I. SUPPLEMENTAL INFORMATION

A. Raman Spectroscopy

Raman spectroscopy performed on the amorphous film is shown in Fig. 1. Only the frequency range of 1200 cm\(^{-1}\) to 1600 cm\(^{-1}\) is shown, as these signals were the strongest and correlate directly to the molecular vibrations. At room temperature, 4 peaks in this frequency range can be clearly identified. The frequencies 1575 cm\(^{-1}\), 1323 cm\(^{-1}\) and 1217 cm\(^{-1}\) arise from ring stretches of the aryl moieties\(^1,2\). However, the signal at 1530 cm\(^{-1}\) is not a vibration of the OPE-1p molecule, therefore it is suspected that this vibration arises from a symmetry element induced by the crystalline packing. As we study the evolution of these Raman signals as a function of temperature this appears to be the case as it is the 1530 cm\(^{-1}\) that shifts most drastically as the crystal approaches its melting point. Tracking these vibrations as a function of temperature, there is a global shift to lower frequencies that all the observed frequencies show as seen in Fig. 1. However, as the melting point of the crystal (407K) is passed, all the raman signals shift strongly to lower frequencies except the 1575 cm\(^{-1}\) mode. This is interpreted as a softening of the crystalline lattice as the melting point is passed.

The 1530 cm\(^{-1}\) mode is not an intrinsic crystal vibration as these tend to be of significantly lower frequency\(^3\). In addition it would be expected that this mode should disappear as the system approached the isotropic liquid and crystal symmetry is lost. This is not the case as the strength 1530 cm\(^{-1}\) mode remains strong even after the crystal has melted completely.

B. Photoluminescence

Our analysis of the PL properties of OPE-1p begins with a detailed fitting of OPE-1p in a dilute toluene solution (\(\sim 1\) pM) using a two-state model accounting for vibronic transitions with 2-D harmonic wells\(^4\),

\[
\frac{I(\omega)}{I(\omega_0)} = \sum_{v_M} \sum_{v_L} \left( \frac{\omega_0 - v_M \omega_M - v_L \omega_L}{\omega_0} \right)^3 \left( \frac{S^v_M}{v_M!} \right) \left( \frac{S^v_L}{v_L!} \right) \exp \left[ -4ln2 \left( \frac{\omega - \omega_0 + v_M \omega_M + v_L \omega_L}{\Delta \omega} \right) \right] \tag{1}
\]

where \(v_M\) and \(v_L\) are the ground state vibrational quantum numbers for the medium and low frequency vibrations, respectively, and the sum is over the first 5 of the medium and first 10 of the low frequency numbers. The vibrational frequencies (\(\omega_M, \omega_L\)), the associated Huang-Rhys factors (\(S_L, S_M\)) and the excited state displacement energy (\(E_{00}\)) can also be determined. The line width (\(\Delta \omega\)) and the PL intensity (\(I(E_{00})\)) are also fit. The quality of the fit is shown in Fig. 2a in the manuscript. We obtain two frequencies corresponding to resonantly coupled vibrations, \(\omega_L = 351 \pm 3\) cm\(^{-1}\) and \(\omega_M = 1559 \pm 6\) cm\(^{-1}\) and their corresponding Huang Rhys factors \(S_L = 2.8 \pm 0.05\) and \(S_M = 0.96 \pm 0.01\). The medium frequency mode we obtained matches the strongest signal in our Raman spectrum in Fig.1 at 1570 cm\(^{-1}\) with less than a 1% difference. This strongly indicates that the excited state decay and even nonradiative pathways relax through ring vibrations.

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FIG. 1: Raman Spectroscopy of OPE-1p drop-cast film at different temperatures. Raman Spectra of OPE-1p at 298K (top) and at 420K (bottom). The frequencies of the 4 identified peaks are tracked as a function of temperature (bottom graphs).