

Supporting Information

Electrochromic polyiminocarbazolylenes with latent hydrogen bonding

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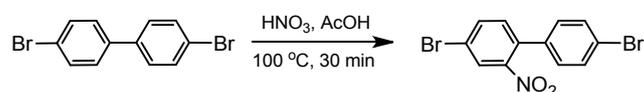
1. Synthesis and ¹H-NMR spectra of **M1**, **M2**, and intermediates
2. ¹H-NMR spectra of polymers **P1-EH**, **P1-BOC**, **P2-EH** and **P2-BOC**
3. UV spectra of polymers **P1-BOC** and **P2-BOC** before and after heat treatment
4. Spectroelectrochemistry of **P1-EH** in the potential range from 0.00 to 0.55 V vs. SCE

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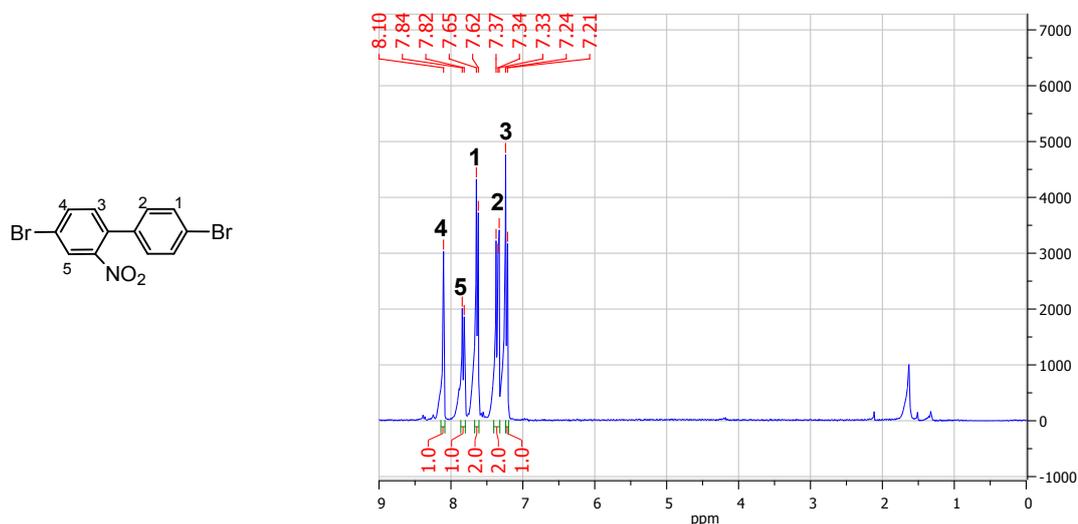
1. Synthesis and $^1\text{H-NMR}$ spectra of M1, M2, and intermediates

4,4'-Dibromo-2-nitrobiphenyl¹



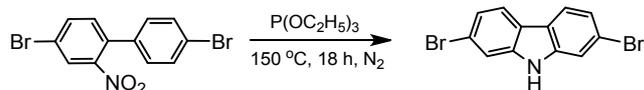
In a 500 ml three-necked flask equipped with reflux condenser and dropping funnel 20,00 g (62,82 mmol) 4,4'-dibromobiphenyl (98 %) were dissolved in 300 ml acetic acid (99,7 %) at $100\text{ }^\circ\text{C}$. Then 92,5 ml fuming nitric acid in 7,5 ml water were slowly added through the dropping funnel, and the mixture was stirred at $100\text{ }^\circ\text{C}$ for 30 min. During stirring the suspension turned red-orange, and nitrogen oxides evolved. The orange solution was cooled to room temperature, while the product precipitated as yellow flakes. The solid was filtered off, washed with ethanol, and recrystallized from ethanol. After drying in vacuo, 21,12 g (94 %; 59,16 mmol) of a yellow solid were obtained. m.p.: $115\text{--}118\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 8.10 (s, 1H), 7.84 (dd, $J = 8.2\text{ Hz}$, 1H), 7.65 (d, $J = 8.4\text{ Hz}$, 2H), 7.37 (m, 2H), 7.24 (d, $J = 8.4\text{ Hz}$, 1H).



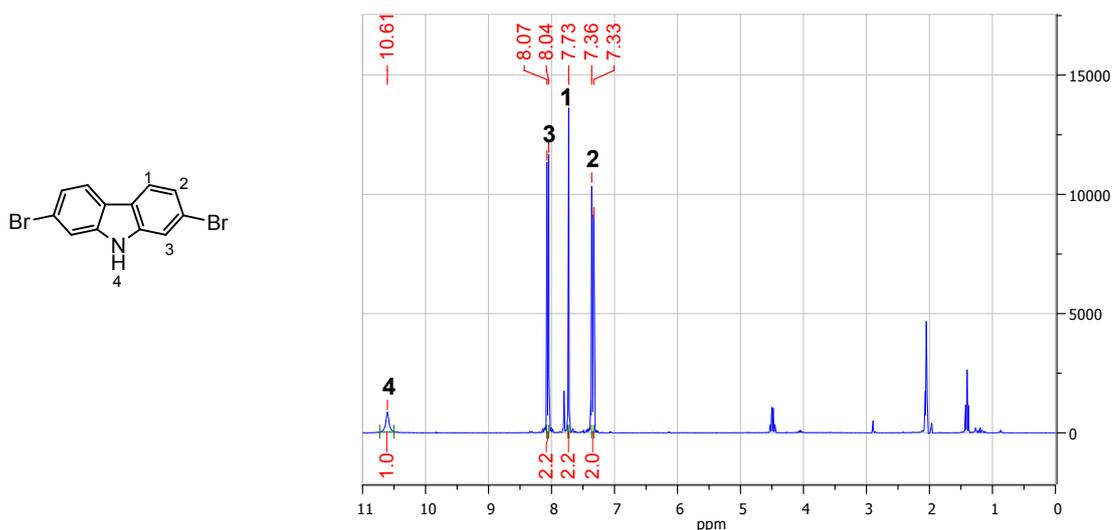
$^1\text{H-NMR}$ spectrum of 4,4'-dibromo-2-nitrobiphenyl in chloroform- d_3 (300 MHz).

2,7-Dibromocarbazole¹



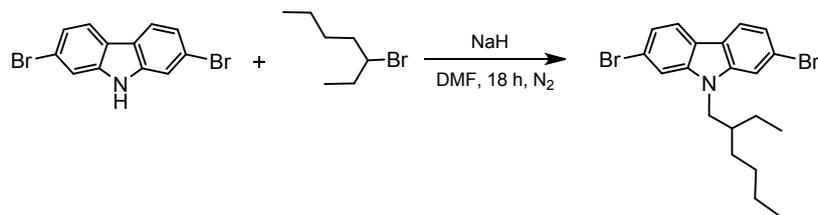
20.0 g (56.02 mmol) 4,4'-dibromo-2-nitrobiphenyl and 75 ml triethylphosphite were put in a 250 ml three-necked flask in nitrogen atmosphere and refluxed at 150 °C for 18 h. Subsequently excess triethylphosphite was distilled off in vacuo using an oil bath (distillation at 75–80 °C). The crude product was purified by column chromatography (20 % ethylacetate in n-hexane) and recrystallized from ethanol. 6.92 g (21.29 mmol, yield: 38 %) of a yellow solid were obtained, m.p.: 219 °C.

¹H-NMR (300 MHz, (CD₃)₂CO): δ (ppm) 10.61 (s, 1H), 8.07 (d, J = 8.42 Hz, 2H), 7.73 (d, J = 1.68 Hz, 2H), 7.36 (dd, J = 1.68 Hz, 2H).



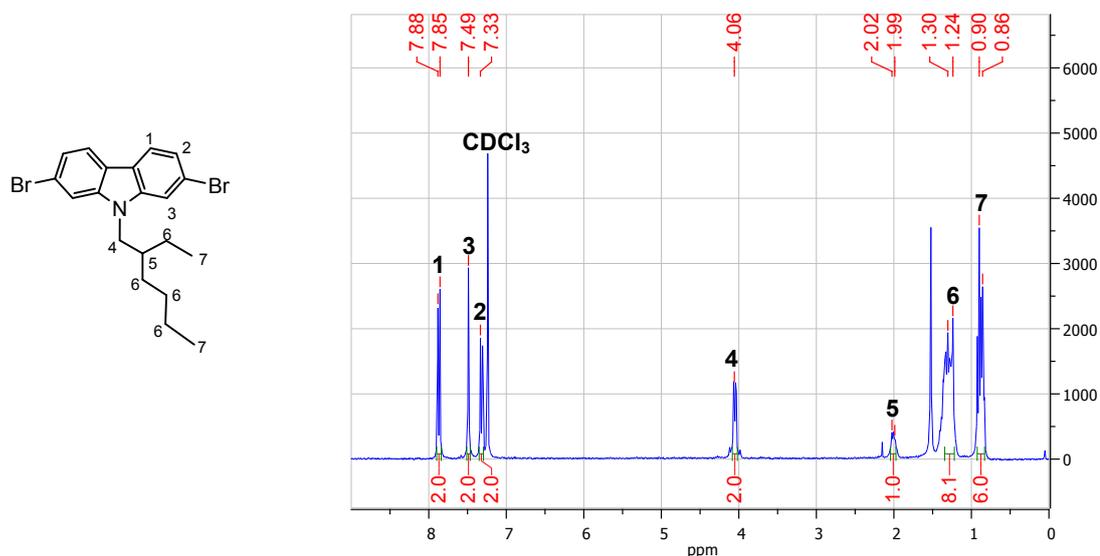
¹H-NMR spectrum of 2,7-dibromocarbazole in aceton-d₆ (300 MHz).

2,7-Dibromo-*N*-(2-ethylhexyl)carbazole (M1)¹



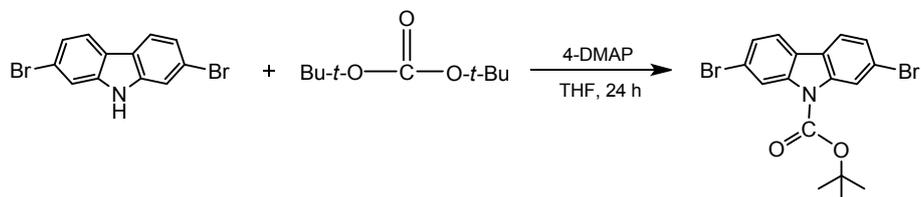
2.68 g (8.26 mmol) 2,7-dibromocarbazole in 27 ml *N,N*-dimethylformamide were filled in a 100 ml three-necked flask in dry nitrogen atmosphere. Then 0.46 g (11.54 mmole, 1.4 eq) sodiumhydride (60 % dispersion in mineral oil) were slowly added to the mixture. After stirring under nitrogen for 30 min 2 ml (10.72 mmole) 2-ethylhexylbromide were added, and the mixture was stirred at room temperature for 18 h. The reaction was quenched by adding 50 ml of distilled water and three-fold extraction with each time 50 ml dichloromethane. The solution was dried over magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by column chromatography (10 % ethylacetate in *n*-hexane) and recrystallized from ethanol. 2.10 g (4.80 mmol, yield: 58 %) of a white solid were obtained, m.p.: 98 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) 7.88 (d, *J* = 8.55 Hz, 2H), 7.49 (d, *J* = 1.29 Hz, 2H), 7.33 (dd, *J* = 1.57, 8.22 Hz, 2H), 4.06 (m, 2H), 2.02 (m, 1H), 1.30 (m, 8H), 0.90 (m, 6H).



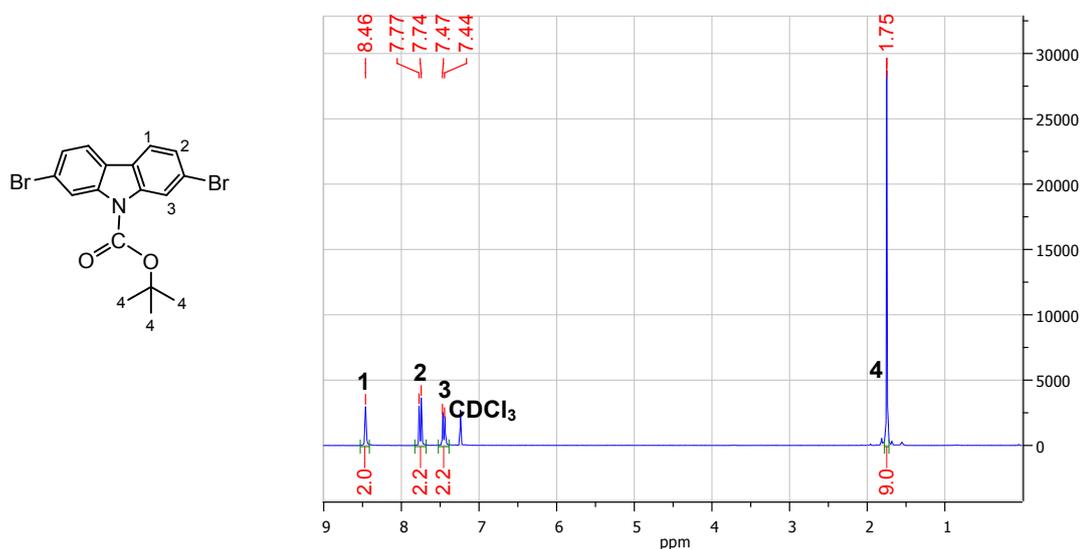
¹H-NMR spectrum of 2,7-dibromo-*N*-(2-ethylhexyl)carbazole in chloroform-*d*₃ (300 MHz).

2,7-Dibromocarbazole-*N*-carbamic acid *t*-butylester (M2)²



In a 100 ml flask 2.69 g (12.31 mmol) di-*t*-butyldicarbonate, 2.00 g (6.15 mmol) 2,7-dibromocarbazole and 0.75 g (6.15 mmol) 4-dimethylaminopyridin (4-DMAP) were dissolved in 62 ml tetrahydrofurane. The yellow solution was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure and the residue was extracted twice with each time 75 ml ethylacetate. Then the solution was washed twice with each time 50 ml 1M aqueous HCl, and twice with each time 100 ml saturated aqueous sodium chloride solution. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. After recrystallisation from ethanol 2.00 g (4.70 mmol, 77 %) of a white solid were obtained. m.p.: 169–171 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) 8.46 (s, 2H), 7.77 (d, J = 8.10 Hz, 2H), 7.47 (dd, J = 8.10 Hz, 2H), 1.75 (s, 9H)



¹H-NMR spectrum of 2,7-dibromocarbazole-*N*-carbamic acid *t*-butylester in chloroform-*d*₃ (300 MHz).

2. ¹H-NMR spectra of polymers P1-EH, P1-BOC, P2-EH and P2-BOC

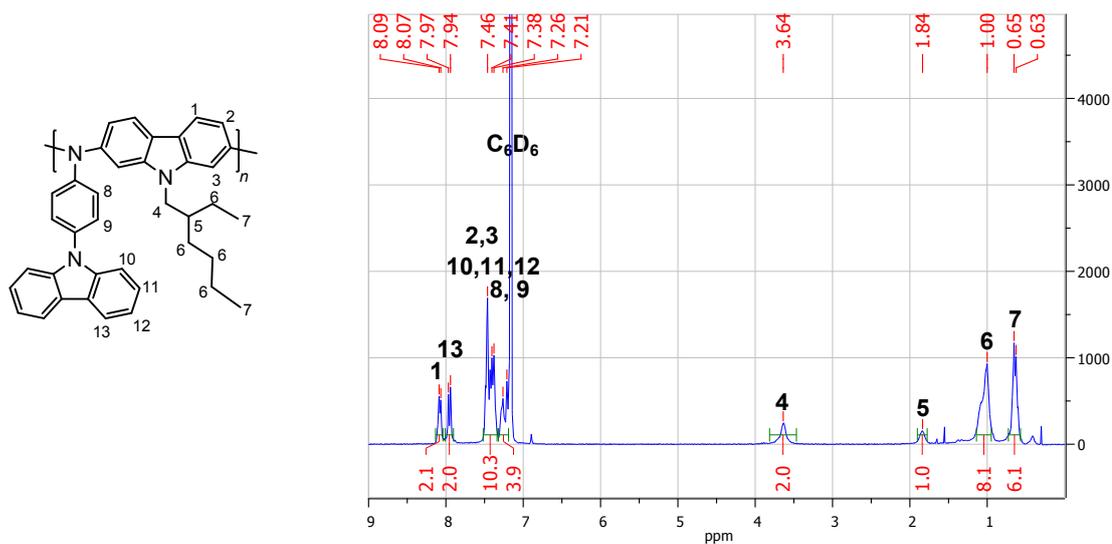


Fig. S1. ¹H-NMR spectrum of P1-EH in benzene-d₆ (300 MHz)

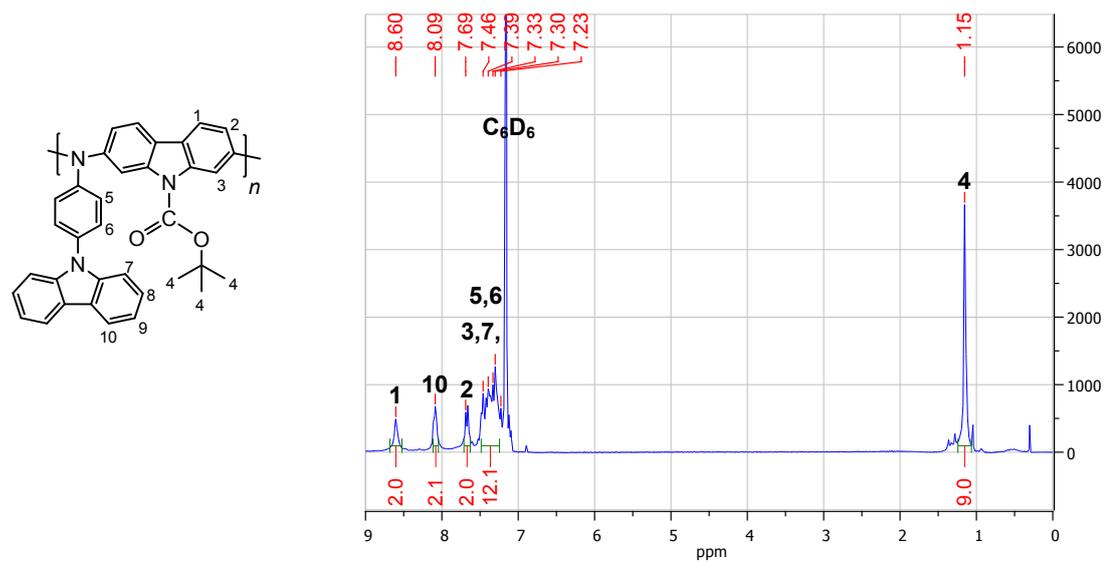


Fig. S2. ¹H-NMR spectrum of P1-BOC in benzene-d₆ (300 MHz)

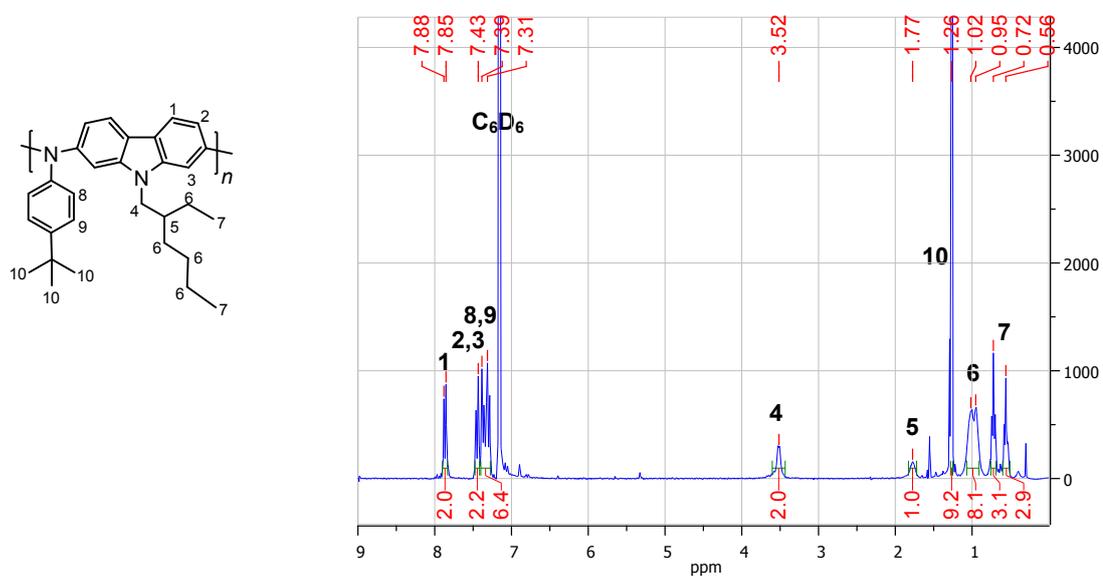


Fig. S3. ¹H-NMR spectrum of **P2-EH** in benzene-d₆ (300 MHz)

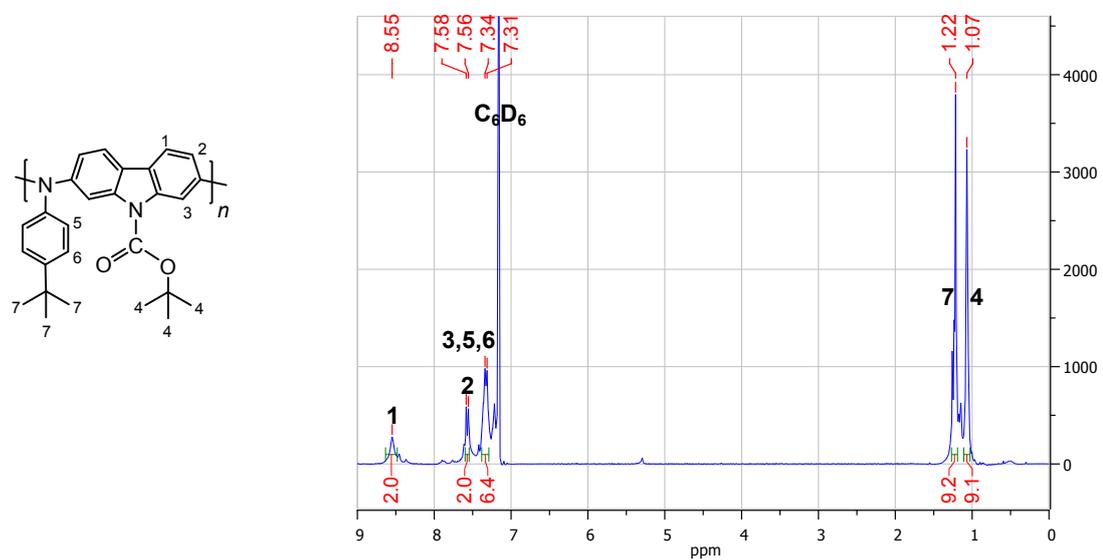


Fig. S4. ¹H-NMR spectrum of **P2-BOC** in benzene-d₆ (300 MHz)

3. UV spectra of polymers P1-BOC and P2-BOC before and after heat treatment

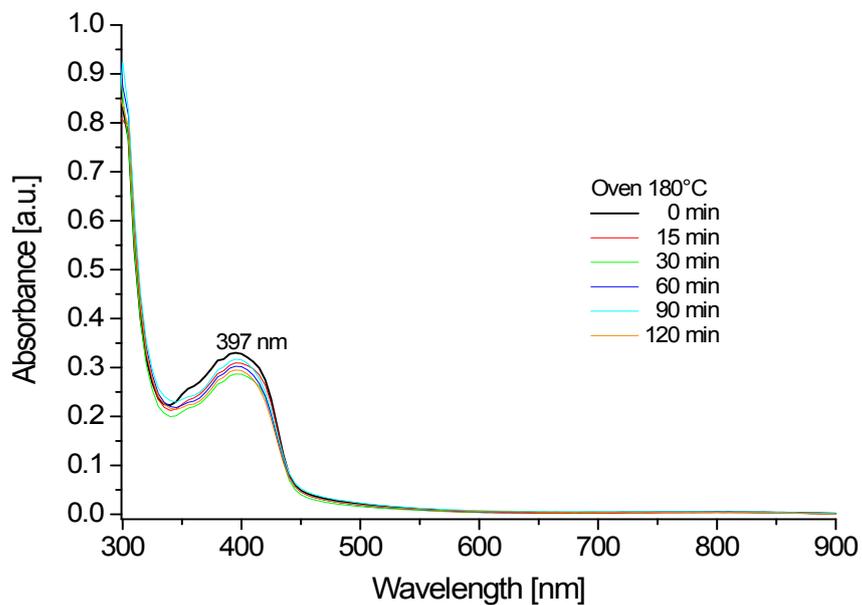


Fig. S5. UV-absorption of a film of **P1-BOC** on ITO-coated glass support prior (black curve) and subsequent to annealing at 180 °C for different time periods (colored curves).

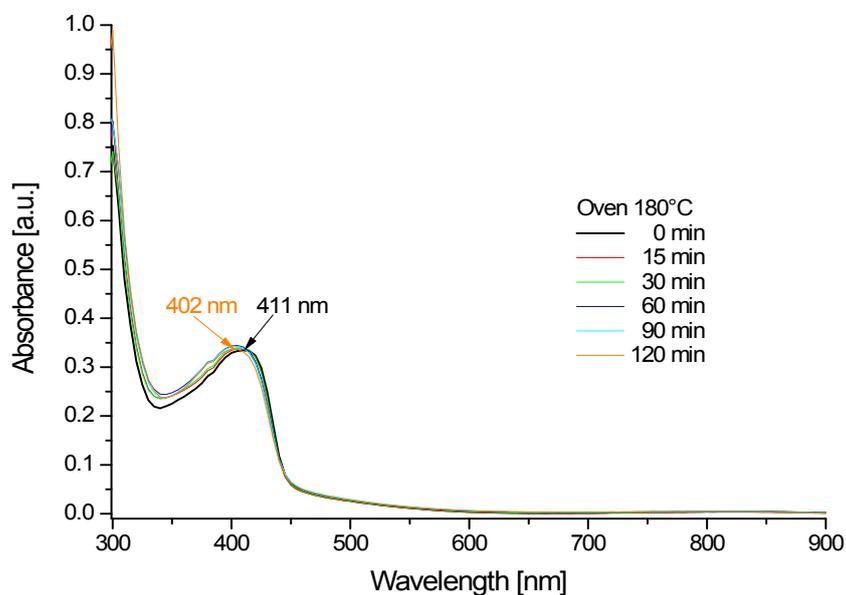


Fig. S6. UV-absorption of a film of **P2-BOC** on ITO-coated glass support prior (black curve) and subsequent to annealing at 180 °C for different time periods (colored curves).

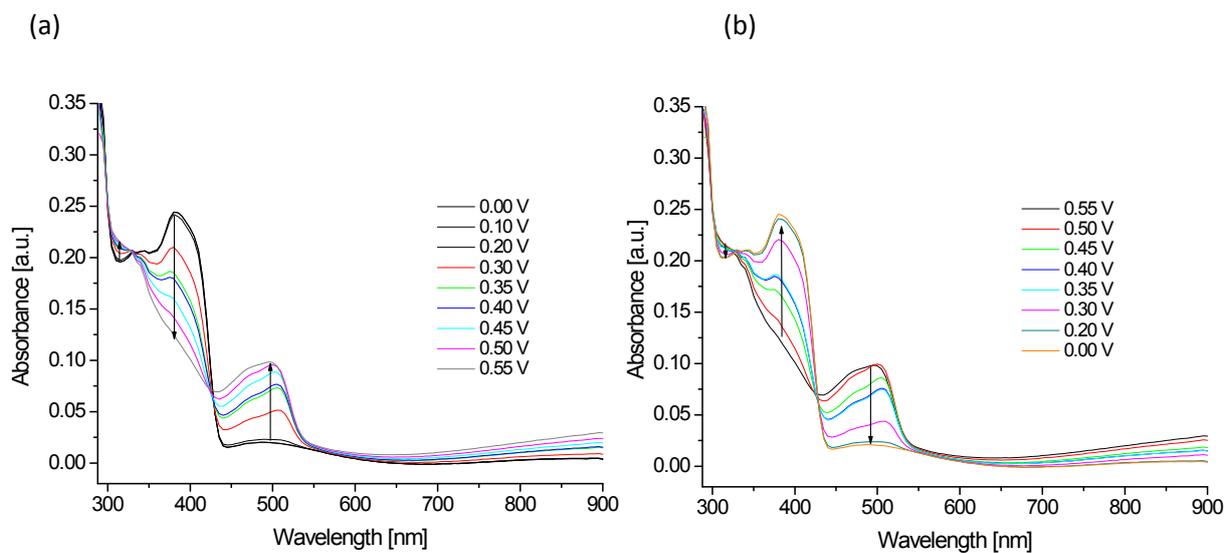


Figure S7. Spectroelectrochemistry of **P1-EH** in the potential range from 0.00 to 0.55 V vs. SCE. The oxidative cycling is completely reversible. UV/Vis-absorption spectra are shown at different, increasing (a) and decreasing potentials (b). Scan rate (UV): 1920 nm/min.

References

1. F. Dierschke, A. C. Grimsdale, K. Müllen, *Synthesis* **2003**, 2470-2472.
2. K.-S. Moon, H.-J. Kim, E. Lee, M. Lee, *Angew. Chem. Int. Ed. Engl.* 2007, **46**, 6807-6810.