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# Influence of P3HT:PCBM ratio on thermal and transport properties of bulk heterojunction solar cells

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## Supplementary Materials

## 1. Photothermal beam deflection spectrometry – theory

### 1.1 *Temperature oscillations*

The temperature ($\vartheta$) distribution of $i$ -layer satisfies the Fourier-Kirchhoff equation [58]:

$$\frac{1}{D_i}\frac{\partial \vartheta_i}{\partial t} = \nabla^2 \vartheta_i + \frac{q_i}{k_i}; D_i = k_i/(c_p\rho) \tag{SM.1}$$

where $D_i$ is thermal diffusivity, $k_i$, $c_p$ and $\rho$are the material thermal conductivity, heat capacity and density, respectively.$q_i$ is the power density of internal heat sources. These heat sources represent the heat produced by the absorption of the excitation light beam (EB). From here on, it was assumed that EB is only absorbed in the central layer comprising P3HT:PCBM and PEDOT:PSS layers. Other layers exhibit negligible light absorption. Thus, for them the Eq.(SM.1) can be rewritten in a form:

$$\frac{1}{D_i}\frac{\partial \vartheta_i}{\partial t} = \nabla^2 \vartheta_i; \tag{SM.2}$$

The incident light of EB is modulated with a frequency $f$ in the range between 0 to $I_0$. As a result, the power density of internal heat sources can be given by [59-64]:

$$q_{si}(z,t) = \frac{\alpha I_0 E_g}{h\upsilon}\left\{\frac{\tau}{2}\left[\nu_{SR} + \frac{1}{\tau}\right] + \left(\frac{h\upsilon}{E_g} - 1\right)[1 + \exp(2i\pi ft)]\right\}\exp(-\alpha z); \tag{SM.3}$$

where $E_g$ is the energy band gap, $\tau$ is the carrier life time, $\upsilon_{SR}$ is the surface recombination velocity, $\alpha$ is the effective optical absorption coefficient of the light absorbing layer. Briefly, Eq.( SM.7) accounts for heat generated by (i) intraband thermalization, (ii) bulk and (iii) surface recombination of photogenerated charge carriers in a semiconducting material [60]. Photogenerated heat is transported to near layers. In fact, the temperature and the heat flux are conserved at the interface between layers, which results in a set of boundary equations:

$$\vartheta_f(z,t)\big|_{z=0} = \vartheta_{s1}(z,t)\big|_{z=0}; \tag{SM.4a}$$

$$\vartheta_{sj-1}(z,t)\big|_{z=l_{sj-1}} = \vartheta_{sj}(z,t)\big|_{z=l_{sj-1}}; \tag{SM.4b}$$

$$\vartheta_{sm}(z,t)\big|_{z\to-\infty} = \vartheta_f(z,t)\big|_{z\to+\infty} = 0; \tag{SM.4c}$$

$$-k_{s1}\frac{\partial\vartheta_{s1}(z,t)}{\partial z}\bigg|_{z=0} = -k_f\frac{\partial\vartheta_f(z,t)}{\partial z}\bigg|_{z=0} \tag{SM.4d}$$

$$-k_{sj-1}\frac{\partial\vartheta_{sj-1}(z,t)}{\partial z}\bigg|_{z=l_{sj-1}} = -k_{sj}\frac{\partial\vartheta_{sj}(z,t)}{\partial z}\bigg|_{z=l_{sj-1}} \tag{SM.4e}$$

A solution of Eqs (SM.1-SM.4) is a set of temperature oscillations in given layers with certain thicknesses $l_{sj}$and thermal properties ($D_{sj}$, $k_{sj}$). The temperature oscillation (TOs) in the fluid above the sample is given by:

$$\vartheta_f(z,t) = \theta\exp\left[-\sqrt{\frac{\pi f}{D_f}}(z+z_0)\right]\cos\left[2\pi\pi-\sqrt{\frac{\pi f}{D_f}}(z+z_0)t+\varphi\right]; \tag{SM.5}$$

where $\theta$ is the amplitude of TOs at the sample's surface and $\phi$is the phase shift between the phase of the sample surface's temperature change and the phase of the pump beam, which is introduced below. $\theta$ and $\phi$ are functions of thermal (thermal diffusivity and conductivity), optical (energy band gap, absorption coefficient), transport (carrier life time) and structural (thickness) properties of light-absorbing layer and other layers constructing the whole sample (Fig. 1) as described by:

$$\theta = \sqrt{(\mathrm{Re}\theta_m)^2 + (\mathrm{Im}\theta_m)^2}; \quad \varphi = \tan\left(\frac{\mathrm{Im}\theta_m}{\mathrm{Re}\theta_m}\right); \quad \theta_m = U_1\exp\left(l_0\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right) + V_1\exp\left(-l_0\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right); \tag{SM.5a}$$

$$U_1 = \frac{U_2}{\sigma_c}\exp\left(2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right) + \frac{V_2}{\sigma_c}\exp\left(-2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right); \; V_1 = U_2\exp\left(2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right) + V_2\exp\left(-2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right); \tag{SM.5b}$$

$$U_2 = \frac{1}{\varepsilon_c}\left\{\frac{\eta_{c1}\alpha_{c2}\alpha_{c3}^{-1}-\eta_{c2}}{\eta_{c3}-\alpha_{c1}\alpha_{c3}^{-1}\eta_{c1}}\exp\left[(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right] + \left(\frac{\varepsilon_{c1}}{\varepsilon_{c3}}\frac{\eta_{c1}\alpha_{c2}\alpha_{c3}^{-1}-\eta_{c2}}{\eta_{c3}-\alpha_{c1}\alpha_{c3}^{-1}\eta_{c1}} + \frac{\varepsilon_{c2}}{\varepsilon_{c3}}\right)\exp\left[-(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]\right\} + -\frac{E_3}{\varepsilon_c}\exp[\alpha(l_1+2l_2)]; \tag{SM.5c}$$

$$V_2 = \frac{1}{\varepsilon_c}\frac{\delta_{c1}}{\delta_{c2}}\left\{\frac{\eta_{c1}\alpha_{c2}\alpha_{c3}^{-1}-\eta_{c2}}{\eta_{c3}-\alpha_{c1}\alpha_{c3}^{-1}\eta_{c1}}\exp\left[(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right] + \left(\frac{\varepsilon_{c1}}{\varepsilon_{c3}}\frac{\eta_{c1}\alpha_{c2}\alpha_{c3}^{-1}-\eta_{c2}}{\eta_{c3}-\alpha_{c1}\alpha_{c3}^{-1}\eta_{c1}} + \frac{\varepsilon_{c2}}{\varepsilon_{c3}}\right)\exp\left[-(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right] - E_3\exp[\alpha(l_1+2l_2)]\right\}; \tag{SM.5d}$$

$$\sigma_c = \exp\left[\sqrt{i\frac{2\pi\pi}{D_{s1}}}(l_0+l_1)\right]\left\{1+\left(\frac{k_{s1}}{k_f}\sqrt{\frac{D_f}{D_{s1}}}-1\right)\left(\frac{k_{s1}}{k_f}\sqrt{\frac{D_f}{D_{s1}}}+1\right)^{-1}\exp\left[2l_1\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right]\right\}; \; \sigma_{c1} = \sigma_c^{-1}\left(\frac{k_{s1}}{k_f}\sqrt{\frac{D_f}{D_{s1}}}-1\right)\left(\frac{k_{s1}}{k_f}\sqrt{\frac{D_f}{D_{s1}}}+1\right)^{-1}\exp\left[2l_0\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right] \tag{SM.5e}$$

$$\delta_{c1} = \sqrt{i\frac{2\pi\pi}{D_{s1}}}\exp\left[2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}-(l_0-l_1)\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right]\sigma_{c1} + \frac{k_{s2}}{k_{s1}}\sqrt{i\frac{2\pi\pi}{D_{s2}}}\exp\left(2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right) - \frac{1}{\sigma_c}\sqrt{i\frac{2\pi\pi}{D_{s1}}}\exp\left[2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}+(l_0-l_1)\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right];$$

$$\delta_{c2} = \frac{1}{\sigma_c}\sqrt{i\frac{2\pi\pi}{D_{s1}}}\exp\left[-2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}+(l_0-l_1)\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right] + \frac{k_{s2}}{k_{s1}}\sqrt{i\frac{2\pi\pi}{D_{s2}}}\exp\left(-2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right) - \sigma_{c1}\sqrt{i\frac{2\pi\pi}{D_{s1}}}\exp\left[-2l_1\sqrt{i\frac{2\pi\pi}{D_{s2}}}+(l_0-l_1)\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right];$$

$$\varepsilon_c = \exp\left[(2l_1+l_2)\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right] + \frac{\delta_{c1}}{\delta_{c2}}\exp\left(-(2l_1+l_2)\sqrt{i\frac{2\pi\pi}{D_{s2}}}\right);$$

$$\varepsilon_{c1}=\frac{\delta_{c1}}{\varepsilon_c\delta_{c2}}\sqrt{i\frac{2\pi\pi}{D_{s2}}}\exp\left[-(2l_1+l_2)\sqrt{i\frac{2\pi\pi}{D_{s2}}}+(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]-\frac{1}{\varepsilon_c}\sqrt{i\frac{2\pi\pi}{D_{s2}}}\exp\left[(2l_1+l_2)\sqrt{i\frac{2\pi\pi}{D_{s2}}}+(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]+$$
$$\frac{k_{s3}}{k_{s2}}\sqrt{i\frac{2\pi\pi}{D_{s3}}}\exp\left[(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}+(l_0-l_1)\sqrt{i\frac{2\pi\pi}{D_{s1}}}\right]$$
$$\varepsilon_{c2}=\frac{E_3}{\varepsilon_c}\sqrt{i\frac{2\pi f}{D_{s2}}}\exp\left[(2l_1+l_2)\sqrt{i\frac{2\pi f}{D_{s2}}}+\alpha(l_1+2l_2)\right]+-\frac{E_3}{\varepsilon_c}\frac{\delta_{c1}}{\delta_{c2}}\sqrt{i\frac{2\pi f}{D_{s2}}}\exp\left[-(2l_1+l_2)\sqrt{i\frac{2\pi f}{D_{s2}}}-(l_1+2l_2)\sqrt{i\frac{2\pi f}{D_{s3}}}\right]+$$
$$\frac{k_{s3}}{k_{s2}}E_3\left[\frac{\tau}{2}\left(\nu_{SR}+\frac{1}{\tau}\right)+\frac{h\upsilon}{E_g}-1\right]\exp[\alpha(l_1+2l_2)]$$
$$\varepsilon_{c3}=-\frac{\delta_{c1}}{\varepsilon_c\delta_{c2}}\sqrt{i\frac{2\pi\pi}{D_{s2}}}\exp\left[(2l_1+l_2)\sqrt{i\frac{2\pi\pi}{D_{s2}}}-(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]+\frac{1}{\varepsilon_c}\sqrt{i\frac{2\pi\pi}{D_{s2}}}\exp\left[(2l_1+l_2)\sqrt{i\frac{2\pi\pi}{D_{s2}}}-(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]+$$
$$\frac{k_{s3}}{k_{s2}}\sqrt{i\frac{2\pi\pi}{D_{s3}}}\exp\left[-(l_1+2l_2)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right];$$
$$\eta_{c1}=-\sqrt{i\frac{2\pi\pi}{D_{s4}}}\frac{k_{s4}}{k_{s3}}\exp\left[(l_1+l_2+2l_3)\sqrt{i\frac{2\pi\pi}{D_{s4}}}\right];$$
$$\eta_{c2}=\frac{\varepsilon_{c2}}{\varepsilon_{c3}}\sqrt{i\frac{2\pi f}{D_{s3}}}\exp\left[-(l_1+2l_2+l_3)\sqrt{i\frac{2\pi f}{D_{s3}}}\right]+E_3\left[\frac{\tau}{2}\left(\nu_{SR}+\frac{1}{\tau}\right)+\frac{h\upsilon}{E_g}-1\right]\exp[\alpha(l_1+2l_2+l_3)]$$
$$\eta_{c3}=\frac{\varepsilon_{c1}}{\varepsilon_{c3}}\sqrt{i\frac{2\pi\pi}{D_{s3}}}\exp\left[-(l_1+2l_2+l_3)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]-\sqrt{i\frac{2\pi\pi}{D_{s3}}}\exp\left[(l_1+2l_2+l_3)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right];$$
$$\alpha_{c1}=\exp\left[(l_1+2l_2+l_3)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]+\frac{\varepsilon_{c1}}{\varepsilon_{c3}}\exp\left[-(l_1+2l_2+l_3)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right];\ \alpha_{c2}=\frac{\varepsilon_{c2}}{\varepsilon_{c3}}\exp\left[-(l_1+2l_2+l_3)\sqrt{i\frac{2\pi\pi}{D_{s3}}}\right]-E_3\exp[\alpha(l_1+2l_2+l_3)];$$
$$\alpha_{c3}=\exp\left[(l_1+l_2+2l_3)\sqrt{i\frac{2\pi\pi}{D_{s4}}}\right];\ E_3=\frac{\alpha I_E E_g}{h\upsilon k_{s3}}\left(\alpha^2-i\frac{2\pi f}{D_{s3}}\right) \quad \text{(SM.5a)}$$

where $I_E$ and $f$ are the intensity and modulation frequency of pumb beam, $\alpha$ and $E_g$ are the absorption coefficient and energy band gap of the examined layer, $D_f$, $k_f$ are the thermal diffusivity and conductivity of air over the whole sample structure, $D_{s1}$, $k_{s1}$, $l_0$ are the thermal diffusivity and conductivity as well as thickness of both glass layers, $D_{s2}$, $k_{s2}$, $l_1$ are the thermal diffusivity and conductivity as well as thickness of nitrogen layer over P3HT:PCBM sample, $D_{s3}$, $k_{s3}$, $l_2$ are the thermal diffusivity and conductivity as well as thickness of P3HT:PCBM material, $D_{s4}$, $k_{s4}$, $l_3$ are the thermal diffusivity and conductivity as well as thickness of ITO layer.

### *1.2 Photodeflection signal*

In BDS technique the sample's surface is periodically heated by a modulated laser beam called excitation beam (EB) [8], what leads to inducing the temperature oscillation (TOs) in the fluid layer adjacent to the sample surface and thus to variation (gradients) in its refraction index, which depends on the optical and thermal properties of the material and fluid above it detected by monitoring the deflection and phase change of a probe beam (PB) propagating above sample close to its surface. One of the main advantages of BDS is the ability to vary the sampling depth by changing the value of modulation frequency f of TOs. This is determined by a quantity called the thermal diffusion length $\mu_{th}$, which defines the distance measured from the surface of the sample into medium that is penetrated by TOs and expressed by:

$$\mu_{th} = (Di/\pi f)^{1/2} \quad \text{(SM.6)}$$

where $D_i$ is the thermal diffusivity of the material, in which TOs propagates ($i$ = s for sample, $i = f$ for fluid over the sample). It turns outthat $\mu_{th}$ depends on the material properties. Thus, by changing the TOs penetration depth, it is possible to obtaininformation about the thickness of the material layer at chosen depth determined by $\mu_{th}$.

As a result of the PB interaction with TOs in the fluid above the sample, its trajectory is changed on the refractive index gradients according to the relation [65]:

$$z_1(\xi,\tau) = n_0^2 s_T \int_0^{\tau} (\tau - \tau') \frac{\partial \vartheta_f}{\partial z} d\tau' , \tag{SM.7}$$

where $n_0$ is the refracting index of undisturbed fluid, $s_T = (1/n_0)(dn/dT)$ – the temperature coefficient of refractive index (thermal sensitivity), $\tau$ is the running complex coordinate along the PB trajectory, $\xi$ is the PB's coordinate in the input plane of the experimental setup ($z = 0$).

The consequence of the change in PB optical path is the change in the PB phase:

$$\Phi_1 = kn_0^2 s_T \int_0^{\tau} \vartheta_f [z(\tau')] d\tau' \tag{SM.8}$$

Thus, the PB intensity changes caused by its interaction with TO results in photodeflection (PD) signal that in case of detection by the use of quadrant photodiode (QP) is given by:

$$S_{PD} = 2K_d \left( \int_0^{+\infty} - \int_{-z0}^{0} \right) dz \int_{-\infty}^{+\infty} dy [\mathrm{Re}(a_1) - k\mathrm{Im}(\Phi_1)] I_0 = A_{PD} \cos(\Omega t + \varphi_f + \varphi_{PD}) \tag{SM.9}$$

Here $K_d$ is the detector constant, $k$ is the wave number of PB and $I_0$ is the light intensity of undisturbed PB.