Supplementary Information for

On the Energetics of Bound Charge-Transfer States in Organic Photovoltaics

Jiangbin Zhang¹, Andreas C. Jakowetz¹, Guangru Li¹, Dawei Di¹, S. Matthew Menke¹,

Akshay Rao¹, Richard H. Friend¹, Artem A. Bakulin^{1,2}

¹ Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom;

KEYWORDS:

Organic Photovoltaics, Binding Energy, Activation Energy, Arrhenius Plot, Driving Energy, Charge Generation, Pump-Push Photocurrent Spectroscopy, Charge Delocalization, Device Characterization, Polymer, Fullerene, Ultrafast Spectroscopy;

LIST:

Figure S1 UV-Vis absorption of films of MDMO-PPV:fullerene derivatives.

Figure S2 PPP response at room temperature (300 K).

Figure S3 Typical raw PPP kinetics without background removal in MDMO-PPV:bPCBM(1:1) device. The background signal is assigned to long-lived trapped states.

Figure S4 Full dataset of pump-push photocurrent spectroscopy.

Table S1 Key device parameters.

² Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom;

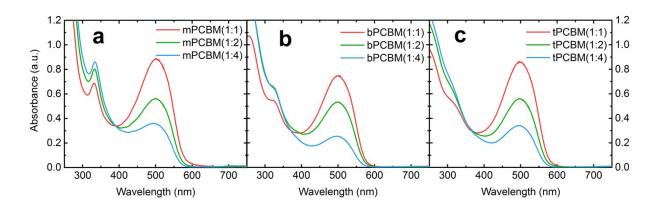


Figure S1 UV-Vis absorption of films of MDMO-PPV:fullerene derivatives (a) mPCBM (b) bPCBM and (c) tPCBM with blend ratios of 1:1, 1:2 and 1:4.

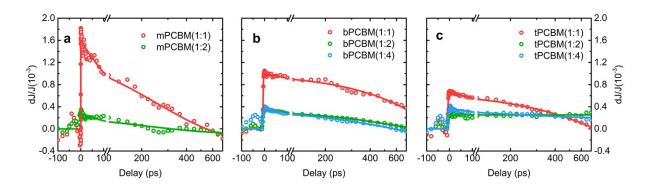


Figure S2 PPP response at room temperature (300 K). (a) MDMO-PPV:mPCBM (b) MDMO-PPV:bPCBM and (c) MDMO-PPV:tPCBM.

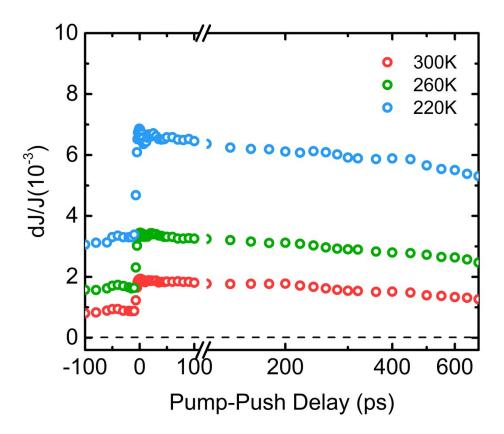
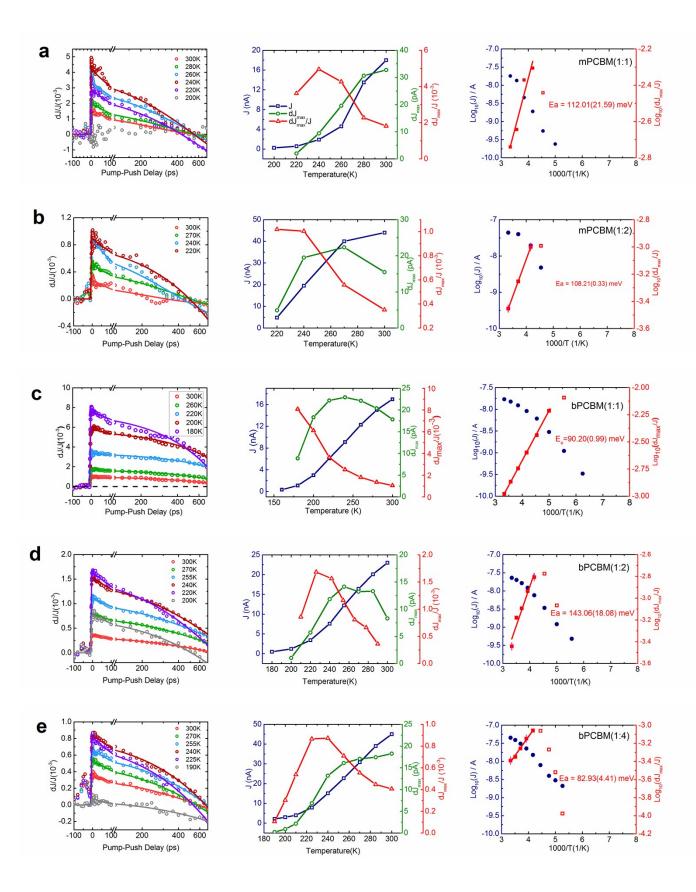


Figure S3 Typical Raw PPP kinetics without background removal in MDMO-PPV:bPCBM(1:1) device. The background signal is assigned to long-lived trapped states and multi-photon excitations.



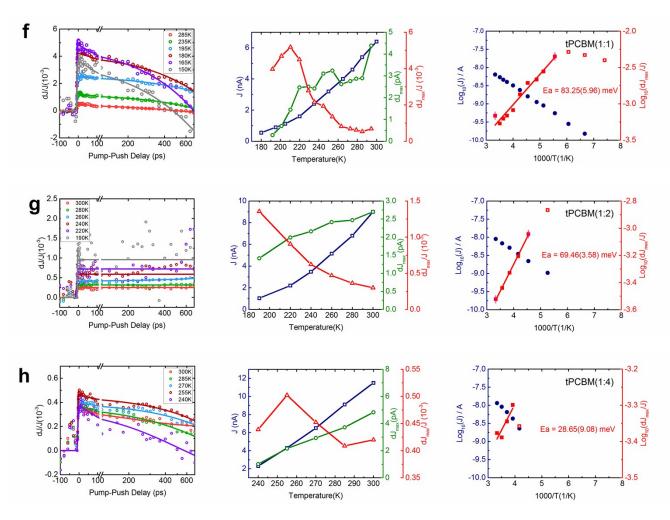


Figure S4 Full dataset of (i) the PPP dynamics in different devices, (ii) temperature dependence of J, dJ_{max} and dJ_{max}/J , and (iii) Arrhenius plots of J and dJ_{max}/J . (a) mPCBM with D-A ratio of 1:1 (b) mPCBM with D-A ratio of 1:2 (d) bPCBM with D-A ratio of 1:2 (e) bPCBM with D-A ratio of 1:4 (f) tPCBM with D-A ratio of 1:1 (g) tPCBM with D-A ratio of 1:2 (h) tPCBM with D-A ratio of 1:4

Table S1 Key device parameters of MDMO-PPV as the donor and three fullerene derivatives (mPCBM, bPCBM and tPCBM) as the acceptors with blend ratios of 1:1, 1:2 and 1:4.

Acceptor	1:1	1:2	1:4
mPCBM	Voc/(V) = 0.91	Voc = 0.87	Voc = 0.84
	$Jsc/(mA/cm^2) = 1.61$	Jsc = 3.62	Jsc = 4.82
	FF=35%	FF=44%	FF=51%
	PCE=0.51%	PCE=1.39%	PCE=2.10%
bPCBM	Voc = 1.00	Voc = 0.98	Voc=0.98
	Jsc = 1.01	Jsc = 1.54	Jsc=2.36
	FF=29%	FF=32%	FF=36%
	PCE=0.29%	PCE=0.49%	PCE=0.83%
tPCBM	Voc = 1.01	*	Voc = 1.01
	Jsc = 0.33		Jsc = 0.76
	FF=25%		FF=29%
	PCE=0.08%		PCE=0.22%

^{*}Even though the tPCBM/1:2 data is absent, from the trend of the data, we can still estimate $Voc \sim 1.01V$, $Jsc \sim 0.5$ mA/cm², $FF \sim 27\%$ and $PCE \sim 0.15\%$.