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Resonance Raman Spectroscopy and Imaging of Push-Pull Conjugated Polymer/Fullerene Blends

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Supporting Information

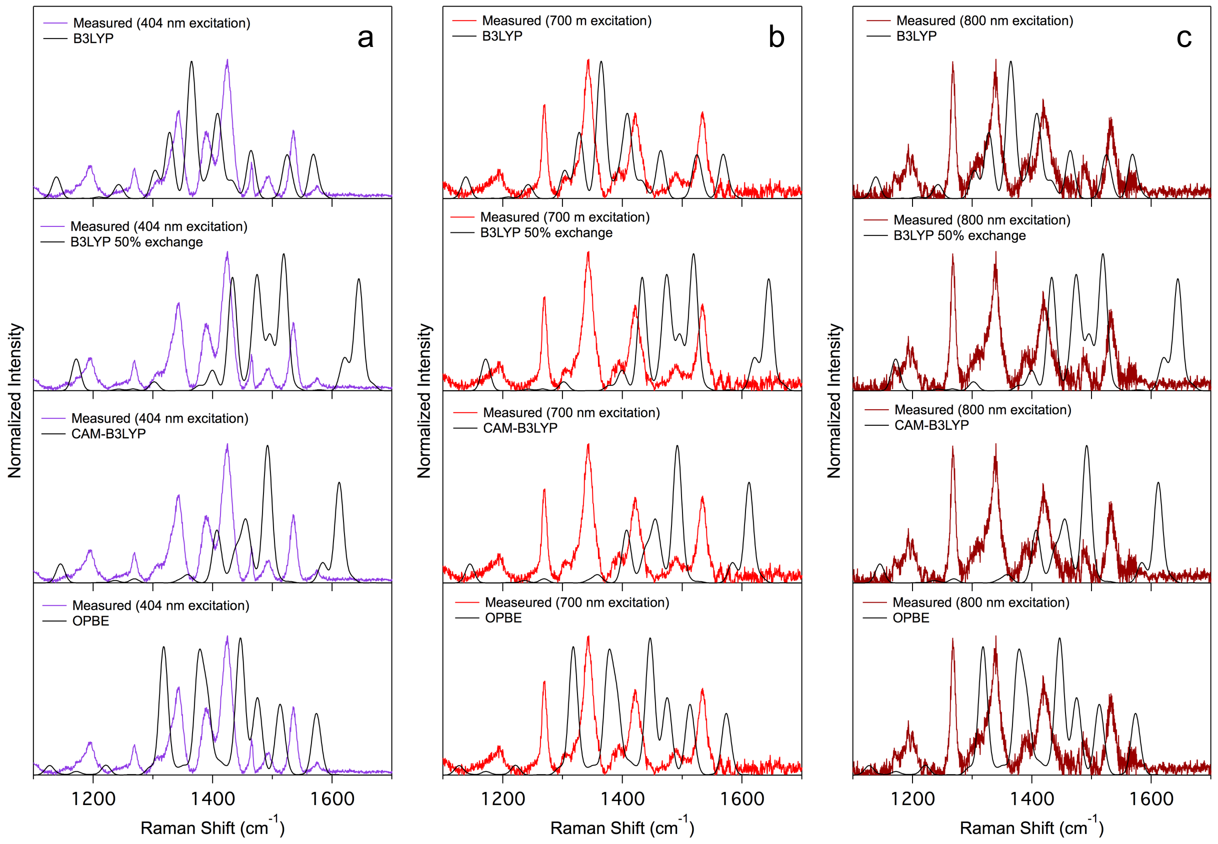

Figure S1. Calculated Raman spectra using B3LYP, B3LYP with reduced exchange energy, CAM-B3LYP, and OPBE functionals compared with measured PCPDTBT:PCBM (1:3) spectra at a) 404 nm, b) 700 nm, and c) 800 nm excitation wavelengths.

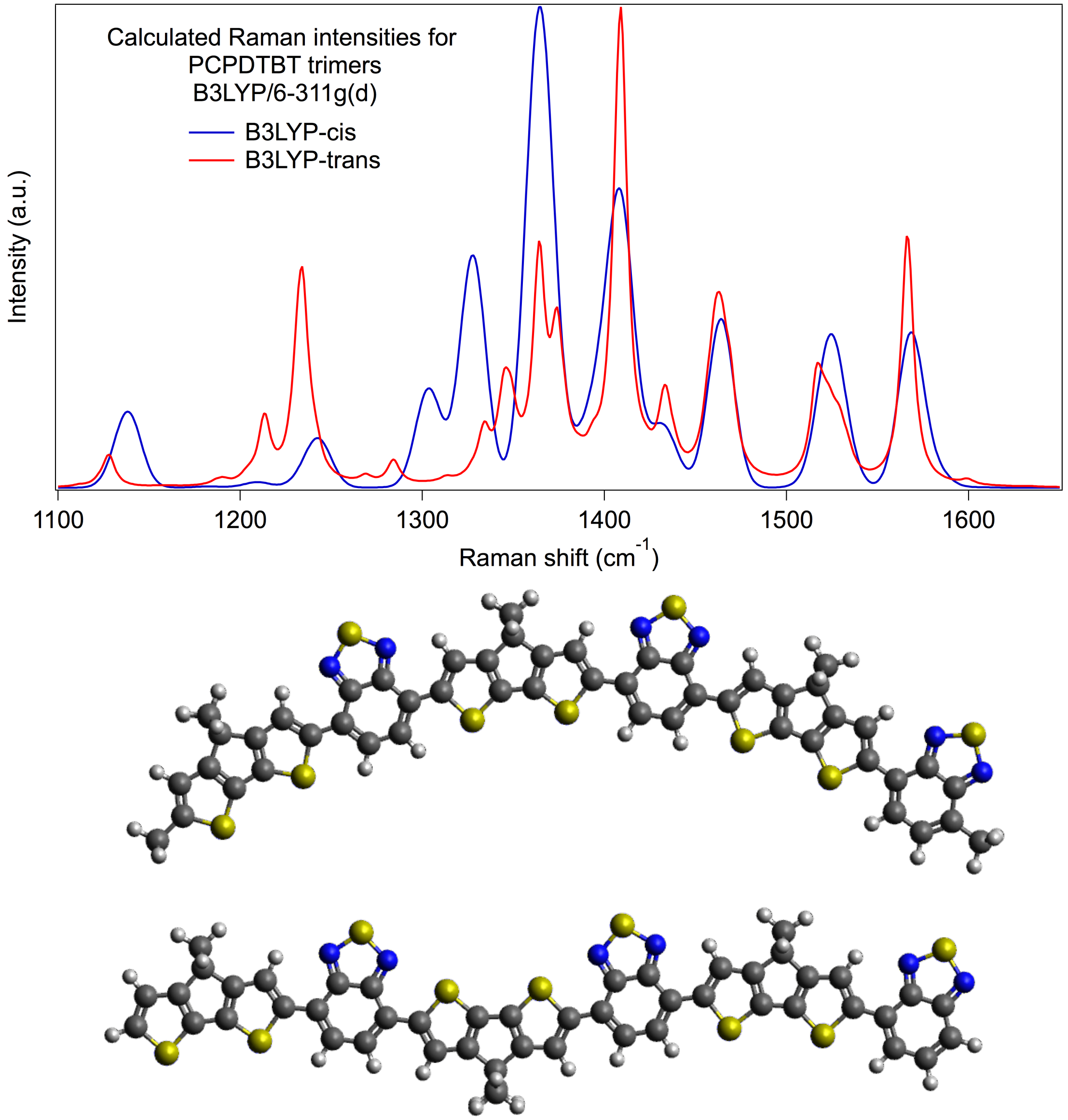

Figure S2. Comparison of cis (syn) and trans (anti) conformations of CPDTBT trimer Raman spectra.

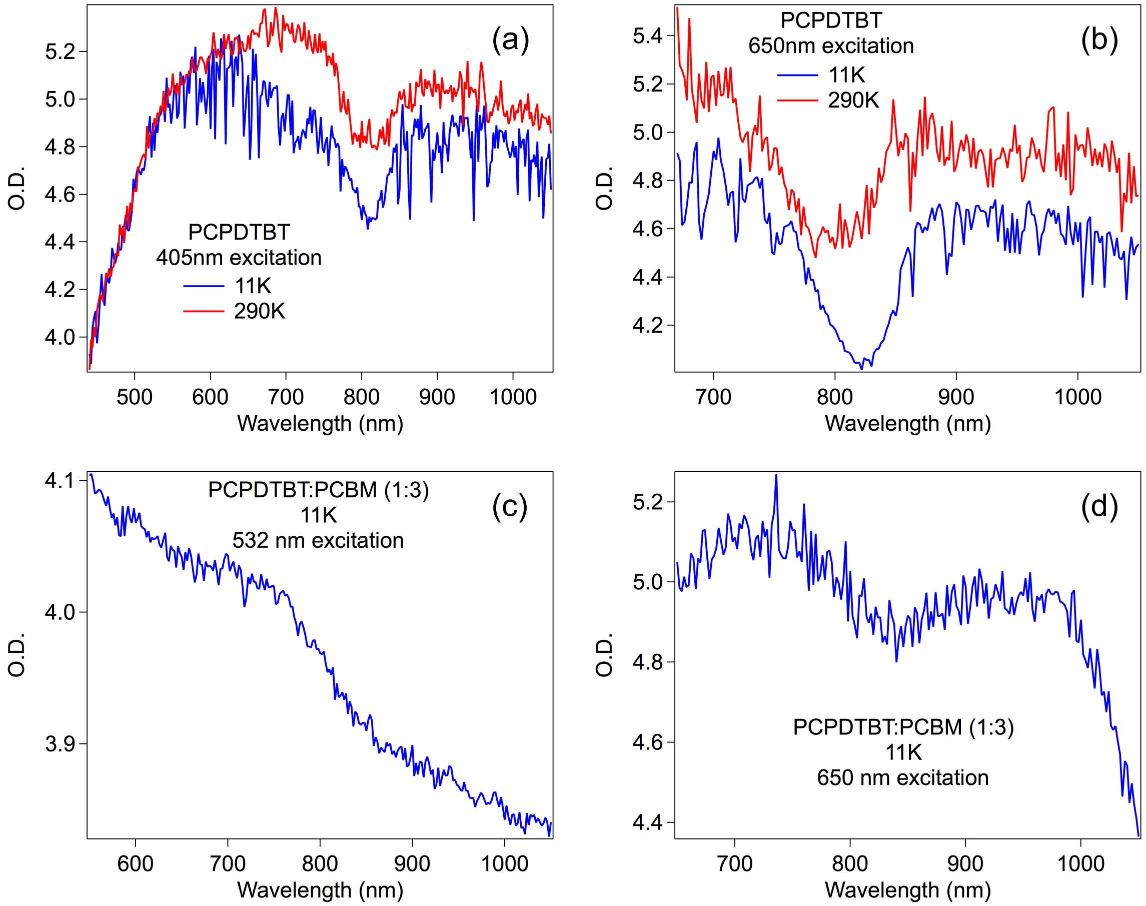

Figure S3. Photoinduced absorption of PCPDTBT films at a) 405 nm and b) 650 nm excitation at 11K and 290K, and for PCPDTBT:PCBM (1:3) blend films at 11K at c) 532 nm and d) 650 nm excitation.

Samples for photoinduced absorption studies were produced by drop casting 5 mg/ml solutions of PCPDTBT and PCPDTBT:PCBM (1:3) (w:w) in chlorobenzene on glass substrates. The setup for collecting the PIA spectra has been described elsewhere in the literature.[1]

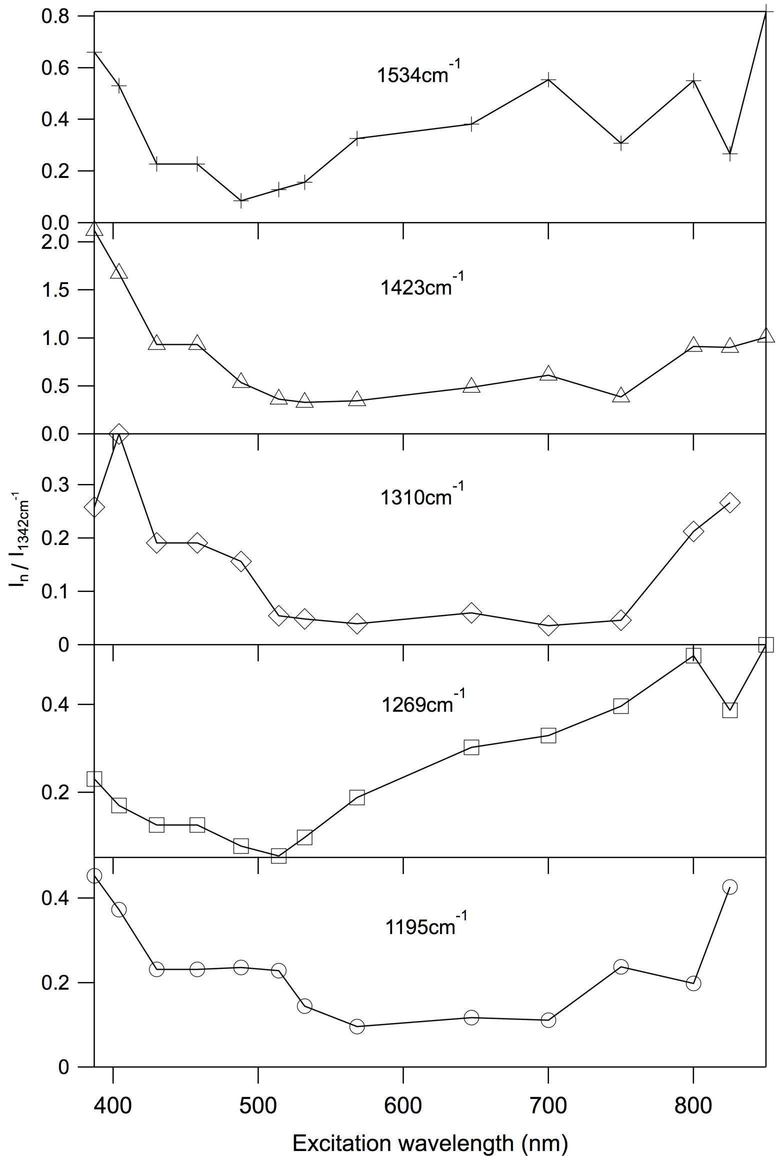

Figure S4. Relative intensities of PCPDTBT skeletal vibrations as a function of excitation wavelength.

The CPDT in-plane C—H wag coupled with the BT symmetric C—H wag at 1195 cm^{-1}, in particular, shows good agreement with the absorption profile, which suggests charge density is delocalized over several D/A units. Interestingly, the 1423 cm^{-1} mode, assigned to the CPDT C-C stretch, shows large increases in relative intensity for increasing excitation energies, suggesting greater localization on this unit, which is consistent with PCBM induced D/A twisting in a mixed phase. Conversely, the 1269 cm^{-1} and 1534 cm^{-1} modes, assigned to the BT symmetric in-plane C—H wag and C-C stretch, respectively, decrease in relative intensity with higher excitation energies. Most importantly, the 1269 cm^{-1} BT C—H wag mode shows very little relative intensity at higher excitation energies but increases dramatically near the NIR region corresponding to the red-shifted component in optical absorption spectra of blends (Fig. 1). Despite the qualitative nature of these trends, they confirm our expectations of structure-induced delocalization over D/A units in PCPDTBT blends. For example, a higher energy mixed phase results in chains that are more localized in nature as opposed to a lower energy phase-separated morphological component where chains are more ordered leading to greater charge transfer character.

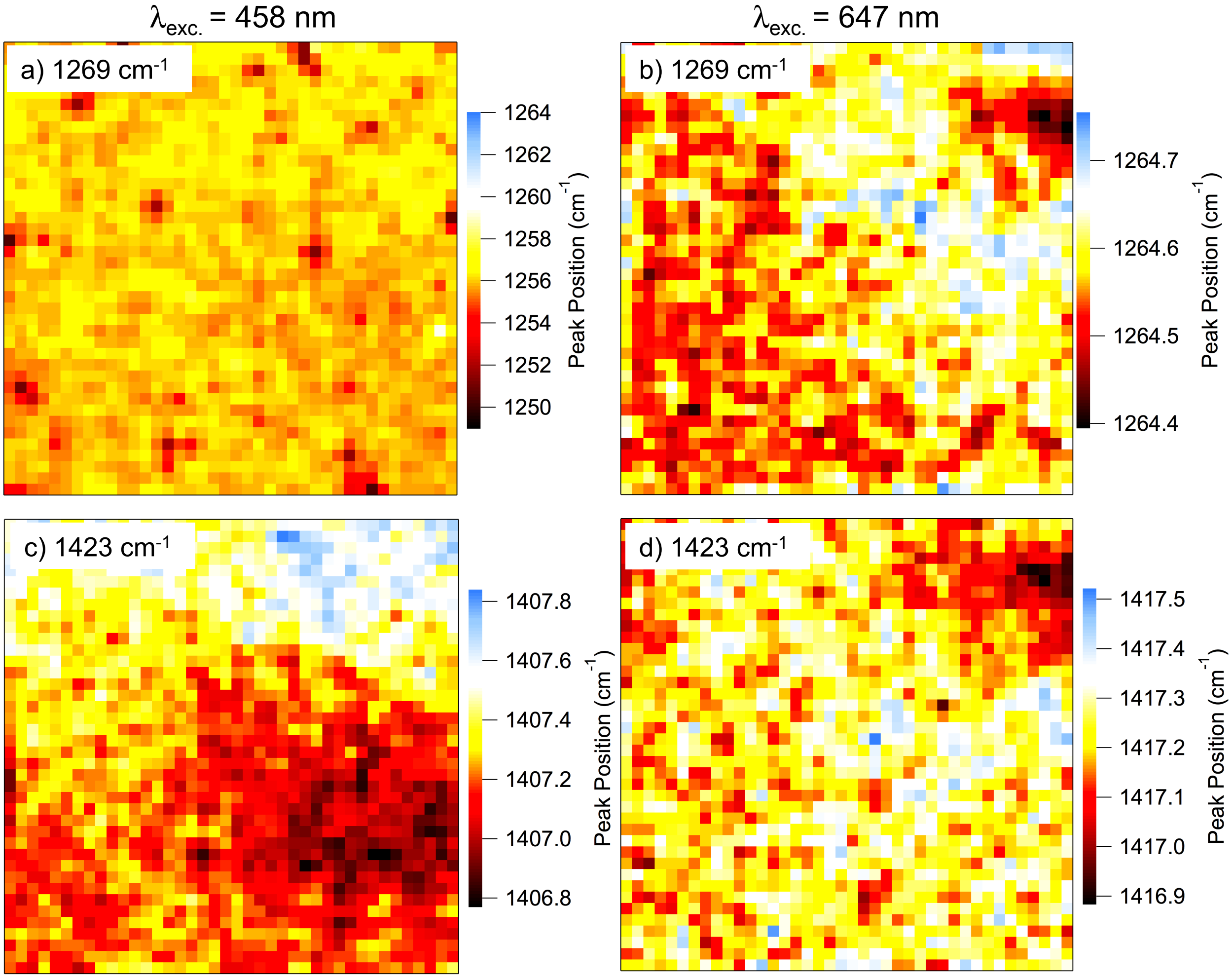

Figure S5. Raman frequency images of acceptor (a, b) and donor (c, d) moiety Raman mode intensities in PCPDTBT:PCBM (10:20 mg/ml) photovoltaic devices at 458 and 647 nm excitation. All images are of the same 10 × 10 μm area as in main article Figure 4. Pixel values represent fitted (Gaussian) peak positions of the indicated modes.

Raman frequency shifts can provide additional information about the local environment of chromophores indicating interactions between PCPDTBT and PCBM. Specifically, it is possible to discern if preferential interactions exist between PCBM ad polymer CPDT and BT groups. Unfortunately, the size of phase segregation hinders reliable correlations between frequency shifts and local morphology difficult. Similarly, there does not appear to be a strong correlation between regions of maximum red-shift and regions of higher PCBM activity for the 1423 cm^{-1} mode at this wavelength. Turning to the donor 1423 cm^{-1} mode, at 647 nm, we see that the area of maximum red shift correlates well with the area of highest PCBM Raman intensity. The BT 1342 cm^{-1} in-plane concert wave C—H wag is much more intense at both 458 and 647nm, allowing for a better comparison between its position and PCBM activity. At 458 nm, the 1342 cm^{-1} mode does not show a strong correlation between areas of maximum red shift and PCBM activity in the ODT-free device. However, like the 1423 cm^{-1} donor-centered mode, there is a strong correlation between areas where the 1342 cm^{-1} mode is most red-shifted and areas of high PCBM activity. These trends suggest that both the donor and acceptor moieties are interacting strongly with PCBM at 647 nm, and may help explain the higher photocurrent production when illuminating the device on resonance with the low-energy absorption band of the polymer. This may indicate more efficient charge generation and separation in these blends with more efficient absorption at this wavelength. With the addition of ODT, we see that these correlations are less clear for both the acceptor and donor modes, which may support the view that both moieties are interacting less with PCBM due to improved phase segregation in these films. Although the interaction between the polymer and fullerene appears to be weaker in ODT treated blends, increased photocurrents are due to improved charge transport.

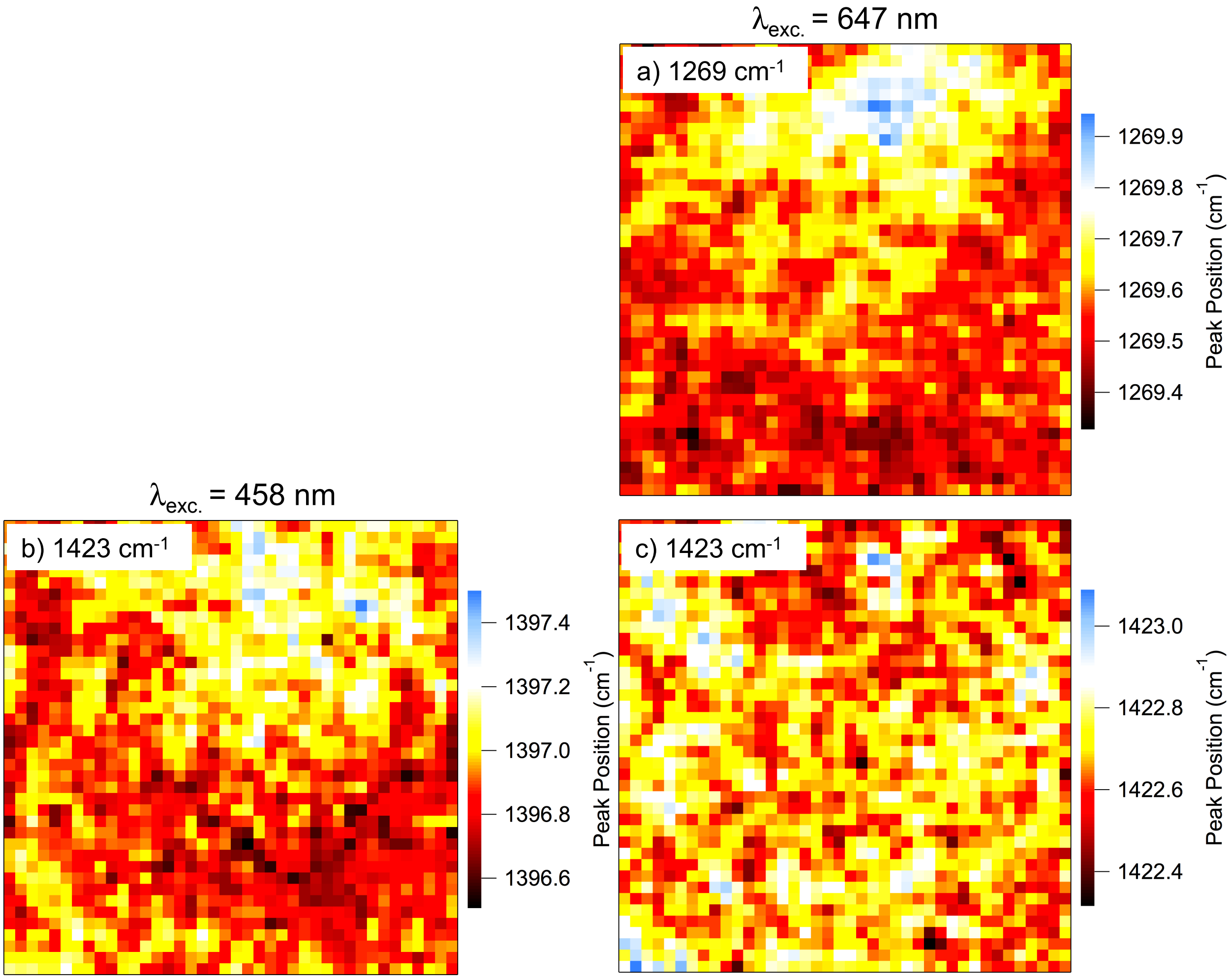

Figure S7. Raman frequency images of acceptor (a, b) and donor (c, d) moiety Raman mode intensities in PCPDTBT:PCBM:ODT (10:20:30 mg/ml) photovoltaic devices at 458 and 647 nm excitation. All images are of the same 10 × 10 μm area as in main article Figure 5. Pixel values represent fitted (Gaussian) peak positions of the indicated modes. The 1269 cm^{-1} acceptor mode is not shown due to weak signal strength at 458 nm.

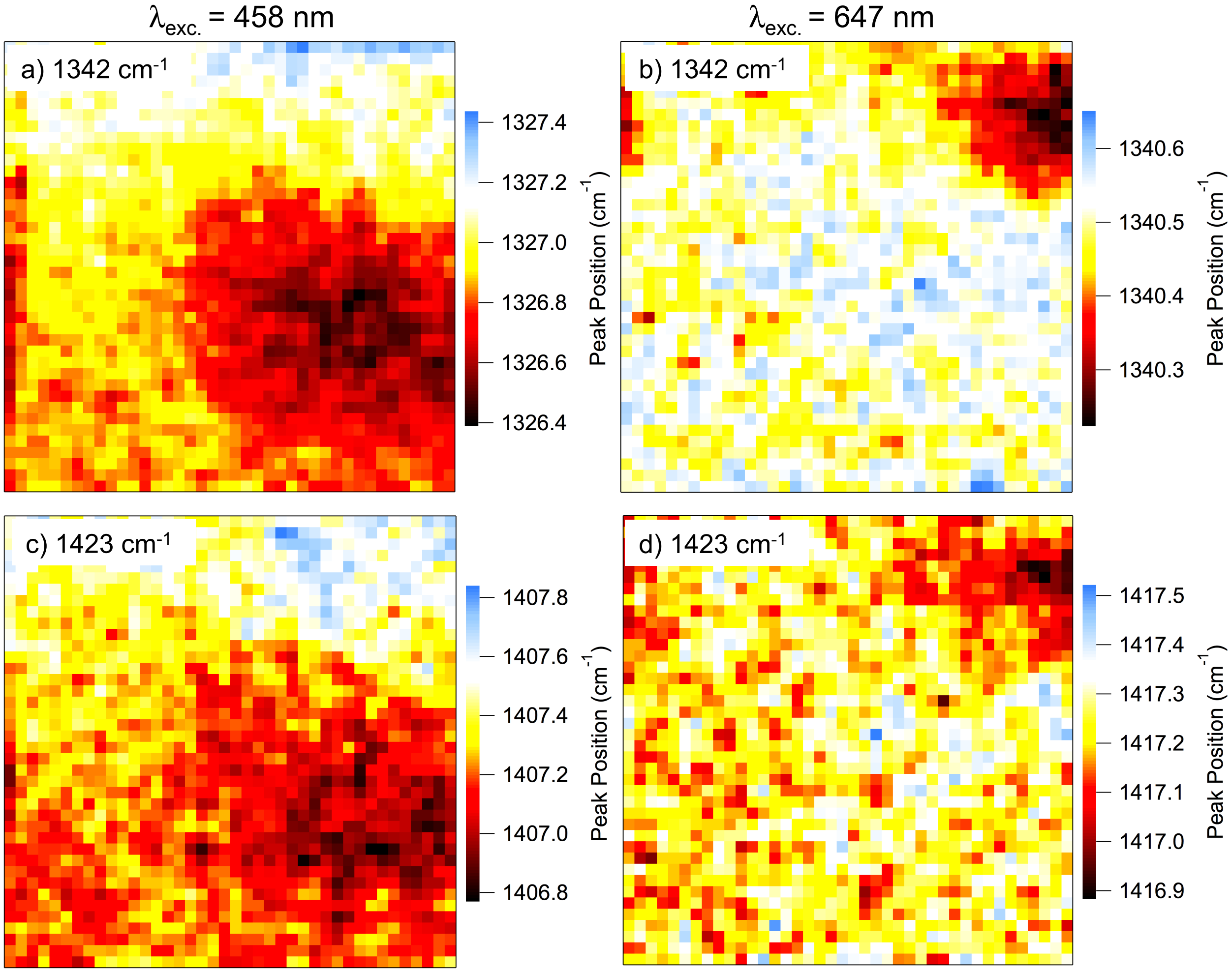

Figure S8. Raman frequency images of acceptor (a, b) and donor (c, d) moiety Raman mode intensities in PCPDTBT:PCBM (10:20 mg/ml) photovoltaic devices at 458 and 647 nm excitation. All images are of the same 10 × 10 μm area as in main article Figure 4. Pixel values represent fitted (Gaussian) peak positions of the indicated modes.

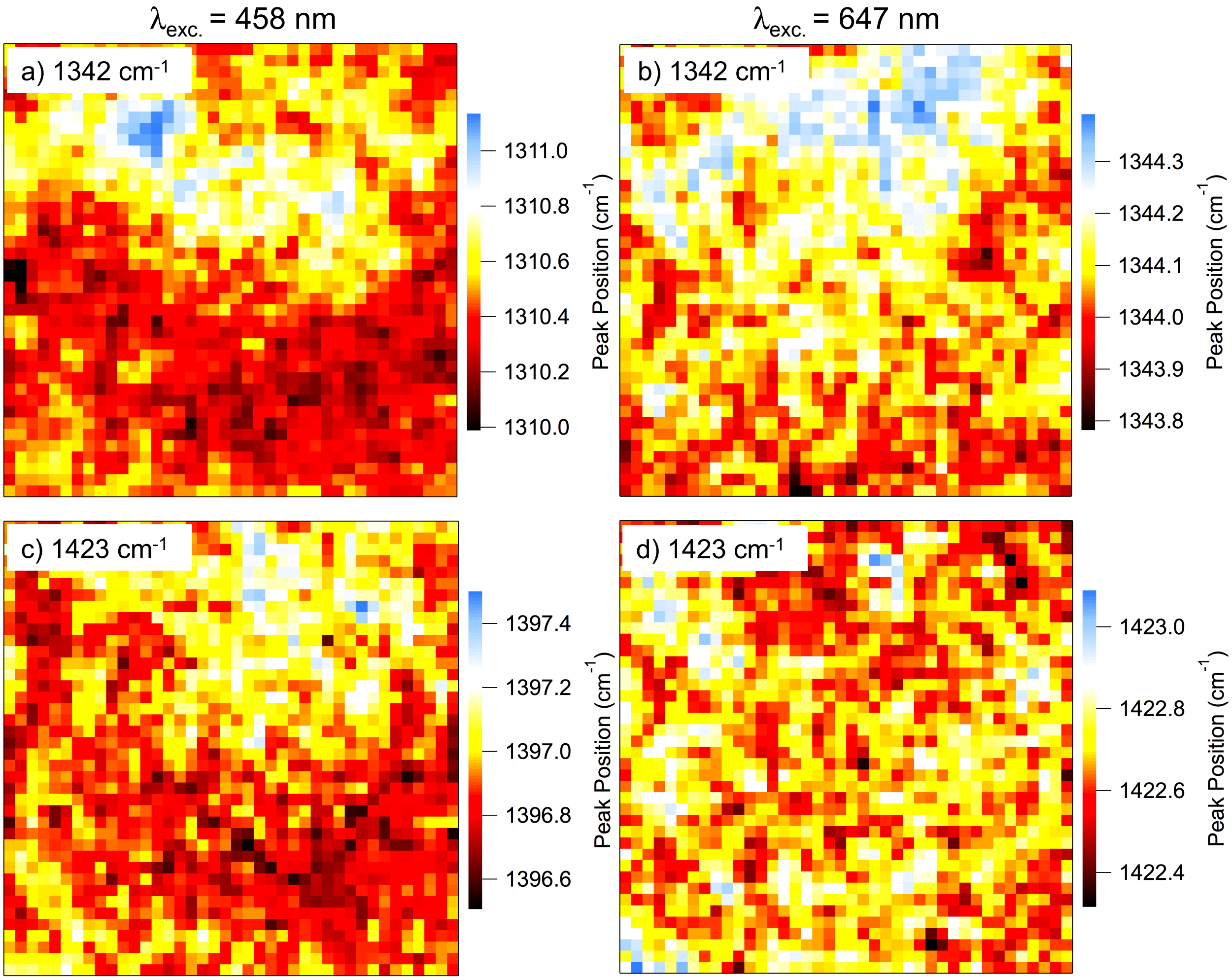

Figure S9. Raman frequency images of acceptor (a, b) and donor (c, d) moiety Raman mode intensities in PCPDTBT:PCBM:ODT (10:20:30 mg/ml) photovoltaic devices at 458 and 647 nm excitation. All images are of the same 10 × 10 µm area as in main article Figure 5. Pixel values represent fitted (Gaussian) peak positions of the indicated modes.

1. Kallel, H.; Latini, G.; Paquin, F.; Rinfret, R.; Stingelin, N.; Silva, C., Background-free quasi-steady-state photoinduced absorption spectroscopy by dual optical modulation. *arXiv:1007.3035v2 [cond–mat.mtrl–sci]* **2010**, 3035.