Extended 2,2′-bipyrroles: new monomers for conjugated polymers with tailored processability

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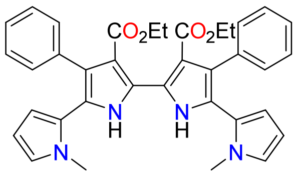
Table of Contents

I. Synthesis

Diethyl 5,5'-dibromo-4,4'-diphenyl-1*H*,1'*H*-[2,2'-bipyrrole]-3,3'-dicarboxylate (0.34 mmol) and 1-methyl-2-(trimethylstannyl)-1*H*-pyrrole (0.85 mmol) were dissolved in 20 ml of dry toluene. Then the solution was flushed with N_2 20 min, $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) was added and flushed 5 min more. The mixture was stirred for 3 hours at 140 ºC in a microwave instrument. The mixture was filtered to separate the precipitated catalyst and the solvent was removed under reduced pressure to obtain a brown oil. The product was obtained washing the brown oil with mixtures of AcOEt and Cy.



1c

Fig. S1. Chemical structure of monomer **1c**.

1c (98%, yellow powder) IR (KBr pellets)/cm^{-1}: 3432, 2982, 1654, 1444, 1410, 1177, 1021, 838, 723, 704. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.36 (s, 2H), 7.27 – 7.16 (m, 10H), 6.55 (dd, *J* = 2.7, 1.8 Hz, 2H), 6.14 (dd, *J* = 3.7, 1.8 Hz, 2H), 6.09 (dd, *J* = 3.7, 2.7 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 4H), 3.24 (s, 6H), 0.84 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 168.60, 136.78, 130.51, 128.49, 127.54, 126.93, 126.19, 124.59, 123.10, 122.71, 111.17, 111.13, 107.88, 60.84, 34.72, 13.46, 0.15. Anal. $C_{36}H_{34}N_4O_4$ Calculated: C73.70 H 5.84 N9.55, Found: C73.68 H5.97 N9.51. UV-Vis λ_{max}/nm (ε/M^{-1}·cm^{-1}) $CHCl_3$: 383 (1.6 · 10^4). m.p.: decomp. 245 ºC.

General methodology for obtaining polymers by chemical coupling (P-1a-c)

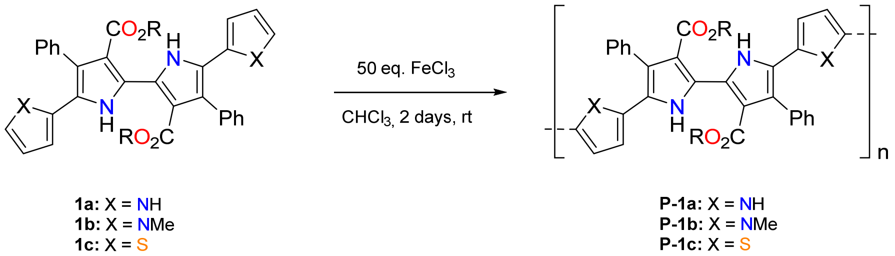


Fig. S2. Chemical oxidative coupling of monomers **1a-c** and chemical structure of polymers **P-1a-c**.

1a-c (1 eq.) was dissolved in 35 ml of dry chloroform and anhydrous $FeCl_3$ (50 eq.) was added in portions, then the solution was stirred for 2 days at room temperature under nitrogen. The solvent was removed under reduced pressure and the obtained solid was suspended in methanol and refluxed 20 min. The mixture was filtrated and solid washed with methanol to eliminate the $FeCl_3$.

The obtained solid was refluxed with THF and filtered to remove the insoluble part of the polymer. The filtrate was concentrated and the product was precipitated with the addition of methanol. Precipitate was cooled at 5 °C overnight and filtered to obtain a powder.

Table S1: properties of weight, absorbance and fluorescence of polymers prepared by chemical oxidation.

Monomer	**M_w[a]**	**M_n[a]**	**PDI[a]**	**Absorbance[b]**	**Emission[c]**	**Quantum Yield[d]**
1a	2300	1100	2.18	369	512	<1%
1b	2600	1100	2.46	408	499	0.04
1c	2300	1000	2.21	457	507	0.12

[a] Estimated from GPC (eluent THF, polystyrene standards). [b] All spectra were recorded in THF at a concentration of 0.1 mg/ml. [c] Emission spectra were measured with excitation at the maximum absorption of each polymer. [d] Quantum yields were determined in THF using a solution of quinine in 0.05M H_2SO_4 ($\Phi_F = 0.546$) as fluorescence standard.

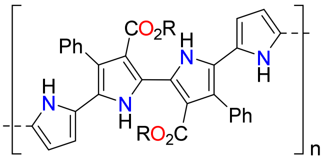


Fig. S3. Chemical structure of polymer **P-1a** (R=Et).

1a (5%) IR (KBr pellet)/cm^{-1}: 3413, 2926, 1719, 1548, 1465, 1384, 1269, 1184, 1093, 1022, 968, 843, 795, 771, 700. UV-VIS: λ_{max} = 369 nm, absorption up to 600 nm.

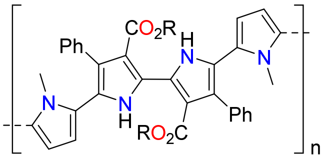


Fig. S4. Chemical structure of polymer **P-1b** (R=Et).

1b (21%) IR (KBr pellet)/cm^{-1}: 3433, 2922, 1669, 1614, 1448, 1419, 1174, 1020, 863, 756, 695. ^{1}H-NMR (400 Mhz, d_6-DMSO) δ: 12.53 (brs, 1H), 9.20 – 8.98 (m, 2H), 7.64 – 7.36 (m, 6H), 4.34 – 3.86 (m, 10H), 1.18 (m, 6H). UV-VIS: λ_{max} = 408 nm, absorption up to 600 nm.

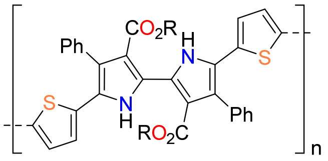
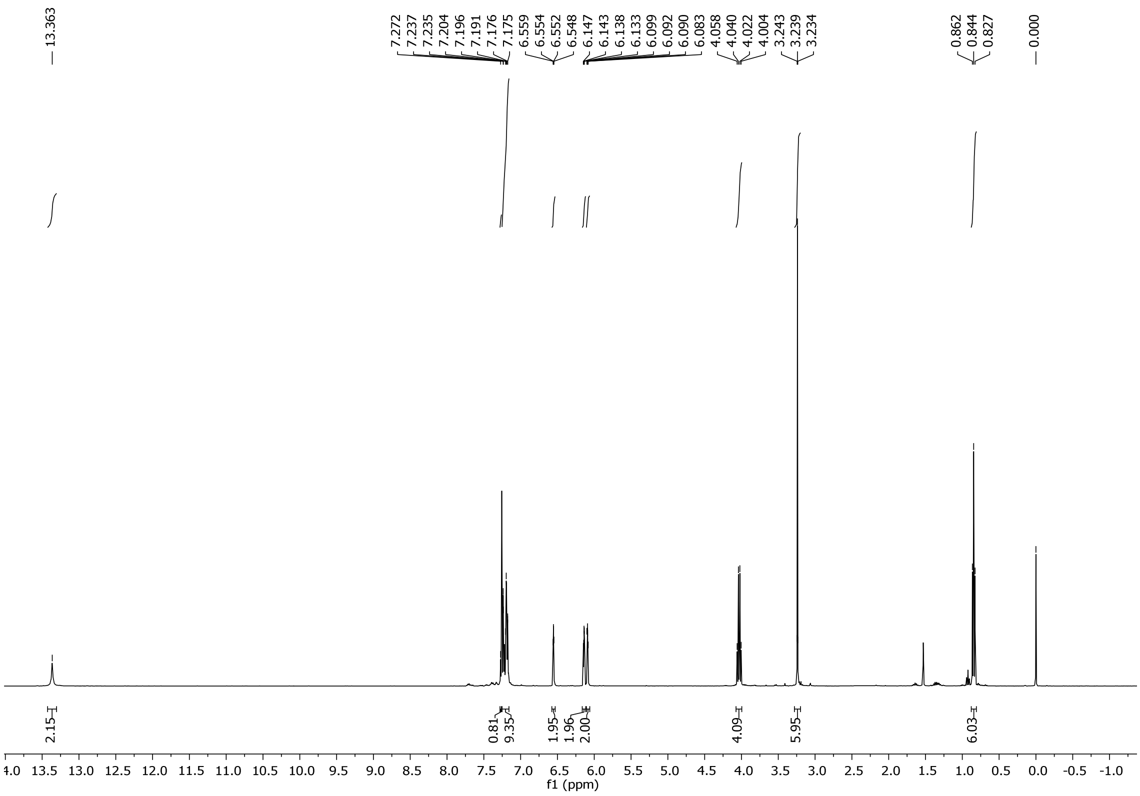


Fig. S5. Chemical structure of polymer **P-1c** (R=Et).

1c (17%) IR (KBr pellet)/cm^{-1}: 3432, 2924, 1658, 1418, 1181, 1063, 930, 794, 770, 699. ^{1}H-NMR (400 Mhz, d$_6$-DMSO) δ: 12.31 (m, 2H), 7.49 – 7.35 (m, 6H), 7.30 – 7.15 (m, 6H), 6.97 (m, 2H), 3.83 (m, 4H), 0.83 (m, 6H). UV-VIS: λ_{max} = 457 nm, absorption up to 515 nm.

II. NMR spectra



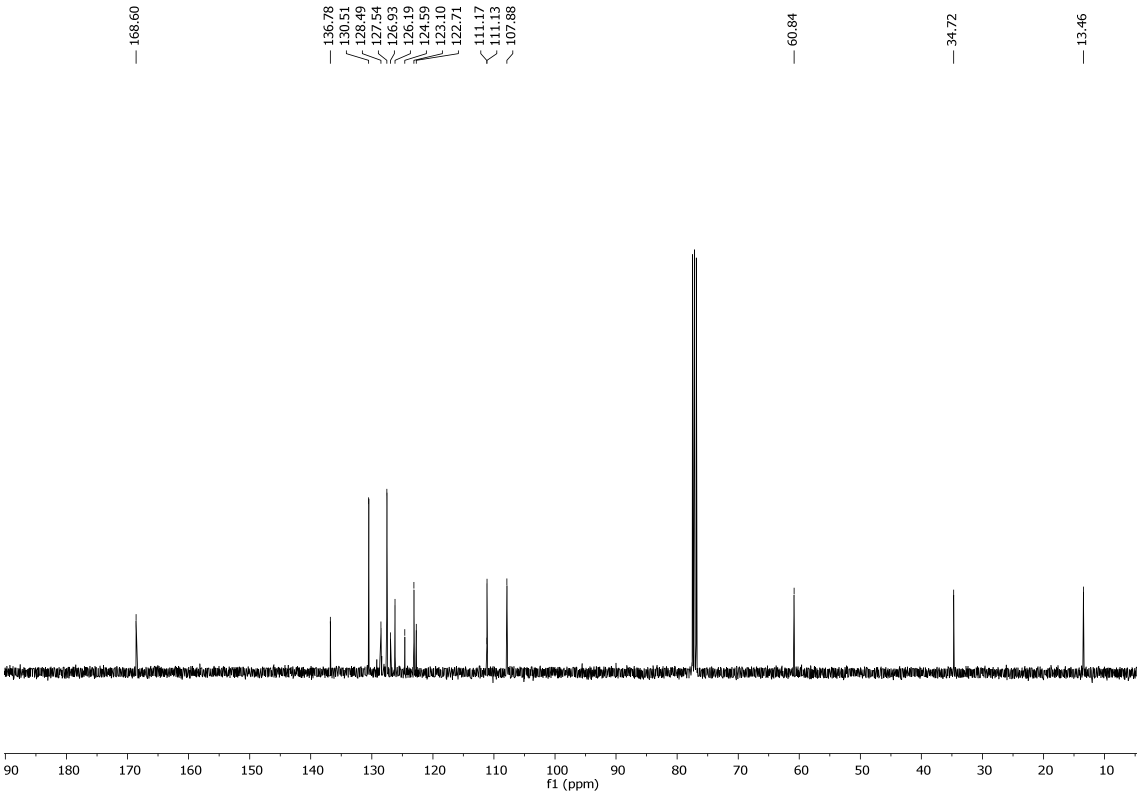


Fig. S6. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of **1c** in CDCl$_3$.

III. Characterization of the polymers prepared by chemical oxidation

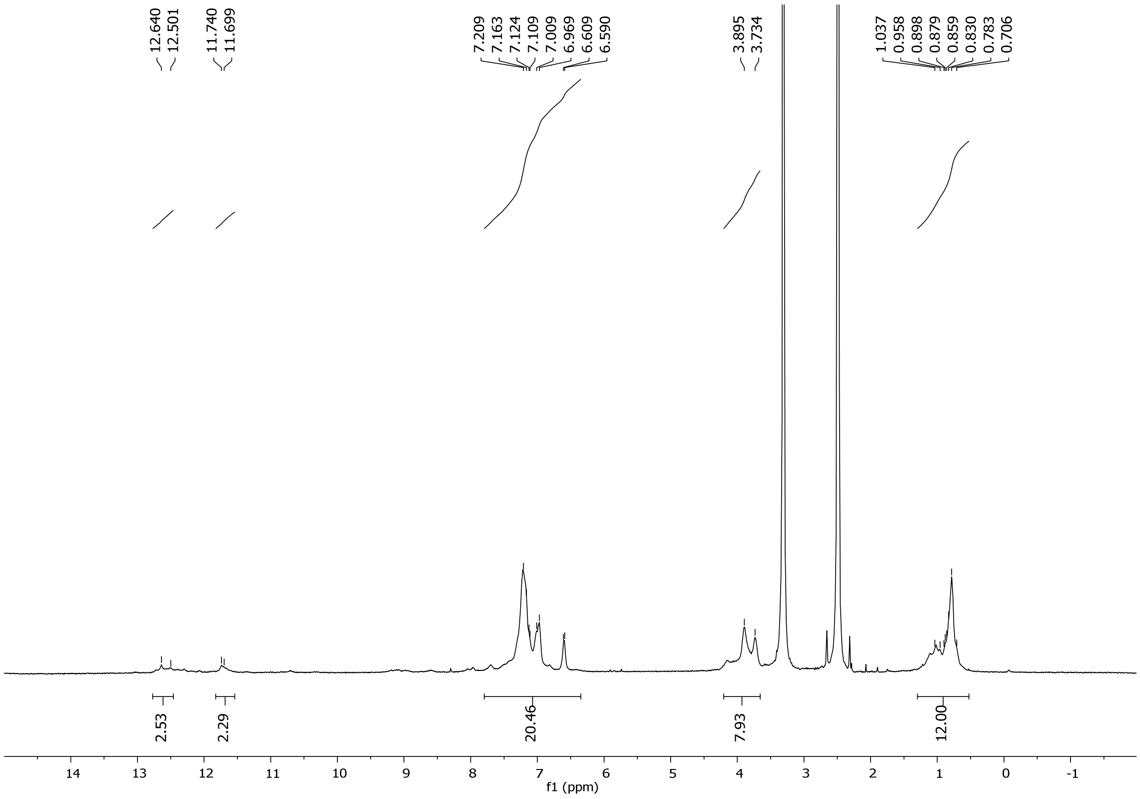


Fig. S7. ^{1}H-NMR spectrum of **P-1a** in DMSO-d$_6$.

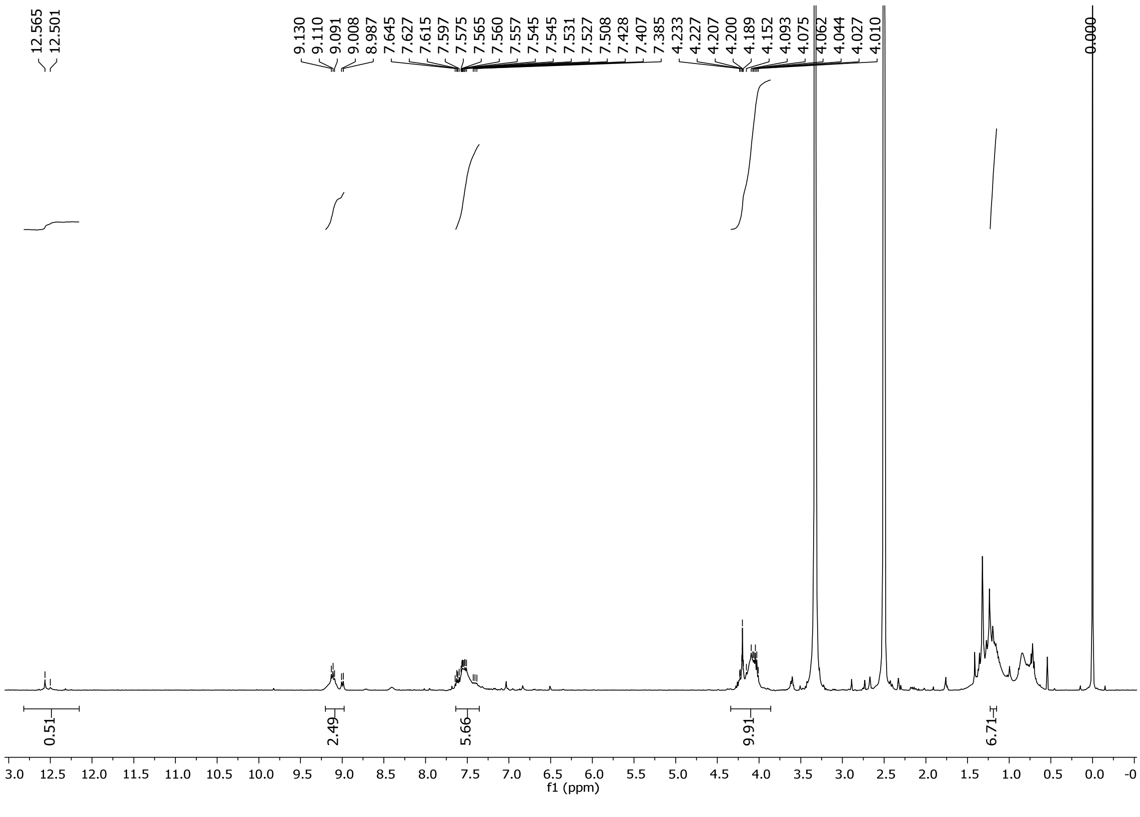


Fig. S8. ^{1}H-NMR spectrum of **P-1b** in DMSO-d$_6$.

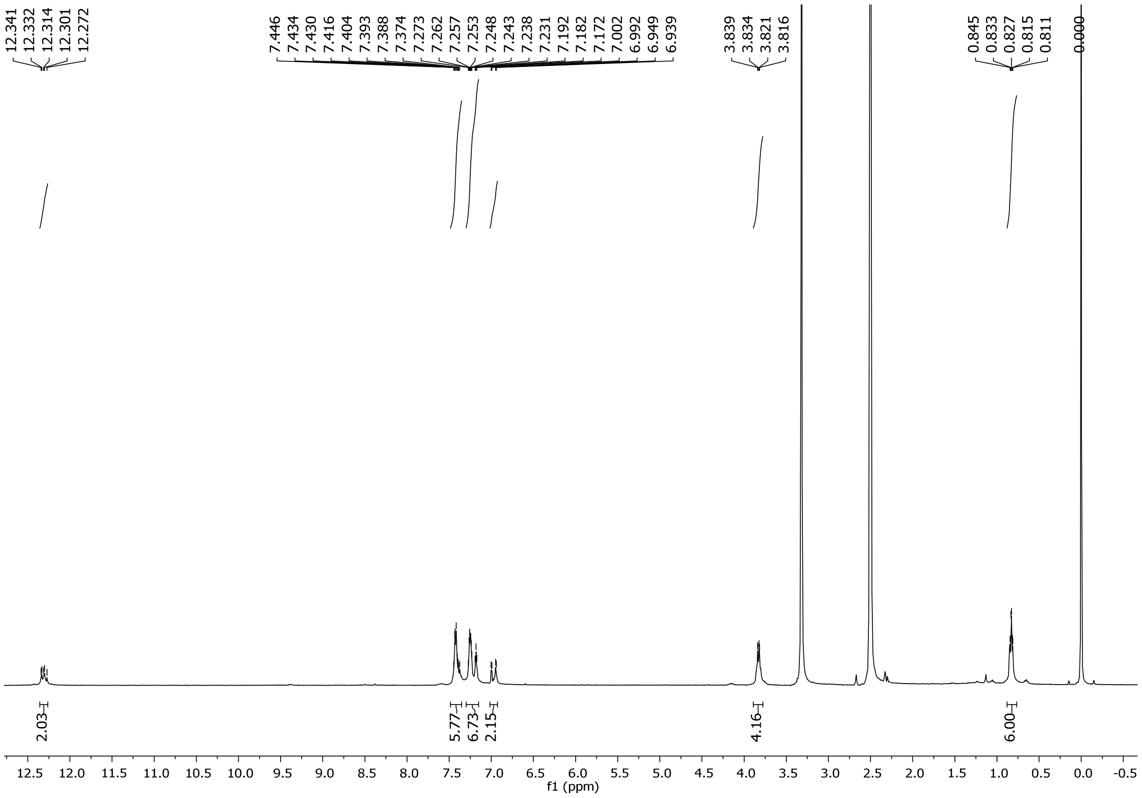


Fig. S9. ^{1}H-NMR spectrum of **P-1c** in DMSO-d$_6$.

IV. Absorption and Fluorescence spectra

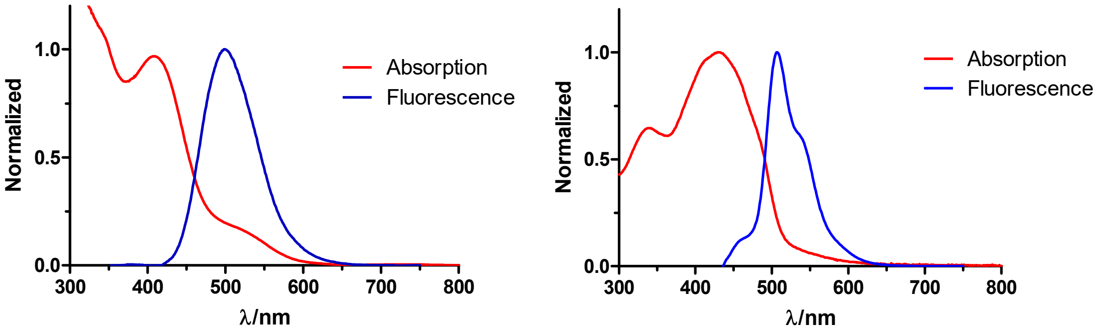
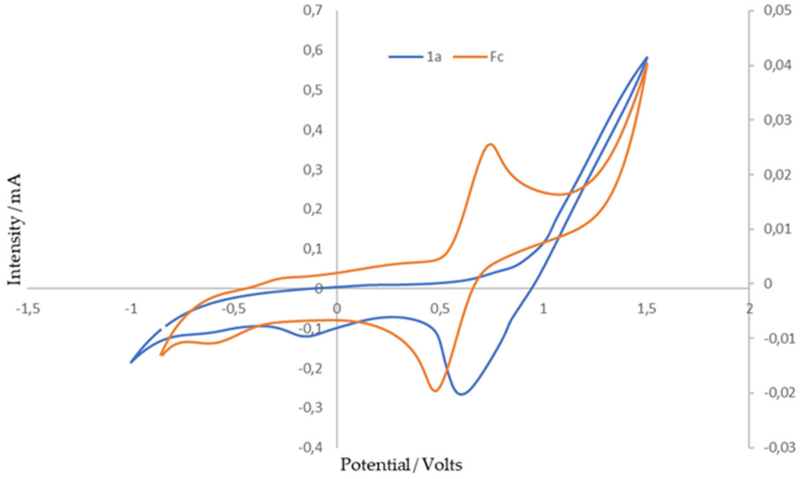


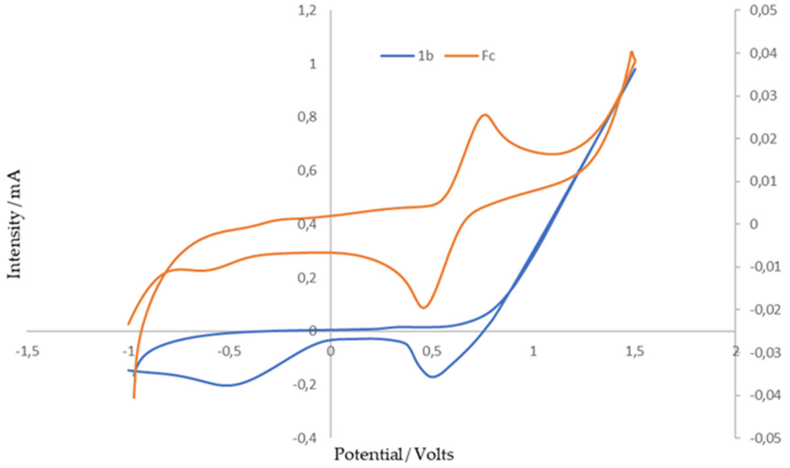
Fig. S10. Absorption and Fluorescence spectra normalized for polymers **P-1b** and **P-1c** in THF.

V. First cyclic voltammetry cycle vs Fc

1a



1b



1c

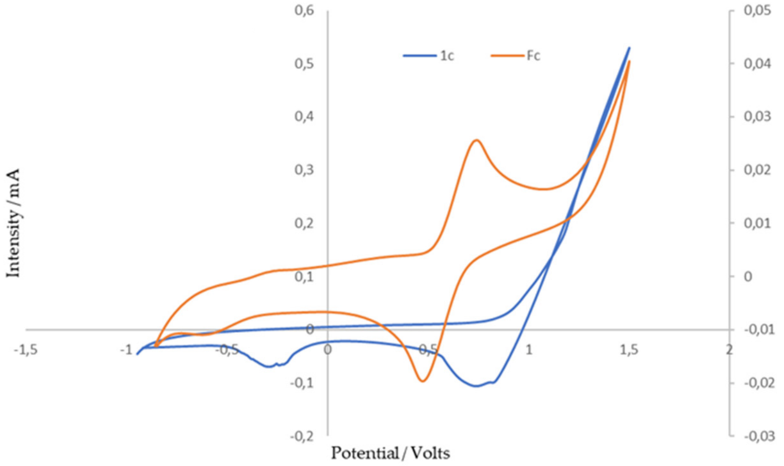


Fig. S11. First cyclic voltammetry of **1a-c** 2,2'-bipyrrole monomers overlapped with Ferrocene/Ferrocenium couple.

VI. MALDI – TOF

Table S2: possible fragmentation peaks

m/z	1a
558.2	Monomer
814.2	Monomer + Tetra butyl ammonium
919.0	Monomer + Tetra butyl ammonium perchlorate
1116.4	Dimer
1370.7	Dimer + Tetra butyl ammonium
1684.7	Trimer
1927.9	Trimer + Tetra butyl ammonium
2227.9	Oligomer n = 4
2786.1	Oligomer n = 5

m/z	1b
586.2	Monomer
656.3	Monomer + Perchlorate - Ethyl group
707.1	Monomer + Perchlorate -2 Ethyl groups
810.3	Monomer + Tetra butyl ammonium
847.3	Monomer + 3Perclorate groups - Esther group
1012.4	Dimer - 2 Phenyl groups - 2 Esther groups
1091.4	Dimer - Phenyl group
1170.5	Dimer
1276.6	Dimer + Perchlorate

m/z	1c
592.2	Monomer
672.0	Monomer + Perchlorate
810.3	Monomer + Tetra butyl ammonium
972.2	Monomer + Tetra butyl ammonium perchlorate - Ethyl group
1182.3	Dimer
1285.3	Dimer + Perchlorate
1443.4	Dimer + Tetra butyl ammonium

VII. Chemical Structures of the polymers

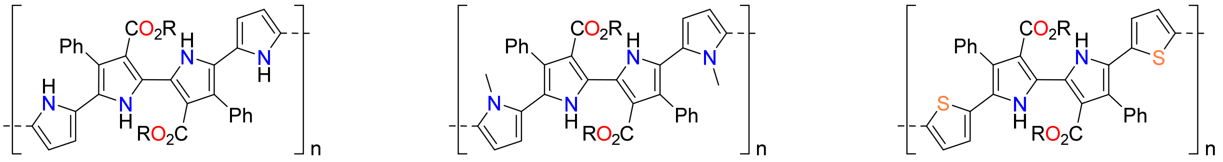


Fig. S12. Chemical structures of 2,2'-bipyrrole based polymers **P-1a-c** (R=Et).