Electronic Supplementary Information

Electromodulation (EM) spectroscopy has been widely used to investigate internal electric fields in organic devices (see ref. S1). In a typical EM measurement, a combined ac and dc bias $V = V_{dc} + V_{ac}\sin(\omega t)$ is applied to the device and changes in the transmission of a probe beam are monitored using phase sensitive lock-in detection. If the origin of the EM signal is electroabsorption (EA) (the Stark effect, SE), the fractional change in transmission is proportional to the third order dc Kerr nonlinear susceptibility and the square of the electric field. The differential transmission is therefore modulated at both the 1st- and 2nd-harmonic frequencies in accordance with eqn (1a) and (1b).

$$I_{\omega} = \left.\frac{\Delta T}{T}\right|_{\omega} \propto 2\,\mathrm{Im}\,\chi^3(\lambda)E_{dc}E_{ac}\sin(\omega t) \qquad \text{1}^{\text{st}}\text{ harmonic} \qquad (1a)$$

$$I_{2\omega} = \left.\frac{\Delta T}{T}\right|_{2\omega} \propto \tfrac{1}{2}\,\mathrm{Im}\,\chi^3(\lambda)E_{ac}^2\cos(2\omega t) \qquad \text{2}^{\text{nd}}\text{ harmonic} \qquad (1b)$$

Under conditions of low carrier injection, the bulk field E_{dc} is related to the dc component of the applied voltage V_{dc} by $E_{dc} = (V_{dc} - V_{BI})/d$ where V_{BI} is the built-in potential, and d is the thickness of the layer. I_{ω} therefore varies linearly with V_{dc} (passing through zero at $V_{dc} = V_{BI}$), and $I_{2\omega}$ is independent of V_{dc}; any deviations from this behaviour indicate non-uniform internal fields arising from the presence of substantial charge in the device.

Ref S1: S.J. Martin, G.L.B. Verschoor, M.A. Webster, A.B. Walker, *Org. Electron.* 2002, **3**(3-4), 129.