Supplementary Information for

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

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

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Table S1 Key device parameters.

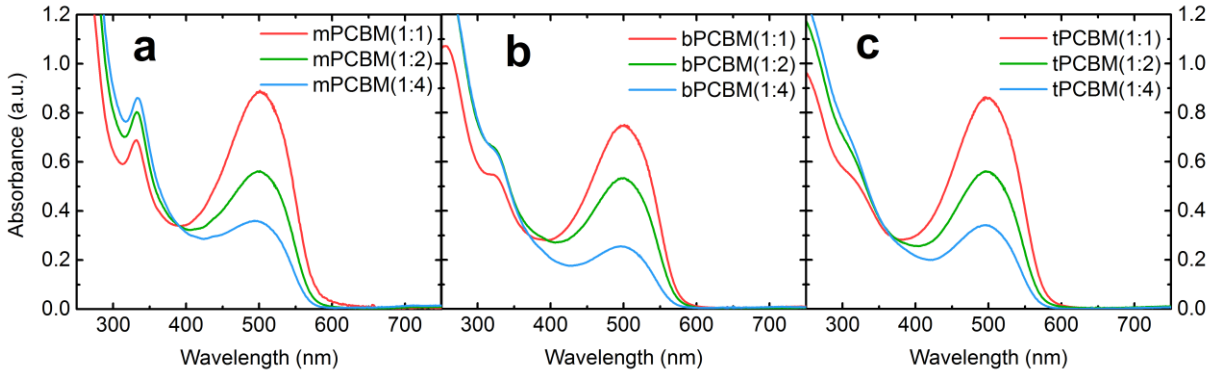


Figure S1 UV-Vis absorption of films of MDMO-PPV:fullerene derivatives (a) mPCBM (b) bPCBM and (c) tPCBM with blend ratios of 1:1, 1:2 and 1:4.

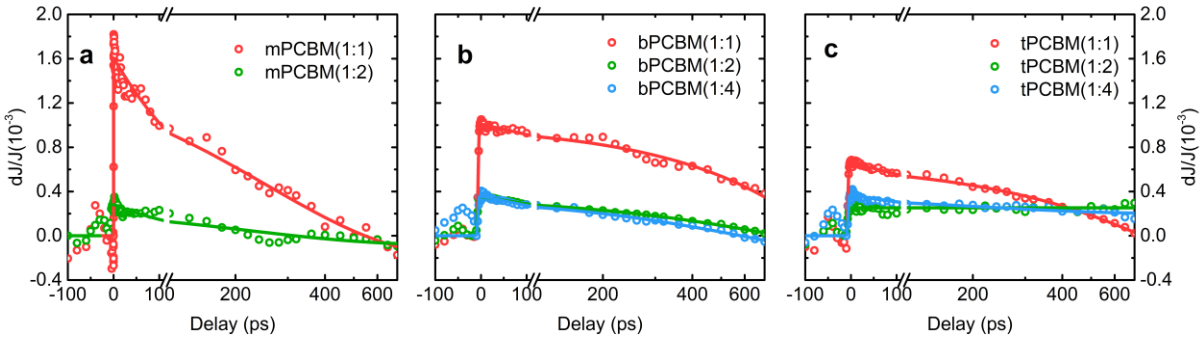


Figure S2 PPP response at room temperature (300 K). (a) MDMO-PPV:mPCBM (b) MDMO-PPV:bPCBM and (c) MDMO-PPV:tPCBM.

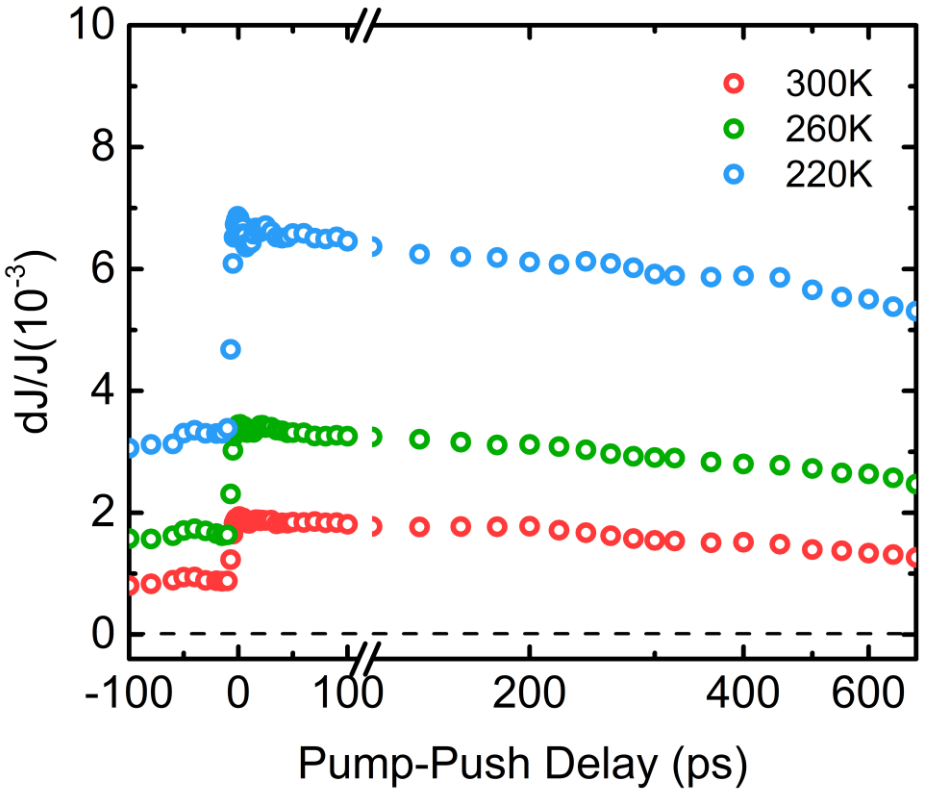
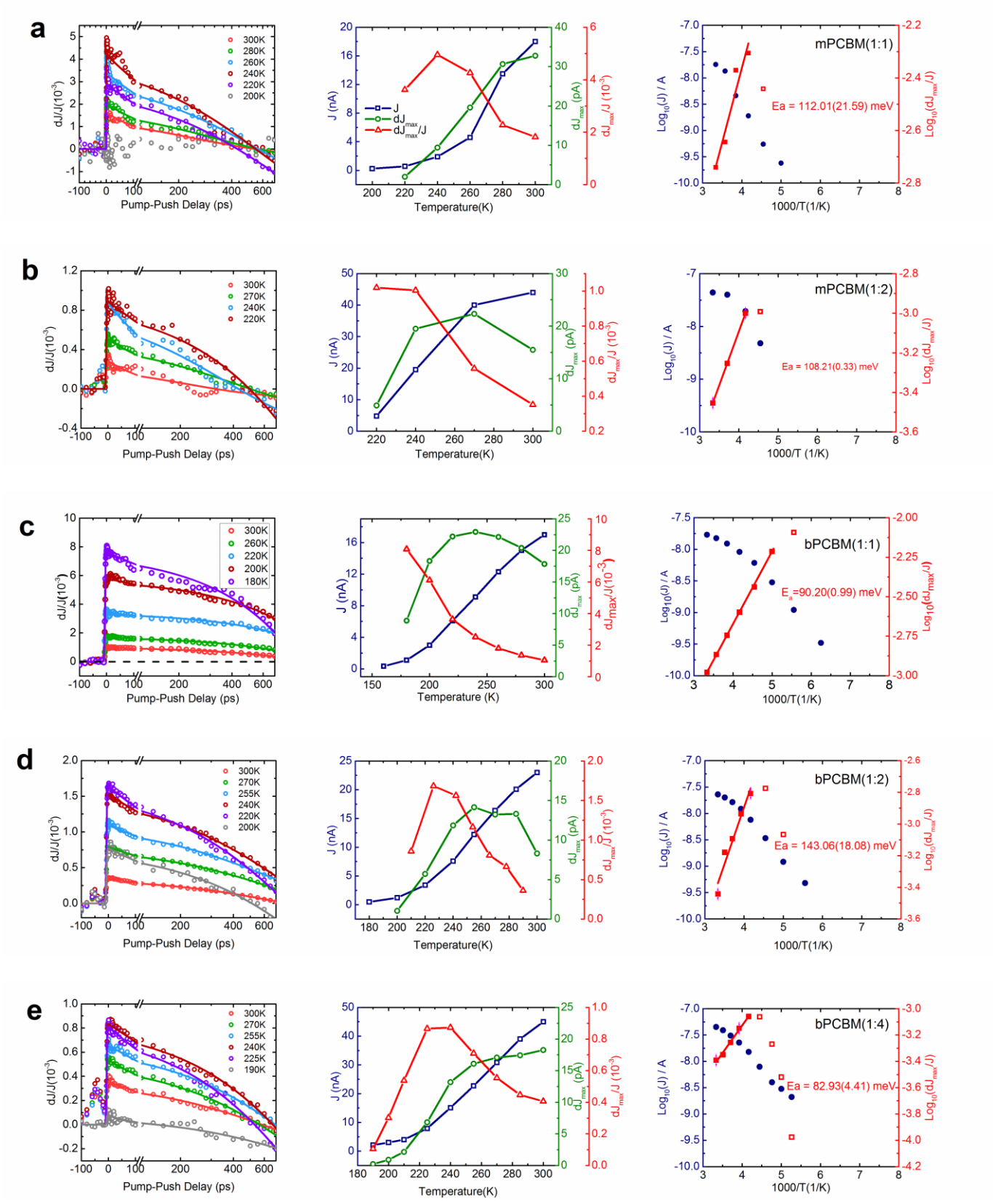


Figure S3 Typical Raw PPP kinetics without background removal in MDMO-PPV:bPCBM(1:1) device. The background signal is assigned to long-lived trapped states and multi-photon excitations.


a
300K
280K
260K
240K
220K
200K
dJ/J(10-3)
Pump-Push Delay (ps)
J (nA)
dJmax (pA)
dJmax/J (10-3)
J
dJmax
dJmax/J
Temperature(K)
mPCBM(1:1)
Ea = 112.01(21.59) meV
Log10(J) / A
Log10(dJmax/J)
1000/T(1/K)
b
300K
270K
240K
220K
mPCBM(1:2)
Ea = 108.21(0.33) meV
c
300K
260K
220K
200K
180K
Temperature (K)
bPCBM(1:1)
Ea =90.20(0.99) meV
d
300K
270K
255K
240K
220K
200K
bPCBM(1:2)
Ea = 143.06(18.08) meV
e
300K
270K
255K
240K
225K
190K
bPCBM(1:4)
Ea = 82.93(4.41) meV

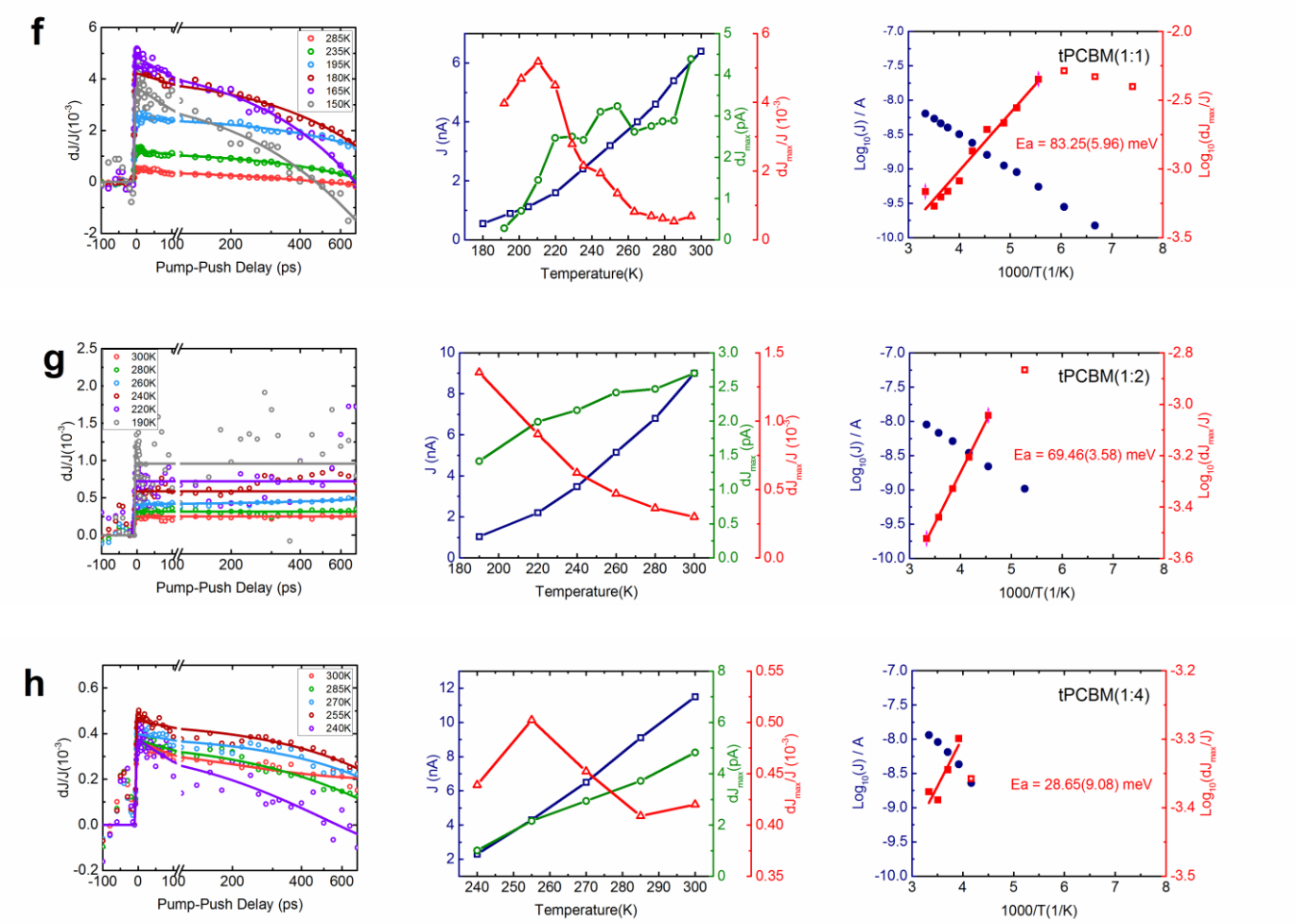


Figure S4 Full dataset of (i) the PPP dynamics in different devices, (ii) temperature dependence of *J*, dJ_{max} and dJ_{max}/J, and (iii) Arrhenius plots of *J* and dJ_{max}/J. (a) mPCBM with D-A ratio of 1:1 (b) mPCBM with D-A ratio of 1:2 (d) bPCBM with D-A ratio of 1:2 (e) bPCBM with D-A ratio of 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 ~ 1.01V, Jsc ~ 0.5 mA/cm^2, FF ~ 27% and PCE ~ 0.15%.