**SUPPLEMENTARY DATA**

**Nanoparticles of Poly(3-hexylthiophene): Toward a Solvent-Independent Performance of Electrochromic Films**

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**Index:**

S1. UV-vis absorption spectra p. 3

S2. Redox charge density & thickness p. 4

S3. Stationary transmittance at 520 nm p. 6

S4. Transmittance spectra p. 8

S5. Switching speed p. 9

S6. Stability test p. 10

S7. Spin-coated P3HT-CHCl3 film p. 11

References p.12

**S1. UV-vis absorption spectra**

The UV-vis spectra (Figure S1) of P3HT-THF and CHCl3 solutions show a featureless broad π-π\* transition absorption band with its maximum at 445 nm, typical for amorphous P3HT. This band is red-shifted to 510 nm for the nanoparticle polymer P3HT (NP) dispersions. The spectra for these dispersions also show the appearance of peaks at 520 nm, 560 nm, and 620 nm, which indicate the existence of vibronic transitions caused by the internal aggregation of the P3HT chains inside the nanoparticles.[1,2] The acquired aggregate structure with its electronic transitions of the P3HT (NPs) in dispersion is maintained when deposited in the form of films onto substrates.[3]



**Figure S1.** Normalized absorbance spectra of P3HT-THF and P3HT-CHCl3 solutions, together with the corresponding nanoparticle-containing P3HT-THF (NP)-H2O and P3HT-CHCl3(NP)-EtOH solutions.

**S2. Redox charge density & thickness**

Figure S2 shows the cyclic voltammograms of the different P3HT film probed for different film thicknesses at a scan rate of 20 mV/s in the potential window from -0.3 to 1.1 V vs. Ag/AgCl reference electrode (RE), calibrated at 0.45 V vs. ferrocene. The surface area exposed to the electrolyte is about 1 cm2.

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**Figure S2**. Cyclic voltamogramms of the different P3HT film series with different film thicknesses (indicated by different colors) taken at a scan rate of 20 mV/s. A) P3HT-CHCl3 B) P3HT-THF C) P3HT-CHCl3(NP) D) P3HT-THF(NP). Respective figures E), F) ,G) and H) represent the linear relations found between resulting redox charge densities and measured thicknesses (colors of each film thickness according to the corresponding cyclic voltammogram).

Redox charge density values in units of mCcm-2 are calculated by the integration of the anodic and cathodic CV curves for each thickness followed by dividing the obtained values by the scan rate and the probed surface area.

**S3. Stationary Transmittance**

Figure S4 show the stationary transmittance curves of the P3HT film series taken at 520 nm in the oxidized and neutral state as a function of the calculated redox charge densities. Experimental data points are fitted by exponential decay functions. The P3HT film series show similar transmittance curves in the oxidized state (Figure S3A), while those in the neutral state (Figure S3B) exhibit larger deviations. The difference between transmittance values in the oxidized and neutral state then provides the contrast curve as a function of the redox charge density as shown in Figure 2 of the main manuscript.

**Gráfico, Gráfico de dispersión

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**Figure S3**. Transmittance values at 520 nm for the P3HT film series taken in their A) oxidized transparent states and B) neutral colored states as a function of the calculated redox charge density. Symbols represent experimental data points. Lines represent the fitted curves according to exponential decay functions. Regression coefficients r2 are indicated for all the film series.

The transmittance curve for P3HT-CHCl3 in the neutral state not only shows overall higher transmittance values but also its exponential fitting curve with lowest regression coefficient strongly deviates from the behavior of all the other films. The different and rather poor transmittance behavior reflects the non-continuous island-like coating of the ITO substrate obtained for this sample by the employed spray-coating process, as demonstrated by the SEM and profilometry results in the main manuscript (Figure 5D and 6D, respectively). The poor transmittance behavior of the spray-coated P3HT-CHCl3 sample in the neutral state thus accounts for the largely different contrast behavior compared to the other P3HT samples, with an apparent shift of the optimum contrast range towards rather high, i.e. out-of-range redox charge density values, as a consequence of unsatisfying fitting results.

**S4. Transmittance spectra**

Figure S4 shows the transmittance spectra of P3HT-THF film acquired in its neutral and oxidized states, reflecting its magenta and transparent pale blue colors, respectively. The transmittance minimum is obtained at 520 nm for the neutral state and provides the reference value at which maximum contrast, i.e. transmittance differences between the oxidized and neutral state is calculated for the different P3HT film series.

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**Figure S4**. Transmittance spectra of a P3HT film in its neutral and oxidized states.

**S5. Switching speed**

The switching speed of the P3HT films has been determined following the experimental procedure described in the experimental section of the main manuscript. Here the films are submitted to potential steps of variable pulse lengths of 15, 10, 5, 2, 1, 0.5 and 0.25 s between -0.3 and 1.1 V. A representative case study for a P3HT-THF film is depicted in Figure S5.

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**Figure S5.** A) Transmittance vs. time plot a P3HT-THF film. B) Contrast vs. pulse length extracted from the previous data and corresponding fitting function from which  values can be obtained.

**S6. Cycling stability**

The cycling stability of the P3HT films has been determined following the experimental procedure described in the experimental section of the main manuscript. Here the films are submitted to a number of potential steps between -0.3 and 1.1 V: 300 cycles of 10 s for each step were applied. A representative case study for a P3HT-THF film is depicted in Figure S6.

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**Figure S6.** A) Transmittance vs. time plot for a P3HT-THF film. B) Contrast vs. number of cycles extracted from the previous data and corresponding fitting function from which  values can be obtained.

**S7. Spin-coated P3HT-CHCl3 film**

Spin-coating of non-nanostructured P3HT-CHCl3 dispersions, provides a continuous film coverage of the ITO substrate, as can be seen by SEM (Figure S7A) and the profilometry curve of a representative film with average film thickness of 77 nm (Figure S7B). Therefore, the electrochromic transmittance and contrast behavior at 520 nm (Figure S7C) now shows more consistent results, comparable to those of the spray-coated films of the other P3HT series. This especially refers to the optimum redox charge density and maximum contrast being achieved. Equally, t90 switching speed (Figure S7D), as well as the cycling stability (Figure S7E) in the optimum redox window reveal a behavior close to the ones of the other spray-coated film series. However, the spin-coated P3HT-CHCl3 film is prone to delamination issues (Figure S7F), compromising the mechanical integrity of the film, and thus as well the contact to the underlying substrate. This results in the non-linear enhancement of the t90 switching and the decrease of the cycle stability, beyond the established optimum redox charge densities window, as can be seen in Figure S7D and S7E, respectively.

The overall electrochromic performance parameters for the spin-coated P3HT-CHCl3 series are summarized in Table S1.

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**Figure S7.** Characterization of spin-coated P3HT films deposited from chloroform. A) SEM image obtained at 30 kX magnification (scale bar 200 nm). B) Profilometry of a representative film with average thickness of 77 nm. C) Transmittance in transparent and colored states, together with resulting contrast, versus redox charge density. D) Switching speeds, represented by t90 values versus redox charge density. E) Cycling stability, represented by the number of cycles corresponding to a 20 % loss of the initial contrast value, i.e. N80 value. F) Images of delaminated films after cycling stability tests.

**Table S1.** Electrochromic performance parameters for spin-coated P3HT-CHCl3 series

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| --- | --- | --- | --- | --- |
|  | **Redox charge density**  **/ mCcm-2** | **Maximum contrast**  **/ %** | **Switching speed t90**  **/s** | **Cycling stability N80** |
| **P3HT-CHCl3** | 2.7 | 48 | 0.48 | 220 |

**REFERENCES**

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