Supplementary Materials for

Molecular doping in organic semiconductors; fully-solution processed, vacuum free doping with metal-complex in orthogonal solvent

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Details of process conditions



SI Fig. S1: Optimization of process temperature. Variation in conductivity for PBTTT doped by F4-TCNQ in acetonitrile (red) and that doped in CT-solv (orange) with respect to process temperature. The thin film of PBTTT was immersed into dopant solvent/solution for 30 mins at given temperatures. Two-terminal conductivity measurements were performed inside an Ar-filled glovebox at 20 °C. The measured conductivity was smaller than that shown in the main text because the effect of contact resistance was not corrected. For the interest of safety, the process temperatures were limited below a boiling point of solvent, *i.e.* < 82 °C for acetonitrile and < 170 °C for CT-solv. The apparent decrease in conductivity for CT-solv at 120 °C is presumably because the process temperature approaches the sublimation temperature of F4-TCNQ (approximately 125 °C). Employing CT-sov can be advantageous because of its high boiling point.

UV-vis absorption spectra in solution



SI Fig. S2: UV-vis absorption spectra in solution. UV-vis absorption spectra for PBTTT-C14 (black), Mo(tfd-COCF₃)₃ (red), and their mixture (blue) in 1,2-dichlorobenzene. Neutral absorptions for Mo(tfd-COCF₃)₃ are found at 288, 400, and 602 nm. These peaks were found in PBTTT-C14/Mo(tfd-COCF₃)₃ solid film (See Fig.S2b), suggesting that there a finite neutral Mo(tfd-COCF₃)₃ remains in the solid film. Apparent doping features are also confirmed in solution; $\pi - \pi^*$ transition at approximately 500 nm in PBTTT becomes bleached, and polaron absorption (a shoulder around 750 nm and a broad tail from 1000 to 2000 nm) appears.

Raman mode assignment



SI Fig. S3: **Raman spectra for PBTTT** Raman spectra for PBTTT-C14 (black), PBTTT/F4-TCNQ (red), and PBTTT/Mo(tfd-COCF₃)₃ (blue).

Mode		Wavenumber (cm	$1^{-1})$	$Description^1$
	This work	Furukawa $et.al.^2$	Francis $et.al.^1$	
А	1391	1390	1392	C=C stretching, thienothiophene core
В	1414	1412	1415	C=C stretching, thiophene ring
\mathbf{C}	1489	1486	1488	C=C/C-C stretching/shrinking

TABLE I: Raman mode assignment for neutral PBTTT. Comparisons of Raman modes for neutral PBTTT.

Mode	Wavenumber (cm^{-1})			Description
	F4-TCNQ	$Mo(tfd-COCF_3)_3$	$\mathrm{FeCl}_3{}^2$	
a	1334	1336	1336	cation PBTTT
b	1383	1379	1383	cation PBTTT
с	1412	N.A.	N.A.	remaining of the neutral mode B
d	1450	1451	1449	cation PBTTT
е	1484	N.A.	N.A.	remaining of the neutral mode C
f	1643	N.A.	N.A.	anion F4-TCNQ

TABLE II: **Raman mode assignment for cation PBTTT.** Comparisons of Raman modes for cation PBTTT. Although the assignment of each vibrational modes is not clear so far, peaks at 1383, 1450, and 1484 cm⁻¹, which are observed commonly for the doped PBTTT, are in good agreement with literature values.

Analysis of coherence factor

In the main text, the fraction of band carriers was determined from the coherence factor based on the recently developed model of Hall effect³ in a mixed transport regime of hopping and band carriers. The model assumes two-channel conduction: the total longitudinal conductivity is given as $\sigma = en_{\text{band}}\mu_{\text{band}} + en_{\text{hopping}}\mu_{\text{hopping}}$, where n_{band} , n_{hopping} and μ_{band} , μ_{hopping} are the corresponding carrier densities and mobilities for band and hopping carriers, respectively. Because the delocalized band-like carrier should have a finite group velocity, they experience the Lorentz force and are accumulated at one side of the channel. In steadystate, there should be no current flow along the transverse direction. Therefore, the Lorentz force is cancelled by an opposite electrical force due to the built-up charges. Because the hopping carriers should not respond to the Lorentz force, but to the electrical force due to the build up charges. Therefore, the total transverse electric field E_y is the sum of the electric fields produced by the charges accumulated at the opposite sides of the channel. This gives the relationship between the transverse (E_y) and longitudinal (E_x) electric fields:

$$E_y = \left(\frac{n_{\text{band}}\mu_{\text{band}}}{n_{\text{band}}\mu_{\text{band}} + n_{\text{hopping}}\mu_{\text{hopping}}}\right)\mu_{\text{band}}BE_x,\tag{1}$$

Then, the measured Hall mobility follows as:

$$\mu_{\text{Hall}} \equiv \frac{E_y}{E_x B} = \mu_{\text{band}} \left(\frac{n_{\text{band}} \mu_{\text{band}}}{n_{\text{band}} + n_{\text{hopping}} \mu_{\text{hopping}}} \right) = \mu_{\text{band}} \frac{\gamma}{\gamma - \gamma\beta + \beta}, \tag{2}$$

where γ is the ratio of the band carrier concentration to the total carrier concentration, $\gamma \equiv n_{\text{band}}/(n_{\text{band}}+n_{\text{hopping}})$, and β is the ratio of the hopping mobility to the band mobility, $\beta \equiv \mu_{\text{hopping}}/\mu_{\text{band}}$. With these two parameters, the longitudinal conductivity can be rewritten as:

$$\sigma = en\mu_{\text{band}}(\gamma - \gamma\beta + \beta), \tag{3}$$

where $n = n_{\text{band}} + n_{\text{hopping}}$ is the total charge density. Equivalently, the effective mobility is:

$$\mu_{\rm eff} \equiv \frac{\sigma}{en} = \mu_{\rm band} (\gamma - \gamma \beta + \beta), \tag{4}$$

Combining Eqs. (2) and (4), the coherence (Hall) factor α , can be expressed as:

$$\alpha = \frac{n}{n_{\text{Hall}}} = \frac{\mu_{\text{Hall}}}{\mu_{\text{eff}}} = \frac{\gamma}{(\gamma - \gamma\beta + \beta)^2},\tag{5}$$

Furthermore, Eqs. (5) and (3) yield

$$\gamma = \alpha \left(\frac{\beta\sigma}{en\mu_{\text{hopping}}}\right)^2.$$
(6)

In Eqs. (5) and (6), there are three unknown parameters that are not experimentally determined: β , γ , and μ_{hopping} . When one of these is reasonably assumed, the other two can be determined.

A detailed semiquantitative analysis presented in the main manuscript is as follows: The experimental coherence factor can be given as $\alpha = n_{/}n_{\text{Hall}}$ (here, the total charge density is equivalent to n_{spin} from spin counting in ESR measurements). Then the relation between γ and β is determined specifically, as shown in Fig. S4, where two examples are plotted: one is for PBTTT/F4-TCNQ system (red) with $\alpha = 1.7$, and another is for PBTTT/Mo(tfd-COCF₃)₃ system with $\alpha = 2.0$. Assuming a reasonable hopping mobility μ_{hopping} of 0.5 cm² V⁻¹ s⁻¹, estimated with a field-effect transistor,^{4,5} the γ , the fraction of band carriers is estimated to be approximately 0.03 (3 %) for PBTTT/F4-TCNQ and 0.20 (20 % for PBTTT/Mo(tfd-COCF₃)₃), respectively.



SI Fig. S4: The function of β as a function of γ given in Eq. 5. Two examples are plotted: one is for PBTTT/F4-TCNQ system (red) with $\alpha = 1.7$, and another is for PBTTT/Mo(tfd-COCF₃)₃ system with $\alpha = 2.0$. α is determined experimentally from the spin counting and the inverse Hall coefficient.

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