

# Synthesis of Poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT) in a Direct Arylation Scheme

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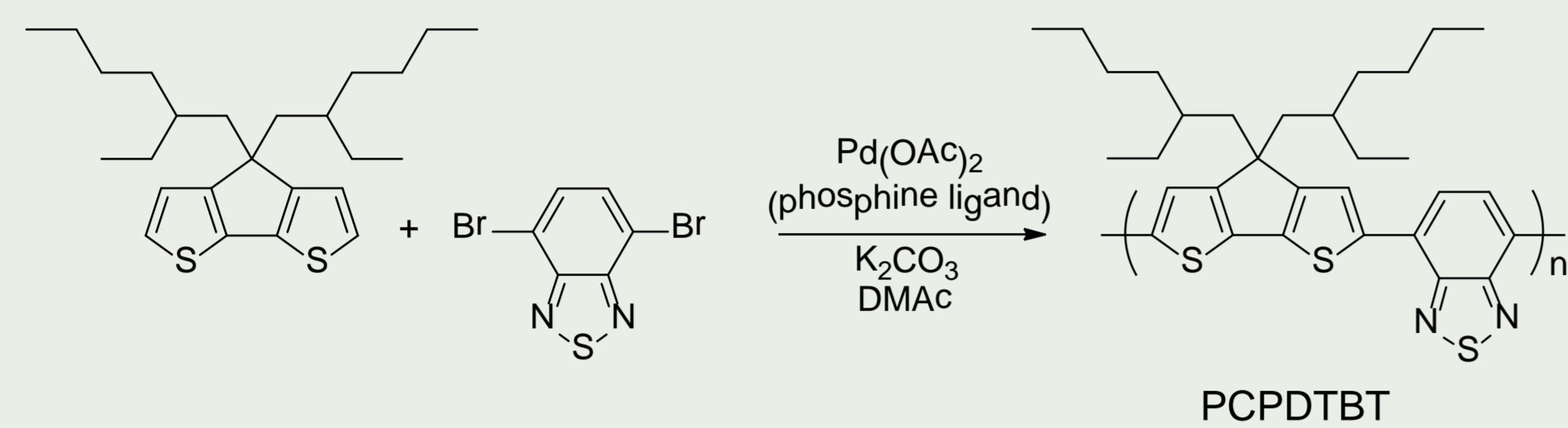
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## Introduction

Recently, direct (hetero)arylation polycondensation (DAP) has attracted increasing interest in the field of conjugated polymer synthesis. DAP allows the formation of aryl-aryl bonds between one unsubstituted and one dihaloarylene monomer without use of organometallic intermediates as arylboronic esters, aryl stannanes or Grignard-compounds. Here we present the first synthesis of poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT) in a DAP scheme starting from 4,4-di(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (CPDT) and 4,7-dibromo-2,1,3-benzothiadiazole as monomers.<sup>[1]</sup>

## Synthesis of PCPDTBT



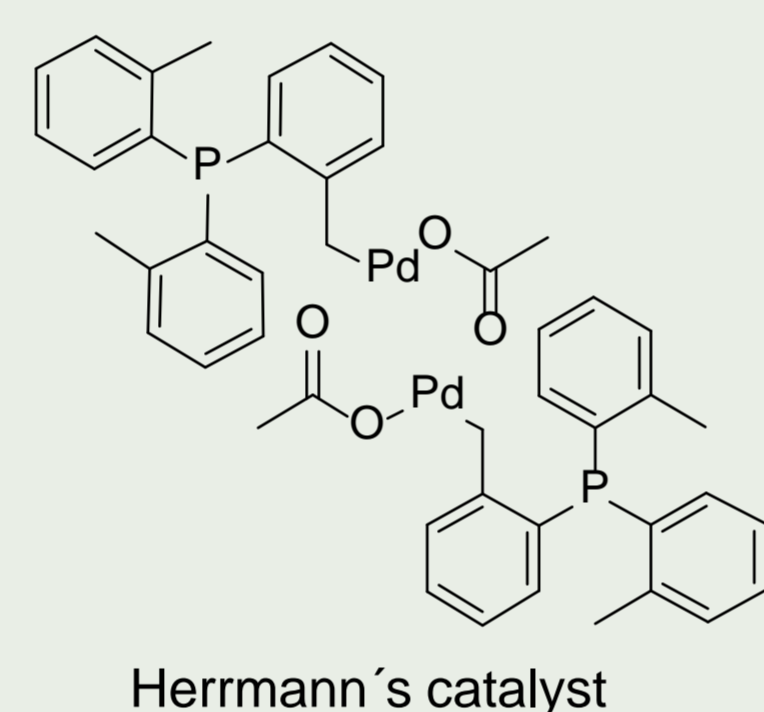
Summary of polycondensation reactions<sup>a</sup>:

entry	Pd(OAc) <sub>2</sub> (mol %)	PCy <sub>3</sub> -HBF <sub>4</sub> (mol %)	solvent	time (h)	M <sub>n</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>	yield (%)
P1	4	8	DMAc	72	24600	3.91	80
P2	4	8	toluene	72	2400	1.56	12
P3	2	4	DMAc	72	22000	3.26	68
P4	4	none	DMAc	72	36800	3.28	42
P5	4	8	DMAc	24	19700	2.78	61
P6	4	none	DMAc	24	40300	3.48	70

<sup>a</sup> Reactions were carried out at 110 °C using Pd(OAc)<sub>2</sub> as catalyst, PCy<sub>3</sub>-HBF<sub>4</sub> as ligand and K<sub>2</sub>CO<sub>3</sub> (1.5 equiv.) as base in DMAc (10 ml). <sup>b</sup> Estimated by gel permeation chromatography (GPC) with polystyrene calibration. <sup>c</sup> The yield is based on the amounts of high molecular weight dichloromethane and chloroform fractions after solvent extraction.

Catalyst screening<sup>d</sup>:

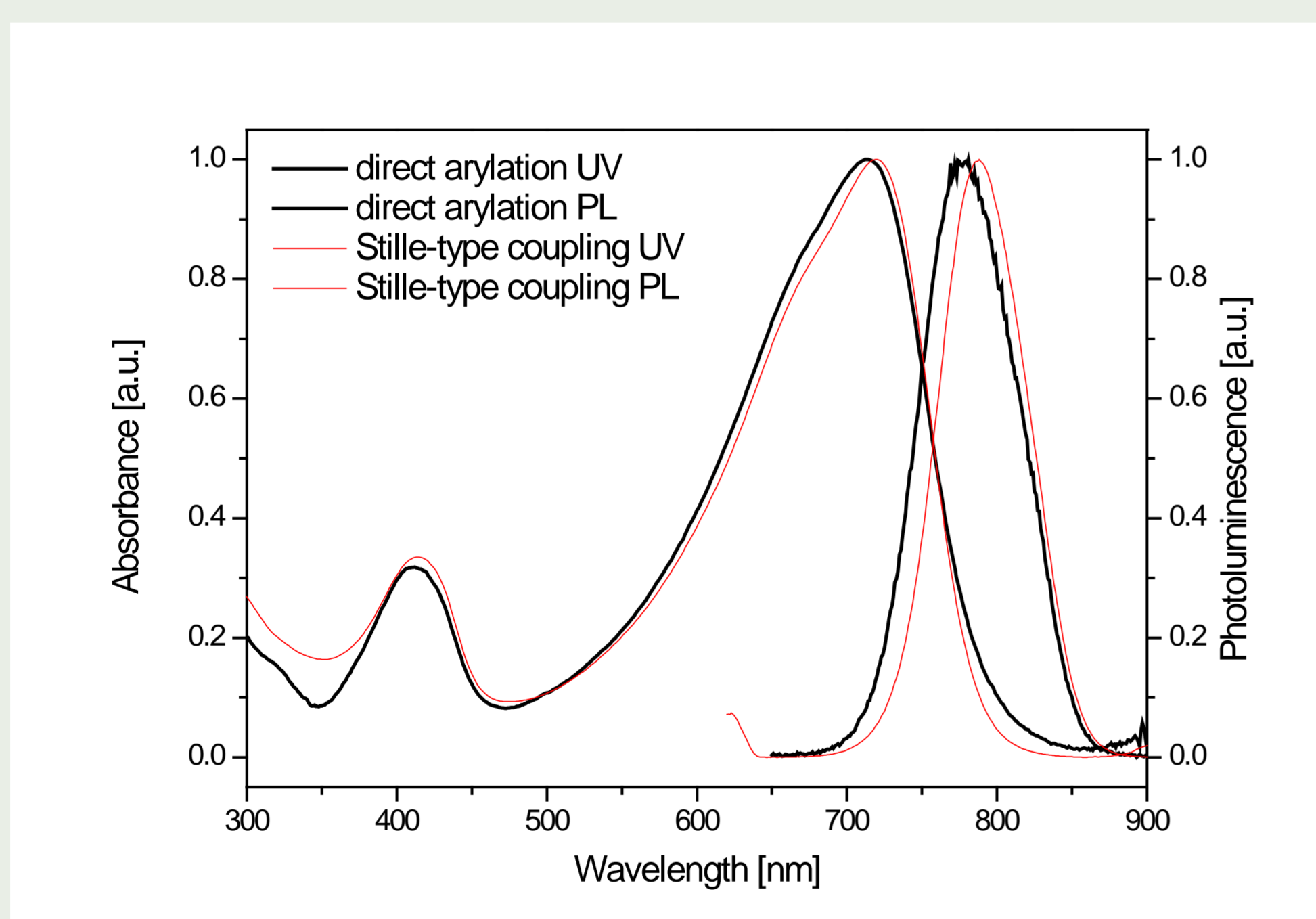
catalyst	time (h)	M <sub>n</sub> [g/mol]	yield (%)
Pd(OAc) <sub>2</sub>	24	40300	70
Pd(dba) <sub>2</sub>	72	-	0
Pd <sub>2</sub> (dba) <sub>3</sub> -CHCl <sub>3</sub>	72	-	0
Herrmann's cat.	72	19100	75



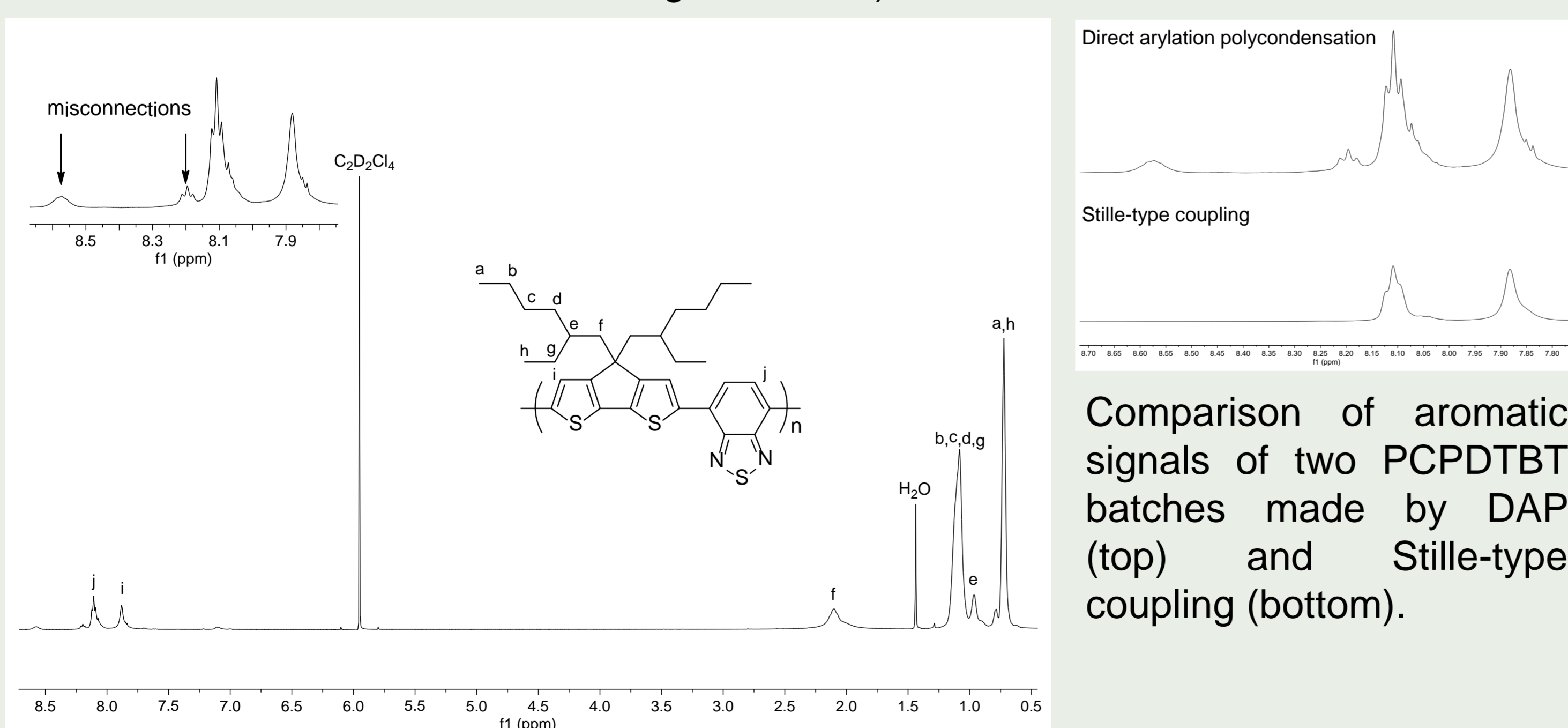
<sup>d</sup> Reactions were carried out at 110 °C using 4 mol % catalyst and 1.5 equiv. K<sub>2</sub>CO<sub>3</sub> as base in DMAc.

## Properties of PCPDTBT

The UV/Vis and PL spectra of PCPDTBT made by DAP and in a standard Stille-type coupling show a slight blue shift for the DAP product, probably caused by misconnections of CPDT units in 3- or 6-position (as indicated by NMR spectroscopy).



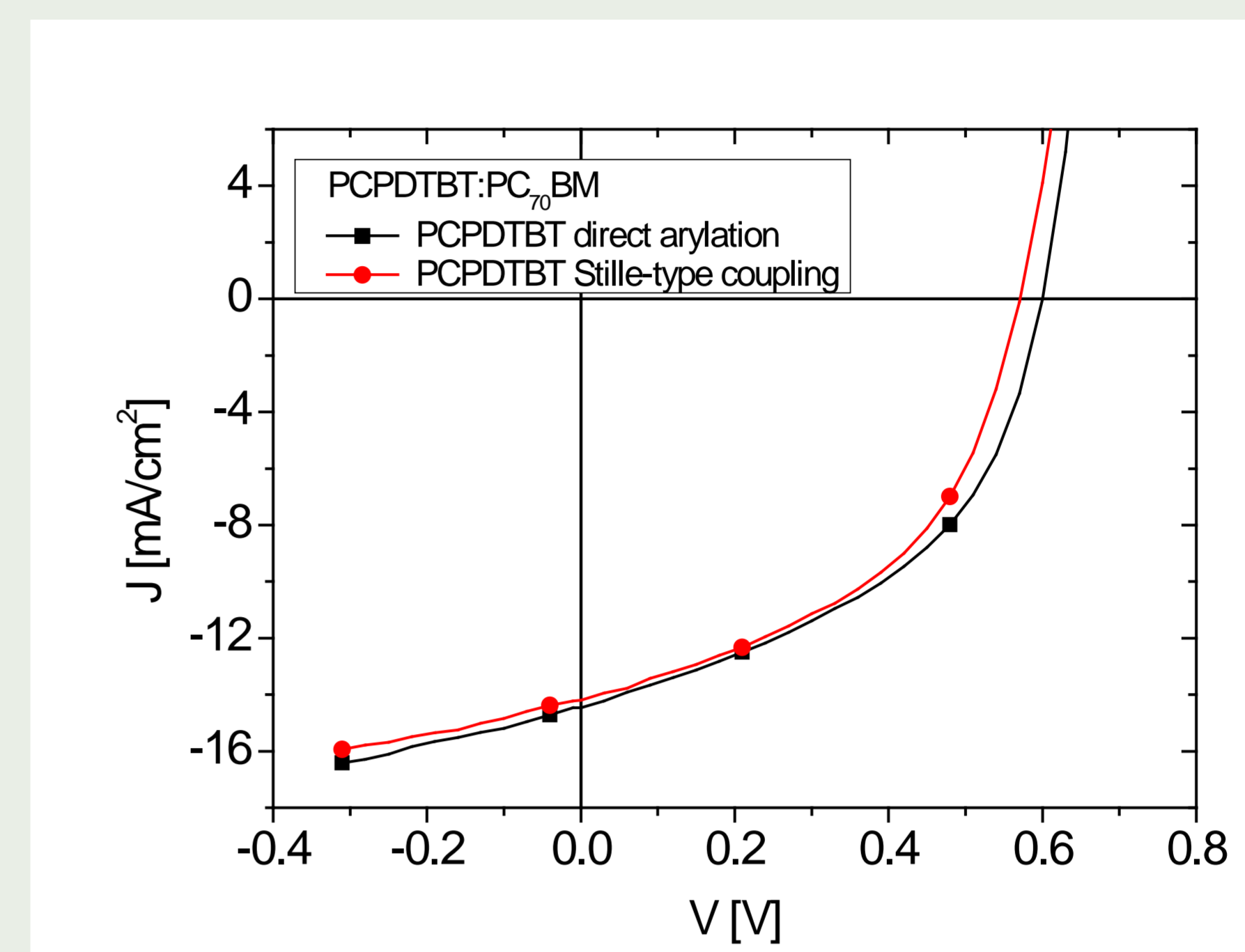
UV/Vis and PL spectra of two PCPDTBT batches made by DAP or Stille-type coupling (solvent: chloroform, excitation wavelength: 620 nm).



Comparison of aromatic signals of two PCPDTBT batches made by DAP (top) and Stille-type coupling (bottom).

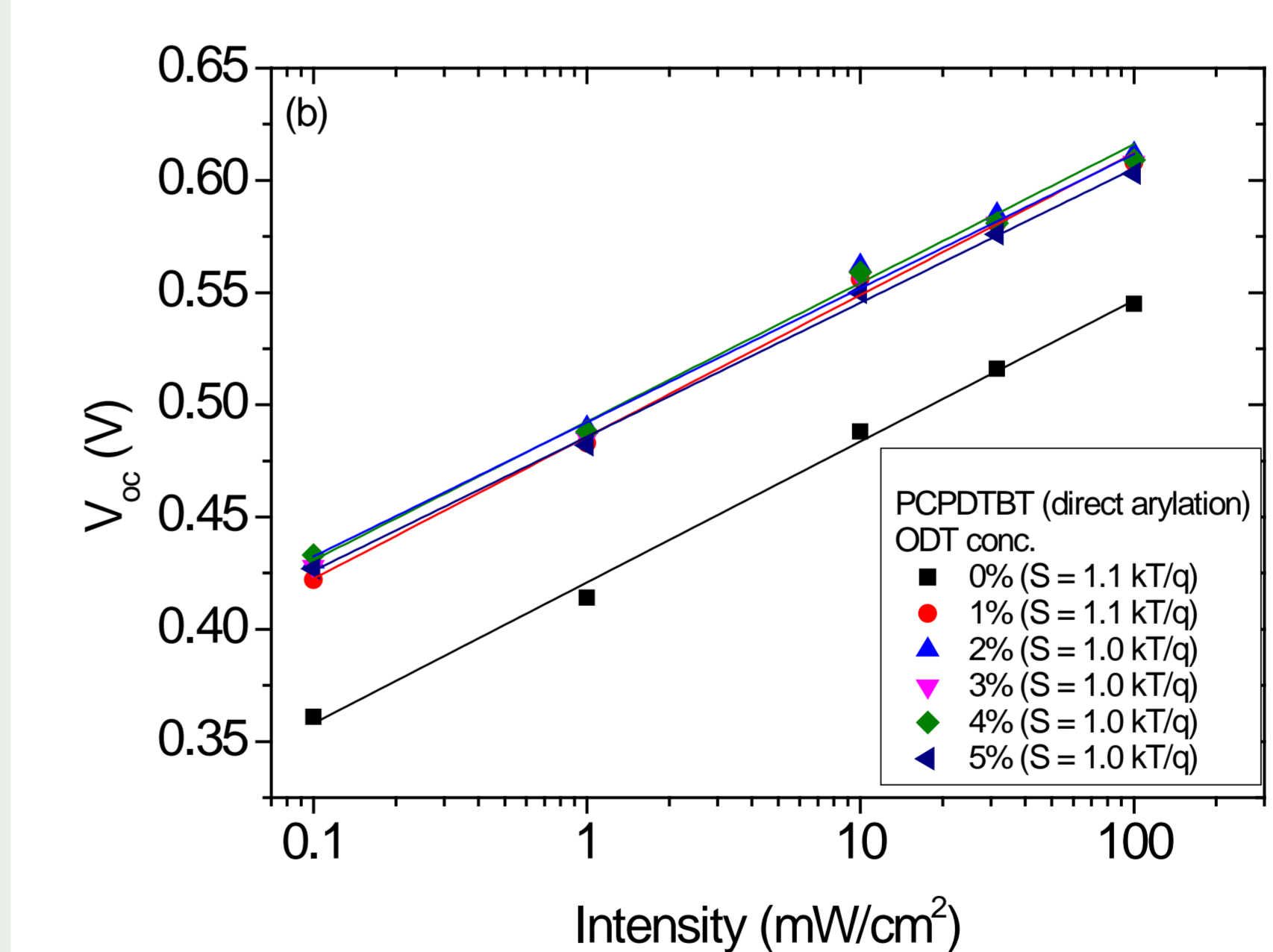
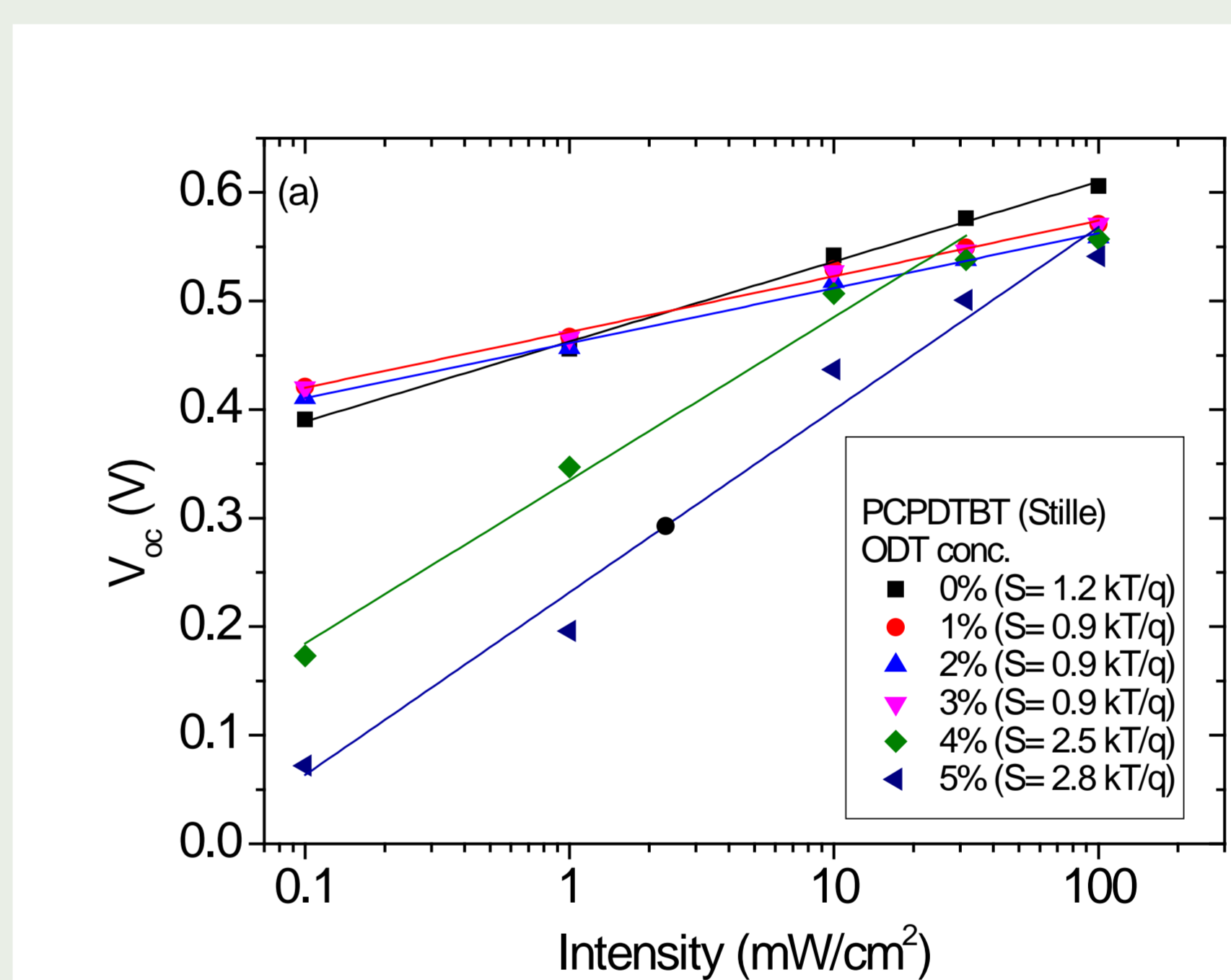
<sup>1</sup>H-NMR spectrum of PCPDTBT made by direct arylation polycondensation (600 MHz, in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80 °C).

## Device characteristics of inverted bulk heterojunction organic solar cells (OSCs):



J/V-characteristics of inverted OSCs with PCPDTBT as donor and PC<sub>70</sub>BM as acceptor (solvent: chlorobenzene, processing additive: octane-1,8-dithiol).

PCPDTBT:PC <sub>70</sub> BM - inverted OSCs	PCE [%]	V <sub>oc</sub> [%]	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	FF [%]
PCPDTBT - Stille-type	3.8	0.57	14.2	46.6
PCPDTBT - direct arylation	4.0	0.60	14.5	45.9



V<sub>oc</sub> vs. logarithmic illumination ln(I) intensity of inverted OSCs based on PCPDTBT/PC<sub>70</sub>BM prepared by (a) Stille-type coupling and (b) by DAP. The slope S of V<sub>oc</sub> vs. ln(I) is close to kT/q indicating the absence of trap assisted recombination due to impurities or defects.<sup>[2-4]</sup> Only for increased amounts of processing additive ODT OSCs based on Stille-type PCPDTBT show an increased S value.

## Conclusion:

Direct arylation polycondensation is a new and efficient method for high molecular weight PCPDTBT synthesis including low catalyst loadings, less reaction steps (green chemistry), and without use of expensive or toxic boronic acids/esters or stannyl compounds.

[1] S. Kowalski, S. Allard, U. Scherf, *ACS Macro Lett.* **2012**, *1*, 465-468.

[2] S.R. Cowan, W. L. Leong, N. Banerji, G. Dennler, A. J. Heeger, *Adv. Funct. Mater.* **2011**, *21*, 3083-3092.

[3] L. J. A. Koster, V. D. Mihailetschi, R. Ramaker, P. W. M. Blom, *Appl. Phys. Lett.* **2005**, *86*, 123509.

[4] M. M. Mandoc, F. B. Kooistra, J. C. Hummelen, B. de Boer, P. W. M. Blom, *Appl. Phys. Lett.* **2007**, *91*, 263505.