Supporting information

Influence of dopant size and doping method on the structure and thermoelectric properties of PBTTT films doped with F$_6$TCNNQ and F$_4$TCNQ

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Figure ES11. a) Concentration dependence of the $F_6TCNNQ^-$ anion absorption spectrum in acetonitrile in the presence of ferrocene. b) absorbance versus $F_6TCNNQ^-$ anion concentration yielding an extinction coefficient $\varepsilon=53700\pm1000 \text{ L Mol}^{-1}\text{ cm}^{-1}$. 
Figure ESI2: Plot of absorbance of the dopant anions vs that of the polarons ($\lambda=2500$ nm).

The linear fit supports integer charge transfer between $C_{12}$-PBTTT and both $F_4$TCNQ and $F_6$TCNNQ.
**Figure ESI3.** Doping kinetics of C$_{12}$-PBTTT thin films doped with 1 mg/ml F$_4$TCNQ and F$_6$TCNNQ. A) and B) represent the time dependence of the absorption for both F$_4$TCNQ and F$_6$TCNNQ anions along the perpendicular directions. C) and D) Evolution of the polaronic bands P1 and P2 in F$_4$TCNQ and F$_6$TCNNQ doped PBTTT C$_{12}$, respectively.
Figure ESI4. A) and B) represents UV–Vis–NIR absorption spectra of oriented C_{12}-PBTTT (before doping) plotted for different angles (every 15°) between the direction of polarization and the rubbing direction. C) and D) Polarized UV–Vis–NIR absorption spectra of F\textsubscript{6}TCNNQ doped PBTTT and F\textsubscript{4}TCNQ doped PBTTT plotted for different angles (every 15°) between the direction of polarization and the direction of rubbing of the film. At 0°, the incident light is parallel to the direction of rubbing (POL // R) whereas at 90° it is perpendicular to the rubbing direction (POL ⊥ R). E) Example of deconvolution of the UV-vis-NIR spectra for C\textsubscript{12}-PBTTT thin films doped with F\textsubscript{6}TCNNQ when the incident polarization angle is 45°. The spectra on
top (blue) result from the overlap of the anionic contribution at 1158 nm, with the polaronic (P2) and N components. The spectra in red contain the sum of all components beneath the anion bands.

Figure ESI5. Polarized UV-Vis-NIR spectra of doped PBTTT thin films (100 nm thick) doped by ICD and dipping in acetonitrile. In the ICD, the thin film is dipped in increasing doping concentration of 0.01, 0.1, 0.5, 1 and 2 mg/ml $F_6$TCNNQ in ACN. To exclude the effect of solvent, another thin film dipped 4 times in ACN and then directly doped by dipping in 2mg/ml $F_6$TCNNQ in ACN.
Figure ESI6. Evolution of the electron diffraction patterns doped $C_{12}$-PBTTT upon incremental concentration doping (A-C) and direct doping with $F_4$TCNQ (D-F). $R$ represents the rubbing direction.
I. Synthesis of 1,3,4,5,7,8-Hexafluorotetracyanonaphthoquinodimethane (F₆TCNNQ).

The synthesis was performed by following the synthetic path given below.

2-Tert-butyl-2-[6-(1,1-dicyano-2,2-dimethyl-propyl)-1,3,4,5,7,8-hexafluoro-naphthalen-2-yl]-malononitrile (compound 1):

In a 50 mL flame dried round bottom flask equipped with magnetic stir bar was added 8 mL of 1,2-dimethoxyethane and NaH 60% in mineral oil (0.65 g, 16.25 mmol). The suspension was cooled on ice bath and a solution of t-butylmalononitrile (1.88 g, 15.38 mmol) in 4mL of dimethoxyethane (DME) was slowly added. The mixture was stirred 20 min at room temperature. Then a solution of octafluoronaphtalene (2 g, 7.35 mmol) in 4 mL of DME was added. The mixture was then refluxed overnight, cooled to room temperature and 80 mL of water was added. The white precipitate was filtered and washed with diethyl ether (Et₂O) to give pure compound 1 with a yield of 96 % (2.6 g).

¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 1.29 (s).

¹⁹F NMR (DMSO-d₆, 400 MHz): δ (ppm) -113.2 (dd, J₉-F = 73.9, 18.1 Hz); -133.7 (d, J₉-F = 21.41 Hz); -147.2 (d, J₉-F = 74.8 Hz).
Figure S1. $^1$H NMR of compound 1 in DMSO-d$_6$. 
**Figure S2.** $^{19}$F NMR of compound 1 in DMSO-$d_6$.

**1,3,4,5,7,8-Hexafluorotetracyanonaphthoquinodimethane (compound 2):**

A 250 mL round bottom flask was charged with 80mL of diphenyl ether and warmed to 260°C. The previous compound 1 (2.6 g) was added in one portion to the flask and the mixture was refluxed for 5 min. The solution was cooled to room temperature, 80 mL of Et$_2$O was added and the organic phase was extracted with 4 % NaHCO$_3$ solution. Aqueous layer acidified with 30 % HCl giving a white solid that was filtered on sintered funnel. This solid was treated with bromine water. The solid, that turned purple, was washed with water and then with Et$_2$O and dried under vacuum to give a purple solid. The solid was then sublimated under vacuum ($P=10^{-6}$ bar, $T_{\text{max}}=280^\circ$C) to give green crystals on the bottom of the collector and purple solid on the top, according to the literature, with a yield of 40 % (0.8 g).

$^{19}$F NMR (Toluene-$d_8$, 400 MHz): $\delta$ (ppm) -137.1 (m, 2F); -103.5 (d, $J_{F,F} = 80$ Hz).
Figure S3. $^{19}$F NMR of compound 1 in DMSO-d$_6$. 