Supporting information for

Balancing steric and electronic effects of bidentate, mixed P,N ligands to control Kumada catalyst transfer polycondensation of a sterically hindered thiophene

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EXPERIMENTAL SECTION

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Chemicals. All reagents were used as received from commercial suppliers. Solvents were purified and dried under argon using conventional methods.¹ Complexes **5-7** were commercially available, whereas complexes **4**,² **8**,³ **9**,⁴ **10**,^{5–7} **11**,⁵ **12**,^{8,9} **13**,^{6–8} **14**¹⁰ and **15**¹¹ were synthesized according to the literature. 2-bromo-3-(2,5-dioctylphenyl)-5-iodothiophene was also synthesized following previously reported procedures.¹²

NMR spectroscopy was done on a Bruker Avance 300 at 300 MHz (¹H) and 75 MHz (¹³C). CDCl₃ or CD₂Cl₂ was used as solvent, lock and internal standard (δ (¹H) = 7.26 ppm; δ (¹³C) = 77.0 ppm for CDCl₃ and δ (¹H) = 5.32 ppm; δ (¹³C) = 53.84 ppm).

SEC measurements were carried out on a PSS SeCurity HP1200 G1310A from PSS with three columns having pore sizes of 10², 10³, and 10⁴ Å and a guard column (PSS). Calibration was done using polystyrene standards. THF was used as eluent at room temperature at a flow rate of 1.0 mL/min.

MALDI-TOF spectrometry was performed on a Bruker Autoflex III TOF/TOF.

Typical procedure of KCTP of PDOPT. A flame-dried Schlenk tube containing 0.1 M 2bromo-5-iodo-3-(2,5-dioctylphenyl)thiophene in dry, degassed THF was cooled to 0 °C under nitrogen. 1.0 eq. *tert*-BuMgCl was added and the mixture was stirred for 1 h. A flame-dried Schlenk tube was charged with the nickel catalyst (ratio 1/100, catalyst/monomer). The Schlenk tube containing the catalyst was put into a pre-heated oil bath and the monomer solution was added in one potion via syringe. For ¹H-NMR and SEC analysis small volume samples were taken. After 4 h, the polymerization was quenched with 5 M HCl in THF. The reaction mixture was diluted with water and THF. The organic phase was washed with water (3 times) and the solvent was evaporated under reduced pressure. The resulting mixture was adsorbed onto silica gel to facilitate Soxhlet extraction. The polymer was purified via Soxhlet extraction with MeOH, acetone and CHCl₃. The CHCl₃ fraction was concentrated under reduced pressure to yield PDOPT. Full characterization of PDOPT has been published elsewhere.¹²



Figure S1. Evolution of the SEC elution profiles with time during PDOPT synthesis with 4



Figure S2. Evolution of the SEC elution profiles with time during PDOPT synthesis with 5



Figure S3. Evolution of the SEC elution profiles with time during PDOPT synthesis with 6



Figure S4. Evolution of the SEC elution profiles with time during PDOPT synthesis with 7



Figure S5. Evolution of the SEC elution profiles with time during PDOPT synthesis with 8



Figure S6. Evolution of the SEC elution profiles with time during PDOPT synthesis with 9



Figure S7. Evolution of the SEC elution profiles with time during PDOPT synthesis with 10



Figure S8. Evolution of the SEC elution profiles with time during PDOPT synthesis with 11



Figure S9. Evolution of the SEC elution profiles with time during PDOPT synthesis with 12



Figure S10. Evolution of the SEC elution profiles with time during PDOPT synthesis with 13



Figure S11. Evolution of the SEC elution profiles with time during PDOPT synthesis with 14



Figure S12. Evolution of the SEC elution profiles with time during PDOPT synthesis with 15



Figure S13. MALDI-ToF spectrum PDOPT produced with **4** (after soxhlet extraction, data from CHCl₃ fraction)



Figure S14. MALDI-ToF spectrum PDOPT produced with **5** (after soxhlet extraction, data from CHCl₃ fraction)



Figure S15. MALDI-ToF spectrum PDOPT produced with **6** (after soxhlet extraction, data from CHCl₃ fraction)



Figure S16. MALDI-ToF spectrum PDOPT produced with 7 (after soxhlet extraction, data from CHCl₃ fraction)



Figure S17. MALDI-ToF spectrum PDOPT produced with **8** (after soxhlet extraction, data from CHCl₃ fraction)



Figure S18. MALDI-ToF spectrum PDOPT produced with **9** (after soxhlet extraction, data from CHCl₃ fraction)



Figure S19. MALDI-ToF spectrum PDOPT produced with 11 (after soxhlet extraction, data from $CHCl_3$ fraction)



Figure S20. MALDI-ToF spectrum PDOPT produced with 13 (after soxhlet extraction, data from $CHCl_3$ fraction)



Figure S21. MALDI-ToF spectrum PDOPT produced with 14 (after soxhlet extraction, data from $CHCl_3$ fraction)



Figure S22. MALDI-ToF spectrum PDOPT produced with 15 (after soxhlet extraction, data from $CHCl_3$ fraction)

Catalyst used	M (kg mol ⁻¹)	M (kg mol ⁻¹)	Ð	Conversion
Catalyst used	masec (Kg.mor)	m _{wsec} (kg.moi)	D	after 4 h (%)
4	7	9	1.27	17
5	6	11	1.67	24
6	9	15	1.56	7
7	11	13	1.23	12
8	9	11	1.25	16
9	7	9	1.30	24
10	15	18	1.15	54
11	14	16	1.18	66
12	16	22	1.34	66
13	14	39	2.75	45
14	8	11	1.49	2
15	9	15	1.66	3

 Table S1. Comparison of the properties of PDOPT samples made in this study (after soxhlet

 extraction, data from CHCl₃ fraction).

THEORETICAL SECTION

1. Computational details

All calculations were performed with GAUSSIAN 09 package (version D 01)¹³ at DFT level of theory (PBEPBE functional).¹⁴ Dispersion corrections were introduced through Grimme's GD3 corrections.¹⁵ Nickel and Bromine atoms were described by the SDD pseudopotentials and associated basis sets,¹⁶ the other atoms were described by 6-31+G** basis sets of Pople.¹⁷ Full geometry optimizations were performed on all the structures. The nature of the encountered minima was checked and all were characterized by a complete set of real frequencies. The reported transition states were characterized by one and only one imaginary frequency. All energies are expressed in kcal.mol⁻¹ and are Gibbs free energies extracted from the frequency calculation. Non-covalent interactions were studied through NCI analysis¹⁸ and topology through ELF analysis¹⁹ using TOPMOD package^{20,21} performed on the optimized geometries wavefunction.

The energies were computed with the separated fragments as references. For example, for the DBP1 monomer, the energy of each complex was computed following **Eq.1**.

 $[Ni(THF)(PyMePPh_2)] + DBP1 \rightarrow [Ni(DBP1)(PyMePPh_2)] + THF(Eq.1)$

$$\Delta G = G([Ni(DBP1)(PyMePPh_2)]) + G(THF) - G([Ni(THF)(PyMePPh_2)]) - G(DBP1)$$

For the sake of comprehension, the atoms in the monomer, the dimer and the trimer were numbered as shown in scheme S1. The Octyl chain was simplified into a Butyl chain to simplify the calculations in DOPT.



Scheme S1. Numbering of the atoms in the monomer DBP1 (up), dimer DBP2 (middle) and trimer DBP3 (bottom). R stands for dibuthylphenyl chains.

For the dimer, three isomers are possible depending on which carbon atoms are the R group: C_3 and C_{10} , C_4 and C_{10} or C_3 and C_9 . Calculations were done on two isomers (DBP2 and DBP2'). For the trimer, calculations were only done on the structure presented in Scheme S1. For all the complexes, several conformers (orientation of the catalyst on the polymer) are possible. Solely the structure of lowest energy will be discussed for each coordination site.

2. ELF Analysis

The Electron Localization Function (ELF) analysis was performed on the free monomer DBP1 and on the complex formed with **5** (with the Ni⁰ atom located on the C₂-C₃ double bond). The results are reported in Table S2.

Basin	Monomer DBP1	Coordination of 5
		on C ₂ -C ₃
S ₁	4.19	4.30
Br	6.62	6.90
Br-C ₂	1.21	0.84
S-C ₃	1.85	1.65
C ₂ -C ₃	3.75	2.35
C ₃ -C ₄	2.44	2.23
C ₄ -C ₅	3.69	3.79
Ni-C ₂	-	1.72
Ni-C ₃	-	1.03

Table S2. Number of electron localized in the sulfur and bromine lone pairs and in the covalent bonds of the thiophene ring in the isolated monomer and in the complex with **5**.

In the isolated monomer DBP1 we retrieve the partial electron delocalization due to the aromaticity of the ring even though from the ELF picture the double bonds are well localized. The C_2 - C_3 and C_4 - C_5 covalent bonds have a strong double bond character with occupancy of respectively 3.75 and 3.69 electrons (e⁻). The multiplicity of the C_3 - C_4 bond is more than single, since 2.44 e⁻ are localized on this bond instead of exactly two. The C_2 -S bond presents an ionic character and is populated by only 1.85 e⁻. This default is associated to an excess of electron in the sulfur lone pair 4.19 e⁻ (instead of 4). The C_2 -Br bond is very weak with only 1.21 e⁻ populated the valence basin.

Coordination of **5** on the C₂-C₃ bond has a dramatic effect on the electronic structure of the ring: all the bonds formed with either C₂ or C₃ are weakened. The multiplicity of the C₂-C₃ bond decreases since it is now almost a single bond, with only 2.35 e⁻ remaining on this covalent bond. This decrease is associated to an increased bond lengthening from 1.383 Å in the monomer to 1.461 Å in the complex. The electron delocalization within the thiophene ring is partially broken as shown by the drop of the C₃-C₄ bond population from 2.44 e⁻ in the monomer to 2.23 e⁻ in the complex. The impact of the coordination to nickel is even greater on the C₂-Br bond which population drops from 1.21 e⁻ to 0.84 e⁻ along with an increase of the Bromine lone pair population. The C₂-Br bond thus becomes more ionic in the complex. Two Ni-C bonds (with C₂ and C₃) appear in the complex with a significant covalent character. It seems that upon coordination, the nickel atom undergoes an oxidation as suggested by its square planar environment which is characteristic of d⁸ cations. Simultaneously, the carbons C₂ and C₃ are reduced and become sp³ as proven by their tetrahedral environment.

	5	10	12
S	-10.7	-16.8	
Br	-1.2	-8.1	
C ₂ -C ₃	-28.2	-33.8	-37.7
C ₃ -C ₄	-16.5ª	-22.0ª	-18.3
C ₄ -C ₅	-29.1	-36.7	-37.9

3. Bonding energies and structures in DBP1

Table S3. Complexation energies in kcal.mol⁻¹ of complex **5**, **10** and **12** on the different sites of the monomer DBP1. a) These structures are transition states.

	5	10
Ni-S	2.944	2.917
Ni-C ₂	2.163	2.075
Ni-C ₃	2.044	2.010
Ni-C ₄	2.044	2.050
Ni-C ₅	2.227	2.234

Table S4. Bond lengths (Å) in the complexes of **5** and **10** on the C_3 - C_4 position of DBP1.

In all structures, the complexes clearly display a η^1 coordination mode when the nickel binds either on the sulfur or on the bromine, or a η^2 coordination mode when it binds on the C-C double bonds. The only questionable cases concern the binding on the C₃-C₄ bond: as the metal is migrating between the C₂-C₃ bond and the C₄-C₅ bond; the coordination pattern is not as clear. In these structures, the thiophene ring is no longer planar but adopt an envelop conformation with the sulfur pointing on the opposite face of the complex. Coordination of the nickel is close to η^4 pattern with non-equivalent Ni-C distances (Table S4), two are shorter (Ni-C₃ and Ni-C₄), one is intermediate (Ni-C₂) and one is longer (Ni-C₅).

Complexation of the neutral Ni⁰ complex on the C₂-C₃ or C₄-C₅ bonds has a critical influence on the nature of the thiophene. Indeed, upon coordination, C₂ and C₃ (or C₄ and C₅ respectively) are no longer pure sp² carbons. C₂ displays a tetrahedral geometry and this change is associated to an increased C₂-C₃ bond distance (from 1.383 Å in the isolated monomer to 1.468 Å in the complex). The C-Br bond is also strongly weakened highlighting, with the C₂-Br (or C₅-Br respectively) bond being almost dissociated from the complex in some cases.

The nickel atom adopts a square planar coordination sphere with the C-Ni bonds being partially covalent as shown by the presence of Ni-C ELF valence basins with significant Ni contributions (Table S3). Roughly, the oxidation of the nickel and a reduction of the C-C double bond occur

upon complexation. This is supported by the geometry around the nickel, which is characteristic of the Ni²⁺ square planar complexes, and by the lengthening of the C-C bond length.

	Monomer DBP1		Dimer DBP2 Dimer DBP		DBP2'	Trimer DBP3				
Bond	5	10	12	5	10	5	10	5	10	12
C ₂ -C ₃	-28.2	-33.8	-37.7	-27.9	-40.3	-30.2	-34.5	-32.6	-34.9	-41.1
C_3-C_4				-	-20.5	-	-23.5	-	-	-
C_3 - C_4^a	-16.5	-22.0	-18.3		-28.0					
C_4-C_5	-29.1	-36.7	-37.9	-29.7	-37.2	-20.6	-32.7	-29.3	-40.7	-38.3
C_5-C_6				-22.2	-26.4	-17.8	-26.8	-32.6	-	-
$C_{6}-C_{10}$				-25.2	-27.4	-	-	-29.3	-30.3	-33.1
$C_{10}-C_{9}$				-11.9	-20.0	-	-	-23.1	-	-
C_9-C_8				-30.2	-35.2	-	-	-32.3	-36.2	-39.7
$C_8 - C_{11}$								-	-	-
C_{11} - C_{15}								-24.7	-36.4	-38.5
$C_{15}-C_{14}$								-	-24.3	-26.3
C ₁₄ -C ₁₃								-30.1	-35.3	-37.4

4. Bonding energies in DBP2, DBP2' and DBP3

Table S5. Complexation energies in kcal.mol⁻¹ of complex **5**, **10** and **12** on the monomer DBP1, dimer DBP2 and trimer DBP3. For each position, only the complexation energy of the most stable conformer is given. For DBP2', positions C_6 - C_{10} , C_{10} - C_9 and C_9 - C_8 were not computed, as they are identical to positions C_2 - C_3 , C_3 - C_4 and C_2 - C_3 respectively for symmetry reasons. See also schemes S2, S3 and S4 for another view of the complexation energy *vs*. binding position. a) These structures are transition states.



Figure S23. Structure of the complex of 10 on DBP2 on C_4 - C_5 bond. Hydrogen atoms are omitted for clarity.

5. Non-covalent interaction analysis



Figure S24. Non-Covalent-Interaction (NCI) analysis performed on the complex of **5** on the C_1 - C_2 position of DBP1. In green are represented Van der Waals dispersive forces and in red steric repulsion.

6. Stuctures

All structures are provided in a separated XYZ file. The structures are named as following: first the ligand bind to the complex, then the complex bonded to the ligand, and finally, the number or type of the atom through which the complex is bonded to the ligand. For example, DAB1_5_2_3 means that this is the structure of the catalyst **5** and the DAB1 ligand bonded on C_2 and C_3 . TS precises that the structure is a transition state. For the oxidative addition, further label are added: RE for the reactant, TS for the transition state and PR for the product.

7. Binding energies vs. binding position



Scheme S2. Binding energies vs. binding position for DBP1



Scheme S3. Binding energies vs. binding position for DBP2

8. Mechanism of the oxidative addition.

	C ₂ -Br			C ₅ -Br		
	Reactant	TS	Product	Reactant	TS	Product
ΔG	-36.7	-26.0	-58.3	-29.0	-25.1	-62.0

 Table S6. Energetics of the oxidative addition of 10 on DBP1 in kcal.mol⁻¹. The energy

 reference corresponds to the separated reactants as presented in Eq. 1.

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