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Nickel-Catalyzed Direct Arylation Polymerization for the Synthesis of Thiophene-Based Cross-linked Polymers

Y. Mohr, A. Ranscht, M. Alves-Favaro, E. Quadrelli, F. Wisser, J. Canivet

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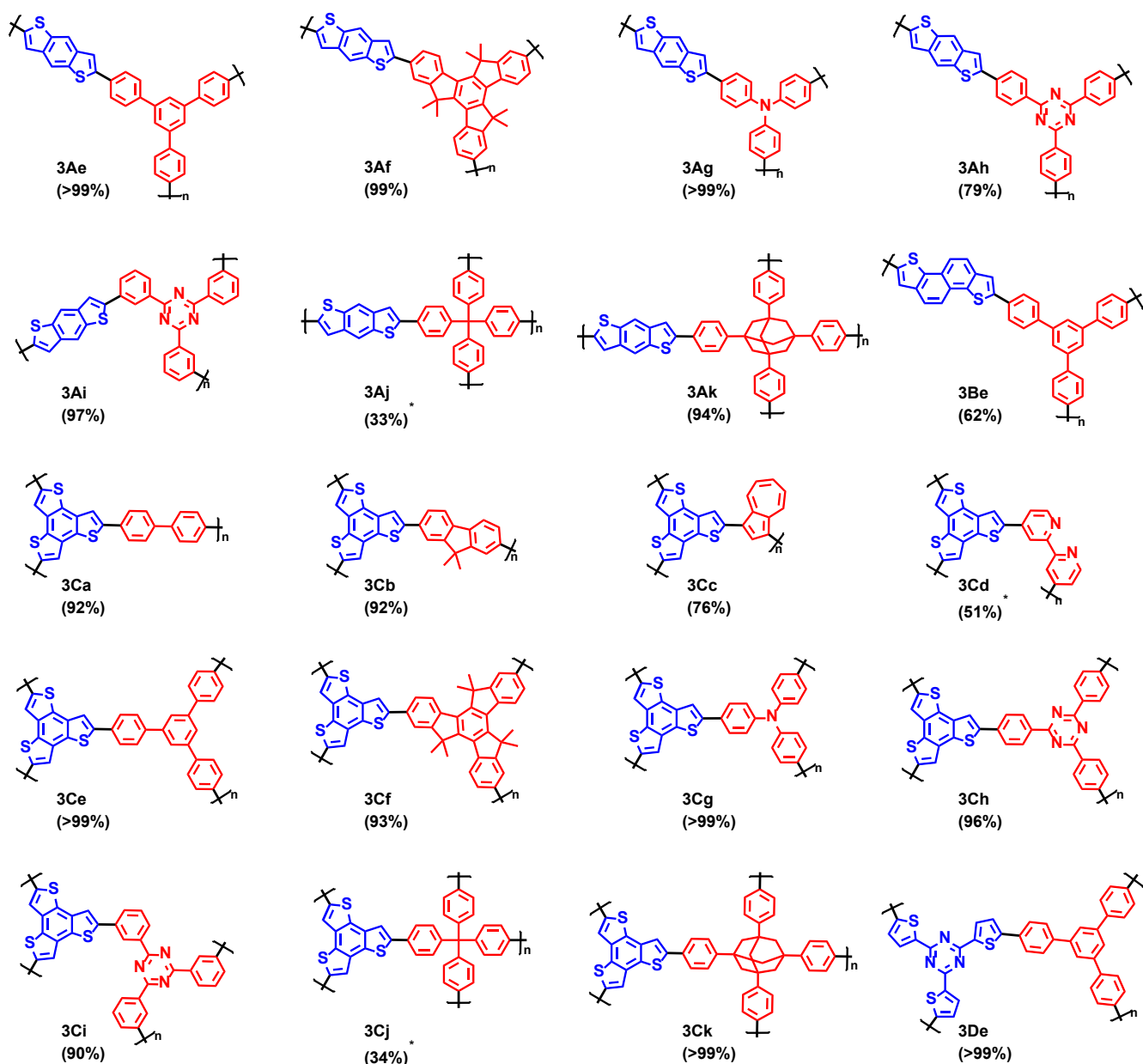
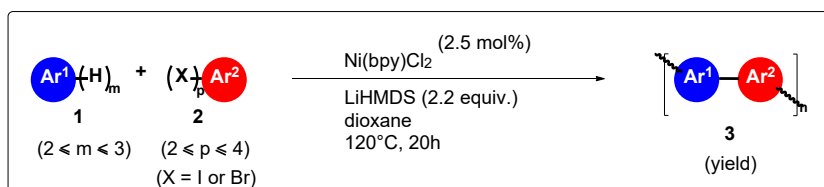
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Scheme 2. Ni-catalyzed direct C-H arylation synthesis of thiophene-based highly cross-linked porous polymers. (Reaction conditions: polyheteroaryl **1** (0.25 mmol), poly(hetero)aryl iodide **2** (0.5 to 1.5 equiv.), NiCl₂·glyme (2.5 mol%), bipyridine (2.5 mol%) and LiHMDS (0.55 mmol) in dioxane (4 mL) at 120°C for 20 hours. Isolated yields are given in brackets. *Aryl bromides are used.)

The porosity of semiconductors is crucial for active site isolation and accessibility for photocatalysis purpose and has also been demonstrated to positively affect the light harvesting efficiency.^[31,32]

Here we report the first example of Ni-catalyzed DARp for the synthesis of porous conjugated organic polymers made by copolymerization of non-activated polytopic thiophenes and aryl halide subunits (Scheme 2). Analogous sulfur-rich organic polymers, synthesized mainly through imine condensation^[33–37] and Pd-catalyzed cross-coupling,^[38–40] already found

applications in light harvesting and electron transport, especially for solar fuels production.^[41,42]

Results and Discussion

The Ni(bpy)Cl₂/LiHMDS catalytic system has been applied to a scope of four non-activated heteroaryl cores (**1A–D**) combined with eleven (hetero)aryl halide electrophiles (**2a–k**) as coupling partners (Figure S1). Under the standard reaction conditions

shown in the Scheme 2, twenty organic polymers have been obtained with yields ranging from 34 to 99%, all having intrinsic porosity and optical properties.

The dimensionality playing a crucial role in the properties of porous semiconductors,^[43] the choice of the molecular structure and composition of the targeted polymers was made to design three-dimensional porous networks, leading to a more limited number of combinations than expected from the total number of substrates. Indeed, the combination of ditopic benzodithiophene **1A** with ditopic electrophiles **2a-d** would have led to linear polymeric networks rather than to porous three-dimensional polymers as targeted here, explaining the restricted series of products **3Ae** to **3Ak**. Also the naphthodithiophene **1B** and 2,4,6-tri(2-thienyl)-1,3,5-triazine **1D** were selected as extended ditopic and tritopic heteroarenes for comparison with model benzodithiophene **1A** and benzotrithiophene **1C**, respectively, in combination with model tritopic iodide 1,3,5-tris(4-iodophenyl)benzene **2e**.

The amount of coupling partners involved in the reaction has been adjusted in each case to get an equimolar ratio of C2-H protons in heteroarenes **1** and halogenides in aryl electrophiles **2**.

All reactions gave rise to solids that are insoluble in common solvents including dichloromethane, dioxane and toluene. Importantly we could not detect any soluble short-chain oligomers in solution using GC analysis.

Most of compounds **3** are obtained with isolated yields higher than 90%, as determined from the solid product weight considering the expected polymer structure, thus demonstrating the high efficiency of the nickel system to catalyze the C-H arylation of (poly)thiophene heteroaryls (Scheme 2). Elemental analysis and NMR spectroscopy data were supporting the expected polymers structures **3** (see Supporting Information). Indeed, solid-state NMR analysis showed the presence of thiophene-based and (hetero)aromatic repeating units and molecular C:N and C:S ratio confirm the expected composition.

Moreover, the degree of cross-linking above 90% (except for **3Ci** and **3Cj** with ca. 70%), as determined from residual halogen content (Table S3), shows the ability of the nickel bipyridine system to give access to highly reticulated networks.

Polymerization reactions performed in the absence of Ni catalyst or LiHMDS base did not lead to product formation. The use of a single substrate, either heteroarene **1A** or aryl electrophiles **2a** or **2e**, under standard conditions reported in Scheme 2, did not give any homocoupled oligomers or polymeric solid.

The aryl bromides **2d** and **2j** gave rise to quite moderate yields with 51% for **3Cd** and 33-34% for **3Aj** and **3Cj**, respectively, most likely due to the lower reactivity of aryl bromides compared to iodides under Ni-catalyzed C-H arylation conditions, in line with report for molecular C-H arylation.^[24]

In addition, all the obtained polymers **3Ae** to **3De** have been evaluated by nitrogen physisorption at 77K (Figures S2-S4). While most of the polymers in series **3A**, **3B** and **3D** show type II/H3 isotherms characteristic for non-porous nanoparticles, most of the materials in series **C** are characterized by type Ib/H4 shaped isotherms. Thus, the apparent surface areas present wide variations depending mostly on the geometry of the coupling partner involved (Table 1). In the **3A** series, **3Af** and **3Ak** stands out for their significant porosity with apparent surface areas of approx. 670 m²/g and 250 m²/g respectively, which most likely arises from ridged tridimensional tri- and

tetratopic node **2f** and **2k**. A similar trend is observed in the **3C** series with the highest porosity measured for **3Cf** (~1070 m²/g) and **3Ck** (~680 m²/g). Overall, the **3C** series gathers porous polymers with high porosity, including **3Cb** (~180 m²/g), **3Cg** (260 m²/g) and **3Ch** (300 m²/g).

Table 1. Textural and optical properties of the polymer series **3**.

compound	Surface Area S _{BET} / m ² ·g ⁻¹	Indirect band gap E _g / eV ^[b]
3Ae	10	2.25
3Af	673	2.27
3Ag	37	n.d.
3Ah	47	2.31
3Ai	34	2.52
3Aj	39	2.23
3Ak	250	2.49
3Be	50	2.32
3Ca	25	2.63
3Cb	182	2.54
3Cc	65	2.16
3Cd	15	2.04
3Ce	371	2.54
3Cf	1066	2.40
3Cg	260	2.44
3Ch	300	2.58
3Ci	37	2.54
3Cj	27	2.34
3Ck	678	2.68
3De	25	2.12

[a] Calculated from nitrogen physisorption isotherms using the BET method.

[b] Calculated from UV-Vis spectra (n.d. = not determined).

In particular **3Ce** having an apparent surface area of approx. 370 m²/g underlines the correlation between rigid tritopic building blocks and porosity, as the other materials in the series **e** (**3Ae**, **3Be** and **3De**) made with ditopic or flexible units show apparent surface area lower than 50 m²/g. The importance of rigid building blocks to achieve materials with a high porosity is demonstrated by ¹H and ¹³C solid-state NMR spectroscopy. Indeed **3Be** (62% yield, 50 m²/g) is highly reticulated with the lowest amount of unreacted C_{Ar}-I groups as deduced qualitatively from ¹³C NMR spectra (Figure S10). Moreover deconvolution of the ¹H NMR data using DMFit,^[44] indicates the lowest amount of residual HMDS groups for **3De** (99% yield, 50 m²/g, see Figures S11 & S12), The HMDS groups are most likely stemming from trapped Ni(HMDS)_x species.^[25,45] In comparison, NMR spectroscopy indicates for **3Ce** (99% yield, 370 m²/g) the presence of an

higher amount of remaining C_{Ar}-I groups than in **3Be** but similar amounts of C_{Ar}-I groups compared to **3Ae** (99% yield, 50 m²/g) and **3De** and significantly less HMDS species than in **3Ae** and **3Be** (for further discussion see SI).

Analogous nitrogen- and sulfur-containing porous polymers made by Pd-catalyzed Stille cross-coupling apparent surface areas between 80 and 700 m²/g have been reported.^[38,39] In particular the analogues of **3Ah** and **3Ch**, reported previously by Bojdys and coworkers as SNP-BDT2 and SNP-BTT2, show similar apparent surface areas of 90 and 400 m²/g, respectively.^[38] The nickel used herein therefore appears as an appealing alternative to precious-metal catalyst counterparts.

As expected from related literature, all these polymer materials possess indirect band gaps.^[46] Indirect optical band gaps have been determined from UV-Vis spectroscopy analysis of the polymers **3Ae** to **3De** (Figures S5-S7). The indirect band gaps range from 2.0 to 2.7 eV, falling in the range of previously reported analogous polymers (Table 1).^[38,39]

Together these results show the versatility of this nickel-catalyzed synthetic pathway to get porous light harvesting materials with controlled donor-acceptor configuration. Such materials like **3Ch**, made with benzotrithiophene (donor) and triazine (acceptor) moieties having an accessible surface area of 300 m²/g and an indirect band gap of 2.58 eV, would be promising candidates for water splitting application, for example.^[39,47]

Conclusion

In conclusion, we demonstrated the wide applicability of a molecular Ni-based C-H arylation catalytic system for the direct arylation polymerization of di- and tri-thiophenyl compounds. Twenty highly cross-linked conjugated porous polymers were obtained with intrinsic porosity and genuine optoelectronic properties. This methodology based on an earth-abundant catalyst opens perspective for the synthesis of a library of conjugated porous polymers based on thiophene units, aiming at facilitating and accelerating the discovery of novel optoelectronic materials.

Experimental Section

For a typical synthesis exemplified for **3Ce**, 32.1 mg (0.125 mmol) benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene **1C**, 87.3 mg (0.125 mmol) 4,4''-diiodo-5'-(4-iodophenyl)-1,1':3',1''-terphenyl **2e**, 142.3 mg (0.825 mmol) lithium bis(trimethylsilyl)amide (LiHMDS) and 2.7 mg (9.4 μmol) Ni(bpy)Cl₂ were added inside a glovebox to a flame dried glass reactor equipped with a magnetic stirring bar. The glass reactor was sealed with a Teflon septum. Outside the glovebox, 5 ml of anhydrous dioxane were added and the reactor was placed in an oil bath preheated to 100°C. The reaction was stirred at 100°C for 20 h. The obtained solid was purified by Soxhlet extraction first using MeOH for 1 day and then CHCl₃ for 3 days. The yellow solid was dried at 80°C under vacuum.

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