Supplementary Information

Fig. SI1 is a schematic representation of the pulsed measurement scheme used to obtain the $J_{\mathrm{ph}}^{\mathrm{pulsed}} - V$ curves. The bias is incremented in equal steps of height ΔV and width Δt and the light source is modulated at a frequency $\omega = 1/\Delta t$ such that the device is in the dark for the first half of each time step and in the light for the second half. The voltage is cycled repeatedly to improve the signal to noise ratio of the measured current by averaging.

Insight into device operation can be obtained from electromodulation (EM) spectroscopy, in which a combined AC and DC bias $V = V_{\mathrm{DC}} + V_{\mathrm{AC}}\sin\omega t$ is applied to the device and changes in the transmission of a probe beam are monitored by lock-in detection. If the origin of the EM signal is electroabsorption (i.e. the Stark effect), the fractional change in the transmission is proportional to the third-order DC Kerr nonlinear susceptibility and the square of the electric field *[6]*. The differential transmission is therefore modulated at the 1st- and 2nd-harmonic frequencies in accordance with Eqs. (SI1) and (SI2):

$$I_{\omega} = \left.\frac{\Delta T}{T}\right|_{\omega} \propto 2\,\mathrm{Im}\,\chi^{(3)}(\lambda)E_{\mathrm{DC}}E_{\mathrm{AC}}\sin\omega t \qquad \textbf{(SI1)}$$

$$I_{2\omega} = \left.\frac{\Delta T}{T}\right|_{2\omega} \propto \tfrac{1}{2}\,\mathrm{Im}\,\chi^{(3)}(\lambda)E_{\mathrm{AC}}^{2}\cos 2\omega t\,. \qquad \textbf{(SI2)}$$

Under conditions of low carrier injection, the bulk field E_{DC} is related to the DC component of the applied voltage V_{DC} by:

$$E_{\mathrm{DC}} = \frac{(V_{\mathrm{DC}} - V_{\mathrm{BI}})}{d} \qquad \textbf{(SI3)}$$

where V_{BI} is the built-in potential, and d is the width of the device. I_{ω} therefore varies linearly with V_{DC} (passing through zero at $V = V_{\mathrm{BI}}$), and $I_{2\omega}$ is independent of V_{DC}.

To perform the electroabsorption measurements, the internal reference signal ($V_{ac}\sin\omega t$) from a *Stanford Instruments SR830 Lock-in Amplifier* and a DC voltage (V_{dc}) from one of its auxiliary outputs were supplied as the inputs to a unity-gain summing amplifier. The output of the amplifier $V = V_{dc} + V_{ac}\sin\omega t$ was applied as a modulation voltage to the solar cell. The monochromated output of a 50 W xenon lamp was focused onto the aluminium cathode of the solar cell (via the glass substrate), and the reflected light refocused onto a Si photodetector with a gain-10^6 Ω trans-impedance amplifier. The amplified output of the photodetector was supplied as an input to the SR830 lock-in amplifier. The first-harmonic electroabsorption response was obtained by locking into the ω frequency component of the detected signal and the second harmonic response by locking into the 2ω component.

Fig. SI2A shows the 1st-harmonic EM spectrum of an annealed ITO/PEDOT:PSS/P3HT:PCBM/Al device, obtained using a 6 kHz 0.3 V AC bias with a DC-offset of -2 V. The spectrum shows a number of oscillatory features with peaks at 538, 578 and 624 nm and nodes at 596 and 558 nm (and additional less well resolved features below 538 nm), typical of electroabsorption (EA). The electroabsorption signal is obscured in forward bias by strong charge-induced absorption features that mask the weaker electroabsorption signal. The inset shows the electromodulation signal measured at a forward bias of 1 V, together with the EA signal that would be expected on the basis of the reverse bias spectrum and Eq. (SI1). The measured signal is much stronger and very different in both shape and phase from the expected EA signal. In consequence, reliable estimates of the built-in potential must be obtained using reverse bias data only.

The DC bias-dependence of the 1st-harmonic EM response at 644 nm is shown in Fig. SI2B using a 6 kHz, 0.3 V AC bias. The1st-harmonic signal varies linearly with the DC bias until a bias of 0 V; it then deviates strongly in the direction of positive $\Delta T/T$, peaks at 0.4 V, passes through zero at

0.65 V, and continues to vary in the direction of negative $\Delta T/T$. The emergence of the charge-induced features at 0 V (at which bias the current is extremely small) suggests they are due to trapped charge rather than injected charge from the electrodes. In order to obtain a reliable estimate of the built-in potential, a line-of-best fit was calculated using the initial twelve reverse-bias data points only and then extrapolated to zero, yielding a value $V_{BI} = 0.59 \pm 0.02$ V (where the errors define a 70 % confidence interval).

Fig. SI3 is a schematic depicting a simple model of a bulk heterojunction solar cell. The effective HOMO of the blend is derived from the HOMO level of the donor and the effective LUMO level of the blend is derived from the LUMO level of the acceptor. The Fermi levels of the electrodes are constrained to lie within the bounds of the effective energy gap due to energy level pinning (see main text). Hence, in this model, the electrodes are expected to behave non-selectively to carriers with easy extraction of electrons and holes at both electrodes.

Fig. SI1 Schematic illustrating the pulsed measurement scheme used to obtain the $J_{ph}^{pulsed} - V$ curves. The bias is incremented in equal steps of height ΔV and width Δt and the light source is modulated at a frequency $\omega = 1/\Delta t$ such that the device is in the dark for the first half of each time step and in the light for the second half. The voltage is cycled repeatedly to improve the signal to noise ratio of the measured current by averaging.

Fig. SI2 **(A) Main -** The reverse-bias 1^{st}-harmonic electromodulation (EM) spectrum of an ITO/PEDOT:PSS/P3HT:PCBM/Al device, obtained with a 6 kHz 0.3 V AC bias at a DC offset of -2 V. **Inset -** The actual forward-bias electromodulation spectrum of the device, obtained with a 6 kHz 0.3 V AC bias at a DC offset of +1 V (black line) and the spectrum that would be expected on the basis of the reverse bias spectrum if the signal were pure electroabsorption (grey line). **(B)** The DC bias dependence of the 1^{st}-harmonic EM response at 644 nm. The signal varies linearly with DC bias in accordance with Eq. SI1 until a DC bias of 0 V and then deviates strongly due to charge-induced modulation. The built-in potential can be determined by using the initial twelve reverse-bias data points – which are not contaminated by charge-induced features – and then extrapolating to zero, yielding a value V_{BI} = 0.59 ± 0.02 V (where the errors define a 70 % confidence interval).

Fig. SI3 Schematic outlining a simple model of a bulk heterojunction solar cell. The effective HOMO of the blend is derived from the HOMO level of the donor and the effective LUMO level of the blend is derived from the LUMO level of the acceptor. The Fermi levels of the electrodes are constrained to lie within the bounds of the effective energy gap due to energy level pinning (see main text). Hence, in this model, the electrodes are expected to behave non-selectively to carriers with easy extraction of electrons and holes at both electrodes.

Fig. SI1

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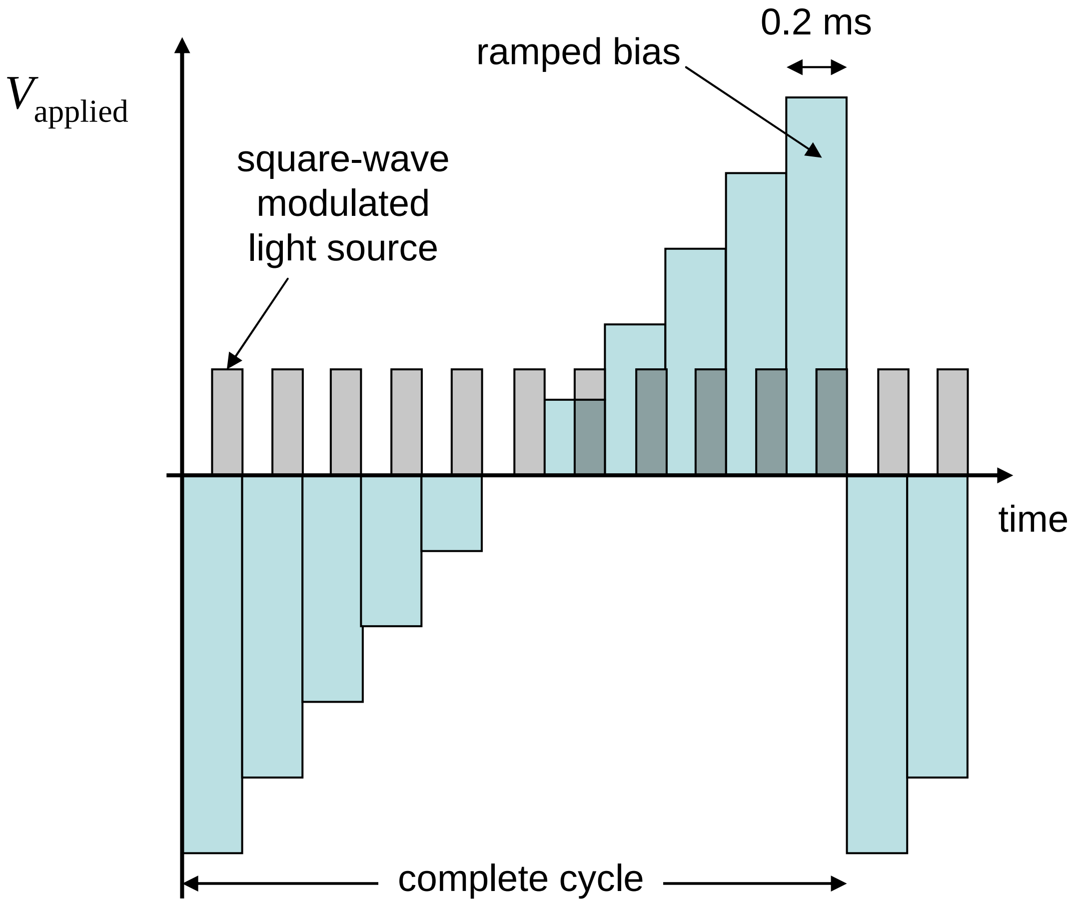
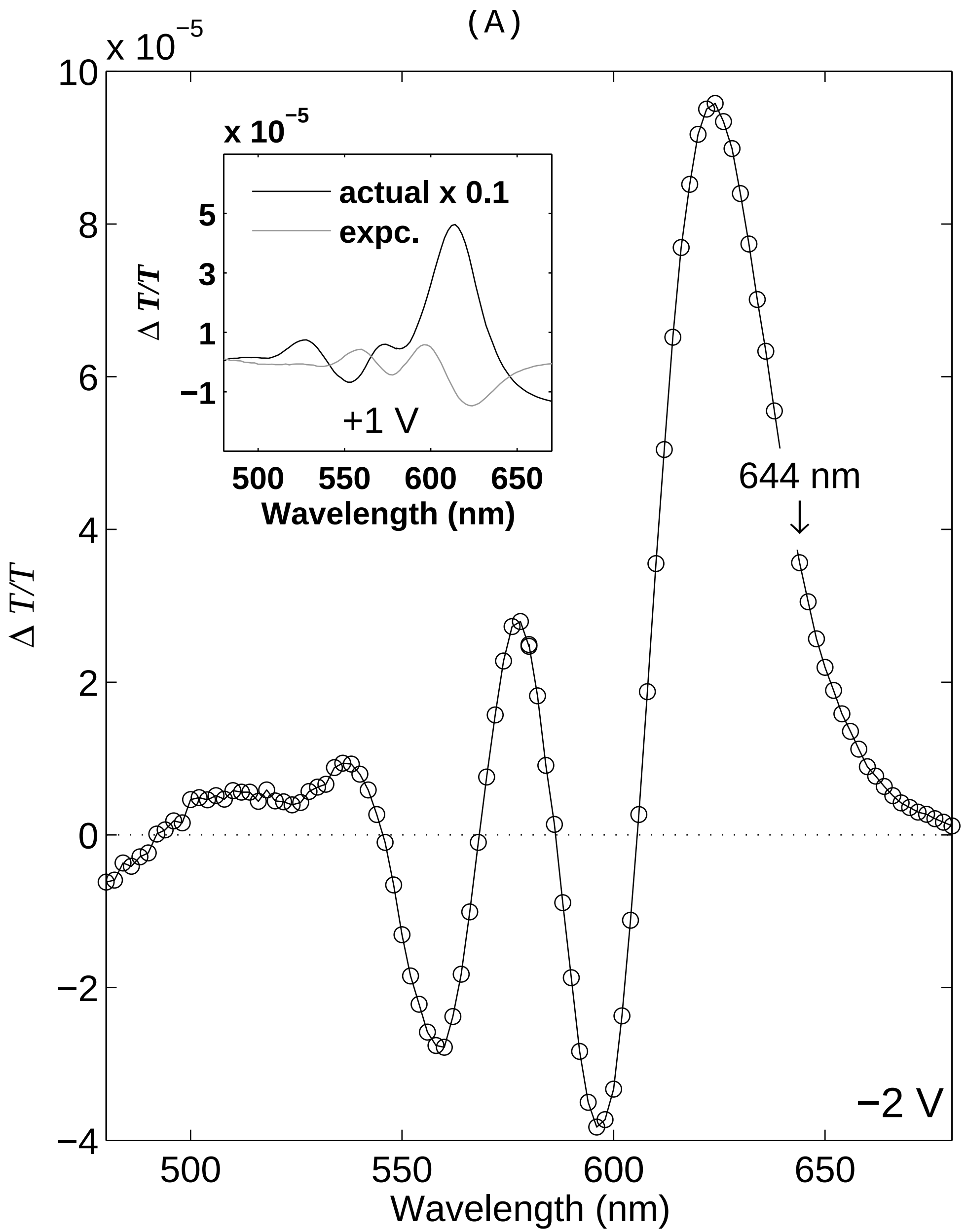
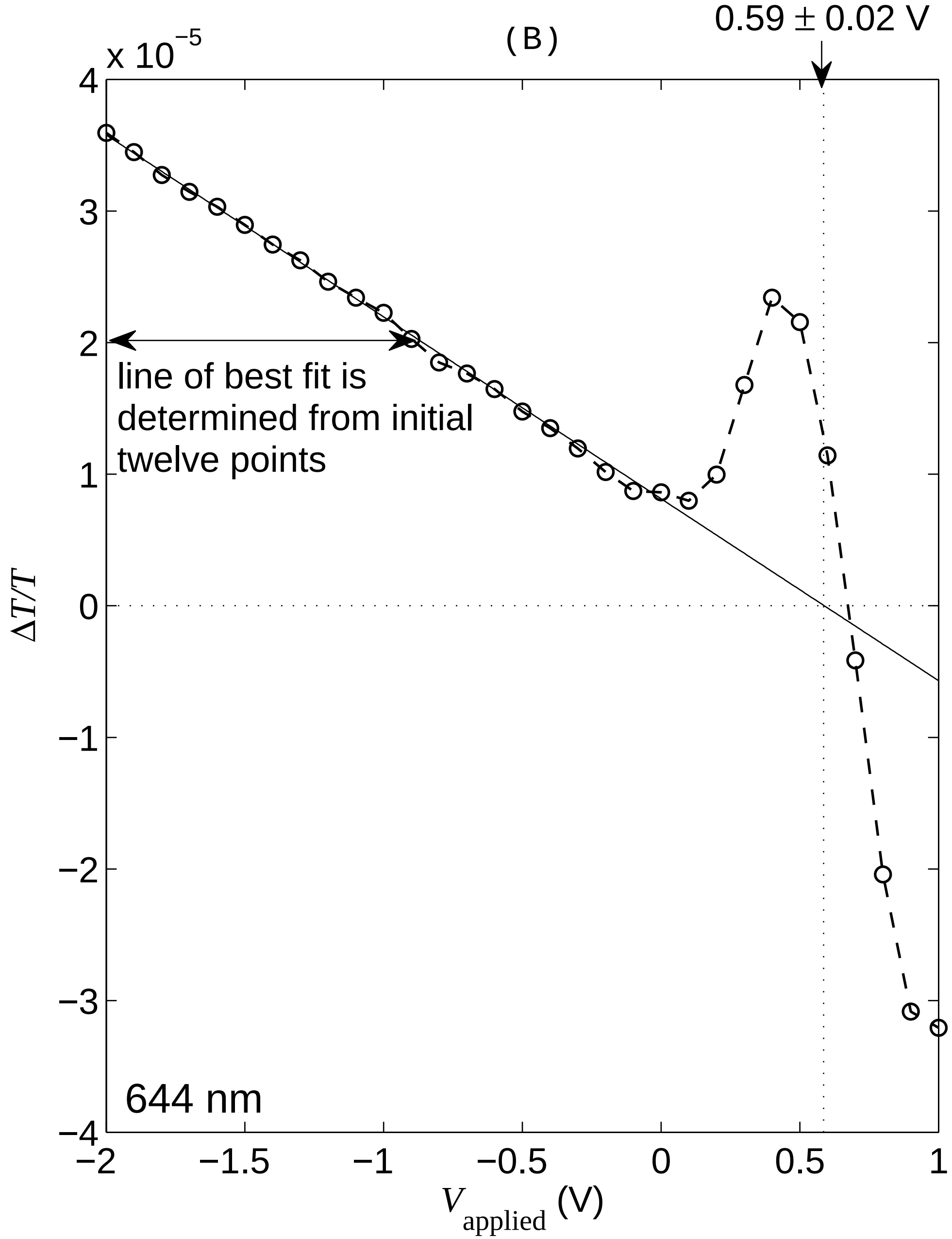


Fig. SI2



(A)
x 10^−5
10
8
6
4
2
0
−2
−4
500
550
600
650
Wavelength (nm)
Δ T/T
644 nm
−2 V
x 10^−5
actual x 0.1
expc.
5
3
1
−1
Δ T/T
+1 V
500
550
600
650
Wavelength (nm)



(B)
0.59 ± 0.02 V
x 10^−5
4
3
2
1
0
−1
−2
−3
−4
line of best fit is
determined from initial
twelve points
644 nm
ΔT/T
−2
−1.5
−1
−0.5
0
0.5
1
V applied (V)

Fig. SI3