

SUPPORTING INFORMATION

Halochromic switch from the 1st to 2nd Near Infrared window of Diazapentalene-Dithienosilole copolymers

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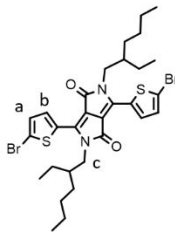
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DPPSeh-Br CDCl₃

7.789
7.778
7.246
7.202
7.192
3.511
3.496
3.454
3.438
2.760
1.781
1.766
1.502
1.493
1.484
1.476
1.468
1.459
1.414
1.403
1.385
1.365
1.349
1.332
1.316
1.240
0.978

7.789
7.778
7.246
7.202
7.192

a b c

7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm

1.00 0.96

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 0.96 2.36 1.09 14.30 8.50

Figure SI2: ^1H NMR spectrum of DAP monomer (CDCl_3 , 400 MHz)

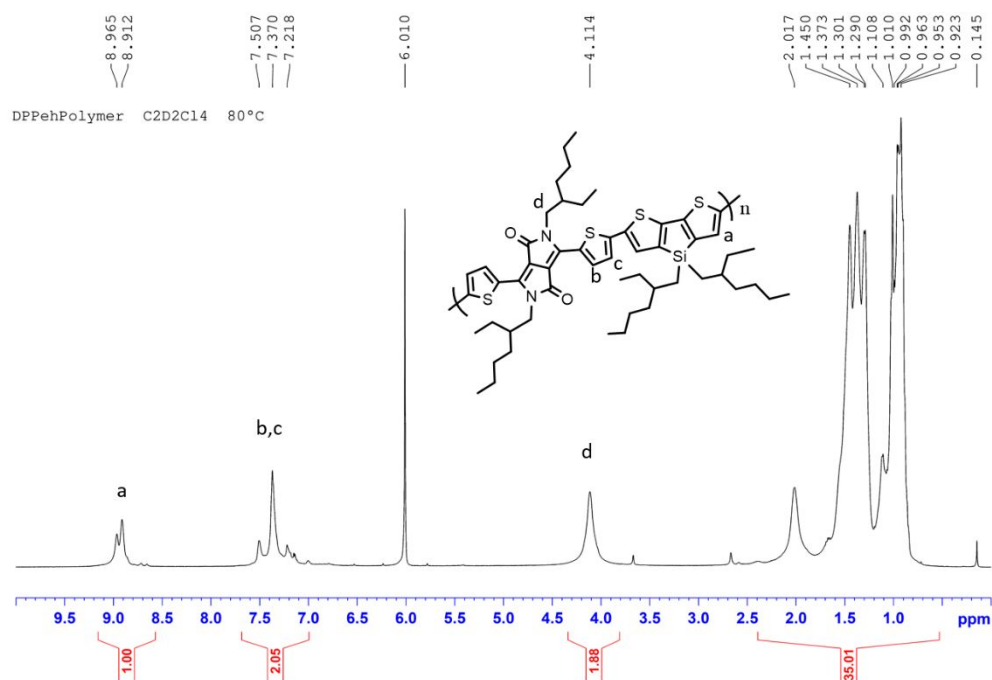


Figure SI3: ^1H NMR spectrum of P(DPP-DTS) ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz)

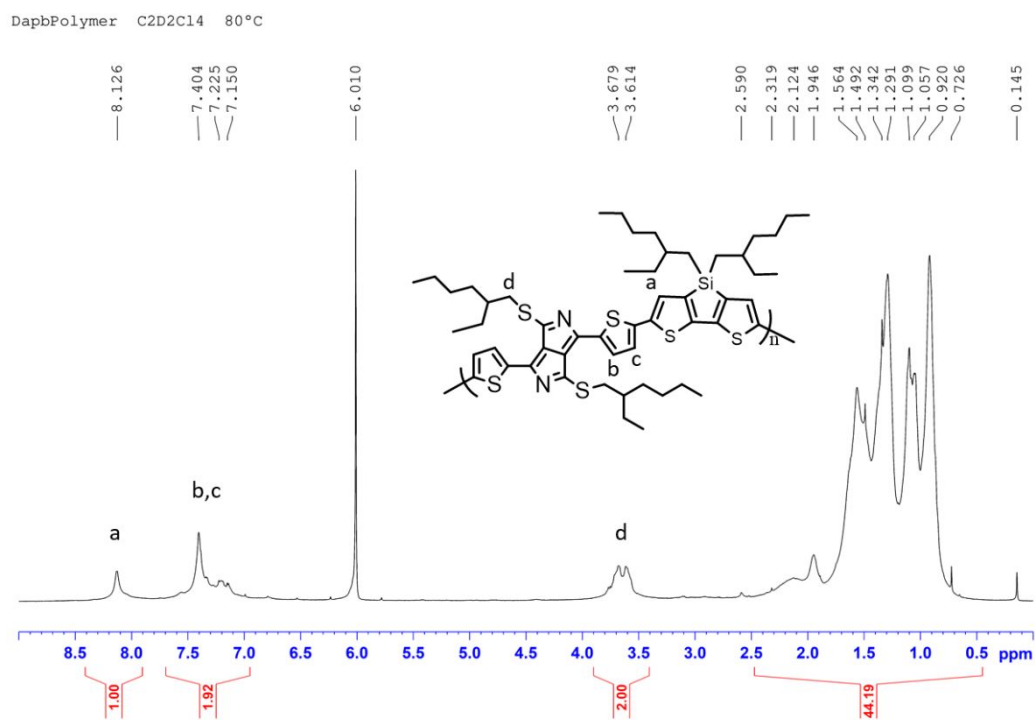


Figure SI4: ^1H NMR spectrum of P(DAP-DTS) ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz)

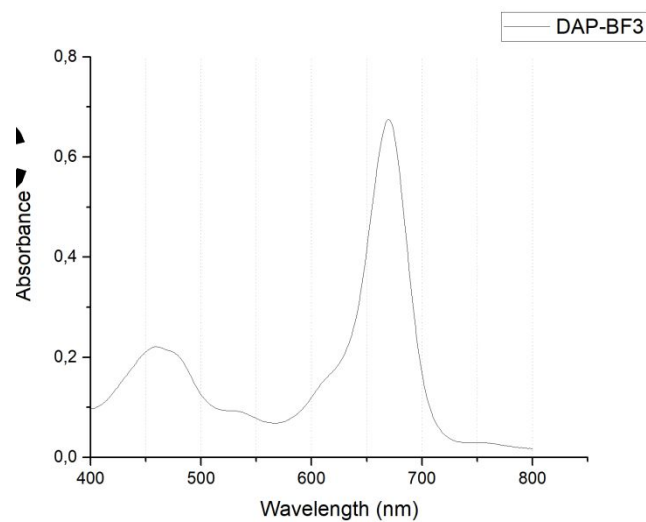


Figure SI5: UV-visible Absorption spectrum of DAP-BF₃ in chloroform solution

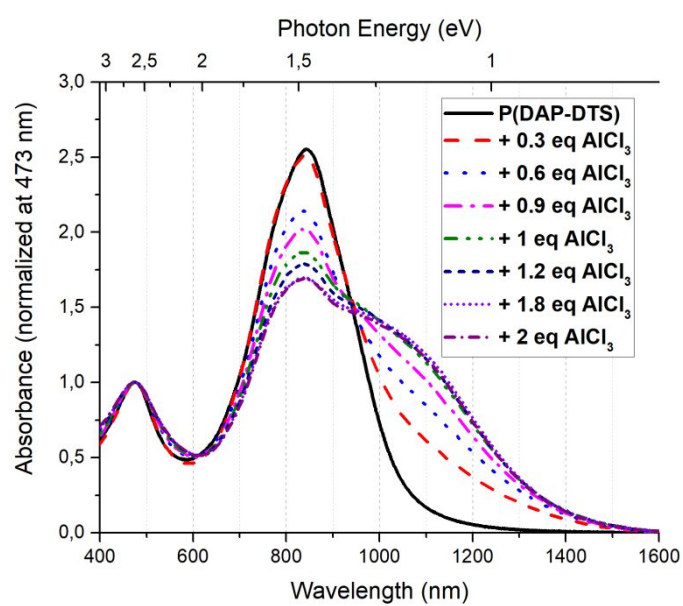


Figure SI6: UV-visible Absorption spectra of P(DAP-DTS)-AlCl₃ in chloroform solution.

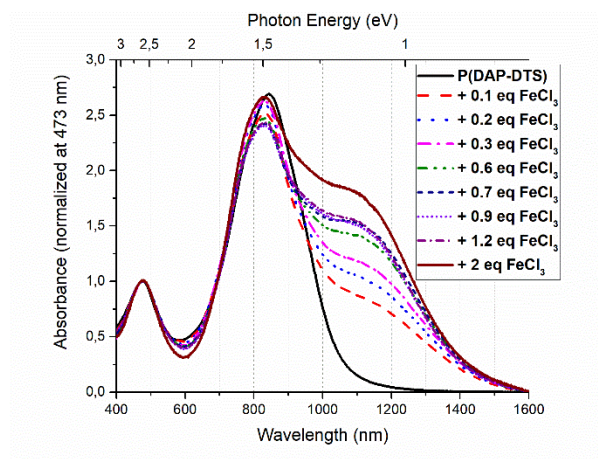


Figure SI7: UV-visible Absorption spectra of P(DAP-DTS)-FeCl₃ in a chloroform solution.

Cyclic Voltammetry (CV). A standard three-electrode electrochemical setup (AUTOLAB PGSTAT 101) consisting of a glassy carbon or a platinum disk as working electrode (2 mm diameter), a platinum foil as counter electrode, and a Ag/AgCl as reference electrode, was used in the electrochemical experiments. At the end of each experiment performed in CH₃CN/Bu₄NPF₆ (0,1 M), the standard potential of the ferrocenium/ferrocene couple, E_{Fe} , was measured, and all potentials were referenced against SCE using a previous determination of $E_{Fe} = 0.41$ V versus SCE in CH₃CN.(ref 1) Polymers were drop casted from a 10 mg/mL polymer solution in chlorobenzene/Bu₄NPF₆ (0,1 M) on the working electrode. CV gives direct information of the oxidation and reduction potentials of materials. The oxidation process corresponds to removal of the electron from the HOMO energy level, while the reduction corresponds to electron addition to the LUMO energy level of the material. Therefore HOMO and LUMO energy levels can be estimated using the empirical equations: $E_{HOMO} = - (E_{ox} + 4,7)$ and $E_{LUMO} = - (E_{red} + 4,7)$, where E_{ox} and E_{red} are respectively the onset potentials for oxidation and reduction peaks relative to SCE and 4,7 the factor connecting SCE to vacuum.(ref 2^[1]). The onset potentials are determined by the tangent method (see supporting information). Only values from the first sweep on a film were used as the film is changed or destroyed during the first oxidation. The scan rate used was 0.1 V.s⁻¹.

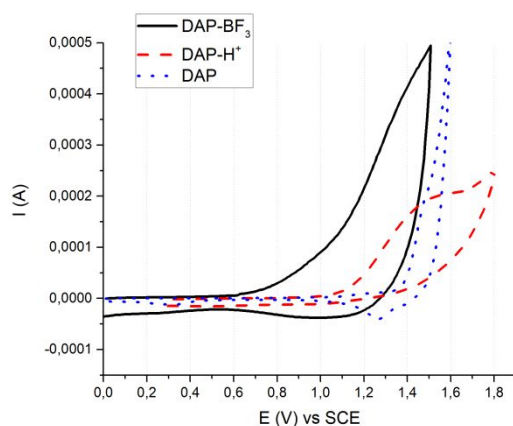


Figure SI8: CV oxidation voltammograms of monomers films performed in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ using a sweep rate of 0.1 V.s^{-1} .

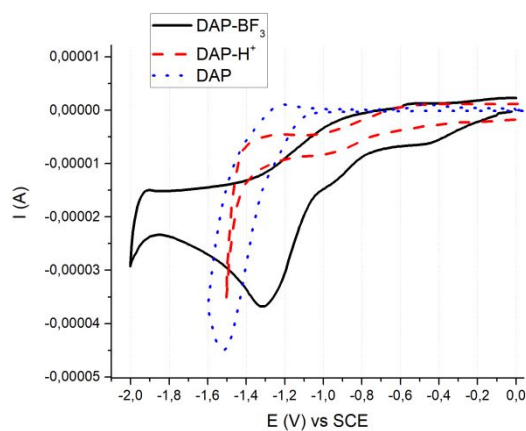


Figure SI9: CV reduction voltammograms of monomers films performed in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ using a sweep rate of 0.1 V.s^{-1} .

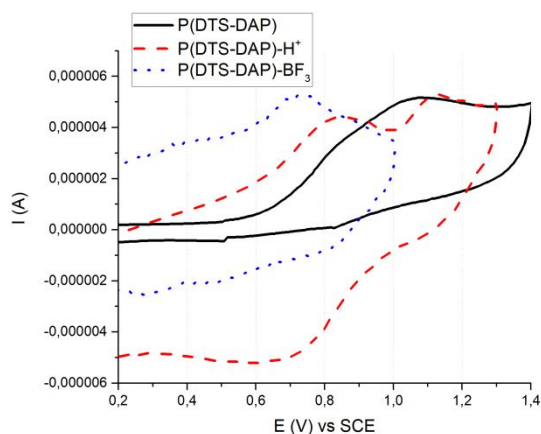


Figure SI10: CV oxidation voltammograms of polymers P(DTS-DAP) films performed in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ using a sweep rate of 0.1 V.s^{-1} .

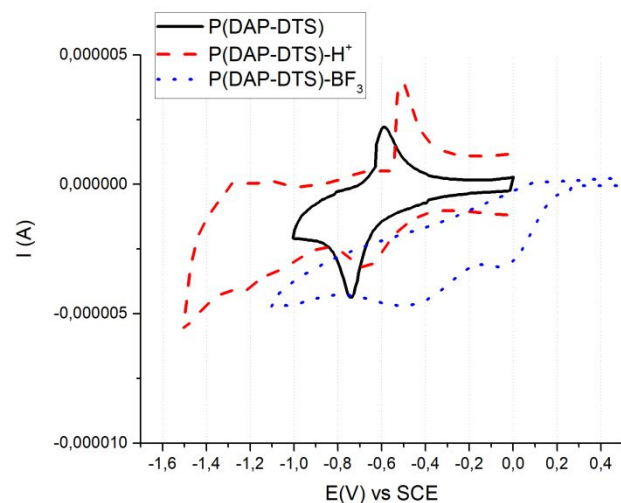


Figure SI11: CV reduction voltammograms of polymers P(DTS-DAP) films performed in 0.1 M Bu₄NPF₆/CH₃CN using a sweep rate of 0.1 V.s⁻¹.

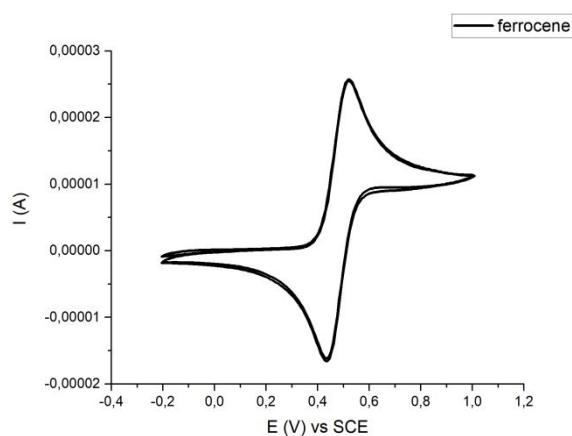


Figure SI12: CV of Ferrocene performed in 0.1 M Bu₄NPF₆/CH₃CN using a sweep rate of 0.1 V.s⁻¹.

Molecular orbitals of monomer units: B3LYP calculations

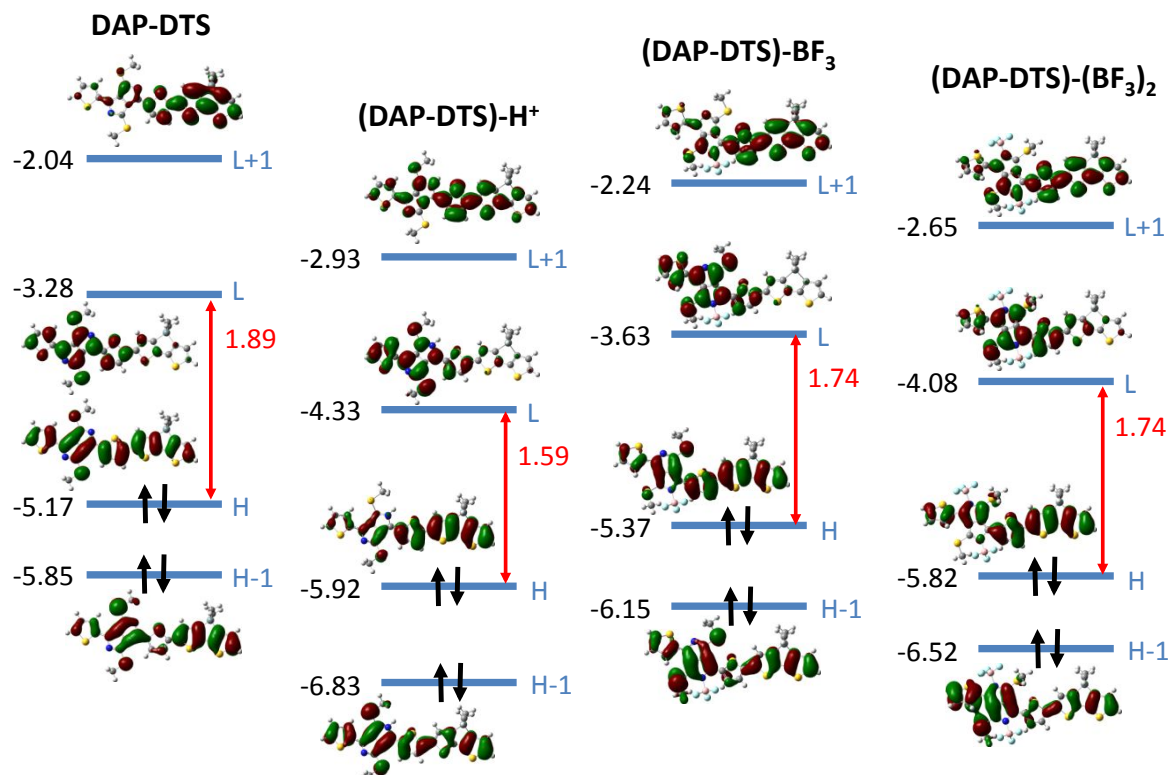


Figure SI13: Frontier energy levels (with energy values in eV) and molecular orbital shapes of DAP-DTS, (DAP-DTS)-H⁺, (DAP-DTS)-BF₃ and (DAP-DTS)-(BF₃)₂ monomers, calculated at the IEFPCM:B3LYP/6-311G(d) level in chloroform.

Bond length alternation

The bond length alternation (BLA) of DAP-DTS monomers has been calculated along the conjugated chain highlighted in red in Figure SI14, using the following expression:

$$BLA_{1\dots N} = 1/(N-2) \sum_{i=1}^{N-2} \{(d_{i+1,i+2} - d_{i,i+1}) \times (-1)^{i+1}\}$$

where N is the number of carbon atoms within the conjugated segment, and $d_{i,j}$ is the interatomic distance between carbons i and j .

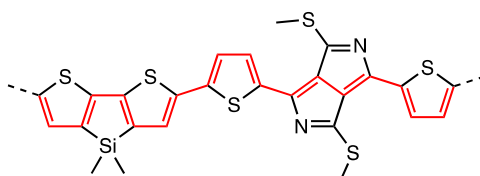


Figure SI14: Structure of the DAP-DTS monomer and (in red) conjugated chain used for calculating the bond length alternation.

Electronic and optical properties of increasingly large oligomers

Table SI1: Frontier orbital energies and electronic gap ($E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$, all values in eV), as well as $S_0 \rightarrow S_1$ transition energies (ΔE_{01} , eV), wavelengths (λ_{01} , nm) and oscillator strengths (f_{01} , dimensionless), calculated at the IEF-PCM:M06-2X/6-311G(d) level in chloroform for increasingly large DAP-DTS oligomers.

N units	E_{HOMO}	E_{LUMO}	E_g	ΔE_{01}	λ_{01}	f_{01}
1	-6.336	-2.802	3.535	1.958	633	1.336
2	-6.095	-2.923	3.173	1.737	714	2.962
3	-6.066	-2.962	3.104	1.712	724	4.529
4	-6.046	-2.982	3.064	1.694	732	6.084
5	-6.044	-2.988	3.056	1.694	732	7.710

Table SI2: Frontier orbital energies and electronic gap ($E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$, all values in eV), as well as $S_0 \rightarrow S_1$ transition energies (ΔE_{01} , eV), wavelengths (λ_{01} , nm) and oscillator strengths (f_{01} , dimensionless), calculated at the IEF-PCM:M06-2X/6-311G(d) level in chloroform for increasingly large (DAP-DTS)-H⁺ oligomers.

N units	E_{HOMO}	E_{LUMO}	E_g	ΔE_{01}	λ_{01}	f_{01}
1	-7.010	-3.915	3.095	1.748	710	1.395
2	-6.986	-4.169	2.817	1.540	805	2.953
3	-7.032	-4.322	2.710	1.506	823	4.788
4	-7.071	-4.426	2.646	1.487	834	6.927
5	-7.105	-4.487	2.618	1.487	834	7.784

Table SI3: Frontier orbital energies and electronic gap ($E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$, all values in eV), as well as $S_0 \rightarrow S_1$ transition energies (ΔE_{01} , eV), wavelengths (λ_{01} , nm) and oscillator strengths (f_{01} , dimensionless), calculated at the IEF-PCM:M06-2X/6-311G(d) level in chloroform for increasingly large (DAP-DTS)-BF₃ oligomers.

N units	E_{HOMO}	E_{LUMO}	E_g	ΔE_{01}	λ_{01}	f_{01}
1	-6.561	-3.118	3.443	1.965	631	1.087
2	-6.377	-3.229	3.148	1.751	708	2.503
3	-6.333	-3.272	3.061	1.710	725	3.840
4	-6.319	-3.291	3.028	1.692	733	5.433

Table SI4: Frontier orbital energies and electronic gap ($E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$, all values in eV), as well as $S_0 \rightarrow S_1$ transition energies (ΔE_{01} , eV), wavelengths (λ_{01} , nm) and oscillator strengths (f_{01} , dimensionless), calculated at the IEF-PCM:M06-2X/6-311G(d) level in chloroform for increasingly large (DAP-DTS)-(BF₃)₂ oligomers.

N units	E_{HOMO}	E_{LUMO}	E_g	ΔE_{01}	λ_{01}	f_{01}
1	-6.887	-3.638	3.249	1.771	700	1.460
2	-6.507	-3.613	2.894	1.541	805	2.545
3	-6.459	-3.681	2.778	1.501	826	4.334
4	-6.448	-3.746	2.702	1.470	844	5.792

Khun fit parameters

Table SI5: Optimized values of the Kuhn fit parameters D_k and E_1 (eV), as calculated at the IEF-PCM:M06-2X/6-311G(d) level in chloroform.

Polymer	D_k	E_1
P(DAP-DTS)	-0.903	5.343
P(DAP-DTS)-H ⁺	-0.913	4.956
P(DAP-DTS)-BF ₃	-0.905	5.419
P(DAP-DTS)-(BF ₃) ₂	-0.924	5.265

Relative energies of (DAP-DTS)-H⁺ and (DAP-DTS)-BF₃ dimers

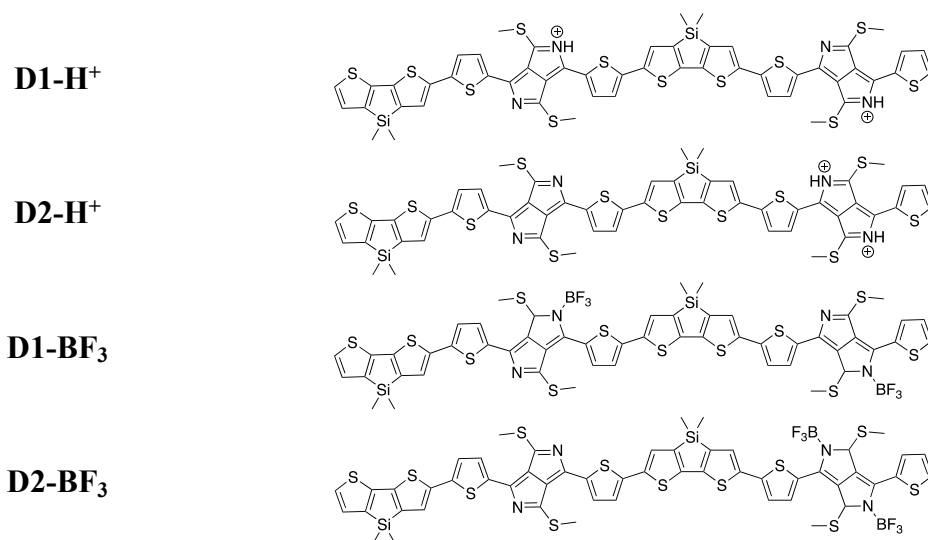


Figure SI15: Chemical structures of (DAP-DTS)-X (X = H⁺ or BF₃) dimers, with X groups located on different (D1) or on the same (D2) DAP unit.

Table SI5: Electronic (E, a.u.) and Gibbs' energies (G, a.u.), as well as relative energy values (ΔE and ΔG , in kcal/mol) of (DAP-DTS)-X structures, calculated at the M06-2X/6-311G(d) level.

	E	ΔE	G	ΔG
D1-H⁺	-7580.906546	/	-7580.239106	/
D2-H⁺	-7580.861959	28.09	-7580.195378	27.54
D1-BF₃	-8229.316951	/	-8228.651094	/
D2-BF₃	-8229.306774	6.41	-8228.639445	7.34

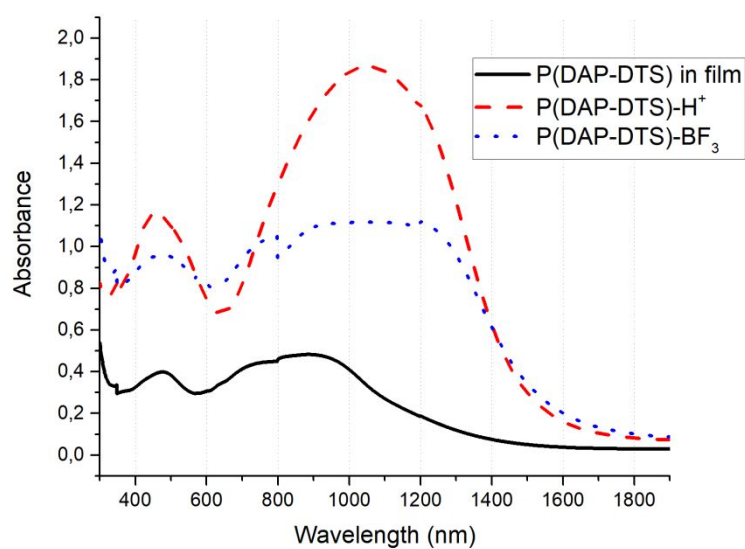


Figure SI16: UV-visible Absorption spectra of P(DAP-DTS) films.

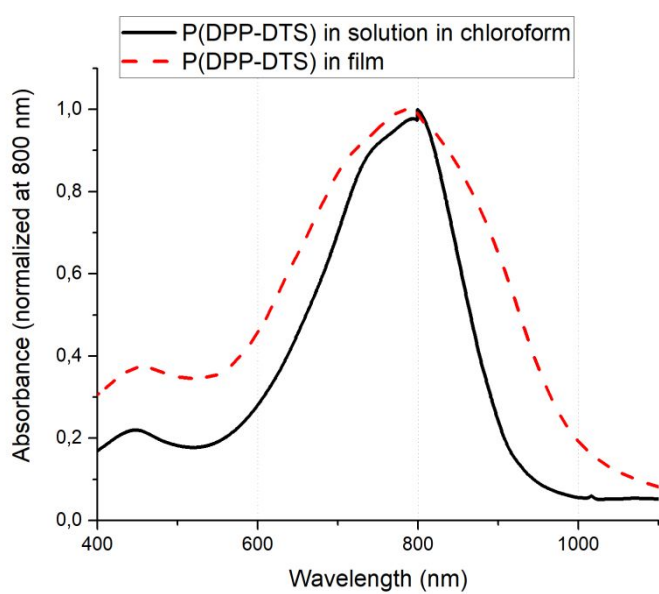


Figure SI17: UV-visible Absorption spectra of P(DPP-DTS).

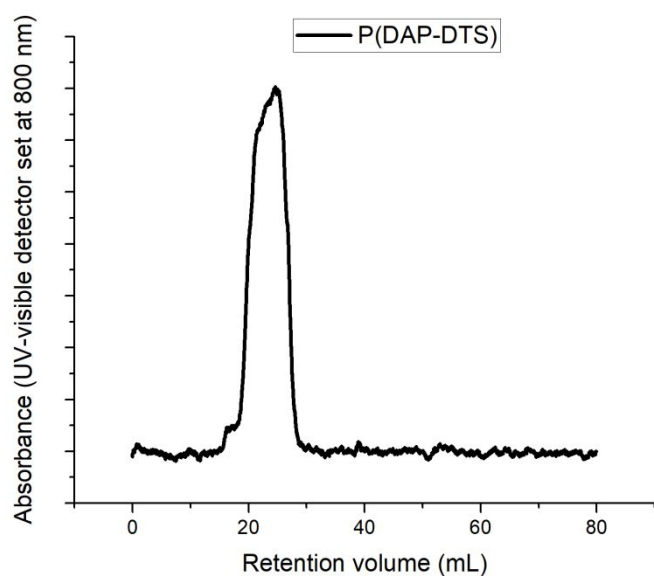


Figure SI18: Size exclusion chromatography of P(DPP-DTS).

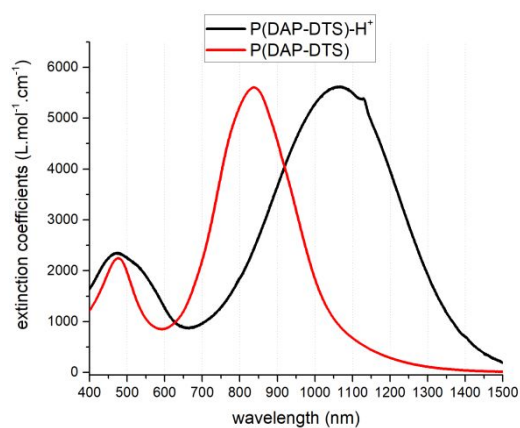


Figure SI19: Absorption electronic spectra of P(DAP-DTS) and P(DAP-DTS) using an excess of HCl in chloroform at RT.