

Resonance Raman Studies of Excited State Structural Displacements of Conjugated Polymers in Donor/Acceptor Charge Transfer Complexes

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SUPPORTING INFORMATION

Figure S1 shows IR spectra of MDMO-PPV, DNF, DDQ and their complexes. MDMO-PPV/DNF IR spectra show contributions from both components and no new transitions are apparent. MDMO-PPV/DDQ spectra also show mostly identical features corresponding to pure MDMO-PPV and DDQ, however, several new peaks appear which arise due to strong CT interactions. In particular, bands at 600, 1044, and 1245 cm^{-1} become apparent in complexes. However, the 600 cm^{-1} band is most prominent in both IR and Raman spectra.

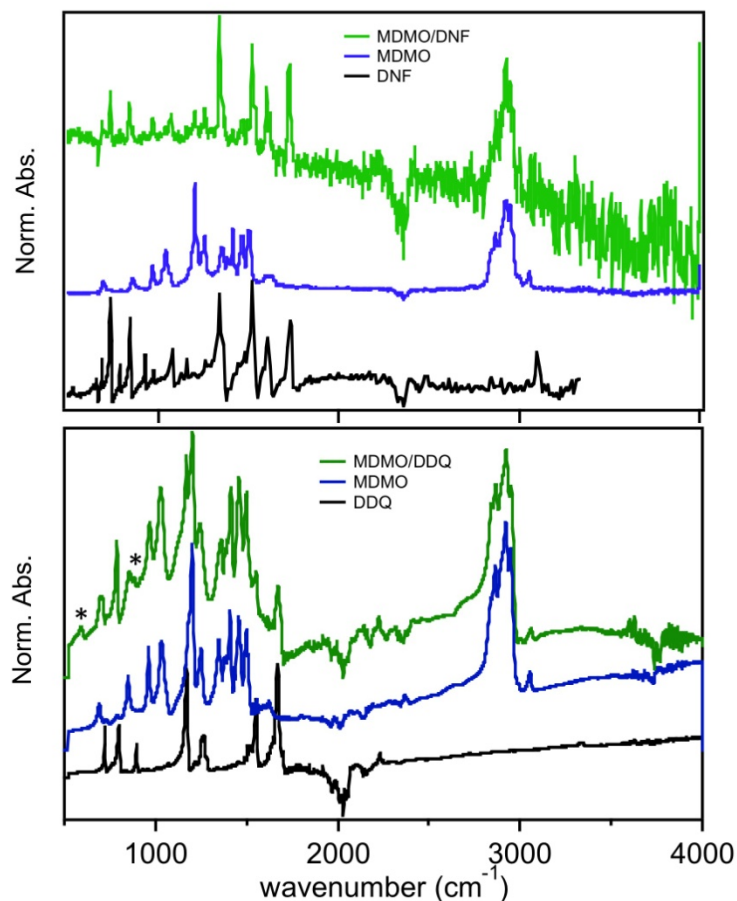


Figure S1. IR spectra of MDMO-PPV/DNF (top panel) and MDMO-PPV/DDQ (bottom panel) complexes.

IR spectra also reveal the C-H stretch region ($\sim 2900\text{-}3000\text{ cm}^{-1}$) which coincides with the 1st overtone region in the Raman spectra. However, these transitions are considerably weaker than overtone intensities due to resonance enhancement effects.

¹H NMR spectra of each complex in solution are shown in Figure S2 along with MDMO-PPV/PCBM blend solutions.

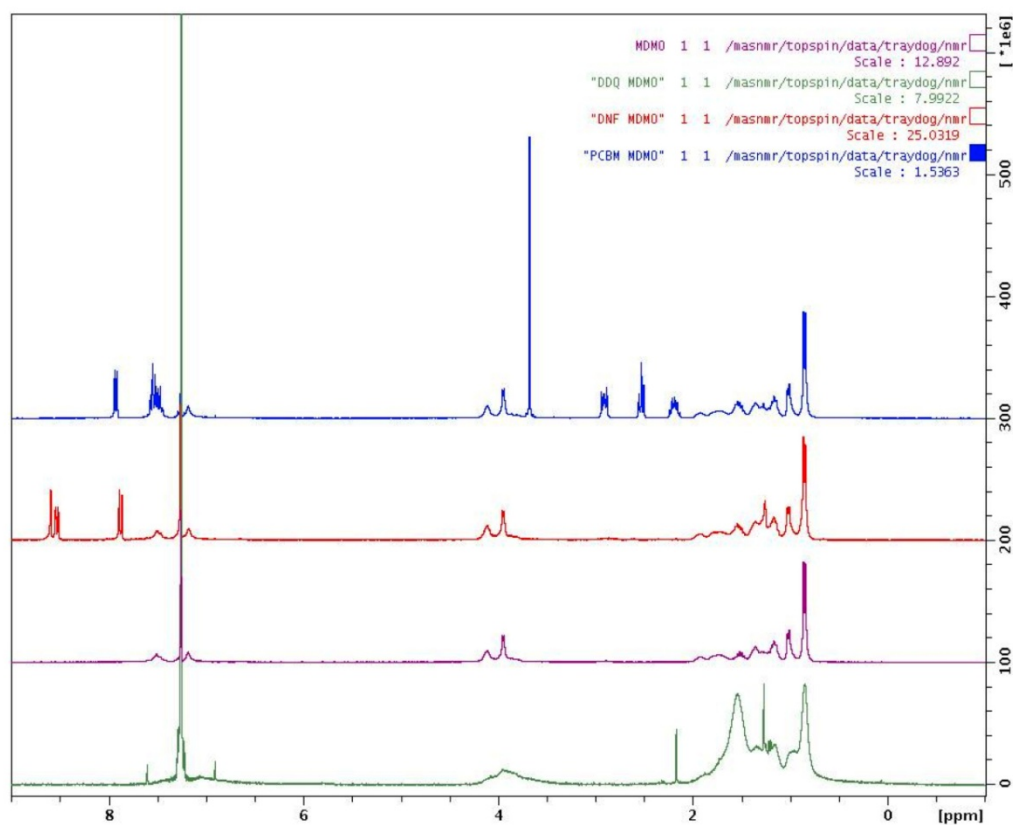


Figure S2. ¹H NMR spectra of MDMO-PPV/PCBM (blue trace), MDMO-PPV/DNF (red trace), MDMO-PPV (purple trace) and MDMO-PPV/DDQ (green trace) complexes.

All blends show characteristic peaks of MDMO-PPV along with acceptors. MDMO-PPV/DDQ complexes demonstrate noticeable broadening possibly due to possible paramagnetic effects. We are currently exploring the association characteristics of MDMO-PPV/DNF and DDQ complexes as well as low temperature measurements to better understand the mechanism of charge transfer in these blends.

Calculations of Raman intensities were generated using eqs. 1-3. Briefly, the fundamental frequency of each mode (described by the index, k) was taken from Table 1 as input in the calculation. The order of each mode, n_k , is inferred from the number of overtones appearing in the Raman spectrum. For example, up to three overtones in the ν_{14} mode are observed so $n_{14} = 4$. The value of the energy of electronic origin, E_{0-0} , is estimated from absorption spectra and we fit the absorption linewidth near the onset region to estimate reasonable values of the phenomenological damping factor, Γ . These values are included in Table 1. Because of the large number of modes involved in the calculation, we use the Savin formula (eq. 4) to estimate the relative displacements using the relative intensities of each mode. This involves a pairwise comparison of intensities and eq. 4 can be used to obtain the relative displacements. Holding the relative displacements fixed we scale these values to obtain a good fit with experiment. We estimate the error in the displacements to be +/- 10% which was determined by changing the scaling factor until the fit no longer agreed with experiment. Combination bands are calculated for up to three modes, namely, ν_6 , $\nu_{9,10}$ and ν_{14} and the overlaps (eq 3) are calculated separately for these transitions but using the same input parameters as fundamentals and overtones.

Because overtones appear in resonance Raman spectra, we can also use the ratios of overtone to fundamental intensities as an additional check on the calculated displacement values. This procedure is described in ref. 15 of the main text and Eq. 1 describes the relation between the ratio of the first overtone and the fundamental integrated intensities (I_{0-2}/I_{0-1}), absorption linewidths, and frequencies to the absolute displacement of each mode. Based on resonance Raman spectra, only the ν_{14} , $\nu_{9,10}$, and ν_6 modes show pronounced overtones that can be used as a check on scaled displacements determined from fitting absorption spectra.

$$\Delta_j^2 = \frac{I_{0-2}^j}{I_{0-1}^j} \frac{4\sigma^2}{\hbar\omega_j} \frac{\varepsilon_1\left(\frac{\omega_e - E}{\sigma}\right)}{\varepsilon_2\left(\frac{\omega_e - E}{\sigma}\right)} \quad (1)$$

Here, σ is the experimental absorption linewidth, $\hbar\omega_j$ is the frequency of mode (j) and ε is an enhancement factor which is a function of the difference between the incident energy and the absorption maximum.

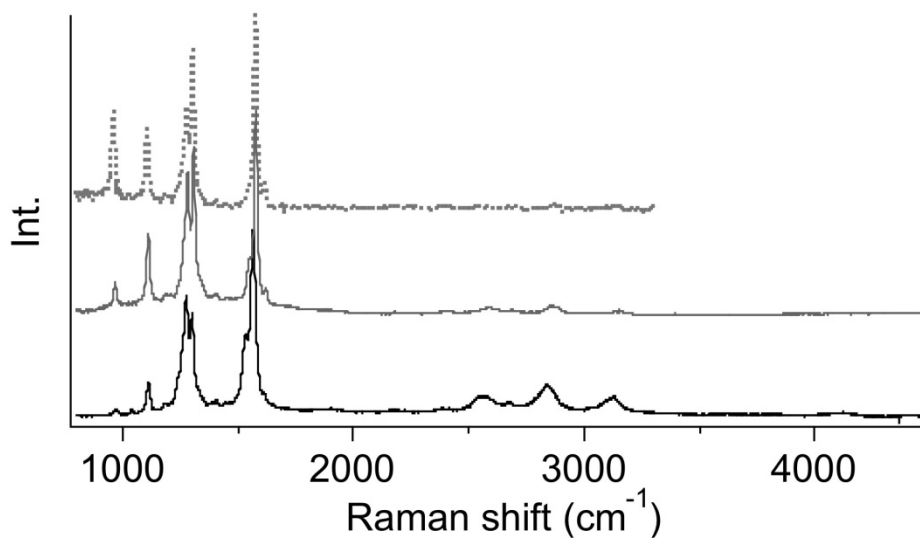


Figure S3. Raman spectra of MDMO-PPV/PCBM (dotted gray trace), MDMO-PPV/DNF (gray solid trace) and MDMO-PPV/DDQ (black solid trace). $\lambda_{\text{exc}}=568$ nm.

We use the Raman data shown in Fig. S3 to determine I_{0-2}/I_{0-1} ratios and, from eq. 1, the ratio of enhancement functions, $\varepsilon_2/\varepsilon_1$ is $\pi/2$ assuming that the laser frequency is on the absorption maximum. These estimates of Δ_j are included in Table 1 of the main text for each resolved overtone.

complex	DDQ	DNF
I_{0-2}/I_{0-1} (ν_{14})	0.19	0.20
I_{0-2}/I_{0-1} ($\nu_{9,10}$)	0.33	0.11
I_{0-2}/I_{0-1} (ν_6)	0.05	-