SUPPORTING INFORMATION

# Nonadiabatic Molecular Dynamics Modeling of the Intrachain Charge Transport in Conjugated Diketopyrrolo-pyrrole (DPP) Polymers

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Derivation of the force applied to nuclear $\alpha$ contributed from the electron dynamics part $\mathbf{F}_\alpha^{dynamic} \equiv -\nabla_{\mathbf{R}_\alpha} \langle \psi(t) | \hat{H} | \psi(t) \rangle$:

1) $\nabla_{\mathbf{R}} \langle \psi(t) | \psi(t) \rangle$

$$\begin{aligned}\langle \psi(t) | \psi(t) \rangle &= \sum_{mn} a_n^*(t) a_m(t) \langle \varphi_n | \varphi_m \rangle = \sum_{mn} a_n^\dagger(t) a_m(t) \delta_{nm} \\ &= \mathbf{A}^\dagger \mathbf{A}\end{aligned}$$

$$\nabla_{\mathbf{R}} \langle \psi(t) | \psi(t) \rangle = \left(\nabla_{\mathbf{R}} \mathbf{A}^\dagger\right) \mathbf{A} + \mathbf{A}^\dagger \nabla_{\mathbf{R}} \mathbf{A} = 0$$

2) $\nabla_{\mathbf{R}_\alpha} \varepsilon_m$:

After expanded on the atomic basis, the matrices equation $\mathbf{HC} = \mathbf{SCE}$ is obtained (see main text), diagonalizing the Hamiltonian, we get

$$\mathbf{HC}_m = \mathbf{SC}_m \varepsilon_m,\ \mathbf{C}_n^\dagger \mathbf{SC}_m = \delta_{nm},\ \mathbf{C}_m^\dagger \mathbf{HC}_m = \varepsilon_m$$

$$\nabla_{\mathbf{R}} \left(\mathbf{C}_m^\dagger \mathbf{SC}_m\right) = \left(\nabla_{\mathbf{R}} \mathbf{C}_m^\dagger\right) \mathbf{SC}_m + \mathbf{C}_m^\dagger \mathbf{S} \nabla_{\mathbf{R}} \mathbf{C}_m + \mathbf{C}_m^\dagger \left(\nabla_{\mathbf{R}} \mathbf{S}\right) \mathbf{C}_m = 0$$

$$\left(\nabla_{\mathbf{R}} \mathbf{C}_m^\dagger\right) \mathbf{SC}_m + \mathbf{C}_m^\dagger \mathbf{S} \nabla_{\mathbf{R}} \mathbf{C}_m = -\mathbf{C}_m^\dagger \left(\nabla_{\mathbf{R}} \mathbf{S}\right) \mathbf{C}_m$$

$$\begin{aligned}\nabla_{\mathbf{R}_\alpha} \varepsilon_m &= \left(\nabla_{\mathbf{R}_\alpha} \mathbf{C}_m^\dagger\right) \mathbf{HC}_m + \mathbf{C}_m^\dagger \left(\nabla_{\mathbf{R}_\alpha} \mathbf{H}\right) \mathbf{C}_m + \mathbf{C}_m^\dagger \mathbf{H} \nabla_{\mathbf{R}_\alpha} \mathbf{C}_m \\ &= \left(\nabla_{\mathbf{R}_\alpha} \mathbf{C}_m^\dagger\right) \mathbf{SC}_m \varepsilon_m + \mathbf{C}_m^\dagger \left(\nabla_{\mathbf{R}_\alpha} \mathbf{H}\right) \mathbf{C}_m + \varepsilon_m \mathbf{C}_m^\dagger \mathbf{S} \nabla_{\mathbf{R}_\alpha} \mathbf{C}_m \\ &= \mathbf{C}_m^\dagger \nabla_{\mathbf{R}_\alpha} \mathbf{HC}_m - \varepsilon_m \mathbf{C}_m^\dagger \nabla_{\mathbf{R}_\alpha} \mathbf{SC}_m\end{aligned}$$

3) $\nabla_{\mathbf{R}_\alpha} \langle \psi(t) | \hat{H} | \psi(t) \rangle$

$$\langle \psi(t) | \hat{H} | \psi(t) \rangle = \sum_m a_m^\dagger(t) a_m(t) \varepsilon_m = \mathbf{A}^\dagger \mathbf{E} \mathbf{A}$$

$$\begin{aligned}\left(\nabla_{\mathbf{R}} \mathbf{A}^\dagger\right) \mathbf{EA} + \mathbf{A}^\dagger \mathbf{E} \nabla_{\mathbf{R}} \mathbf{A} &= \left(\nabla_{\mathbf{R}} \mathbf{A}^\dagger\right) \mathbf{AA}^\dagger \mathbf{EA} + \mathbf{A}^\dagger \mathbf{EAA}^\dagger \nabla_{\mathbf{R}} \mathbf{A} \\ &= \mathbf{A}^\dagger \mathbf{EA} \left(\left(\nabla_{\mathbf{R}} \mathbf{A}^\dagger\right) \mathbf{A} + \mathbf{A}^\dagger \nabla_{\mathbf{R}} \mathbf{A}\right) \\ &= 0\end{aligned}$$

$$\begin{aligned}\nabla_{\mathbf{R}_\alpha} \langle \psi(t) | \hat{H} | \psi(t) \rangle &= \left(\nabla_{\mathbf{R}_\alpha} \mathbf{A}^\dagger\right) \mathbf{EA} + \mathbf{A}^\dagger \mathbf{E} \nabla_{\mathbf{R}_\alpha} \mathbf{A} + \mathbf{A}^\dagger \left(\nabla_{\mathbf{R}_\alpha} \mathbf{E}\right) \mathbf{A} \\ &= \mathbf{A}^\dagger \left(\nabla_{\mathbf{R}_\alpha} \mathbf{E}\right) \mathbf{A} \\ &= \sum_m a_m^\dagger(t) a_m(t) \nabla_{\mathbf{R}_\alpha} \varepsilon_m\end{aligned}$$

$$\nabla_{\mathbf{R}_\alpha}\left\langle \psi(t)\middle|\hat{H}\middle|\psi(t)\right\rangle = \sum_m a_m^\dagger(t)\,a_m(t)\left(\mathbf{C}_m^\dagger \nabla_{\mathbf{R}_\alpha}\mathbf{H}\mathbf{C}_m - \epsilon_m \mathbf{C}_m^\dagger \nabla_{\mathbf{R}_\alpha}\mathbf{S}\mathbf{C}_m\right)$$

$$= \sum_m a_m^\dagger(t)\,a_m(t)\sum_{\mu\nu}\left(c_{m\mu}^\dagger \nabla_{\mathbf{R}_\alpha} H_{\mu\nu} c_{\nu m} - \epsilon_m c_{m\nu}^\dagger \nabla_{\mathbf{R}_\alpha} S_{\mu\nu} c_{\nu m}\right)$$

$$= \sum_{\nu\mu}\sum_m\left(c_{\nu m} a_m^\dagger(t)\,a_m(t)\,c_{m\mu}^\dagger \nabla_{\mathbf{R}_\alpha} H_{\mu\nu} - c_{\nu m} a_m^\dagger(t)\,a_m(t)\,\epsilon_m c_{m\mu}^\dagger \nabla_{\mathbf{R}_\alpha} S_{\mu\nu}\right)$$

$$= \sum_{\mu\nu}\left(\rho'_{\nu\mu}\nabla_{\mathbf{R}_\alpha} H_{\mu\nu} - \rho'^{\epsilon}_{\nu\mu}\nabla_{\mathbf{R}_\alpha} S_{\mu\nu}\right)$$

where $\rho'_{\nu\mu} \equiv \sum_m c_{\nu m} a_m^\dagger(t)\,a_m(t)\,c_{m\mu}^\dagger$ , $\rho'^{\epsilon}_{\nu\mu} \equiv \sum_m c_{\nu m} a_m^\dagger(t)\,a_m(t)\,\epsilon_m c_{m\mu}^\dagger$

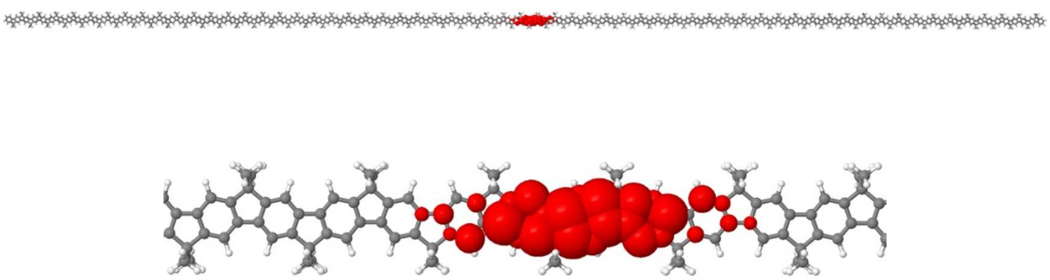
$$H_{\mu\nu} \equiv H_{\mu\nu}^0 + H_{\mu\nu}^1 = \left\langle \phi_\mu\middle|\hat{H}_0\middle|\phi_\nu\right\rangle + \frac{1}{2} S_{\mu\nu}\sum_{\zeta}^{N}\left(\gamma_{\delta\zeta} + \gamma_{\beta\zeta}\right)\Delta q_\zeta \quad \text{(see ref 49 in main text)}$$

4) The force $\mathbf{F}_\alpha^{dynamic}$ from the dynamic part can be written as:

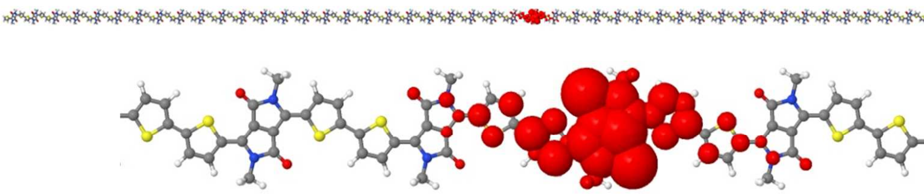
$$\mathbf{F}_\alpha^{dynamic} = -\sum_{\mu\nu}\left(\rho'_{\nu\mu}(t)\left(\nabla_{\mathbf{R}_\alpha} H_{\mu\nu}^0 + \nabla_{\mathbf{R}_\alpha} H_{\mu\nu}^1\right) - \rho'^{E}_{\nu\mu}(t)\nabla_{\mathbf{R}_\alpha} S_{\mu\nu}\right)$$

$$= -\sum_{\mu\nu}\rho'_{\nu\mu}(t)\nabla_{\mathbf{R}_\alpha} H_{\mu\nu}^0 - \left(\rho'^{\epsilon}_{\nu\mu}(t) - \frac{H_{\mu\nu}^1}{S_{\mu\nu}}\right)\nabla_{\mathbf{R}_\alpha} S_{\mu\nu} + \frac{1}{2} S_{\mu\nu}\nabla_{\mathbf{R}_\alpha}\left(\gamma_{\delta\alpha} + \gamma_{\beta\alpha}\right)\Delta q_\alpha$$

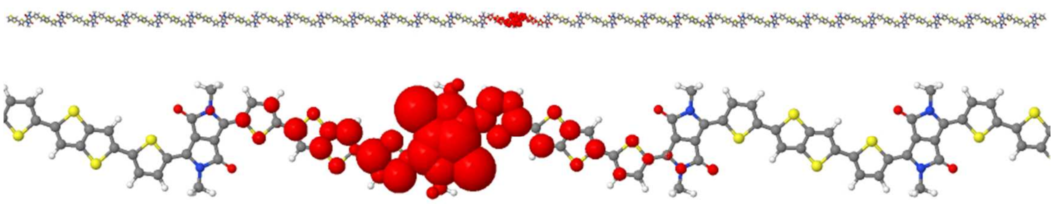
LPPP



DPP_DPP



DPP_cTT



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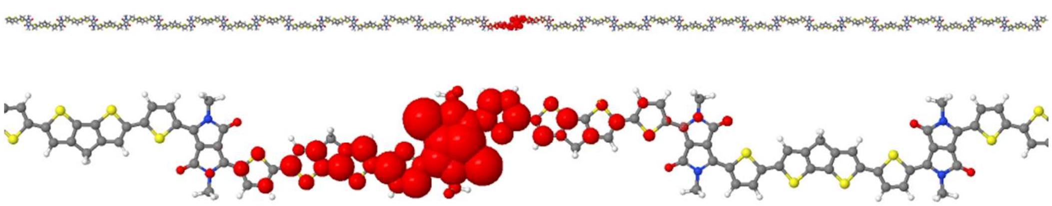
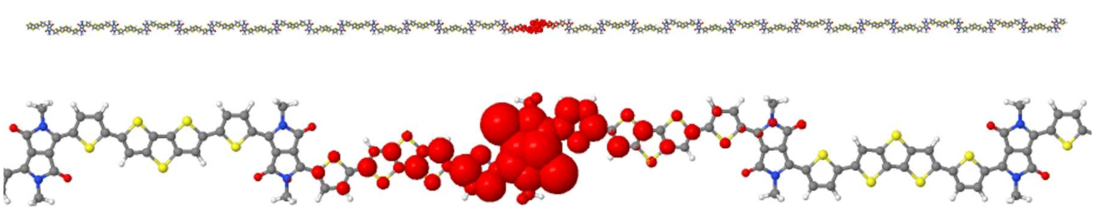
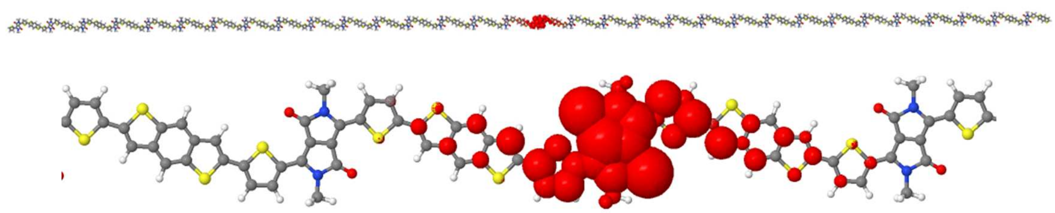


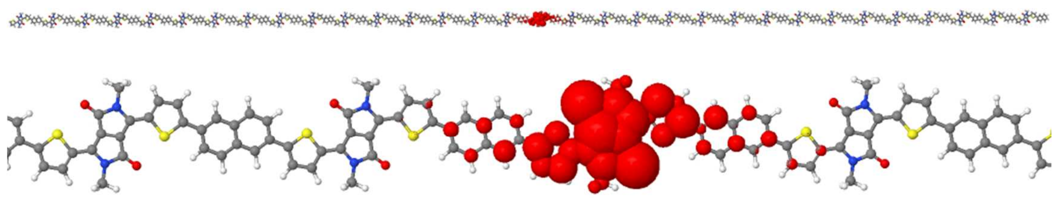
DPP_f3T



DPP_BDT



DPP_NPT



DPP_CBZ

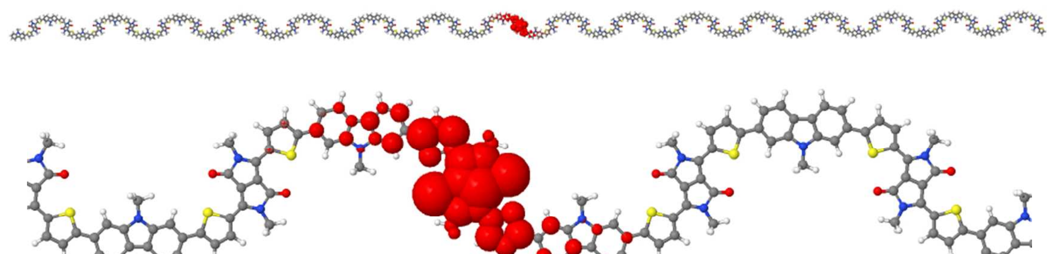


Figure 1S Charge distribution for the polymers at the initial time which is highlighted by the red color

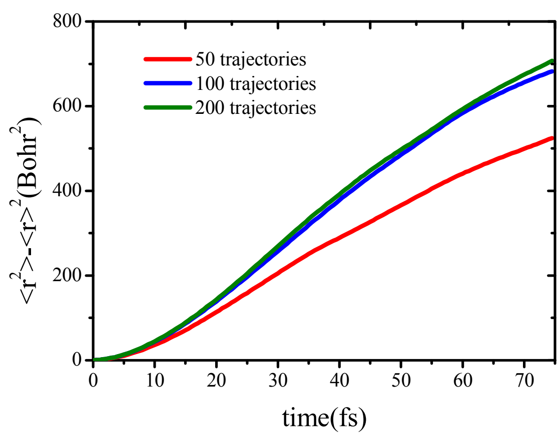



Figure 2S Convergence test for diffusion distance in DPP_CBZ copolymer with 50, 100 and 200 trajectories

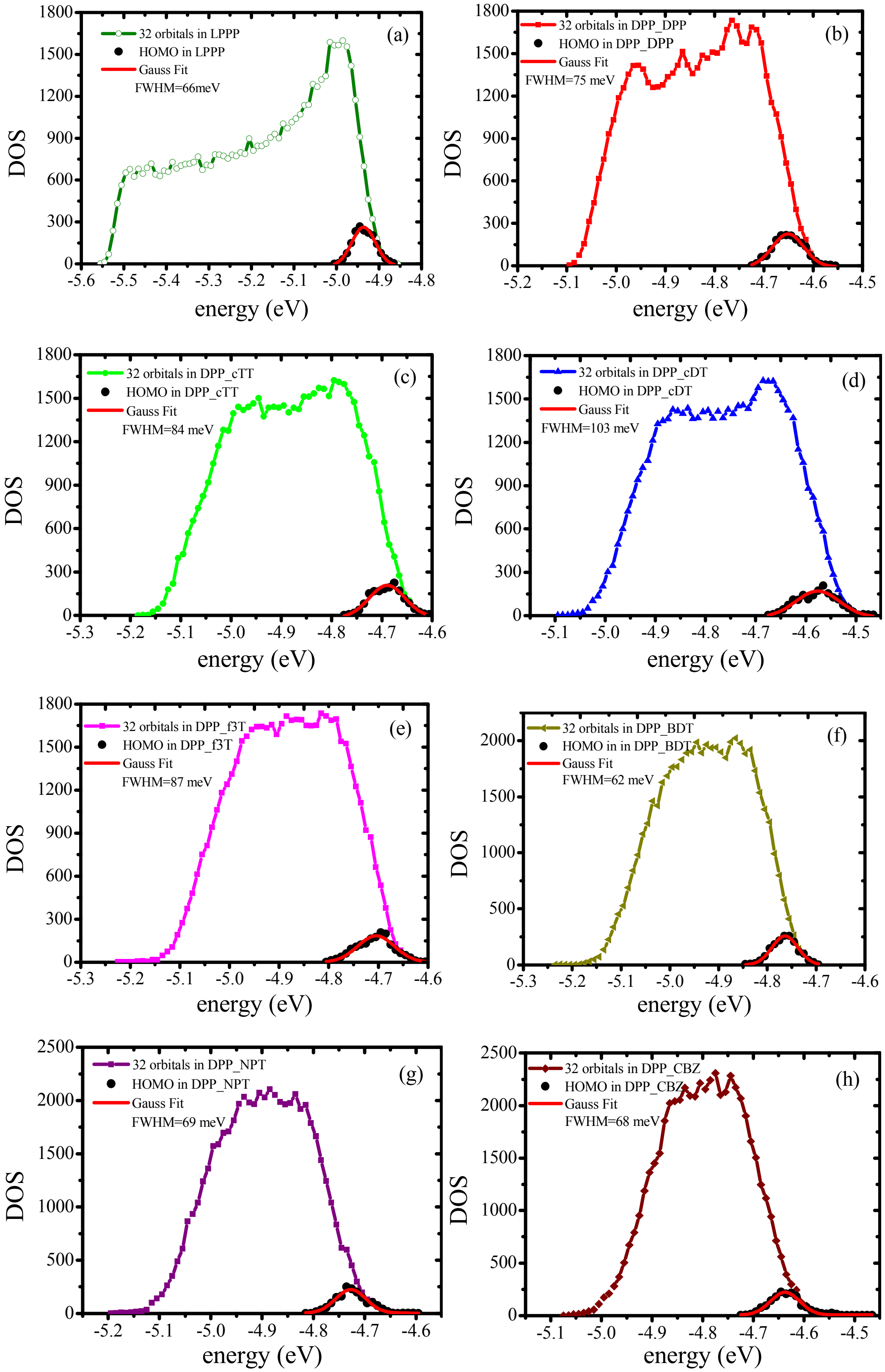



Figure 3S the density of states from 32 orbitals, HOMO and Gaussian fit for HOMO distribution

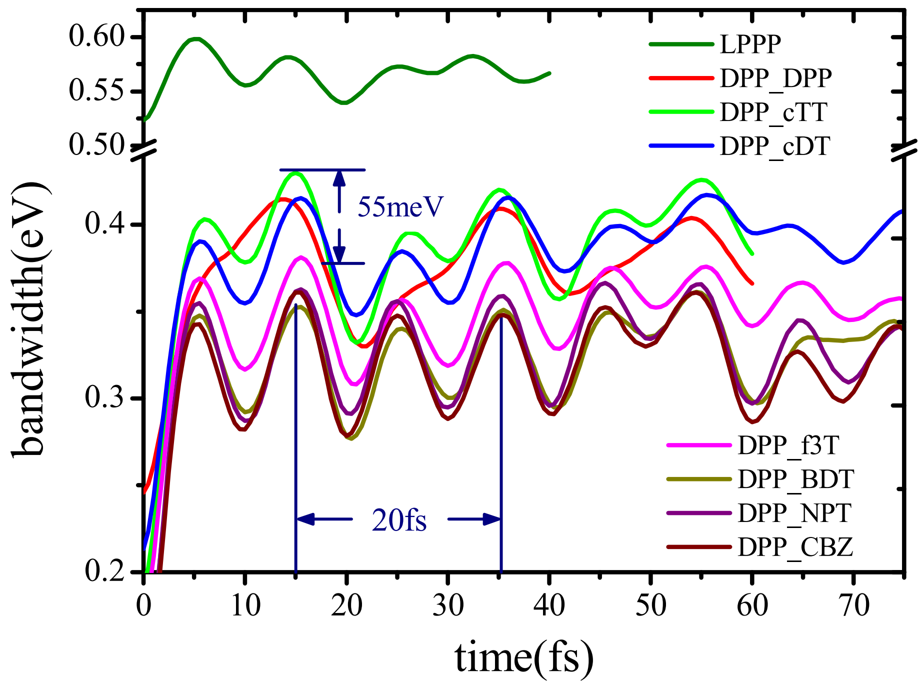



Figure 4S time evolution for the bandwidth with contribution from 32 molecular orbitals

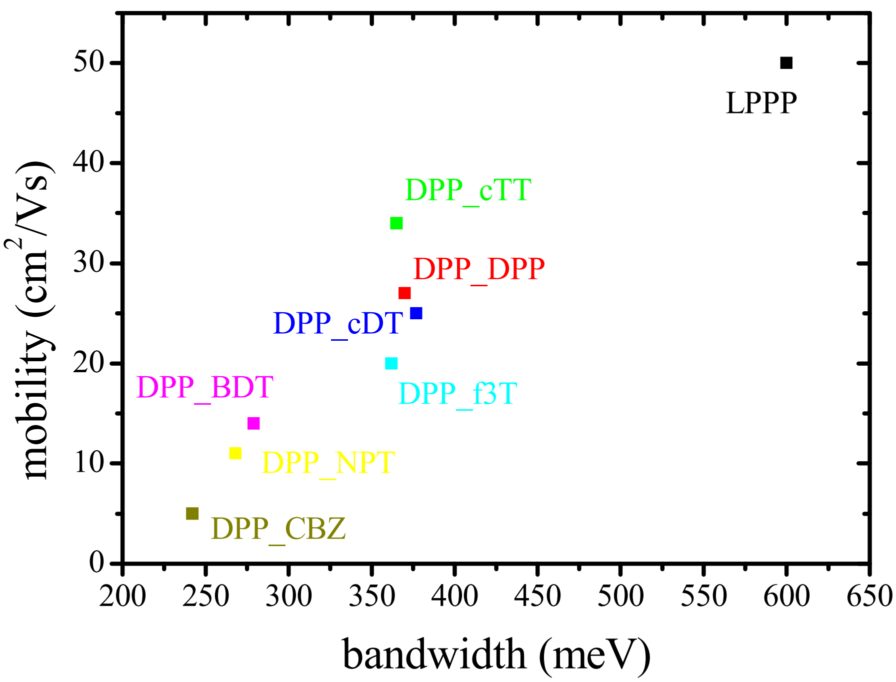



Figure 5S the carrier mobilities *versus* bandwidth for the conjugated polymers