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

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**Abstract:** An earth-abundant nickel(II) bipyridine catalyst, combined with lithium hexamethyldisilazide as base, demonstrates its wide applicability in the direct arylation polymerization of di- and tri-thiophene heteroaryls with poly(hetero)aryl halides. With a nickel catalyst loading of 2.5 mol%, a series of twenty highly cross-linked organic polymers are obtained with 34 to 99% yields. Using mixed polytopic coupling partners allows obtaining alternating and optically active thiophene-based solids with intrinsic porosity.

## Introduction

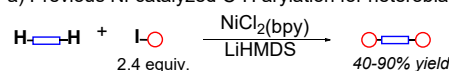
Conjugated polymers have shown to be key components in (opto)electronic devices with applications ranging from light capture to sensing and photo-/electrocatalysis.<sup>[1-8]</sup>

Among synthetic methods, the direct arylation polymerization (DAP) relies on a C-H/C-X biaryl coupling strategy and allows for reduced synthetic steps and waste compared to traditional biaryl coupling, like Suzuki-Miyaura and Stille-Migita reactions.<sup>[9-16]</sup> The last decade shows the expansion of the site-selective DAP methodology to prepare a variety of mostly linear conjugated polymers.<sup>[13-16]</sup> However, despite crucial advances to increase DAP overall sustainability,<sup>[10,17]</sup> the developed processes rely on transition metal catalysis, most often on palladium catalysts. There is thus a need for earth-abundant catalytic systems able to promote DAP.

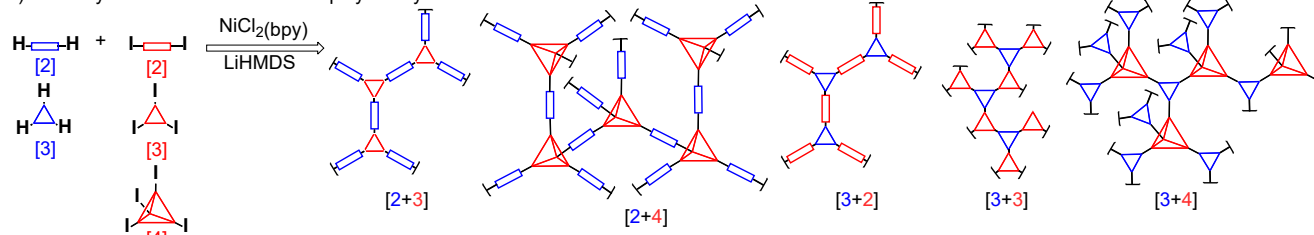
Inspired by molecular C-H arylation catalysis,<sup>[18]</sup> Thompson and coworkers developed copper-catalyzed DAP for the synthesis of conjugated linear polymers.<sup>[19]</sup> An optimized protocol described a Cu-phenanthroline catalyst loading of 5 mol% to get 20 to 80% yield at 140°C in the presence of potassium carbonate as base in a mixture of amide and aromatic solvents.<sup>[20,21]</sup> Mori and coworkers developed nickel-based systems using phosphine/carbene ligands for polythiophene synthesis from halogeno-thiophenes *via* Grignard-type intermediates.<sup>[22,23]</sup> Similarly, we recently reported the nickel 2,2'-bipyridine (bpy) catalyzed direct C-H arylation of thiophenes and indole (Scheme 1a).<sup>[24,25]</sup> A variety of arylthiophenes has been obtained with 100% selectivity towards thiophene's C2 position in ethereal solvents in the presence of lithium hexamethyldisilazide (LiHMDS) as base.

Advantageously avoiding the homocoupling reaction, this Ni-catalyzed C-H arylation would allow for alternating units though orthogonal synthesis strategy to prepare periodic, sequential conjugated copolymers. Such perfectly alternating conjugated polymers, without homocoupling pattern affecting light absorption and charge transport, are of a great interest for semiconductors and optoelectronics.<sup>[26-30]</sup> Furthermore, to introduce porosity within such polymeric networks, we envisioned alternating di-/trifunctional heteroarenes and tri-/tetrafunctional (hetero)aryl electrophiles to get three dimensional polymeric frameworks with intrinsic porosity (Scheme 1b).

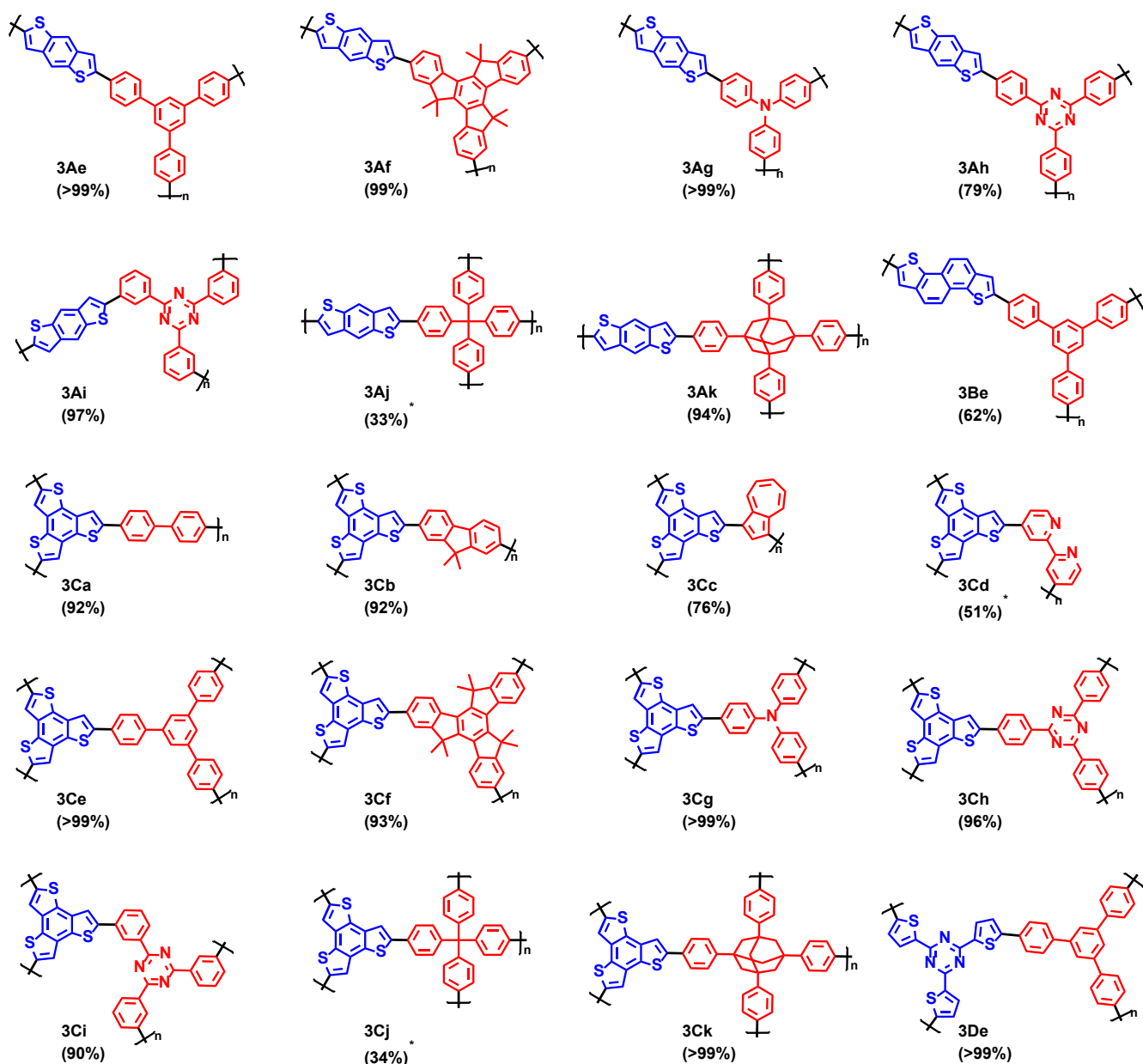
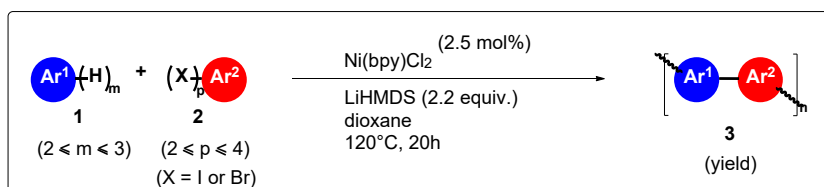
a) Previous Ni-catalyzed C-H arylation for heterobiaryl synthesis<sup>21</sup>



b) Ni-catalyzed DAP for cross-linked polymer synthesis



**Scheme 1.** From heterobiaryls to conjugated porous polymers with controlled topology through Ni-catalyzed C-H arylation.



**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.), NiCl<sub>2</sub> · 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.<sup>[31,32]</sup>

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<sup>[33–37]</sup> and Pd-catalyzed cross-coupling,<sup>[38–40]</sup> already found

applications in light harvesting and electron transport, especially for solar fuels production.<sup>[41,42]</sup>

## Results and Discussion

The Ni(bpy)Cl<sub>2</sub>/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,<sup>[43]</sup> 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.<sup>[24]</sup>

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 m<sup>2</sup>/g and 250 m<sup>2</sup>/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 m<sup>2</sup>/g) and **3Ck** (~680 m<sup>2</sup>/g). Overall, the **3C** series gathers porous polymers with high porosity, including **3Cb** (~180 m<sup>2</sup>/g), **3Cg** (260 m<sup>2</sup>/g) and **3Ch** (300 m<sup>2</sup>/g).

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

compound	Surface Area S <sub>BET</sub> / m <sup>2</sup> ·g <sup>-1</sup>	Indirect band gap E <sub>g</sub> / eV <sup>[b]</sup>
<b>3Ae</b>	10	2.25
<b>3Af</b>	673	2.27
<b>3Ag</b>	37	n.d.
<b>3Ah</b>	47	2.31
<b>3Ai</b>	34	2.52
<b>3Aj</b>	39	2.23
<b>3Ak</b>	250	2.49
<b>3Be</b>	50	2.32
<b>3Ca</b>	25	2.63
<b>3Cb</b>	182	2.54
<b>3Cc</b>	65	2.16
<b>3Cd</b>	15	2.04
<b>3Ce</b>	371	2.54
<b>3Cf</b>	1066	2.40
<b>3Cg</b>	260	2.44
<b>3Ch</b>	300	2.58
<b>3Ci</b>	37	2.54
<b>3Cj</b>	27	2.34
<b>3Ck</b>	678	2.68
<b>3De</b>	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 m<sup>2</sup>/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 m<sup>2</sup>/g. The importance of rigid building blocks to achieve materials with a high porosity is demonstrated by <sup>1</sup>H and <sup>13</sup>C solid-state NMR spectroscopy. Indeed **3Be** (62% yield, 50 m<sup>2</sup>/g) is highly reticulated with the lowest amount of unreacted C<sub>Ar</sub>-I groups as deduced qualitatively from <sup>13</sup>C NMR spectra (Figure S10). Moreover deconvolution of the <sup>1</sup>H NMR data using DMFit,<sup>[44]</sup> indicates the lowest amount of residual HMDS groups for **3De** (99% yield, 50 m<sup>2</sup>/g, see Figures S11 & S12), The HMDS groups are most likely stemming from trapped Ni(HMDS)<sub>x</sub> species.<sup>[25,45]</sup> In comparison, NMR spectroscopy indicates for **3Ce** (99% yield, 370 m<sup>2</sup>/g) the presence of an

higher amount of remaining C<sub>Ar</sub>-I groups than in **3Be** but similar amounts of C<sub>Ar</sub>-I groups compared to **3Ae** (99% yield, 50 m<sup>2</sup>/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 m<sup>2</sup>/g have been reported.<sup>[38,39]</sup> 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 m<sup>2</sup>/g, respectively.<sup>[38]</sup> 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.<sup>[46]</sup> 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).<sup>[38,39]</sup>

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 m<sup>2</sup>/g and an indirect band gap of 2.58 eV, would be promising candidates for water splitting application, for example.<sup>[39,47]</sup>

## 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)Cl<sub>2</sub> 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 CHCl<sub>3</sub> for 3 days. The yellow solid was dried at 80°C under vacuum.

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**Keywords:** nickel • catalysis • C-H arylation • thiophene • conjugated polymer

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