Supporting Information

The optical signatures of molecular-doping induced polarons in poly(3-hexylthiophene-2,5-diyl): individual polymer chains *versus* aggregates

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XPS peak fitting:

High-resolution S 2p peaks were deconvoluted into two components, (1) neutral sulfur and (2) sulfur in a positively charged environment (polarons). Peak fitting was performed in CasaXPS software, using a Shirley background and mixed Gaussian – Lorentzian peak shapes.

Each component was fitted as a doublet of S $2p_{3/2}$ and S $2p_{1/2}$ using the following constraints that were optimized by fitting an undoped P3HT film:

- Doublet ratio was held constant at $\frac{A\ [S\ 2p1/2]}{A\ [S\ 2p3/2]} = 0.5$
- The separation of the doublets was optimized to a value of 1.2 eV.
- Optimized peak shape mixing ratio was 0.30 (Lorentzian to Gaussian)

The sulfur in the positively charged environment was set to 0.6 eV higher binding energy as relative to the neutral sulfur component. The results of the fitted peaks are shown in Table S1.

Table S1: Fitting results of the S 2p high-resolution peaks.

Sample	1:4 doped P3HT	1:4 doped P3HT filtered	1:40 doped P3HT	1:40 doped P3HT filtered
Component 1 (neutral sulfur)				
Position (eV) (S $2p_{3/2}$)	163.0	163.0	162.9	163.2
Width (eV)	0.78	0.78	0.78	0.78
Component 2 (sulfur in the positively charged environment)				
Position (eV) (S $2p_{3/2}$)	163.6	163.6	163.5	163.8
Width (eV)	0.78	0.78	0.78	0.78

Table S2: Quantification of XPS data. Calculation of polaron density is based on the assumption that polarons are delocalized in the intrachain direction of P3HT over 4 monomer units,[1] the ratio of polarons/Sulfur atoms can be estimated according to the table below

Dopant ratio	condition	S^+/S^{tot}	Polaron/S^{tot}	Distance in monomer units
1:4	as-is	0.17	0.0425	24
1:4	F200	0.06	0.015	67
1:40	as-is	0.09	0.0225	44
1:40	F200	0.10	0.025	40

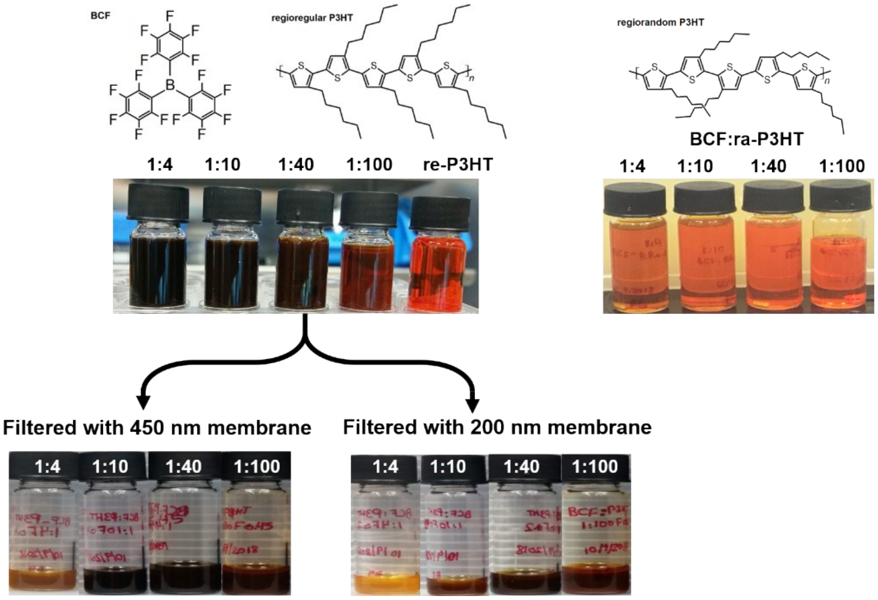

Figure S1: The chemical structure of the materials used in this work, along with the images showing the colour change in BCF:re-P3HT and BCF:ra-P3HT solutions with increasing dopant ratio (at a fixed absolute concentration). Fully soluble P3HT in solution exhibits a dark orange colour, which gradually changes to a black suspension with increasing dopant ratio for BCF:re-P3HT, whereas no change is observed in BCF:ra-P3HT. Changes in the colour of re-P3HT suspensions upon filtration with membranes of two sizes F450 and F200 are shown, in which an obvious change is seen at high dopant ratios of 1:4 and 1:10, whereas no distinct change is observed for lower dopant ratios of 1:40 and 1:100.

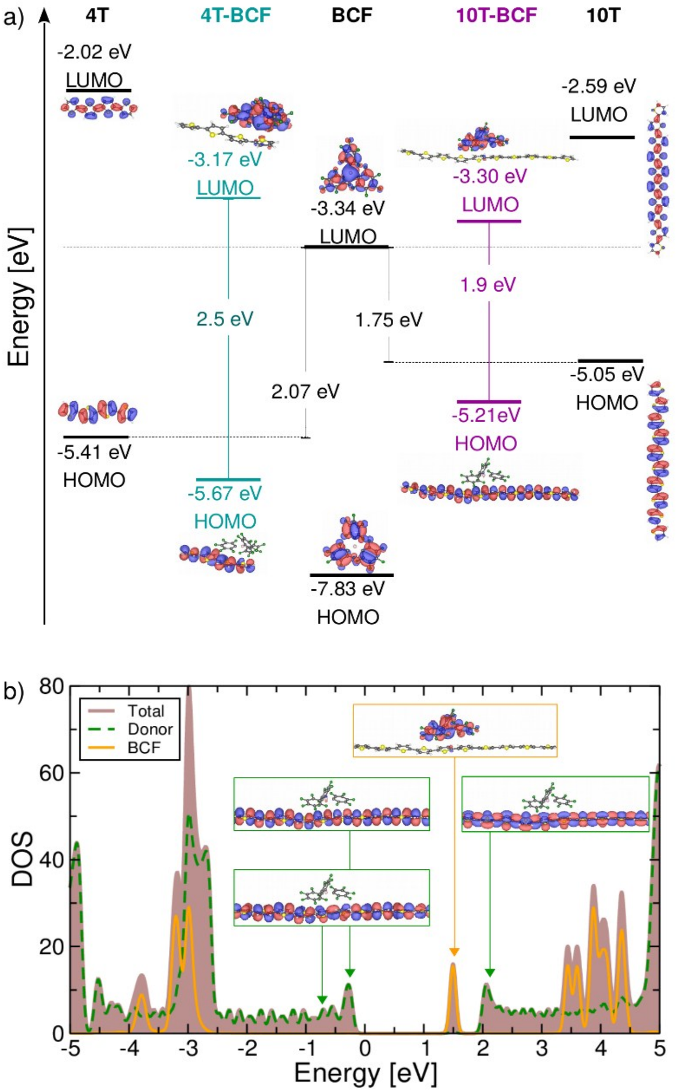

Figure S2: a) Energies and spatial distribution of the frontier orbitals of BCF with respect to the considered thiophene oligomers and the resulting D/A complexes computed from density functional theory. b) Density of states (DOS) representing the total as well as the donor and acceptor contributions of BCF-doped polythiophene. The spatial distribution of selected states close to the frontier are shown in the inset.

We performed first-principles calculations in the framework of density-functional theory (DFT) to investigate the charge transfer in donor/acceptor complexes formed by BCF-doped thiophene chains. For this purpose, we considered both, a polythiophene (PT) chain, modeled by a unit cell of 10 thiophene rings repeated periodically in the conjugation direction, and isolated thiophene oligomers including 4 and 10 rings. The results of our analysis reveal that no hybridization is present between the frontier orbitals of the donor and the acceptor. While the individual BCF and nT molecules exhibit a type-II level alignment (see Fig. S2a) with the frontier states of the D/A system energetically comprised between the HOMO and the LUMO of the constituents as in the case of F4TCNQ doped nT,[2–4] the HOMO and the LUMO of the doped system are segregated on the donor and the acceptor, respectively. We note that the conjugation length of the thiophene chain does not play a role here, as confirmed also from the analysis of the BCF-doped PT (see Fig. S2b). In this case, we calculate the density of states (DOS) of the system projected over the single constituents. The total contribution is also shown for comparison. From this plot shown in Fig. S2b we can see that, at least in the gap region, the states associated to BCF are segregated from those of the donor. Remarkably, also at lower (higher) energies in the valence (conduction) region, the contributions of BCF are shaped as sharp peaks rather than broad features typical of hybridized systems.

The absence of orbital hybridization rules out the possibility of doping occurring via partial charge transfer between the donor and the acceptor. For a more quantitative assessment of the degree of charge transfer in the ground state, we calculate the Hirshfeld partial charges in all the D/A systems represented in Fig. S2 and we subtract them the values associated to the isolated constituents. In this way, we find a charge transfer of the order of 10^{-2} in the nT/BCF systems and of the order of 10^{-2} in BCF-doped PT. These results indicate that essentially no charge transfer occurs in the ground state between the thiophenes and BCF.

Theoretical background and computational details

All calculations are carried out from DFT with the all-electron code FHI-aims,[5] adopting the hybrid functional PBE0[6] to optimize the geometries (until the Hellmann-Feynman forces are smaller than 10^{-3} eV/Å) and to compute the electronic properties. In the case of PT/BCF the geometry optimization is performed within the generalized gradient approximation for the exchange-correlation functional using the Perdew-Burke-Ernzerhof (PBE) parameterization.[7] Van der Waals interactions are included with the Tkatchenko-Scheffler scheme.[8] The Brillouin zone sampling of the periodic PT/BCF system is performed with a 6x1x1 **k**-grid. The optimized lattice parameters of the unit cell, which contains 10 thiophene rings and one BCF molecule, are 39.00 Å in the periodic direction and 26.16 Å in the non-periodic direction, where about 42 Å of vacuum are included to avoid interaction between the replicas. The dipole correction is applied to prevent artificial electrostatic interactions between the replicas.

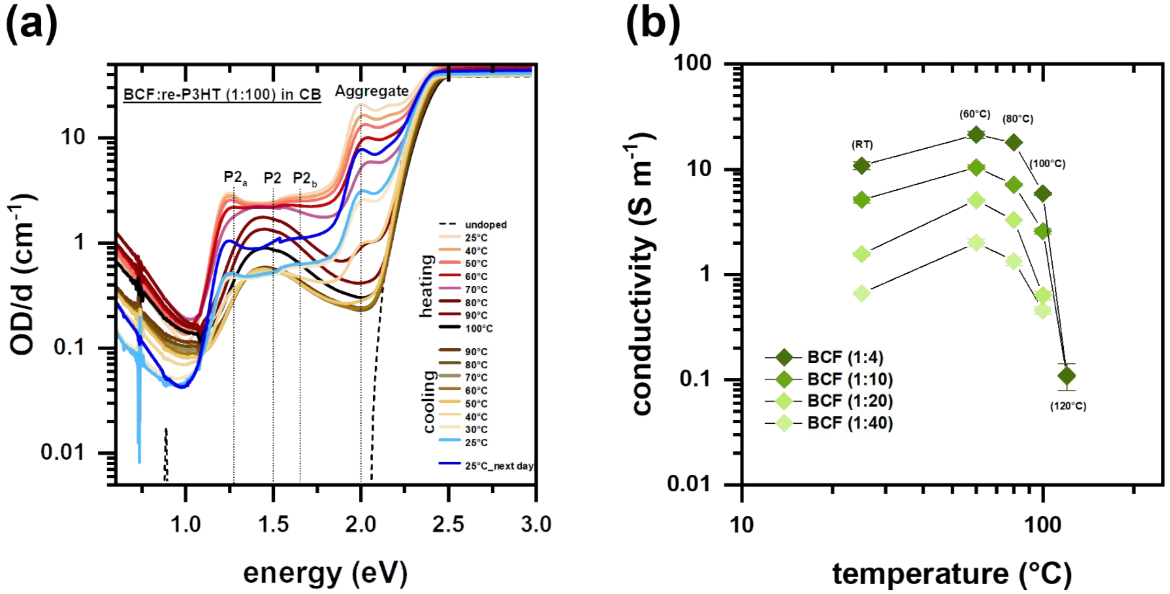

Figure S3: Temperature dependence of (a) Optical absorption spectra of BCF:re-P3HT (1:100) in chlorobenzene solution and (b) electrical conductivity of BCF:re-P3HT thin films at different dopant *ratio. The optical absorption measurements were taken at the specified temperature after allowing the solution to equilibrate for 10 minutes. (re-P3HT (at 2.15 mg/ml) and BCF solutions (0.93 mg/ml) in chlorobenzene were individually prepared in the glove box, and subsequently blended in the ratio 1:100. The final concentration of rreP3HT was 2 mg/ml).*

Details of conductivity measurements:

BCF:re-P3HT solutions of specific doping ratios were prepared by blending P3HT solution (at 20 g/L in CF) with the required volume of BCF solution (at 20g/L, 10g/L or 5 g/L), such that the final concentration of P3HT was ca. 11-15 g/L in the doped solution. Films were subsequently prepared by spin coating the solutions at 2000 rpm for 50 seconds onto pre-cleaned glass substrates. The film thickness was ca. 120nm, as measured using a profilometer (Veeco Dektak). Conductivity was measured on a home-built four point-probe (4PP) setup. After the initial measurement at room temperature (RT), the films were heated for 15 minutes at each temperature, then cooled for 10 minutes, and subsequently measured. In the figure, the data points refer to the mean value of the conductivity measured at 6 different regions on the film (and the error bar is the standard deviation from the mean value). Solution preparation, spin coating, and conductivity measurement was done in inert nitrogen atmosphere.

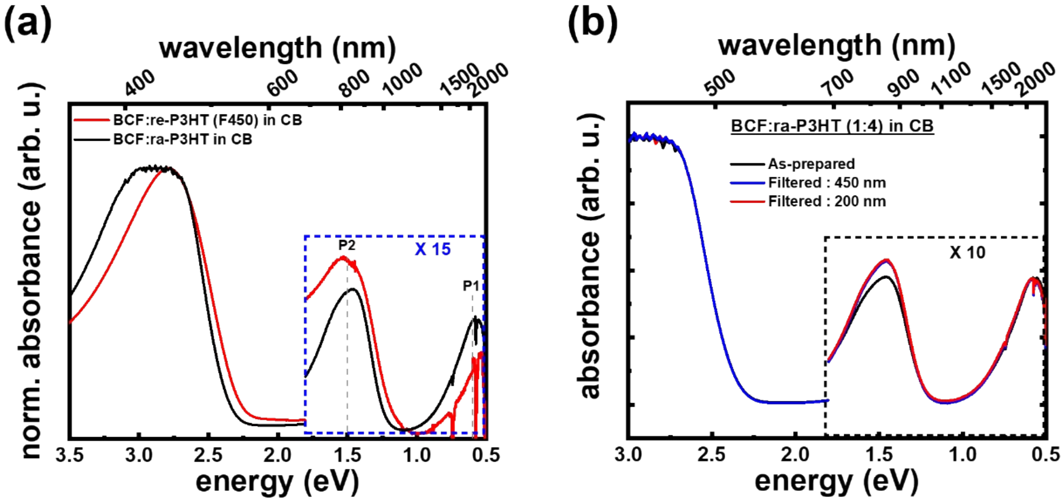

Figure S4: Optical absorption spectra of BCF:P3HT (1:4) in (a) doped single chains in solution of ra-P3HT (black) and filtered re-P3HT suspension (red) – inset is a zoom into the absorption features of the polarons – and (b) optical absorption spectra of BCF:ra-P3HT (1:4) before and after filtration with F450 and F200. Ra-P3HT solution is prepared at the absolute concentration of 2 mg/ml.

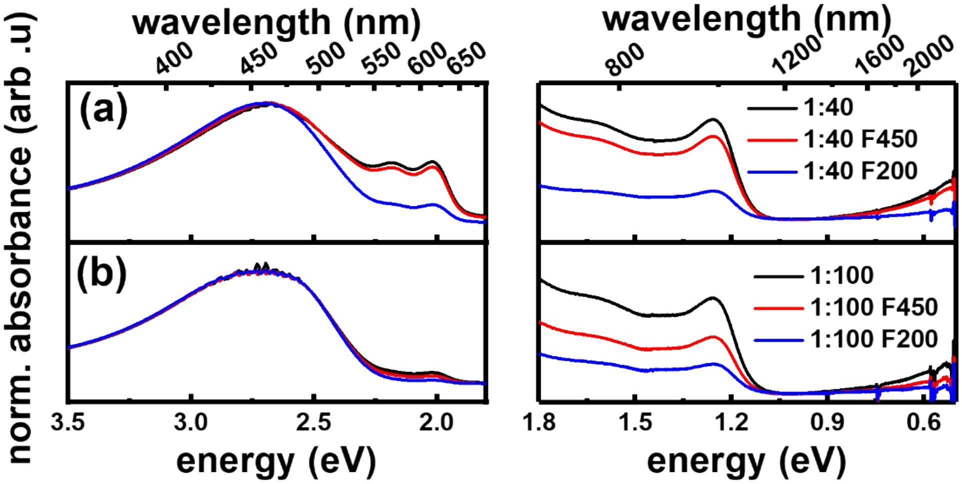

Figure S5: Changes of optical absorption spectra of BCF doped P3HT suspensions with filtration for absolute concentration of 1 mg/ml for (a) dopant ratio of 1:40 and (b) 1:100.

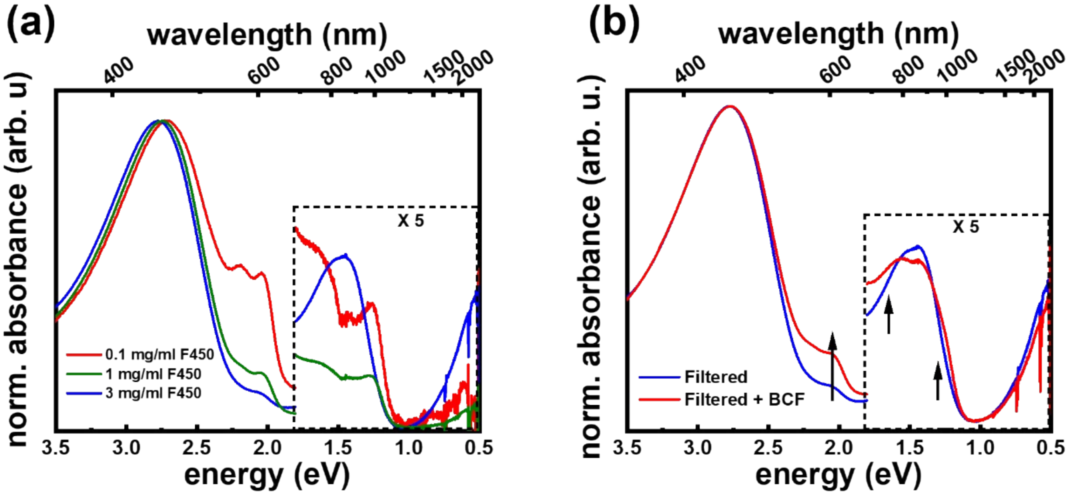

Figure S6: Optical absorption spectra of (a) filtered BCF doped P3HT (1:4) solutions prepared at different absolute concentrations and (b) filtered (1:4) doped P3HT solutions prepared at an absolute concentration of 3 mg/ml before and after the addition of BCF solution. The comparision in panel (a) indicates that increasing the absolute concentration increases the size of the aggregates in the suspension, and thus can be effectively removed upon filtration for the high absolute concentration of 3 mg/ml.On the other hand,, filtration of lower absolute concentrations (0.1 and 1 mg/ml) with the same size of filter, resulted in the absorption features of polarons in aggregated P3HT, meaning that aggregates form at lower soluation concentration can pass the filter. Panel (b) shows the possibility of reaggregating doped P3HT in filtered solutions with the addition of the dopant. The arrows indicate the positions of the neutral aggregates absorption (2.1 eV) and the positions of the absorption features of polarons in aggregated P3HT (1.65 eV and 1.3 eV).

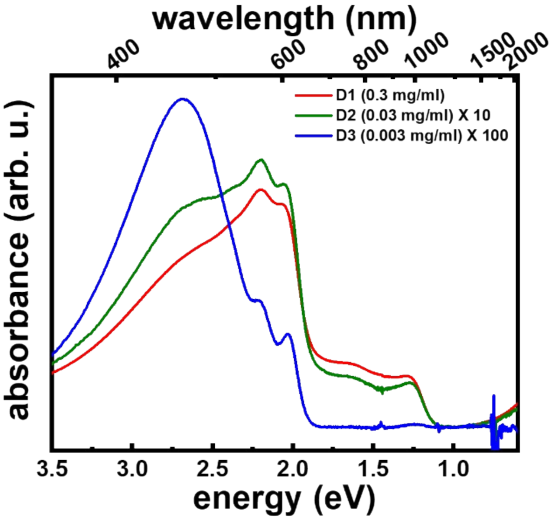

Figure S7: Effect of dilution of BCF doped RRe-P3HT (1:4) starting from an absolute concentration of 3 mg/ml. In all cases the absorption features of the polaron in aggregated P3HT as well as neutral aggregated P3HT are present. This indicates the stability of the aggregates (both neutral and doped) is enhanced with the presnce of dopant.

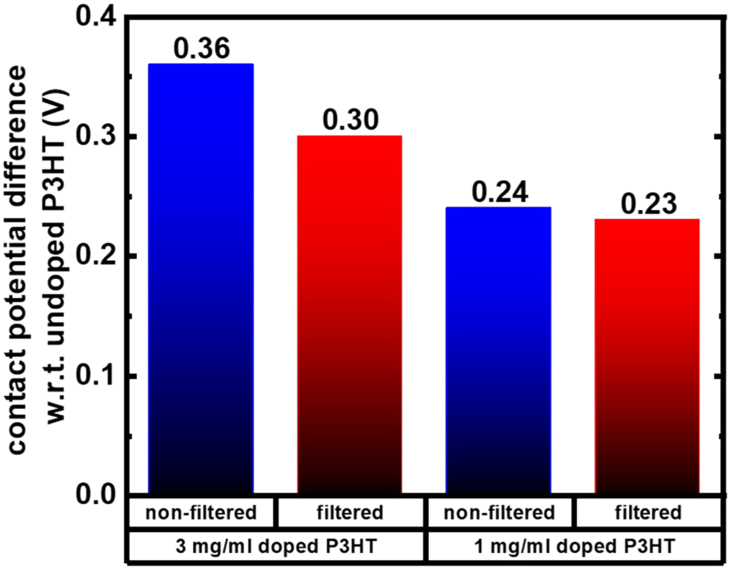

Figure S8: Contact potential difference with reference to undoped P3HT (0V) in thin films of P3HT spin-coated from filtered and non-filter suspensions at two different dopant concentrations. All data are for doped films with 1:4 dopant ratio.

References:

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