Synthesis of π-Expanded, Diketopyrrolopyrrole-Based Conjugated Polymers

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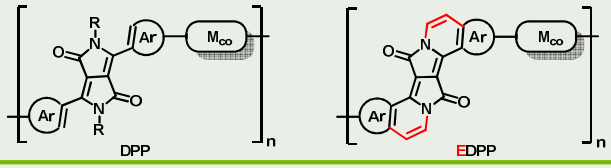
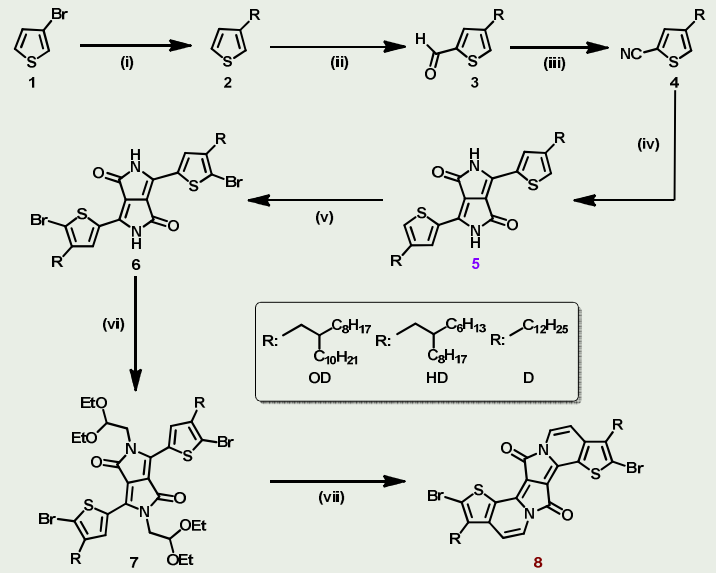
Introduction:

Due to their superb properties, diketopyrrolopyrrole (DPP)-containing copolymers are currently one of the most widely used donor materials for the active layer of high efficiency organic photovoltaic devices (OPV).[1] The implementation of an additional vinylene bridge between aromatic substituents and amide nitrogens of the DPP unit leads to a π-expanded diketopyrrolopyrrole chromophore (EDPP) with unique optical properties.[2] Moreover the EDPP unit can be used for the formation of new conjugated donor-acceptor-type ladder polymers (cLPs).[3]

General Structure of DPP and EDPP Copolymers



Synthetic Pathway to EDPP-T

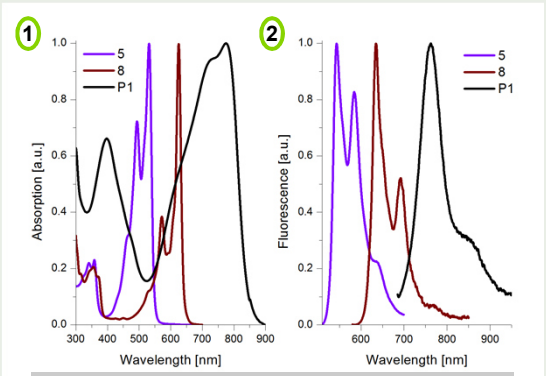


(i) I-R, Mn, $CoBr_2$, (*p*-tolyl)$_3$P, TFA , DMAc, Py, 70 °C **(ii)** LDA, DMF, THF, -78 °C **(iii)** $NH_{3\,(aq)}$, I_2, THF **(iv)** DIPS, Na, $FeCl_3$ *tert*-Amyl alcohol,110 °C **(v)** NBS, TFA, $CHCl_3$ **(vi)** Bromoacetal, K_2CO_3, DMF, 120 °C **(vii)** TFSA, $CHCl_3$, 60 °C

Comparison of the Optical Properties of 5,8 and P1

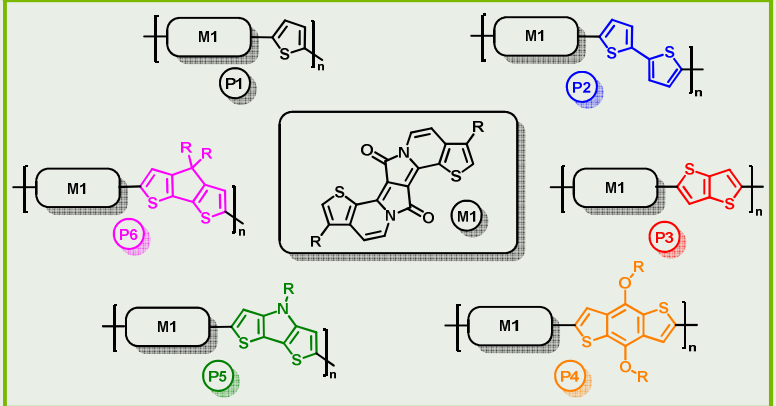
From left to right: saturated solutions of 5,8 and P1 in Chloroform

From left to right: saturated solutions of 5,8 and P1 in Chloroform, in the dark, excited at 380 nm



1. Normalized absorption spectra of 5,8 and P1 in chloroform.
2. Normalized photoluminescence spectra of 5,8 and P1 in chloroform

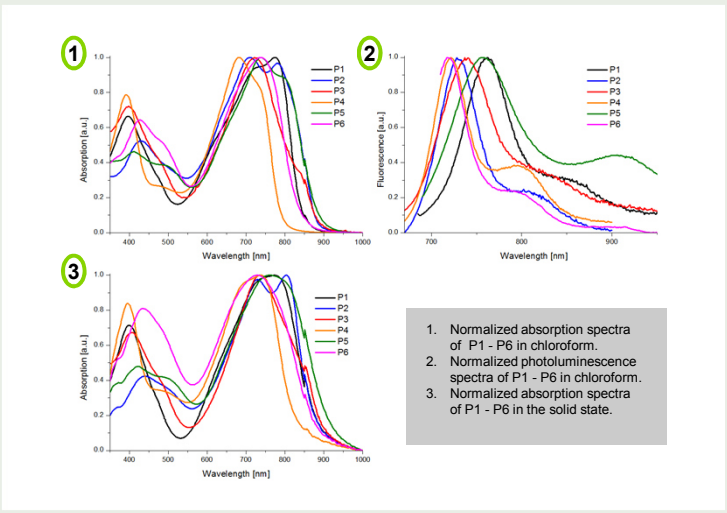
Novel EDPP-Based Donor-Acceptor-Type Copolymers



Molecular Weight,Optical and Electronical Properties of the Copolymers

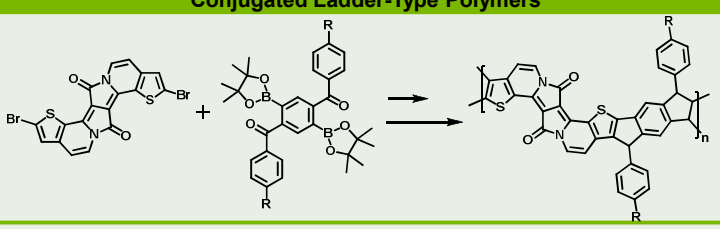
	R	Mn [kDa][a]	Mw [kDa][a]	PDI	HOMO [eV][b]	LUMO [eV][c]	Bandgap [eV][d]
P1	HD	23.1	49.6	2.1	-5.00	-3.31	1.69
P2	OD	14.6	30.0	2.1	-5.08	-3.35	1.73
P3	HD	10.4	18.2	1.8	-4.83	-3.18	1.65
P4	OD	23.3	63.5	2.7	-5.21	-3.40	1.81
P5	D	7.5	10.3	1.4	-5.18	-3.58	1.60
P6	D	9.6	87.7	9.1	-5,19	-3.47	1.72

[a]determined by GPC in THF.; [b]estimated by photoelectron spectroscopy with a photoelectron spectrometer AC-2.; [c]E_g^{opt} – optical HOMO (AC-2).; [d]calculated based on the onset of the absorption band in the solid state absorption spectrum by adding a correction factor of 0.3 eV for the exciton binding energy.



1. Normalized absorption spectra of P1 - P6 in chloroform.
2. Normalized photoluminescence spectra of P1 - P6 in chloroform.
3. Normalized absorption spectra of P1 - P6 in the solid state.

Outlook: Synthesis Scheme for the Generation of EDPP-Based, Conjugated Ladder-Type Polymers



Conclusion:

We have successfully synthesized six novel donor-acceptor-type copolymers containing the thiophene-based EDPP building block. All polymers show absorption and fluorescence features that are extended into the near infrared region with number average molecular weights of up to 23000. Also cLPs that contain EDPP units are promising for future work.

References:
[1] W. Li, K. H. Hendriks, M. M. Wienk, R. A. J. Janssen, *Acc. Chem. Res.*, **2015**, 49, 78 – 85.
[2] M. Grzybowski, E. Glodkowska-Mrowka. T. Stoklosa, D. T. Gryko, *Org. Lett.*, **2012**, 14 (11), 2670 – 2673.
[3] K.-J. Kass, M. Forster, U. Scherf, *Angew. Chem., Int. Ed.*, **2016**, 55, 7816–7820.