Supporting Information to

"Comprehensive picture of p-doping P3HT with the molecular acceptor F_4TCNQ"

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I. OPTICAL ABSORPTION SPECTROSCOPY

A. Reference spectra

In order to evaluate the optical spectra of F_4TCNQ-doped P3HT layers and solutions, proper reference spectra of the neat charged compounds are indispensable. The P3HT polaron reference spectrum was prepared by exposing the P3HT powder to I_2 vapor. The doped polymer was then dissolved in chloroform. The spectrum of this solution, plotted in Fig. 3b of the article, serves as a reference of the relative absorption of P3HT polarons in F_4TCNQ-P3HT blends.

In order to determine the absolute amount of F_4TCNQ anions in our samples, we use the extinction coefficient spectra of neutral F_4TCNQ and ionized F_4TCNQ bound in a charge transfer salt which we have taken from Dixon et al. (Ref. 1 in this Supporting Information). For integrity of our analysis, we compare these spectra with our own measurements. Close accordance is exhibited between the published spectrum of a crystal of neutral F_4TCNQ and our measurement of $0.01\,\mathrm{g/l}$ F_4TCNQ dissolved in chloroform (CF) in terms of the shape of the spectra and the absolute value of the extinction coefficient (thick solid and dashed lines in Fig. 1a, respectively). Preparation of a neat reference sample for obtaining the F_4TCNQ anion absorption is unfortunately not straightforward. We have prepared a solution of $0.01\,\mathrm{g/l}$ F_4TCNQ in tetrahydrofuran (THF) and added ca. $4\,\mathrm{\mu l}$ of a $1\,\mathrm{g/l}$ potassium iodide solution in water (K^+I^-) in order to reduce a significant, but unknown, amount of the F_4TCNQ molecules. Again, excellent accordance of the shapes of the specific F_4TCNQ anion absorption in the NIR (between 1 and $2\,\mathrm{eV}$) is exhibited between our measured spectrum and the literature data (thick solid and dashed lines in Fig. 1b, respectively). As concluded from these comparisons, we can use the spectra published in Ref. 1 as absolute references in order to measure the content of neutral F_4TCNQ and F_4TCNQ anions in our blends.

Note that the algebraic decomposition analysis cannot be directly performed on the spectra of F_4TCNQ-P3HT layers, because the NIR absorption of the F_4TCNQ anions is affected by the polymer matrix in terms of a broadening of the absorption bands and strong tails. This can be seen in Fig. 1b, thin dashed lines, for a sample that incorporates F_4TCNQ anions in an inert matrix of poly(methyl methacrylate) (PMMA). Therefore, in order to evaluate the number of P3HT-F_4TCNQ charge transfer pairs in the doped layers, we proceed as de-
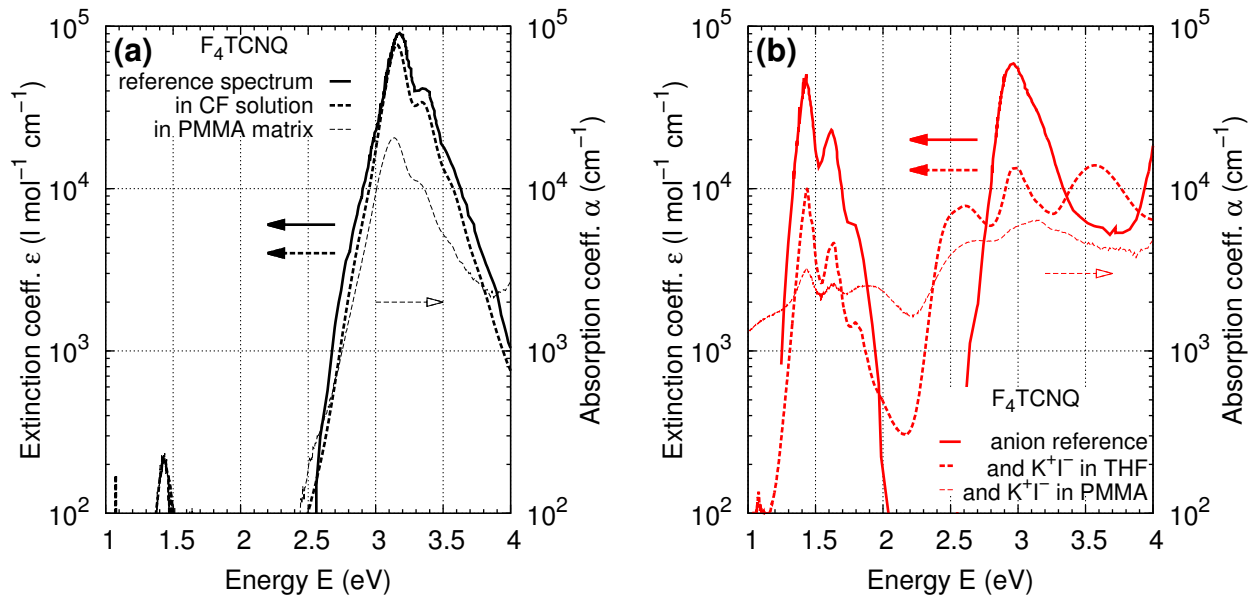
FIG. 1. Reference[1] and experimental extinction and absorption coefficient spectra of (a) neutral and (b) singly negatively charged F_4TCNQ. Solutions were prepared at $0.01\,g/l$ in chloroform (a) and tetrahydrofuran (b). Thin film samples were prepared from a blend of one F_4TCNQ molecule per 100 repeat units of poly(methyl methacrylate). F_4TCNQ was reduced by adding a little amount of a water-based potassium iodide solution to the F_4TCNQ-THF solution.

scribed in the article, i.e., we apply the extinction coefficient of the P3HT-F_4TCNQ charge transfer pairs which we have priorly determined in solution.

B. Decomposition of the solution spectra

Absorption spectra of the F_4TCNQ-P3HT blends in chloroform have been algebraically decomposed in the NIR into the F_4TCNQ anion and P3HT polaron parts (Figs. 2-4). Interestingly, the fraction of intentionally applied F_4TCNQ molecules that has been recovered as F_4TCNQ anions in the analysis is a function of the solution concentration. Depending on the initial concentration of the undoped P3HT solution, we recover $50 - 83\%$ (at $2\,g/l$), $42 - 67\%$ (at $0.5\,g/l$), and $6 - 16\%$ (at $0.025\,g/l$) of the F_4TCNQ molecules as anions (see Tables I-III). For the $0.025\,g/l$-based solutions, we observe the specific absorption bands of neutral F_4TCNQ between 3 and $3.5\,eV$. A rough analysis of these bands using the reference extinction coefficient spectrum recovers $73 - 93\%$ of the applied F_4TCNQ as neutral

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molecules. Similar observations have been made by Parashchuk et al.[2] for poly(methoxy-5-(20-ethylhexyloxy)-1,4-phenylene-vinylene), MEH-PPV, doped with the organic acceptor 2,4,7-trinitrofluorenone, TNF. The authors inferred that the dopants do not penetrate into the polymer coils in dilute solutions, resulting in only few charge transfer pairs being formed at the surface of these coils. At higher solution concentrations, dopants do enter and charge transfer occurs with interior polymer units as well. It is worth to note that the typical P3HT concentration in solutions which we have used to prepare solid samples is in the range of $0.5 - 30\,\mathrm{g/l}$, which is in a regime where most of the F_4TCNQ dopants underwent charge transfer with P3HT.
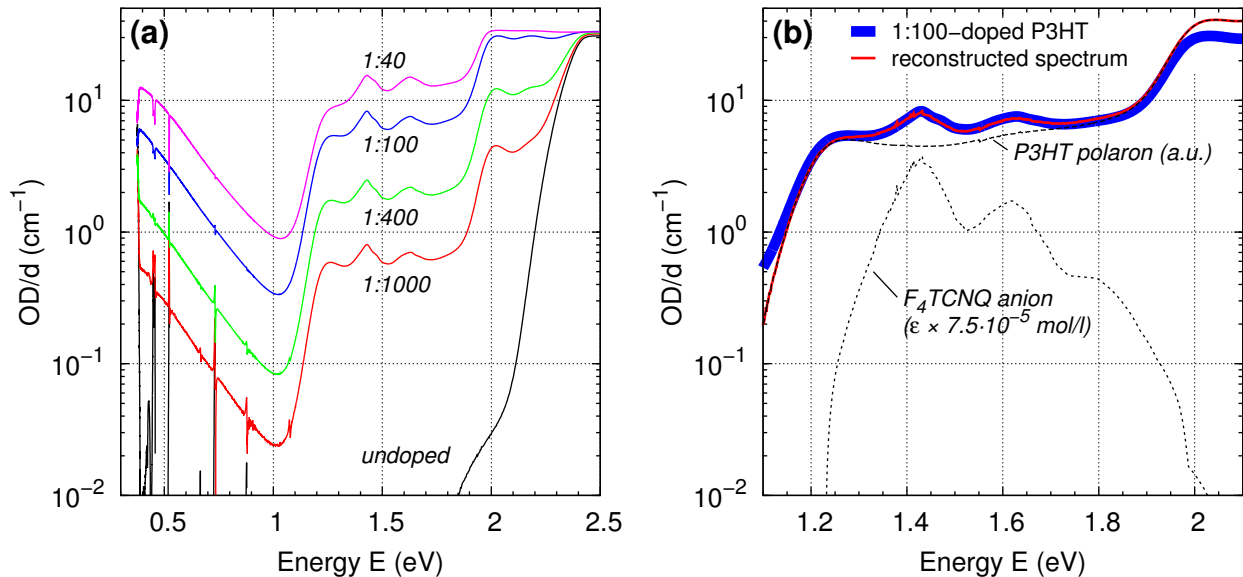

FIG. 2. (a) Absorbance-per-length of undoped and F_4TCNQ-doped P3HT solution in chloroform. The undoped P3HT solution sample had a concentration of $2\,\mathrm{g/l}$. (b) Reconstruction of the P3HT polaron/F_4TCNQ anion absorption of the 1:100-doped P3HT sample from reference spectra. The F_4TCNQ anion spectrum is reprinted with permission from Ref. 1. Copyright 1989 American Chemical Society.

TABLE I. Concentrations of ionized F_4TCNQ found in a blend with P3HT in chloroform at various doping ratios. The undoped P3HT solution sample had a concentration of $2\,g/l$.

Doping ratio	P3HT repeat units[a] (mol/l)	F_4TCNQ[a] (mol/l)	F_4TCNQ^-[b] (mol/l)	ionized fraction
1:1000	1.19×10^{-5}	1.19×10^{-5}	6.0×10^{-6}	0.50
1:400	1.18×10^{-5}	2.96×10^{-5}	2.0×10^{-5}	0.68
1:100	1.13×10^{-5}	1.13×10^{-4}	7.5×10^{-5}	0.66
1:40	1.03×10^{-5}	2.58×10^{-4}	1.8×10^{-4}	0.70

[a] intentionally applied amount in solution

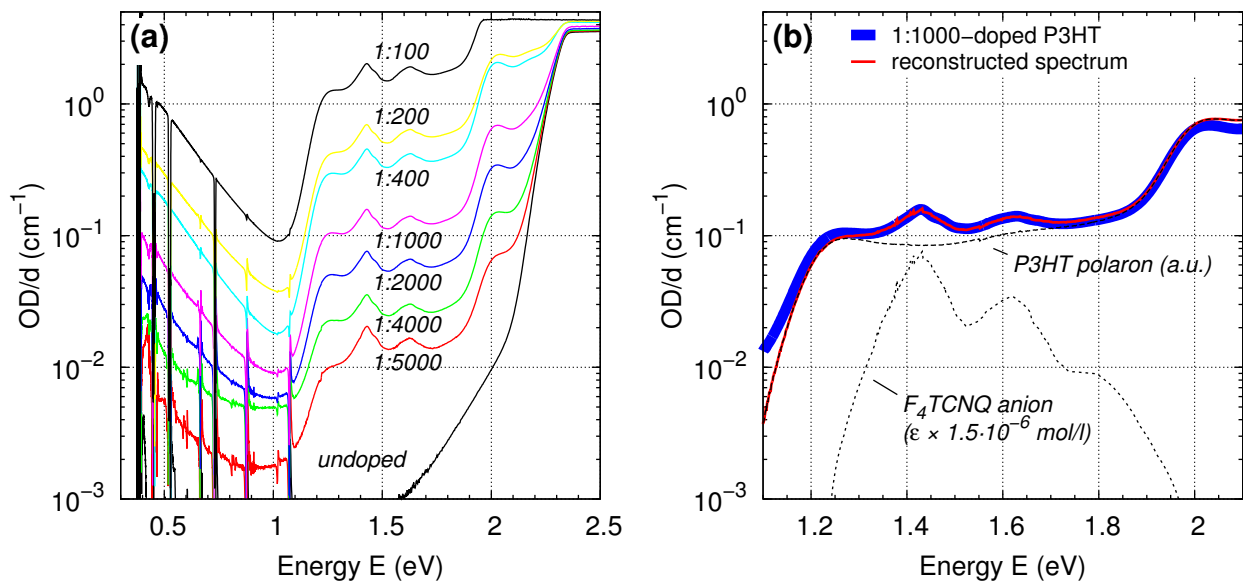[b] measured by decomposition of the optical spectra

FIG. 3. (a) Absorbance-per-length of undoped and F_4TCNQ-doped P3HT solution in chloroform. The undoped P3HT solution sample had a concentration of $0.5\,g/l$. (b) Reconstruction of the P3HT polaron/F_4TCNQ anion absorption of the 1:1000-doped P3HT sample from reference spectra.

TABLE II. Concentrations of ionized F_4TCNQ found in a blend with P3HT in chloroform at various doping ratios. The undoped P3HT solution sample had a concentration of $0.5\,\mathrm{g/l}$.

Doping ratio	F_4TCNQ^{-a} (mol/l)	F_4TCNQ^b (mol/l)	ionized fraction
1:5000	2.5×10^{-7}	6.0×10^{-7}	0.42
1:4000	3.5×10^{-7}	7.5×10^{-7}	0.47
1:2000	7.0×10^{-7}	1.5×10^{-6}	0.47
1:1000	1.5×10^{-6}	2.9×10^{-6}	0.52
1:400	5.0×10^{-6}	7.5×10^{-6}	0.67
1:200	7.5×10^{-6}	1.3×10^{-5}	0.58
1:100	2.0×10^{-6}	3.0×10^{-5}	0.66

[a] measured by decomposition of the optical spectra

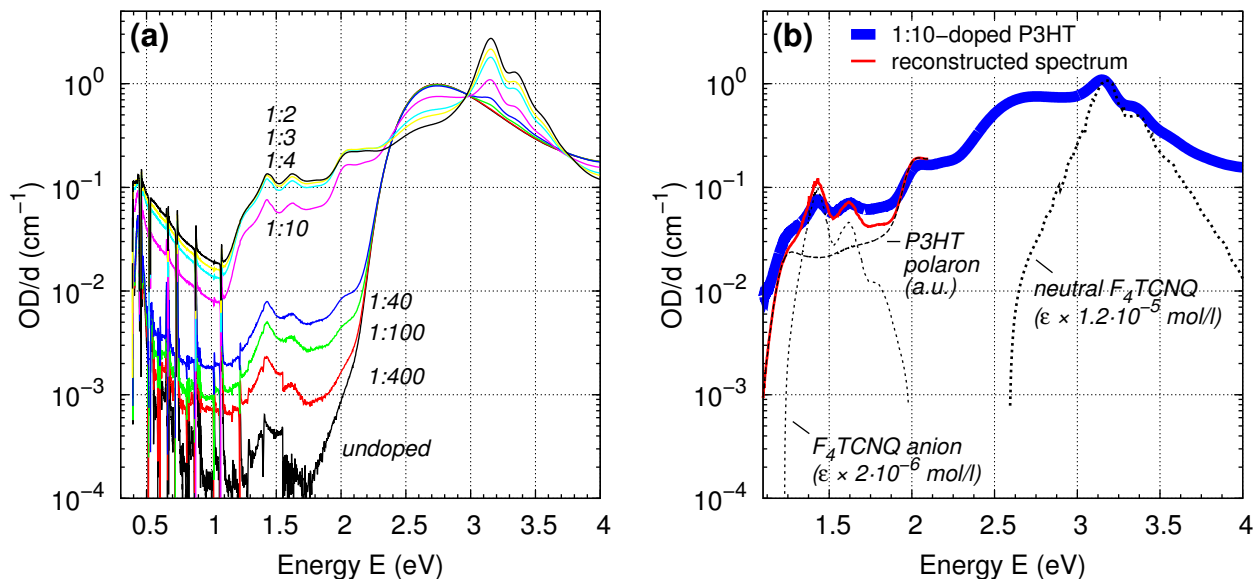[b] intentionally applied amount in solution

FIG. 4. (a) Absorbance-per-length of undoped and F_4TCNQ-doped P3HT dilute solution in chloroform. The undoped P3HT solution sample had a concentration of $0.025\,\mathrm{g/l}$. (b) Reconstruction of the P3HT polaron/F_4TCNQ anion and neutral F_4TCNQ absorption of the 1:10-doped P3HT sample from reference spectra.

TABLE III. Concentrations of ionized F_4TCNQ found in a blend with P3HT in chloroform at various doping ratios. The undoped P3HT solution sample had a concentration of $0.025\,g/l$.

Doping ratio	F_4TCNQ^{-a} (mol/l)	F_4TCNQ^{a} (mol/l)	F_4TCNQ^{b} (mol/l)	ionized fraction	
1:100	1.2×10^{-7}	–	1.5×10^{-6}	0.08	–
1:40	2.0×10^{-7}	–	3.6×10^{-6}	0.06	–
1:10	2.0×10^{-6}	1.2×10^{-5}	1.3×10^{-5}	0.16	0.93
1:4	3.0×10^{-6}	2.0×10^{-5}	2.7×10^{-5}	0.11	0.75
1:3	2.3×10^{-6}	2.4×10^{-5}	3.2×10^{-5}	0.07	0.74
1:2	2.3×10^{-6}	3.0×10^{-5}	4.1×10^{-5}	0.06	0.73

[a] measured by decomposition of the optical spectra
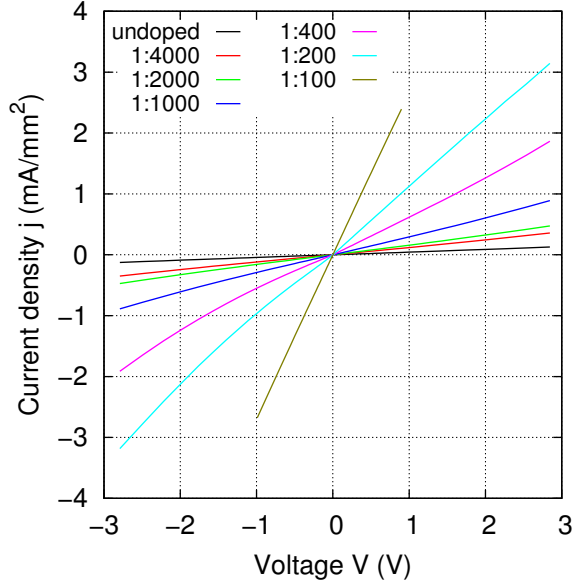[b] intentionally applied amount in solution

FIG. 5. *I-V* characteristics of undoped and F_4TCNQ-doped P3HT hole-only devices.

II. HOLE-ONLY *I-V* CHARACTERISTICS

Hole-only devices of undoped and F_4TCNQ-doped P3HT layers with a PEDOT:PSS bottom electrode and a MoO_3/Al top electrode exhibit symmetric *I-V* characteristics (Fig. 5). Positive voltages refer to hole injection from the PEDOT:PSS electrode. Conductivities were extracted by using a linear fit within 0 to +1 V.

[1] D. Dixon, J. Calabrese, and J. Miller, J. Phys. Chem. **93**, 2284 (1989).

[2] O. D. Parashchuk, A. Y. Sosorev, V. V. Bruevich, and D. Y. Paraschuk, JETP Lett. **91**, 351 (2010).