The UV−vis spectra of $NDITh_2$ and $NDIFu_2$ in $CHCl_3$ solution are shown in Figure 1a. Both compounds show absorption bands typical for $\pi-\pi^*$ transitions of the NDI core between 350 and 400 nm and a $\pi-\pi^*$ charge transfer (CT) band between 400 and 600 nm. Interestingly, the CT band of $NDIFu_2$ is more intense and red-shifted in comparison to $NDITh_2$, and a possible explanation can be found in the different torsion angles between NDI and Fu/Th. A similar trend has been observed in porphyrin copolymers with either furan or thiophene, in which the furan copolymer allowed for enhanced planarization due to smaller steric repulsion.[61] If planarity is not influenced upon replacing sulfur by oxygen, the usual influence on the optical properties is a blue shift.[62] Hence, we can assign the red-shifted and more intense CT band of $NDIFu_2$ to the enhanced planarity compared to $NDITh_2$ enabled by reduced steric repulsion of the smaller furan.

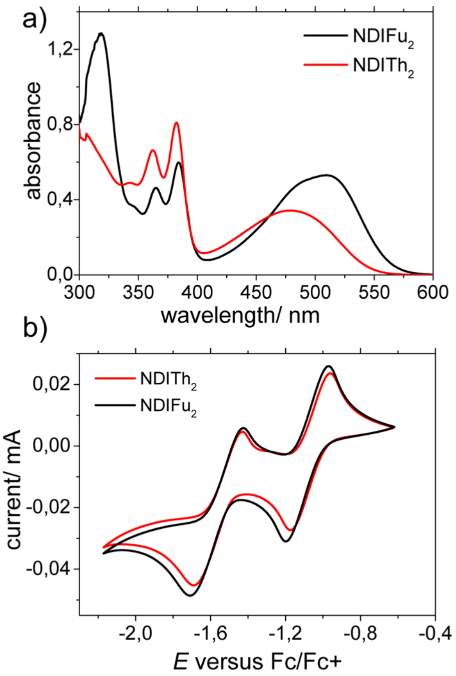
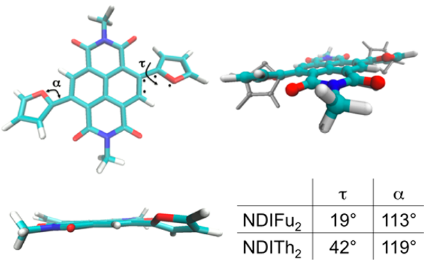


Figure 1. (a) UV−vis spectra of $NDIFu_2$ (black) and $NDITh_2$ (red) in $CHCl_3$ (c = 0.02 mg/mL) and (b) cyclic voltammograms in 0.1 M $TBAPF_6$ dichloromethane.

Further support into this dependence is given by density functional theory (DFT). Literature data of PNDIT2 copolymers show the NDI/Th dihedral angle to be 42° as a result of steric hindrance between the imide oxygen and the proton of the thiophene ring.[54,55] Because of the shorter carbon−oxygen bond of furan, $NDIFu_2$ should exhibit a reduced dihedral angle. DFT calculations (B3LYP/6-31G**) were used to investigate the molecular and electronic structure of $NDIFu_2$, highlighting the differences with respect to $NDITh_2$ (the long alkyl chains were replaced by methyl groups). Figure 2 reports the optimized structure of $NDIFu_2$ and the main geometrical parameters considered, e.g., the valence angle α (α = X−C−C, X = O, S) and the dihedral angle τ (τ = X−C−C−C). Notably, τ is 19° for $NDIFu_2$ vs 42° for $NDITh_2$, indicating a much more planar structure for the furan-based molecule as a



	τ	α
$NDIFu_2$	19°	113°
$NDITh_2$	42°	119°

Figure 2. Left: B3LYP/6-31G**-optimized structure (top and side views) of $NDIFu_2$. Top right: superposition between $NDIFu_2$ and $NDITh_2$ (gray scale) optimized structures. Bottom right: dihedral (τ) and valence (α) angles for $NDIFu_2$ and $NDITh_2$.

result of the reduced steric hindrance in $NDIFu_2$ compared to $NDITh_2$.

The electronic interaction between NDI and furan is thus enhanced compared to NDI and thiophene. The topology of the frontier molecular orbitals (HOMO and LUMO, Figure 3) is similar for both species, and the orbital energies are slightly different, leading to a HOMO−LUMO gap of 2.61 eV for $NDIFu_2$ and 2.66 eV for $NDITh_2$ (Table 2). The reduced energy gap of the furan based species explains the red-shifted low energy band in the UV−vis spectrum. From the UV−vis spectra, optical gaps of 2.20 and 2.26 eV are extracted for $NDIFu_2$ and $NDITh_2$, respectively, reflecting the same general trend of the energy gap. Although close in value, the LUMO energies predicted by DFT are not paralleled by the CV data showing almost the same value of 3.72 eV (Table 2). However, the most significant difference between $NDIFu_2$ and $NDITh_2$ is found in the intramolecular electronic coupling t between Fu/Th and NDI, which is computed as half the energy splitting between HOMO and HOMO−1.[63,64] t is 0.328 eV for $NDIFu_2$ and 0.211 eV for $NDITh_2$ and thus larger for the furan-based species, leading, in principle, to superior charge transport properties in $NDIFu_2$-based materials compared to $NDITh_2$ (Table 2). The lower torsional and valence angles for $NDIFu_2$ are ultimately relevant in determining the intra- and intermolecular structure of polymer chains based on this D−A−D unit. Supramolecular organization in the solid state, $\pi-\pi$ stacking, and charge and exciton mobility are indeed beneficially affected by planar and ordered polymer structures.[65] We have recently found that the incorporation of $NDIFu_2$ into conjugated polymers with F_4 ($PNDITh_2F_4$) via direct arylation polycondensation leads to a drastically reduced $\pi-\pi$ stacking distance compared to the $NDITh_2$ analogue $PNDITh_2F_4$, while electron transport was enhanced for the latter.[51] Whether these structure function relationships are general features in a variety of other copolymers and materials is the subject of ongoing investigations. Here, the effect of furan or thiophene on the intra- and intermolecular contributions to charge transport will be especially interesting to investigate.

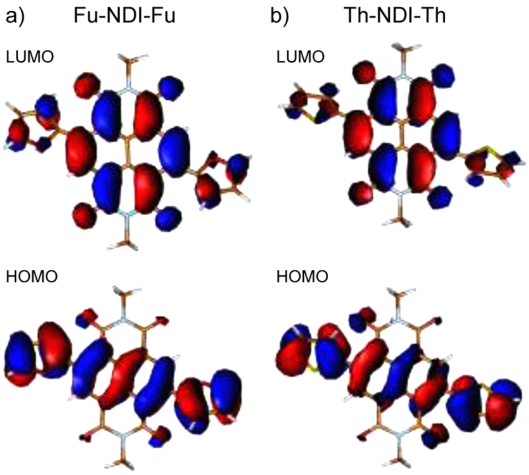


Figure 3. Topologies of the frontier molecular orbitals of (a) $NDIFu_2$ and (b) $NDITh_2$ obtained from DFT calculations at the B3LYP/6-31G** level. The N-substituent is a methyl group in all cases.

In conclusion, we have established simple direct arylation protocols for the reactions between unsubstituted thiophene or furan with popular acceptor bromide building blocks for the synthesis of conjugated materials. Our findings provide a base on which D−A−D-type conjugated building blocks can be obtained from inexpensive starting materials to be used in any optical or electronic application or to be further functionalized or copolymerized in direct arylation polycondensations. Given the large differences in price with respect to the tributylstannylated compounds needed for Stille reactions (Th is cheaper by a factor of ~50 and Fu by a factor of ~150) combined with environmentally more benign Fu and Th, the herein developed DA protocols clearly rival classical methods and may be further extended toward more diverse and complex conjugated architectures. Linking the NDI skeleton to furan leads to enhanced planarity and electronic coupling, which is rather unusual among known NDI-based motifs.

■ EXPERIMENTAL SECTION

General Experimental Methods. Alkylated 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis(2-octyldodecyl)diimide ($NDIBr_2$) was prepared according to a previously reported method.[48] Dichloromethane (DCM) was dried over calcium hydride under argon and distilled before use. All other chemicals and solvents were purchased from commercial suppliers and were used as received. Purification of the products was done by column chromatography using silica gel (230−400 mesh). Analytical TLC was performed on silica gel G/GF 254 plates. NMR spectra were recorded at 300, 282, and 75 MHz (^1H, ^{19}F, and ^{13}C) with ^1H broadband decoupling for ^{13}C and ^{19}F. $CDCl_3$ was used as solvent and internal standard ($\delta(^1H)$ = 7.26 ppm; δ (^{13}C) = 77.0 ppm). Signal assignments are based on the evaluation of correlations in $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, and $^1H-^{13}C$ HMBC spectra. 2D NMR spectra were recorded using standard pulse programs of the TOPSPIN 2.1 software package. High-resolution mass spectrometry was performed using an orbitrap analyzer (electrospray ionization, spray voltage: 3−5 kV). For cyclic voltammetry measurements, a standard commercial electrochemical analyzer with a three-electrode single-compartment cell was used with a Ag/AgCl electrode, a Pt disc, and a Pt wire as reference, working, and auxiliary electrode, respectively. Measurements were carried out in dichloromethane at a concentration of $<10^{-2}$ M with $TBAPF_6$ as supporting electrolyte and ferrocene as internal standard.

General Method for the Synthesis of $BTFu_2$ or $BTTh_2$. Under an N_2 atmosphere, a mixture of $BTBr_2$ (100 mg, 0.34 mmol) and PivOK (143.02 mg, 1.02 mmol) was dissolved in 3.4 mL of a degassed mixture of DMAc and toluene (1:1) (or 3.4 mL of degassed pure DMAc in the case of $BTTh_2$) in a high-pressure vial. Then the desired equivalent of degassed furan or thiophene was added, followed by the addition of catalyst (Pd_2dba_3, 7.79 mg, 2.5 mol %, or $Pd(OAc)_2$, 3.82 mg, 5 mol %). The high pressure vial was placed into a preheated oil bath and stirred for the desired time. After the mixture was cooled to room temperature, the solvent was evaporated under high vacuum and the crude product was dissolved in THF and filtered. It was further

Table 2. HOMO/LUMO Energies and Electronic Coupling Values (t) from DFT (B3LYP/6-31G), Optical Band Gaps, and Cyclic Voltammetry Data of $NDIFu_2$ and $NDITh_2$**

	HOMO (DFT) (eV)	LUMO (DFT) (eV)	energy gap (DFT) (eV)	electronic coupling t (eV)	optical gap (solution UV−vis) (eV)	LUMO (CV) (eV)
$NDIFu_2$	−5.79	−3.18	2.61	0.328	2.20	−3.72
$NDITh_2$	−5.98	−3.32	2.66	0.211	2.26	−3.73

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purified by column chromatography (dichloromethane/isohexane = 1:2) to obtain the products as orange crystalline solids.

4,7-Bis(2-furanyl)-2,1,3-benzothiadiazole (BTFu$_2$) (68.5 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.01 (s, 2H, H_6), 7.67 (dd, ^3J = 3.4, ^4J = 0.7, 2H, H_3), 7.58 (dd, ^3J = 1.8, ^4J = 0.7, 2H, H_1), 6.62 (dd, ^3J = 1.8, ^3J = 3.4, 2H, H_2). ^{13}C NMR (75 MHz, $CDCl_3$): 151.3 (C_7), 150.1 (C_4), 142.8 (C_1), 123.5 (C_6), 121.8 (C_5), 112.4 and 112.1 (C_2, C_3).

4,7-Bis(2-thienyl) 2,1,3-benzothiadiazole (BTTh$_2$) (73.6 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.17 (dd, ^3J = 3.7, ^4J = 1.1, 2H, H_3), 7.89 (s, 2H, H_6), 7.46 (dd, ^3J = 5.1, ^4J = 1.1, 2H, H_1), 7.22 (dd, ^3J = 3.7, ^3J = 5.1, 2H, H_2).

General Method for the Synthesis of HO-NDI-Fu and HO-NDI-Br. Under an N_2 atmosphere, a mixture of $NDIBr_2$ (100 mg, 0.115 mmol, for R= 2-hexyldecyl) and PivOK (50.48 mg, 0.36 mmol) was dissolved in 2 mL of degassed DMAc in a high-pressure vial, and then the desired equivalent of degassed furan was added, followed by the addition of $Pd(OAc)_2$ (3.82 mg, 5 mol %). The vial was placed in a preheated oil bath and stirred for 30 h. After the mixture was cooled to room temperature, the solvent was removed by evaporation and the residue was purified by flash chromatography (dichloromethane/isohexane = 1.3:1) to afford the product as red solid. HO-NDI-Br is obtained as a yellow-orange solid in the same way except that furan and the catalyst are omitted. For R = 2-octyldodecyl, 100 mg (0.101 mmol) of $NDIBr_2$ was used, and the other reagents were adjusted accordingly.

2-Hydroxy-6-(2-furanyl)naphthalene-1,4,5,8-tetracarboxylic-N,N′-bis(2-octyldodecyl)diimide (HO-NDI-Fu) (74 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): 12.86 (s, 1H, OH), 8.89 (s, 1H, H_7), 8.29 (s, 1H, H_3), 7.62 (d, ^3J = 1.7 Hz, 1H, H_{18}), 7.10 (d, J = 3.3 Hz, 1H, H_{16}), 6.63 (dd, ^3J = 1.7 Hz, ^3J = 3.3 Hz, 1H, H_{17}), 4.12 (d, ^3J = 7.2 Hz, 2H, $H_{aR'}$), 4.08 (d, J = 7.2 Hz, 2H, H_{aR}), 1.97 (m, 2H, H_b), 1.5−1.1 (48H, $H_{c\text{-}g,c'\text{-}g'}$), 0.86 ppm (12H, $H_{h,h'}$). ^{13}C (75 MHz, $CDCl_3$): 168.7 (C_{11}), 164.0 (C_2), 162.7 (C_{12}), 162.1 and 162.1 ($C_{13,14}$), 150.9 (C_{15}), 144.0 (C_{18}), 134.8 (C_7), 132.2 (C_6), 129.5 (C_4), 127.0 (C_9), 124.8 (C_3), 123.6 (C_8), 122.4 and 122.3 (C_5, C_{10}), 112.8 (C_{16}), 112.1 (C_{17}), 105.2 (C_1), 45.0 (C_{aR}), 44.4 ($C_{aR'}$), 36.5 (C_b), 31.9 ($C_{f,f'}$), 31.6 ($C_{c,c'}$), 30.0−29.2 ($C_{e,e'}$), 26.4 ($C_{d,d'}$), 22.6 ($C_{g,g'}$), 14.1 ppm ($C_{h,h'}$). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{58}H_{88}N_2O_6$ 909.671515, found 909.6453.

2-Hydroxy-6-bromonaphthalene-1,4,5,8-tetracarboxylic-N,N′-bis(2-hexyldecyl)diimide (HO-NDI-Br) (57.5 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): 12.88 (s, 1H, OH), 8.92 (s, 1H, H_7), 8.34 (s, 1H, H_3), 4.13 (d, ^3J = 7.2 Hz, 2H, $H_{aR'}$), 4.11 (d, ^3J = 7.2 Hz, 2H, H_{aR}), 1.98 (m, 2H, H_b), 1.5−1.1 (48H, $H_{c\text{-}g,c'\text{-}g'}$), 0.85 ppm (12H, $H_{h,h'}$). ^{13}C NMR (75 MHz, $CDCl_3$): 168.4 (C_{11}), 164.1 (C_2), 161.8 (C_{12}), 161.6 and 161.2 (C_{13}, C_{14}), 139.0 (C_7), 128.7 (C_4), 126.8 (C_9), 125.4 (C_3), 124.1, 124.0, and 123.9 (C_5, C_6, C_8), 123.2 (C_{10}), 105.4 (C_1), 45.4 (C_{aR}), 44.6 ($C_{aR'}$), 36.5 (C_b), 31.9 and 31.8 ($C_{f,f'}$), 31.6 ($C_{c,c'}$), 30.0−29.3 ($C_{e,e'}$), 26.3 ($C_{d,d'}$), 22.6 ($C_{g,g'}$), 14.1 ppm ($C_{h,h'}$). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{46}H_{69}BrN_2O_5$ 809.4463, found 809.4496.

General Method for the Synthesis of NDIFu$_2$ or NDITh$_2$. Under an N_2 atmosphere, a mixture of $NDIBr_2$ (100 mg, 0.115 mmol, for R= 2-hexyldecyl), K_2CO_3 (47.66 mg, 0.34 mmol), and PivOH (11.75 mg, 0.12 mmol) was dissolved in 2 mL of degassed toluene in a high-pressure vial, and then the desired equivalent of degassed furan or thiophene was added, followed by the addition of catalyst (Pd_2dba_3, 5.26 mg). The vial was placed in a preheated oil bath and stirred for the desired time. After the mixture was cooled to room temperature, solvent was removed by evaporation and the residue was purified by flash chromatography (dichloromethane/isohexane = 1.3:1) to afford $NDIFu_2$ and $NDITh_2$ as red and orange-red solids, respectively. For R = 2-octyldodecyl, 100 mg (0.101 mmol) of $NDIBr_2$ was used, and the other reagents were adjusted accordingly.

2,6-Bis(2-furanyl)naphthalene-1,4,5,8-tetracarboxylic-N,N′-bis(2-hexyldecyl)diimide (NDIFu$_2$) (92 mg, 95%, entry 20 with 20 equuiv of furan). ^{1}H NMR (300 MHz, $CDCl_3$): 9.04 (s, 2H, $H_{3/7}$), 7.67 (d, ^3J = 1.5, 2H, H_{18}), 7.31 (d, ^3J = 3.4, 2H, H_{16}), 6.63 (dd, ^3J = 1.5, ^3J = 3.4, 2H, H_{17}), 4.13 (d, J = 7.3, 4H, H_a), 1.99 (m, 2H, H_b), 1.5−1.1 (48H, $H_{c\text{-}g,c'\text{-}g'}$), 0.86 (12H, $H_{h,h'}$). ^{13}C (75 MHz, $CDCl_3$): 162.7 ($C_{12/14}$), 162.6 ($C_{11/13}$), 150.8 (C_{15}), 144.6 (C_{18}), 134.5 ($C_{2/6}$), 134.1 ($C_{3/7}$), 127.2 ($C_{9/10}$), 125.8 ($C_{4/8}$), 121.1 ($C_{1/5}$), 114.6 (C_{16}), 112.4 (C_{17}), 45.1 (C_a), 36.6 (C_b), 31.8 and 31.7 ($C_{f,f'}$), 31.7 ($C_{c,c'}$), 30.0−29.3 ($C_{e,e'}$), 26.4 ($C_{d,d'}$), 22.6 ($C_{g,g'}$), 14.1 ($C_{h,h'}$).

2,6-Bis(2-thienyl)naphthalene-1,4,5,8-tetracarboxylic-N,N′-bis(2-octyldodecyl)diimide (NDITh$_2$) (80 mg, 80%, entry 25 with 15 equuiv of Thiophene). ^{1}H NMR (300 MHz, $CDCl_3$): 8.76 (s, 2H, $H_{3/7}$), 7.56 (dd, ^3J = 5.1, ^4J = 1.1, 2H, H_{18}), 7.31 (dd, ^3J = 3.6, ^4J = 1.1, 2H, H_{16}), 7.19 (dd, ^3J = 5.1, ^3J = 3.6, 2H, H_{17}), 4.07 (d, J = 7.3, 4H, H_a), 1.96 (m, 2H, H_b), 1.5−1.1 (64H, $H_{c\text{-}g,c'\text{-}g'}$), 0.86 (12H, $H_{h,h'}$). ^{13}C (75 MHz, $CDCl_3$): 162.4 ($C_{12/14}$), 162.2 ($C_{11/13}$), 140.7 (C_{15}), 140.1 ($C_{2/6}$), 136.5 ($C_{3/7}$), 128.3 (C_{16}), 128.0 (C_{18}), 127.4 ($C_{9/10}$), 127.3 (C_{17}), 125.3 ($C_{4/8}$), 123.3 ($C_{1/5}$), 44.8 (C_a), 36.4 (C_b), 31.8 ($C_{f,f'}$), 31.5 ($C_{c,c'}$), 30.0−29.3 ($C_{e,e'}$), 26.3 ($C_{d,d'}$), 22.6 ($C_{g,g'}$), 14.0 ($C_{h,h'}$).

General Method for the Synthesis of F$_4$Fu$_2$ or F$_4$Th$_2$. Under an N_2 atmosphere, a mixture of F_4Br_2 (100 mg, 0.325 mmol) and PivOK (114 mg, 0.82 mmol) was dissolved in 1.7 mL of a degassed mixture of DMAc and toluene (1:1) (or 1.7 mL of degassed pure DMAc or toluene) in a high-pressure vial. Then the desired equivalent of degassed furan or thiophene was added, followed by the addition of catalyst (Pd_2dba_3 (7.2 mg, 2.5 mol %) or $Pd(OAc)_2$ (3.7 mg, 5 mol %). The high-pressure vial was heated and stirred for the desired time. After the mixture was cooled to room temperature, the solvent was evaporated under high vacuum and the crude product was purified by column chromatography (isohexane) to obtain the products as white crystalline solids.

1,4-Bis(2-furanyl)-2,3,5,6-tetrafluororobenzene (F$_4$Fu$_2$) (52 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.64 (dd, ^3J = 1.8, ^4J = 0.7, 2H, H_1), 6.98 (m by J_{HH} and J_{HF}, 2H, H_3), 6.59 (dd, ^3J = 1.8, ^3J = 3.5, 2H, H_2). ^{13}C NMR (75 MHz, $CDCl_3$): 143.9 (C_1), 143.4 (dm, $^1J_{CF}$ = 256, C_6), 142.5 (C_4), 114.1 (m, C_3), 111.7 (C_2), 109.1 (m, C_5). ^{19}F NMR (282 MHz, $CDCl_3$): −142.4. MS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_6F_4O_2$ 283.0377, found 283.0361.

1,4-Bis(2-thienyl)-2,3,5,6-tetrafluororobenzene (F$_4$Th$_2$) (59 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.68 (d, ^3J = 3.8 Hz, 2H, H_3), 7.57 (dd, ^3J = 5.2 Hz, ^4J = 1.1 Hz, 2H, H_1), 7.21 ppm (dd, ^3J = 3.8 Hz, ^3J = 5.2 Hz, 2H, H_2); small J_{HF} splitting for H_2 and H_3. ^{13}C (75 MHz, $CDCl_3$): 144.0 (dm, $^1J_{CF}$ = 256 Hz, C_6), 130.2 (C_3), 128.3 (C_1), 127.9 (C_4), 127.4 (C_2), 112.5 ppm (m, C_5); small J_{CF} splitting for C_1 and C_3. ^{19}F (282 MHz, $CDCl_3$): −140.8 ppm.

Computational Details. Ground-state geometries for $NDIFu_2$ and $NDITh_2$ were optimized at the B3LYP/6-31G** level of theory. Frequency calculations were made to verify the stability of the equilibrium structures, and no imaginary eigenvalues were found. All calculations were carried out with Guassian09.[66]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra with signal assignments and details of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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