New Core-Extended Naphthalene Diimide (NDI)-based Polymers

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Abstract

Napthalene diimide (**NDI**)-based materials are among the most-studied imide-containing semiconductors for high-performance applications.[1] For example, the group of A. Facchetti synthesized the core-linked **P(NDI2OD-T2)** (figure 1) that showed very high electron mobilities (up to ~0.85 $cm^2 V^{-1} s^{-1}$) in polymer-based thin film transistors.[2] In addition, there is interest in polymers and alternating copolymers based on so-called core-extended **NDI**s, in which, for example, aromatic or heteroaromatic rings (like thiophene) are annelated to the **NDI** core (e.a. **P(NDTI2DT-T2)**, figure 1). Such **NDTI**-related materials show a very rigid and planar structure and have been used as *n*-channel, *p*-channel, or ambipolar semiconductors.[3] Additionally, **P(NDTI2DT-T2)**, for example, shows an intense absorption band in the near-infrared (NIR) region that makes it promising for NIR-luminescent devices. Suraru *et al.* first synthesized the core-extended carbazole[2,3-*b*]carbazole-6,7:13,14-tetracarboxylic acid diimide (**CCDI**) analogon (figure 2).[4] Monomeric *N*-diisopropylphenyl substituted **CCDI** showed *p*- or *n*-type charge transfer behavior, depending on the transistor architecture. We have now synthesized a series of **CCDI** based polymers and alternating copolymers (figure 2) and investigated their electronic and optical properties such as the absorption behavior in solution and in the solid state. Additionally, we estimated their HOMO-energy levels by atmospheric pressure photoelectron spectroscopy.

Core-linked and Core-extended NDIs[1,2]

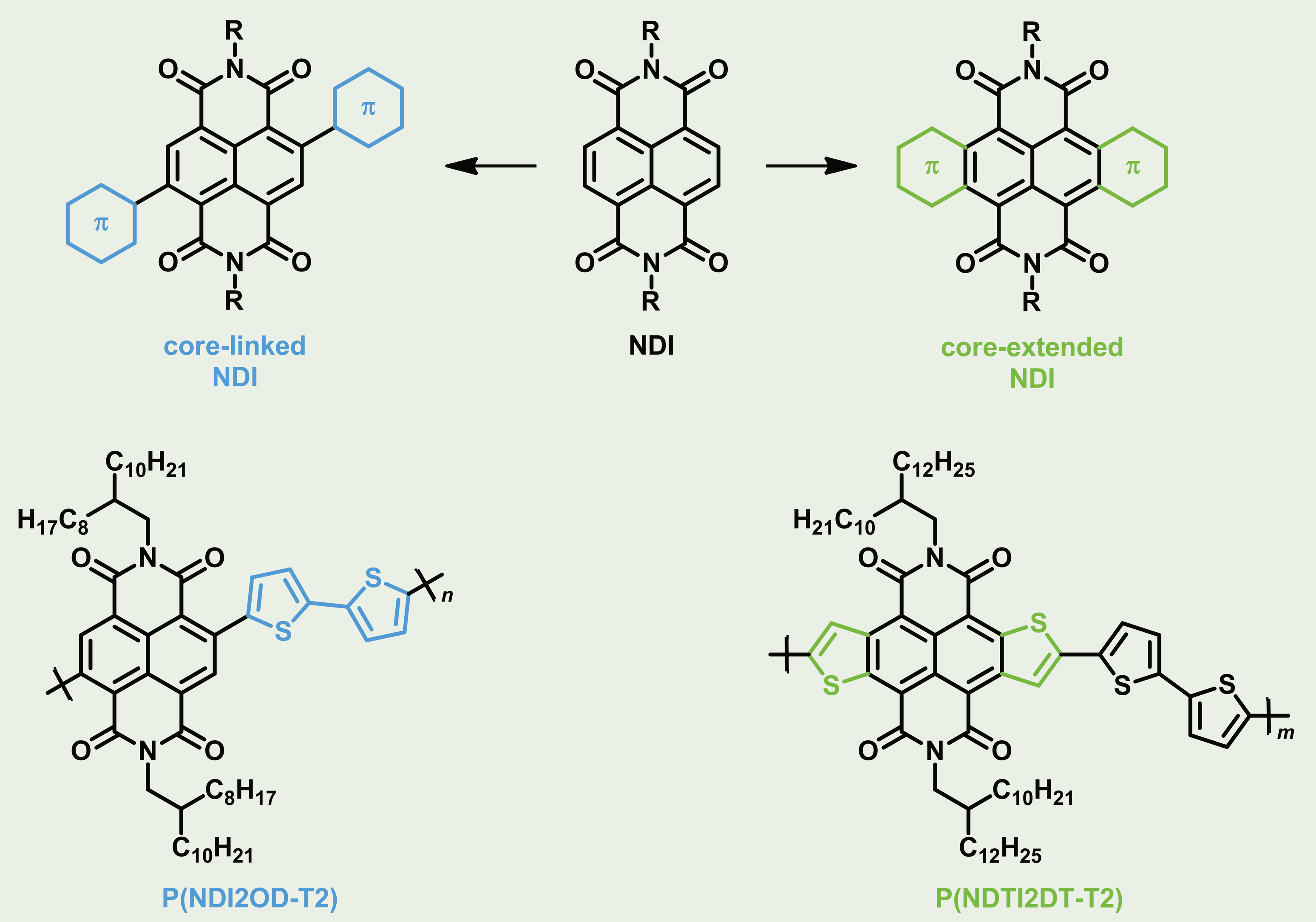


Figure 1 Examples of core-linked and core-extended **NDI**-based polymers.

CCDI-based Core-extended NDIs

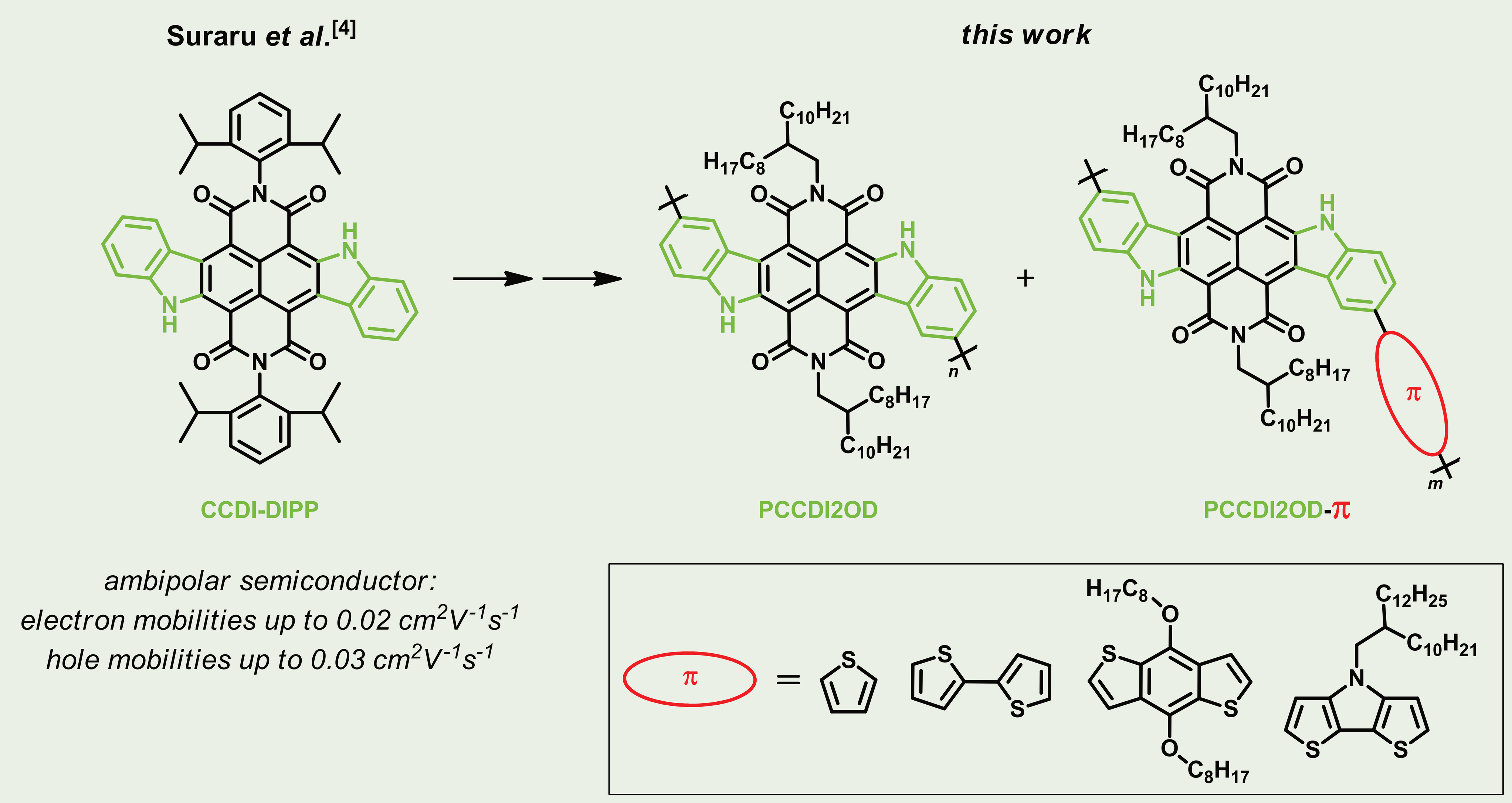


Figure 2 Structures of **CCDI-DIPP** and the **CCDI**-based polymers in this work.

Synthesis of the CCDI-based Monomer[4,5]

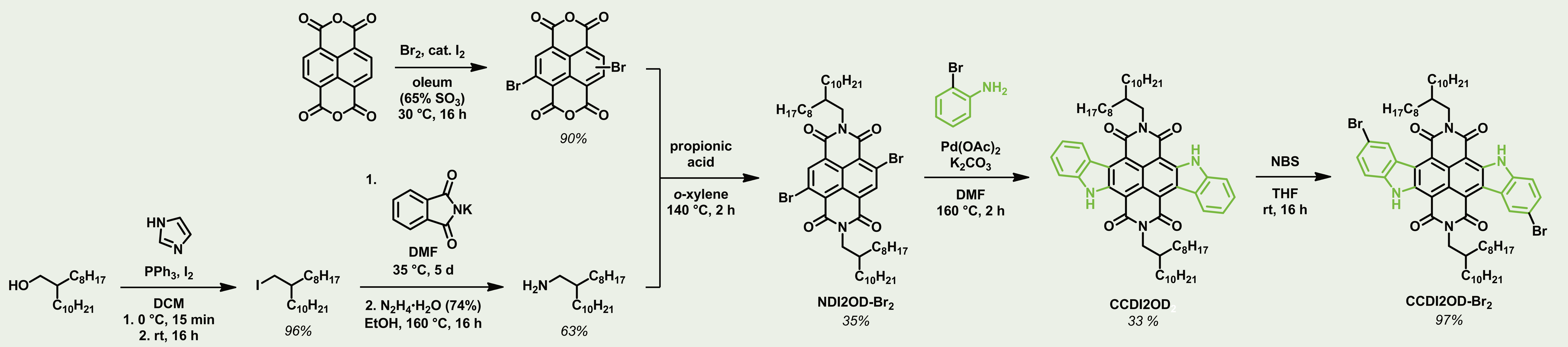
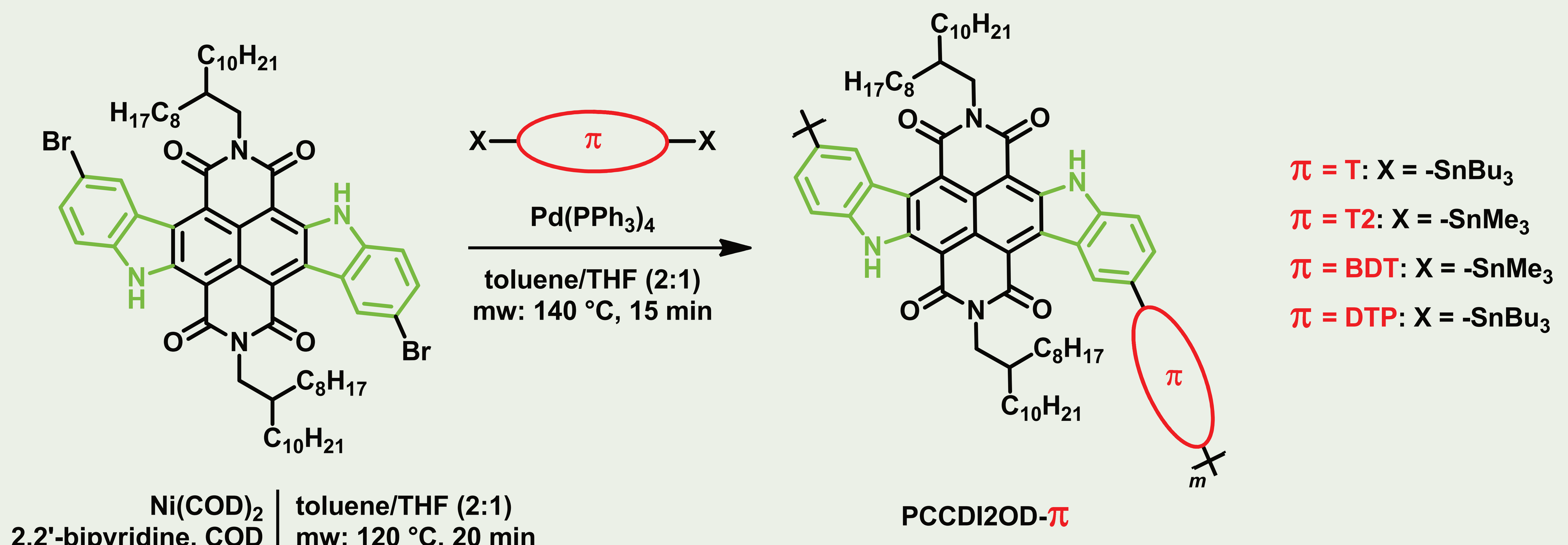
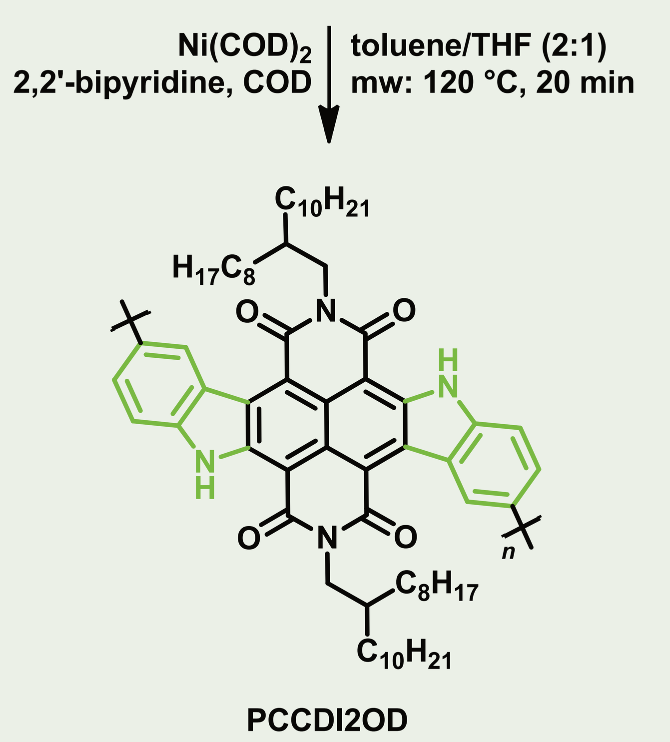


Figure 3 Synthesis of the **CCDI**-based dibromo monomer starting from commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride and 2-octyldodecan-1-ol.

Synthesis of a CCDI-based Homopolymer and CCDI-based Alternating Copolymers





	fraction (yiel [%])	M_n/ M_w[a] [g/mol]	PDI[b] (M_w:M_n)	HOMO[c]/ LUMO[d] [eV]	E_g [eV]
PCCDI2OD	CB (58)	22000/ 81000	3.7	-5.45/ -3.68	1.78
PCCDI2OD-T	DCM (64)	2400/ 4600	1.9	-5.28/ -3.56	1.72
PCCDI2OD-T2	$CHCl_3$ (20)	2100/ 3300	1.6	-5.21/ -3.50	1.71
PCCDI2OD-BDT	$CHCl_3$ (44)	5900/ 27300	4.6	-5.31/ -3.55	1.76
PCCDI2OD-DTP	DCM (37)	5200/ 12900	2.5	-5.16/ --	--

[a] due to solubility and aggregation problems the molecular weights were calculated using GPC at 135 °C and trichlorobenzene as eluent
[b] PDI = polydispersity index
[c] HOMO = highest occupied molecular orbital: estimated by atmospheric pressure photoelectron spectroscopy
[d] LUMO = lowest unoccupied molecular orbital: calculated from the estimated HOMO the optical bandgap E_g

Figure 4 Synthesis of the **CCDI**-based polymers; molecular weights and electronic properties are summerized in the table; with: mw = microwave, **T** = thiophene, **T2** = bithiophene, **BDT** = benzodithiophene, **DTP** = dithienopyrrole.

Optical Spectra of CCDI-based Polymers

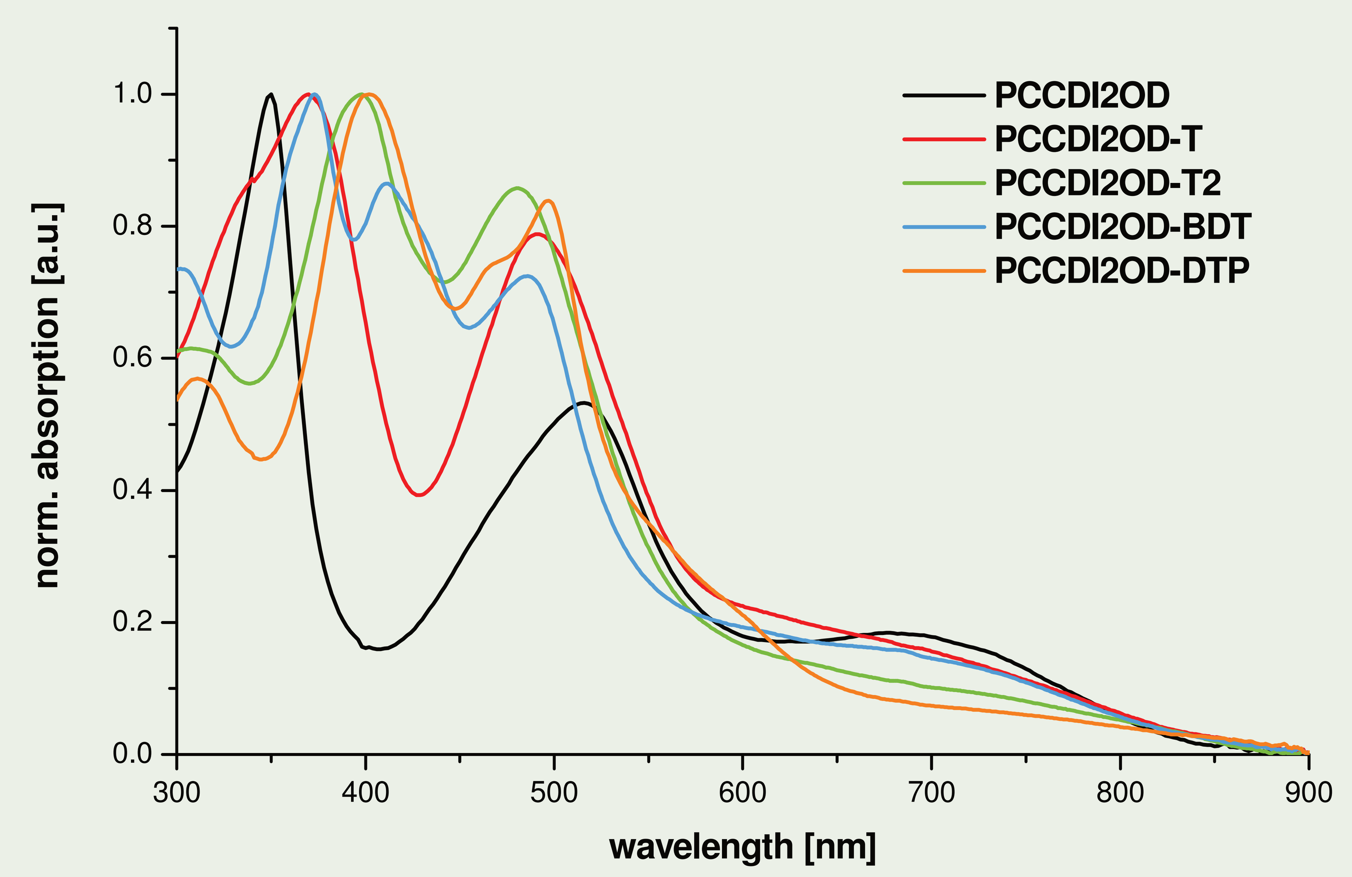


Figure 5 Normalized UV/Vis spectra of the **CCDI**-based polymers in solid state.

Conclusion and Outlook

- successful synthesis of new **CCDI**-based polymers
- further investigations of electron and hole mobilities in thin film transistors
- possible application of **PCCDI** as acceptor or donor material in organic solar cells

References

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