DA-type semiconducting Oligomers and Copolymers with NIR absorption for Optoelectronic Devices

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Introduction

Devices based on organic semiconducting polymers may enable compatibility with flexible substrates, large-area and low-cost production. Althought the solar spectrum covers a wavelenght range from ultraviolet to near-infrared (NIR), most of the reported components of bulk heterojunction type organic solar cells show a HOMO-LUMO gap ≥ 2.0 eV. For this reason, the resulting cells only able to harvest visible light, limiting the performance of polymer-based solar cells (PSCs). We present **five novel low band gap semiconducting donor-acceptor copolymers showing a broad absorption band that is extended up to 1200 nm.** The synthetic strategy uses suitable acceptor and donor building blocks, thus extending the absorption bands into the NIR. The copolymers show sufficient solubility for solution processing at room temperature.

Low Bandgap DA-type Copolymers via Stille Coupling Polycondensation

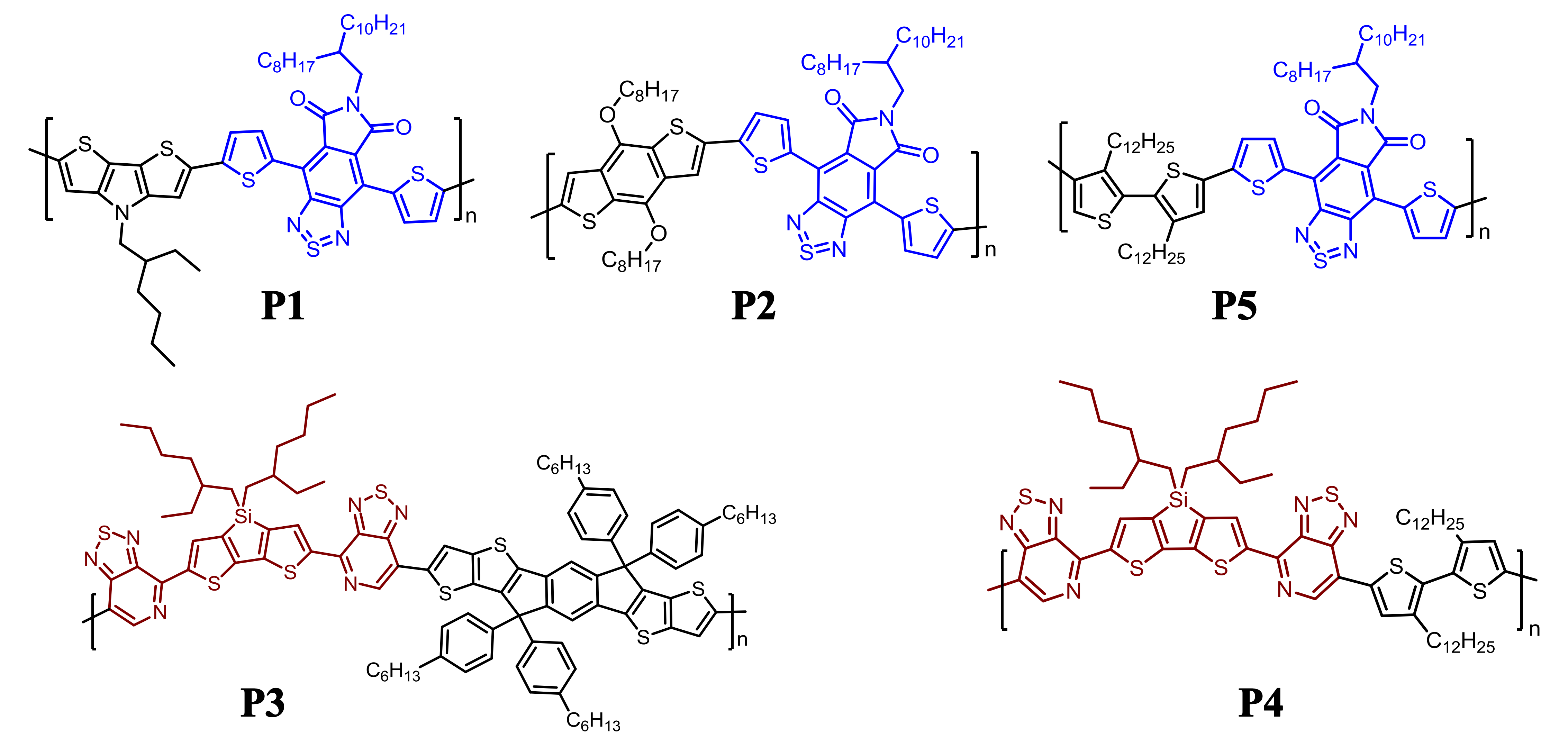


Figure 1: Chemical structures of the novel low bandgap DA-type copolymers

Absorption Spectra of the Copolymers

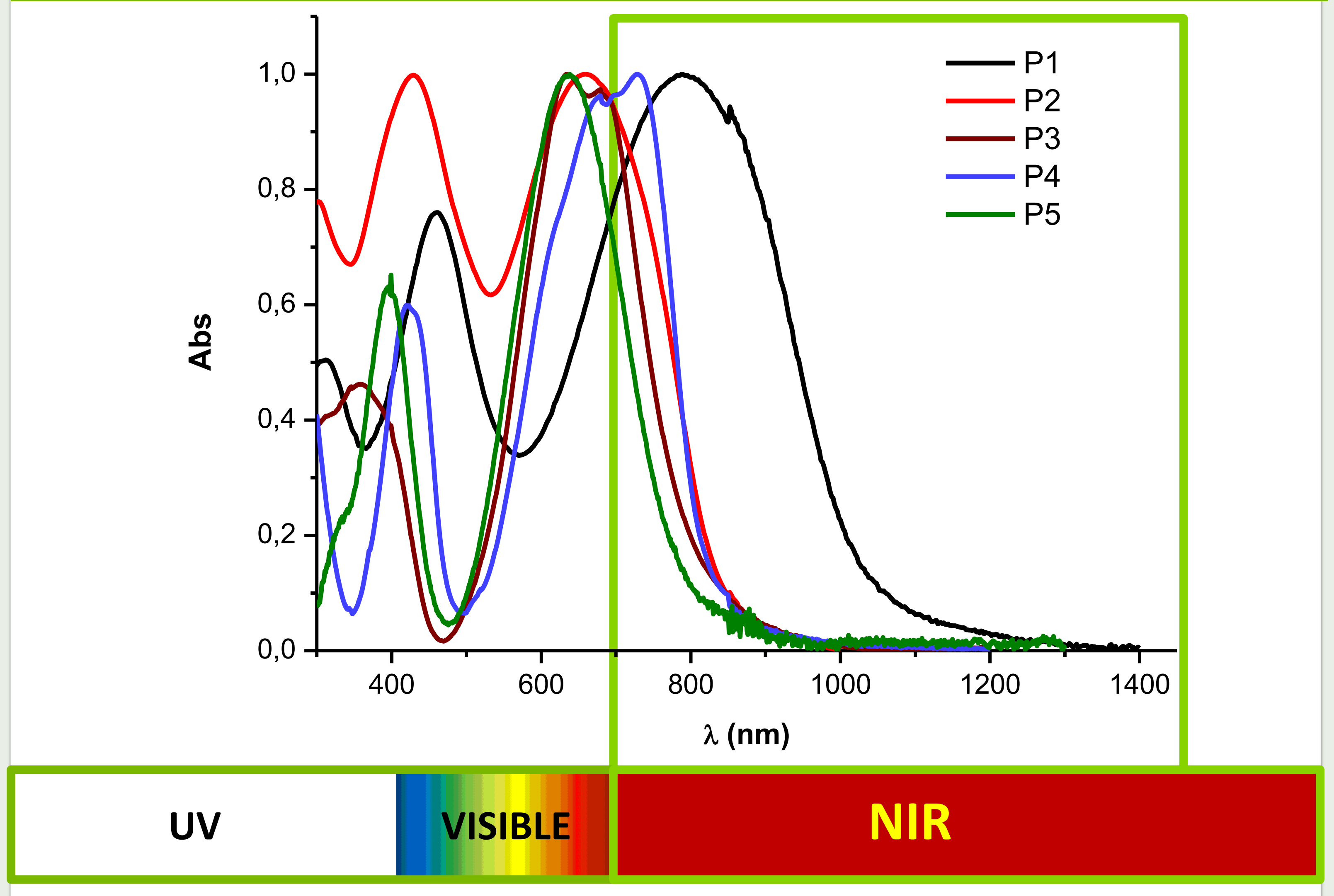


Figure 4: UV/Vis absorption spectra of P1-P5 in the solid state

Molecular Weight and Electronic Properties

	Mn[a] (g/mol)	Mw[a] (g/mol)	PDI	HOMO[b] (CV, eV)	LUMO[b] (CV, eV)	HOMO[c] (AC-2)	LUMO[d] (opt)	E_g^{elec} (eV)	$E_g^{opt,e}$ (eV)
P1	11400	21000	1.8	-5.44	-4.47	-4.85	-3.67	0.97	1.18
P2	18300	166000	9.0	-5.54	-4.15	-5.05	-3.59	1.39	1.46
P3	6800	9400	1.4	-5.44	-3.60	-5.33	-3.48	1.84	1.85
P4	36800	120600	3.3	-5.34	-3.71	-5.28	-3.41	1.63	1.87
P5	14400	20600	1.4	-5.51	-3.81	-5.28	-3.42	1.70	1.86

[a]determined by GPC, P1 and P4 in DCB at high temp., P2, P3 and P5 in $CHCl_3$ at rt.; [b]estimated by cyclic voltammetry, WE:Pt, solution 0.1M of TBAP in $CHCl_3$.; [c]determined by photoelectron spectroscopy with a photoelectron spectrometer AC-2.; [d]E_g^{opt} - optical HOMO (AC-2).; [e]calculated based on the onset of the absorption band in the solid state absorption spectrum by substracting a correction factor of 0.3 eV.

Table 1: Summary of optoelectronic properties

Photo- and Electroluminiscence, as well as PLEDs Performance of P2

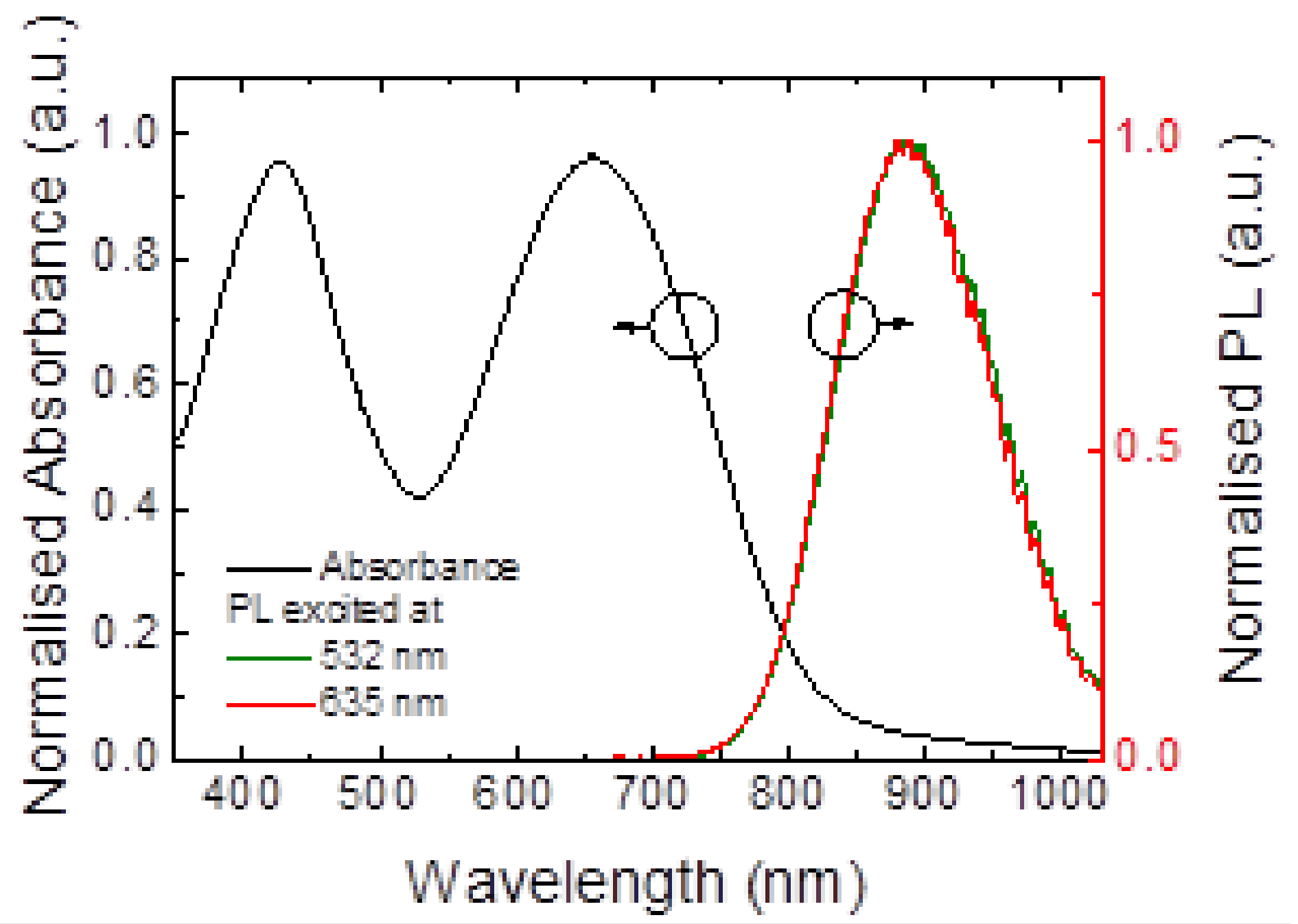


Figure 2: Normalised absorbance and PL spectra for the thin film of P2 with thickness ~100 nm.

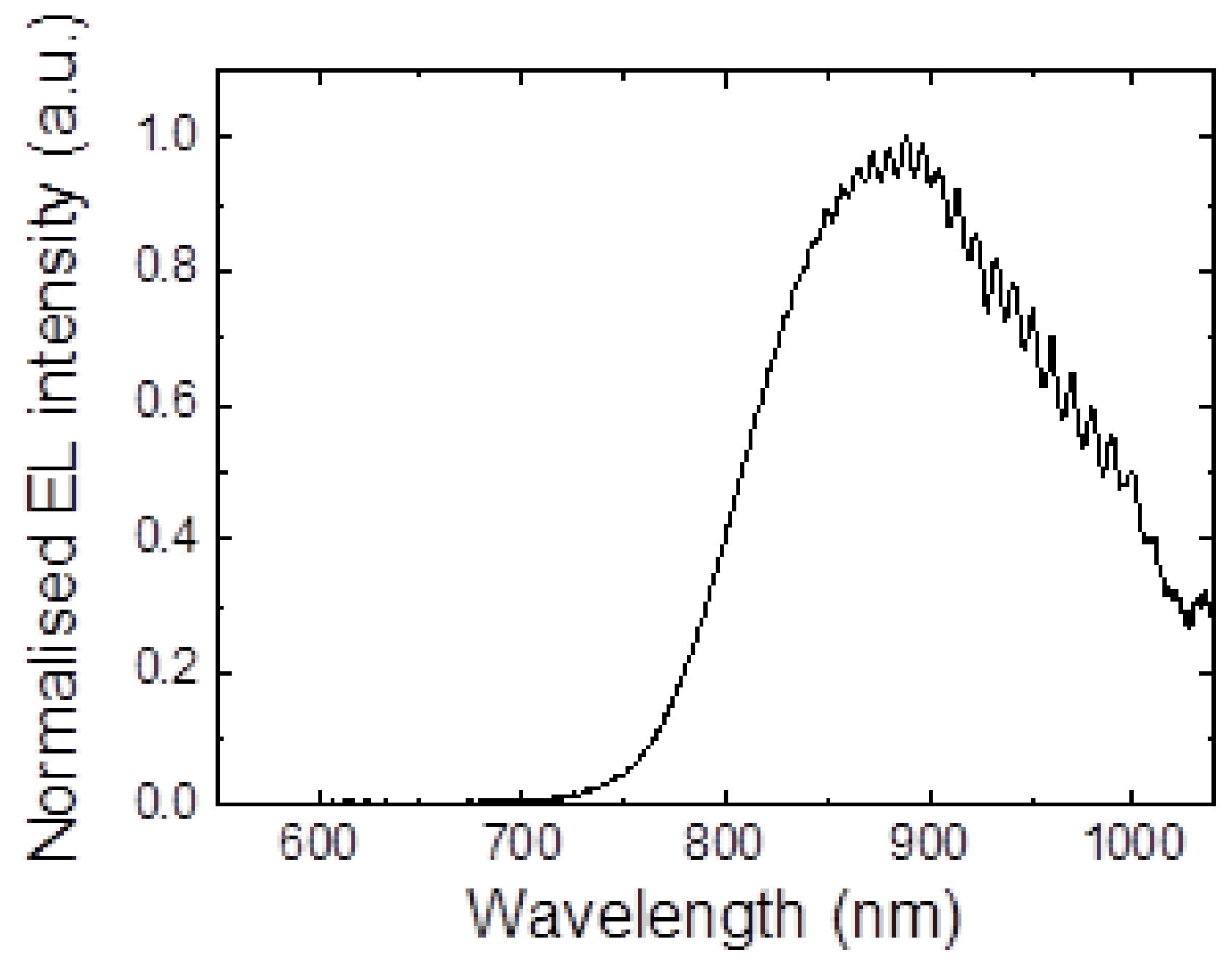
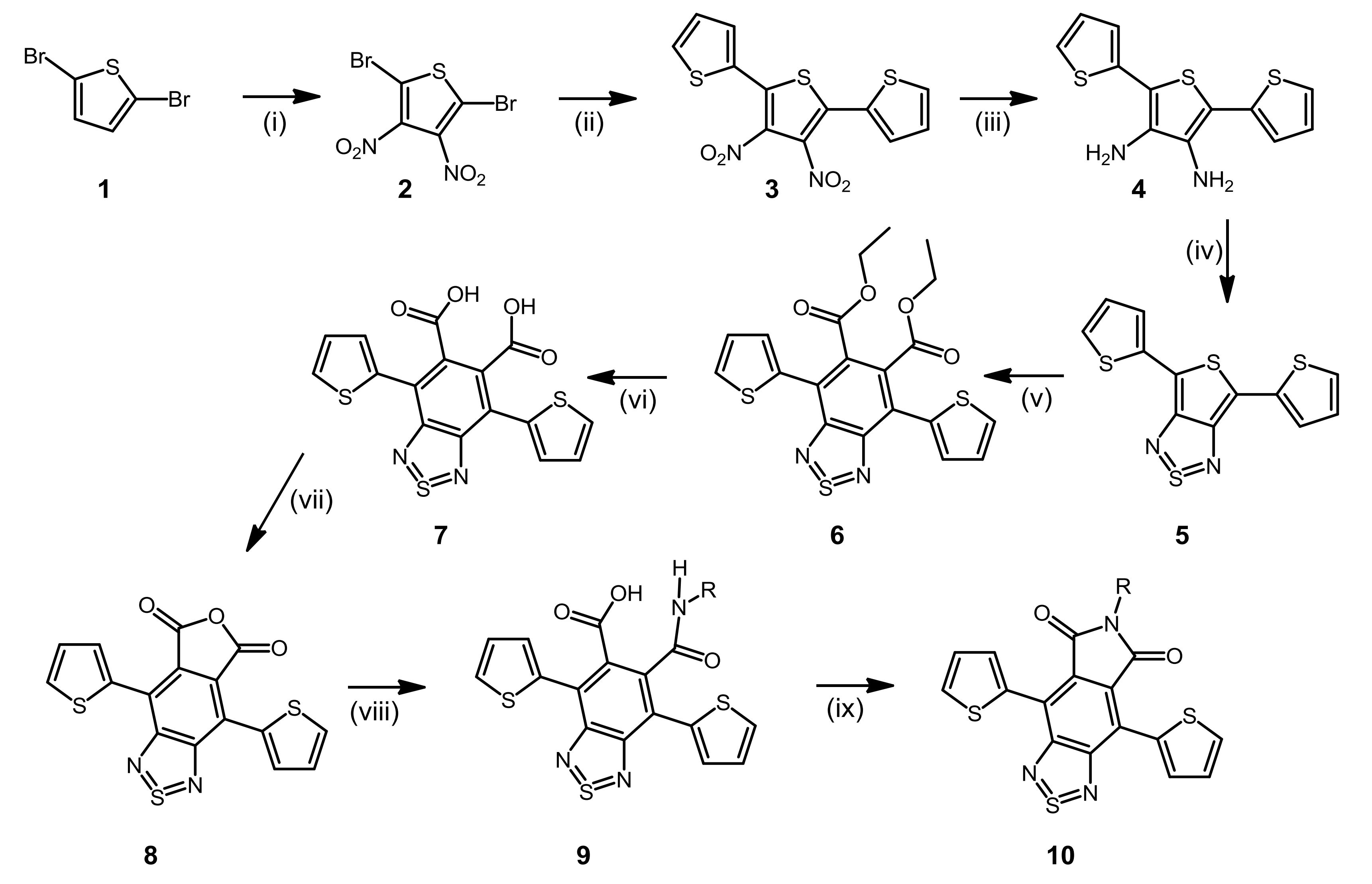


Figure 3: Electroluminescence (EL) spectrum of P2

Polymer	Max EQE (%)	V_{ON}[a] (V)	Radiance[b] (mW/m^2)	PL peak (nm)	EL peak (nm)
P2	0.039±0.007	1.3±0.2	415.2±205.7	880	870

Table 2: Summary of PLEDs performance (PLEDs with ITO/PEDOT:PSS anodes and Ca/Al cathodes). [1]
[a]Intercept of the radiance-voltage curve with the x-axis in a semi-log plot. [b]Measured at 5V.

Synthetic Example: Synthesis of Acceptor Building Block 10



(i) H_2SO_4, HNO_3, 0°C **(ii)** 2-(tributylstannyl)thiophen, DMF **(iii)** $SnCl_2 \cdot 2H_2O$, EtOH, H_2O **(iv)** chlorotrimethylsilan, thionylaniline, py **(v)** diethyl but-2-ynedioate, toluene **(vi)** NaOH, EtOH **(vii)** acetic anhydride, xylene, 130°C **(viii)** acetic acid, acetic anhydride, 100°C **(ix)** NBS, DMF

Scheme 1: Synthesis of N-alkyl-4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic imide

CONCLUSIONS

- Five novel low bandgap DA-type semiconducting copolymers presented
- The copolymers show broad absorption up to 1200 nm and NIR emission
- The presented copolymers are promising candidates for optoelectronic devices as NIR-emitting PLEDs

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References:(1) O. Fenwick et al., *Nano Letters* 11, *2451-2456*, **2011**. (2) Wang, L.; Cai, D.; Zheng, Q.; Tang, C.l; Chen, S-C.; Yin, Z. *ACS Macro Lett.* 2, *605−608*, **2013**.

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