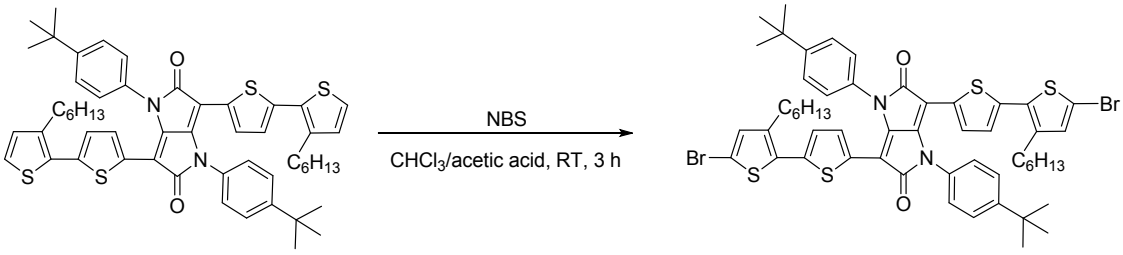
Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Electrochemical Polymerization of 1,3,4,6-Tetraarylpyrrolo[3,2-*b*]pyrrole-2,5-dione (IsoDPP) Derivatives

Irina Welterlich and Bernd Tieke*

Synthesis of M1'



M1 **M1'**

200 mg (1 eq, 0,22 mmol) **M1** were dissolved in 100 mL $CHCl_3$/AcOH (1:1 v/v), stirred at room temperature for 10 min, and cooled to 0 °C. Then 83 mg (2,1 eq, 0,46 mmol) NBS were added in small portions within 30 min. After stirring for 3 h the reaction was quenched with 20 mL water, and diluted with 30 mL DCM. Then the organic layer was washed once with 5 % aqueous $NaHCO_3$, and three times with saturated NaCl solution, and dried over $MgSO_4$. Then the solvent was removed under reduced pressure. The residue was purified upon precipitation from methanol. 201 mg (86 %) of a bordeaux-red powder of **M1'** were obtained.

m.p.: 260-262 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7,48-7,46 (d, l-4H); 7,28-7,26 (d, k-4H); 6,84 (s, h-2H); 6,68-6,67 (d, i-2H); 6,34-6,33 (d, j-2H); 2,63-2,54 (t, e-4H); 1,56 (m, d-4H); 1,35-1,27 (m, a,c-30H); 0,88 (t, b-6H).

Analysis for $C_{54}H_{58}Br_2N_2O_2S_4$ (1055.1 g/mol):calc.. C, 61,47; H, 5,54; N, 2,66; found:C, 61,68; H, 5,56; N, 2,62.**UV/Vis** [nm]: 333, 485 (DCM); 350, 524 (film). **PL** [nm]: 646 (DCM); λ_{exc} = 450.

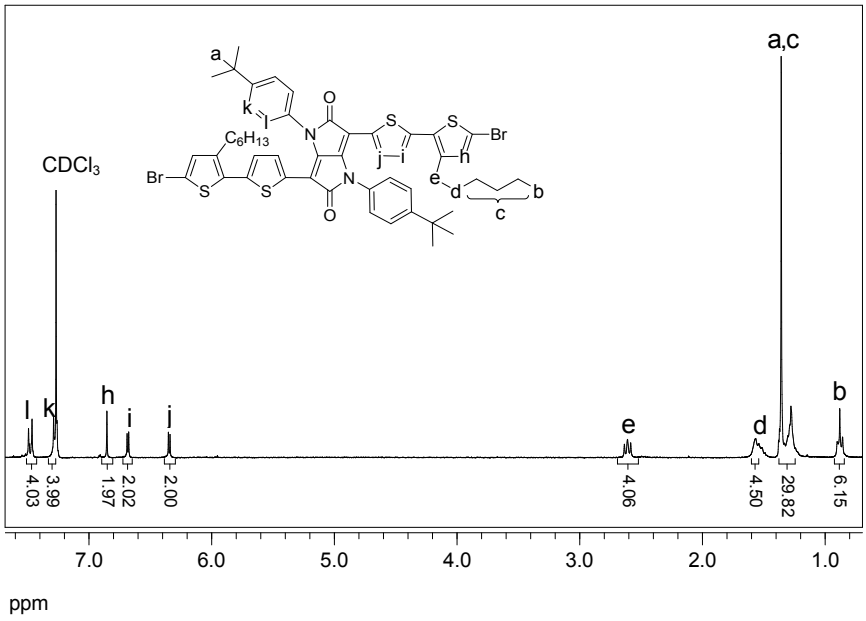
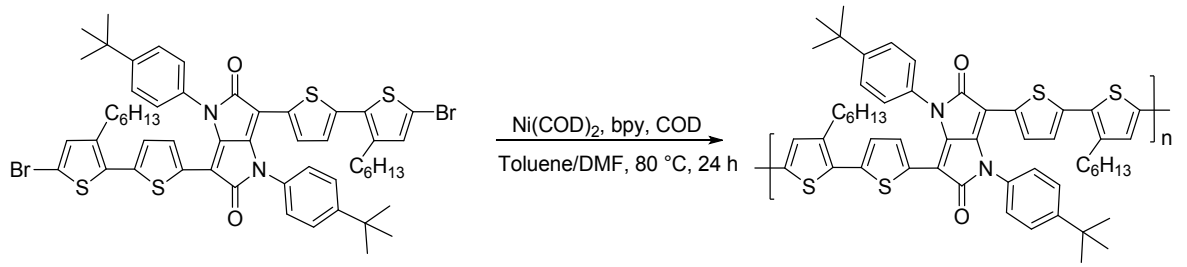


Fig. **S2:** ^{1}H-NMR-spectrum of **M1a** in $CDCl_3$.

Synthesis of P1´



M1a **P1**

100 mg (0,95 mmol) **M1a** were dissolved in 3 ml toluene. In a separate Schlenk flask, 260 mg (0,73 mmol) bis(1,5-cyclooctadien)nickel(0), 114 mg (0.73 mmol) 2,2´-bipyridine and 1,4 mL cyclooctadiene(COD) were dissolved in 2,5 ml DMF. Then the catalyst mixture was stirred at 80 °C for 30 min, treated with the monomer solution, and stirred at 80 °C for 48 h. After cooling to room temperature, the reaction mixture was poured in a 1:1 mixture of methanol/1 M aqueous HCl, stirred at room temperature for 2 h and treated with 100 ml DCM. Then 100 ml Milli-Q-water were added. The organic phase was separated, washed three times with Milli-Q-water, another three times with an aqueous EDTA-solution (5 %), and dried over $MgSO_4$. Then the solvent was removed in vacuo. The solid residue was dissolved in 2 mL DCM and precipitated in 100 ml MeOH. The precipitate was filtered off and dried in vacuo. 23 mg (28 %) of abordeaux-red powder of P1‘ were obtained. **GPC** (THF, 45 °C): M_w = 17,4 kg/mol, M_n = 8,4 kg/mol, PD = 2,07.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7,48 (bs, l-4H); 6,90-6,33 (m, k,l,j,h-10H); 2,66 (bs, e-4H); 1,60 (bs, d-4H); 1,36-1.25 (m, a,c-30H); 0,87 (bs, b-6H). **UV/Vis** [nm]: 477 (toluene), 491 (film). **ε**(477) [L mol^{-1} · cm]: 18356. **PL** [nm]: 667 (toluene); λ_{exc} = 450, PL quantum yield **Φ** [%]: 0,7 (toluene)

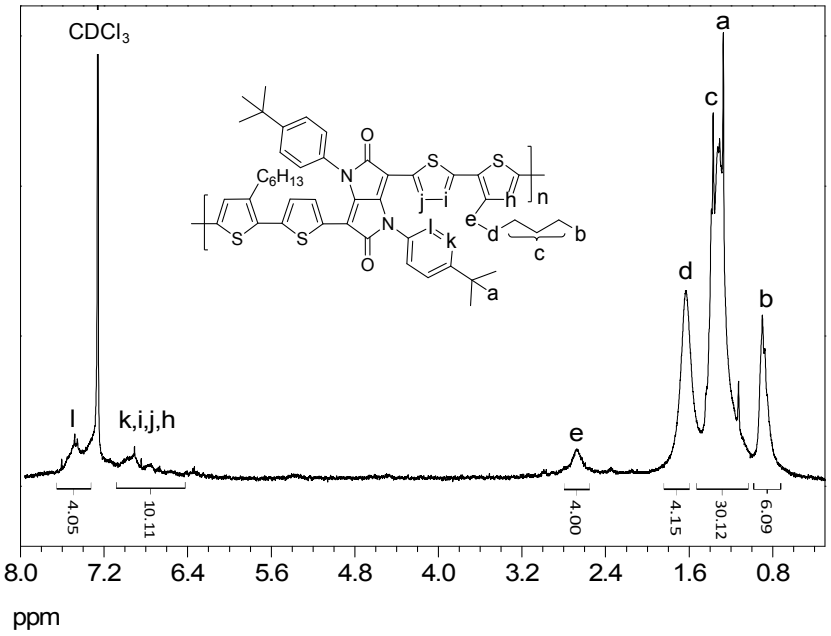


Figure S2: ^{1}H-NMR spectrum of **P1´** in $CDCl_3$.

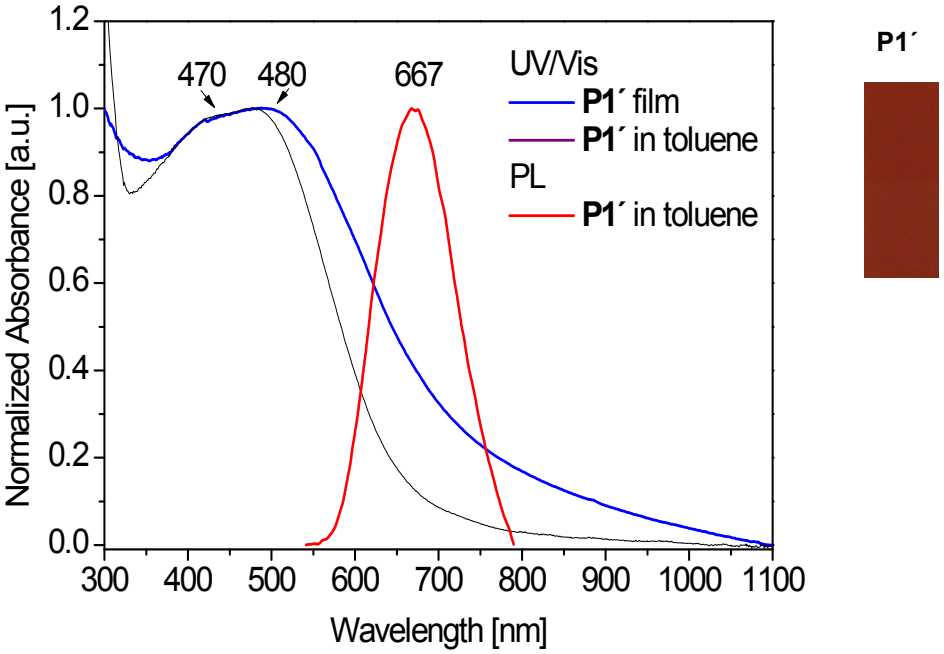


Figure S3: UV/Vis absorption and emission spectra of **P1´** in toluene and as film, and color of polymer solution in toluene.

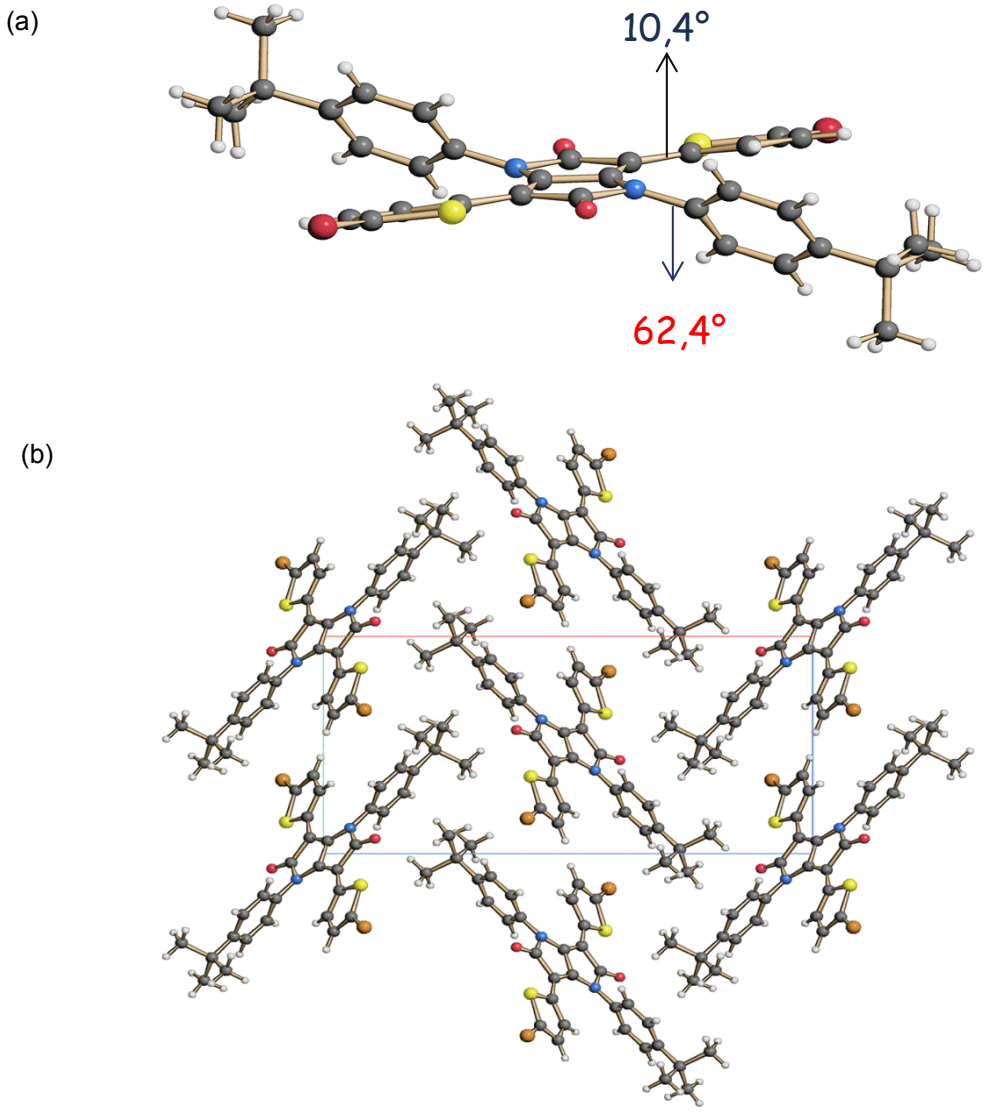


Figure S4: Crystal structure of **1a**. Molecular conformation in crystal lattice (a) and projection along c-axis (b). The N-, S-, O-, C-, Br-, H-atoms are show in blue, yellow, red, grey, brown and white colour.

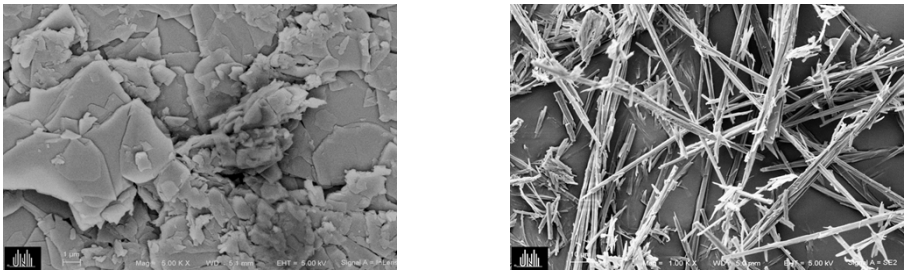


Figure S5: SEM images of monomers **M1** and **M2.**

Table S4: Crystal data and structure refinement of **1a**

Identification code	iwel54_benzol
Empirical formula	C_{34} H_{30} Br_2 N_2 O_2 S_2
Formula weight	722.54
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 6.8071(6) Å α = 90°.
	b = 21.415(2) Å β = 102.159(3)°.
	c = 10.9248(10) Å γ = 90°.
Volume	1556.9(2) $Å^3$
Z	2
Density (calculated)	1.541 g/cm^3
Absorption coefficient	2.772 mm^{-1}
F(000)	732
Crystal size	.2 x .03 x .03 mm^3
Theta range for data collection	1.90 to 26.99°.
Index ranges	-8<=h<=8, -25<=k<=27, -10<=l<=13
Reflections collected	7775
Independent reflections	3234 [R(int) = 0.0768]
Completeness to theta = 26.99°	95.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3234 / 0 / 193
Goodness-of-fit on F2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1102
R indices (all data)	R1 = 0.0741, wR2 = 0.1309
Largest diff. peak and hole	0.891 and -0.551 $e.Å^{-3}$