



HAL
open science

Organic Semiconductor Materials via Simplified Synthetic Pathways

Jérémie Grolleau, Stéphanie Legoupy, Frédéric Gohier, Pierre Frère

► **To cite this version:**

Jérémie Grolleau, Stéphanie Legoupy, Frédéric Gohier, Pierre Frère. Organic Semiconductor Materials via Simplified Synthetic Pathways. 2nd International Symposium on C-H activation, 2014, Rennes, France. 2014. hal-03344878

HAL Id: hal-03344878

<https://hal.univ-angers.fr/hal-03344878>

Submitted on 15 Sep 2021

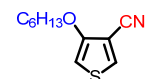
HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Introduction

In the field of organic semi-conductors (OSC) developed for organic photovoltaic cells (OPV), the environmental impact of the synthesis of organic materials has recently been highlighted.¹ Indeed, the synthetic procedures for the conception of organic semiconductors are essentially based on organometallic couplings or Wittig type reactions giving toxic byproducts. Moreover, the purification of polymers or small molecules often uses large amounts of solvent without ensuring the high level of purity required for semiconductors. The use of direct heteroarylation for the synthesis of conjugated systems is now well established and allows to decrease the environmental impact to do OSCs.² In this context, we have focused on the synthesis of new materials for OPV based on the dissymmetric 3-alkoxy-4-cyanothiophene building block³ by using green procedures. We present here the synthesis of donor – acceptor (D-A) and D-A-D derivatives⁴ and the studies of their electronic properties.

Dissymmetric block

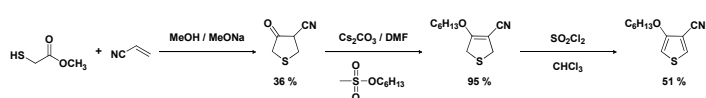


Green Approach for OPV

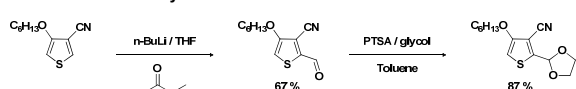


Synthesis of Precursors

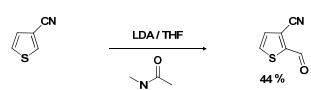
Dissymmetric block



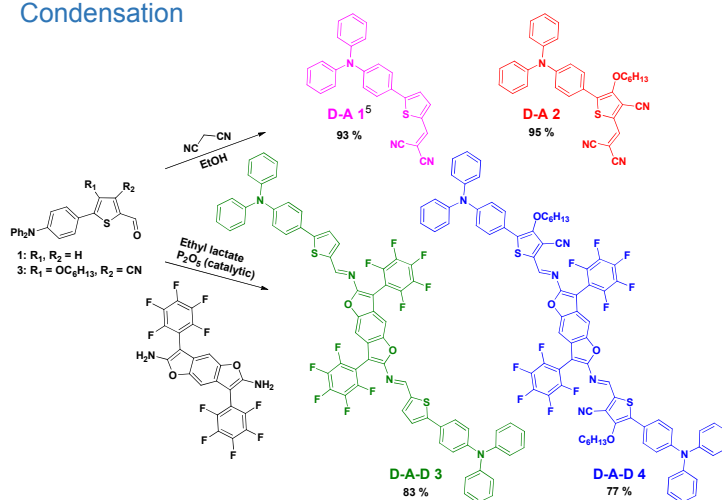
Functionalization of Dissymmetric block



Functionalization of 3-cyano-thiophene

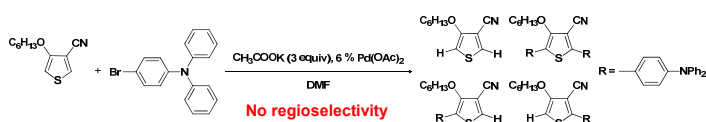


Condensation

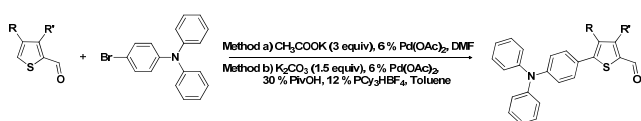


Direct Heteroarylation

Direct Arylation on Dissymmetric block

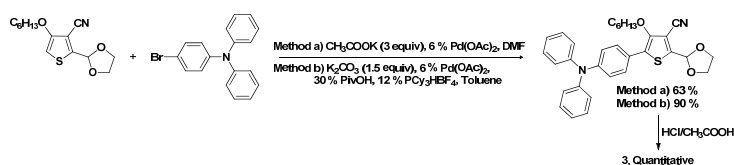


Direct Arylation with 4-bromotriphenylamine

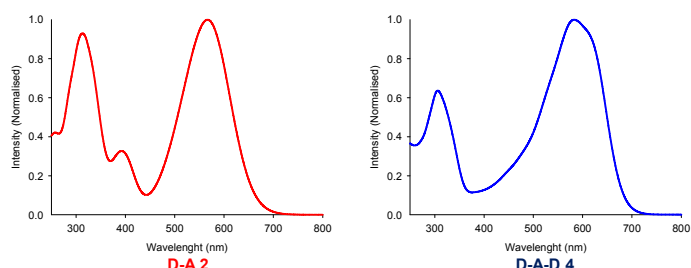


Substrate	Product	Yield
		Method a) 28% Method b) 92%
		Method a) 12% Method b) 93%
	Aldehyde degradation	

Direct Arylation with 4-bromotriphenylamine on Protect Aldehyde



Optical Spectroscopy



Compound	λ_{max} (nm)	ϵ (M ⁻¹ .cm ⁻¹)	ΔE^{opt} (eV)
D-A 1 ⁵	501	33900	2.47
D-A 2	567	27 700	2.19
D-A-D 3	536	82 400	2.32
D-A-D 4	582	85 200	2.14

UV – Visible Spectra of compounds D-A 2 4.10⁻⁵ M and D-A-D 4 1.10⁻⁵ M in CH₂Cl₂

Conclusion - Outlook

- We synthesized a new series of D-A and D-A-D materials by following a green approach: direct heteroarylation and condensation.
- The effect of cyano group on building block shows a GAP diminution.
- The optical and electrochemical properties suggest a possible application as donor semiconductors in organic solar cells.

Bibliography

- (a) Burke, D. J.; Lipomi, D. J. *Energy Environ. Sci.* **2013**, 6, 2053; (b) Osedach, T. P.; Andrew, T. L.; Bulovic, V. *Energy Environ. Sci.* **2013**, 6, 711.
- (a) Schipper, D. J.; Fagnou, K. *Chem. Mater.* **2011**, 23, 1594; (b) Mercier, L. G.; Leclerc, M. *Acc. Chem. Res.* **2013**, 46, 1597.
- Hergu n, N.; Mallet, C.; Savitha, G.; Allain, M.; Fr re, P.; Roncali, J. *Org. Lett.* **2011**, 13, 1762.
- (a) Leli ge, A.; Grolleau, J.; Allain, M.; Blanchard, P.; Demeter, D.; Rousseau, T.; Roncali, J. *Chem. Eur. J.* **2013**, 19, 9948; (b) Moussalem, C.; Gohier, F.; Mallet, C.; Allain, M.; Fr re, P. *Tetrahedron* **2012**, 68, 8617; (c) Moussalem, C.; Segut, O.; Gohier, F.; Allain, M.; Fr re, P. *ACS Sustainable Chem. Eng.* **2014**, 2, 1043.
- Leli ge, A.; Regent, C.-H. L.; Allain, M.; Blanchard, P.; Roncali, J. *Chem. Commun.* **2012**, 48, 8907.