ADVANCED ENERGY MATERIALS

Supporting Information

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Using Ultralow Dosages of Electron Acceptor to Reveal the Early Stage Donor–Acceptor Electronic Interactions in Bulk Heterojunction Blends

*Carr Hoi Yi Ho, Sin Hang Cheung, Ho-Wa Li, Ka Lok Chiu, Yuanhang Cheng, Hang Yin, Mau Hing Chan, Franky So, Sai-Wing Tsang, and Shu Kong So**

Supporting Information

Title: Using Ultra-Low Dosages of Electron Acceptor to Reveal Electronic Interactions Between Donors and Acceptors

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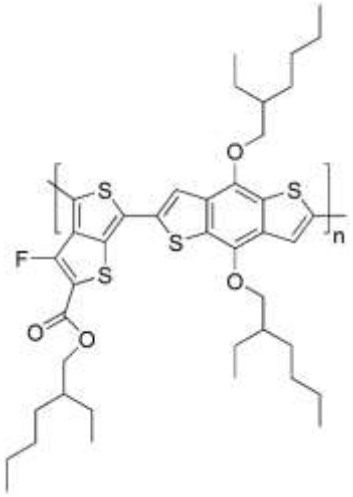
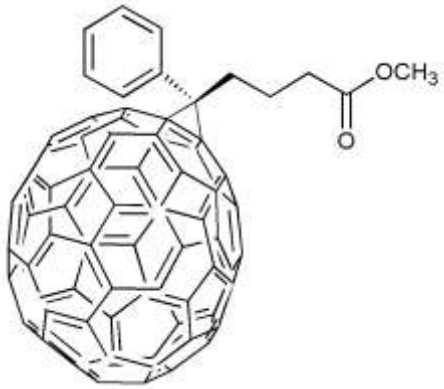
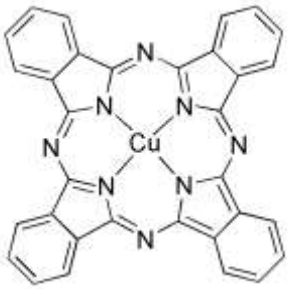


(a)

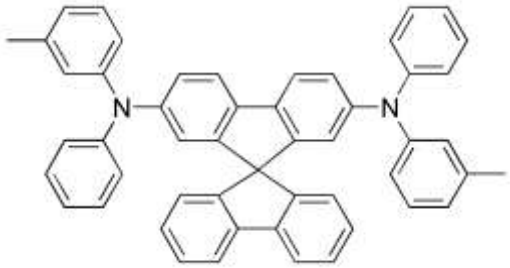


(b)

(c)



(d)



(e)

Figure S1. Chemical structures of (a) PTB7, (b) $PC_{71}BM$, (c) DIO (d) copper(II) phthalocyanine (CuPc), and (e) N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-9,9-spirobifluorene (Spiro-TPD).

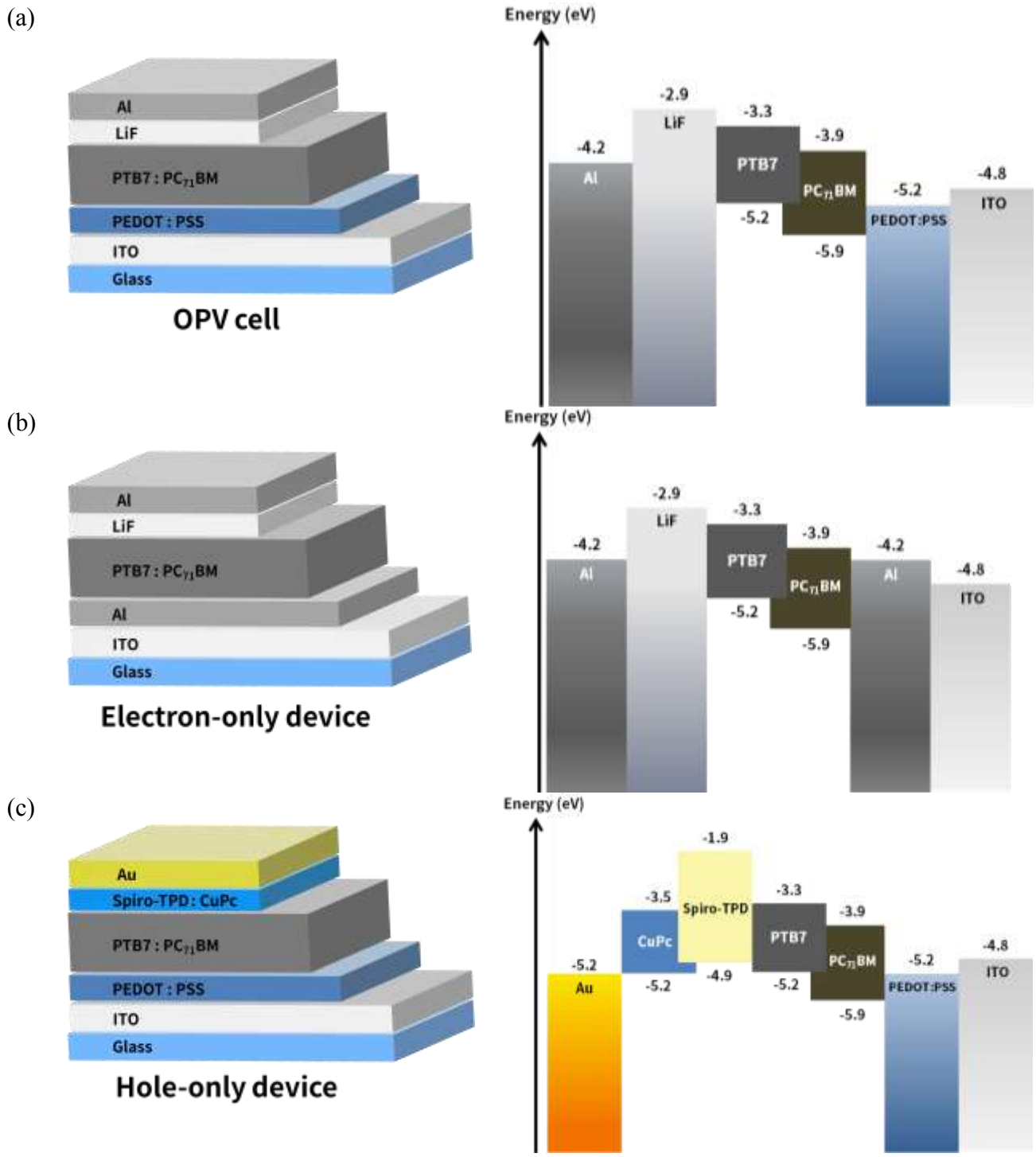


Figure S2. Device structures of BHJ of PTB7:$PC_{71}BM$. (a) OPV cell, (b) electron-only, and (c) hole-only device for carrier transport evaluation, and their schematic energy levels. In (b), the interlayer of spiro-TPD:CuPc act as an electron-blocking and trapping layer. In (c), a thin layer of CB is spin-coated on the bottom Al electrode for better wetting.

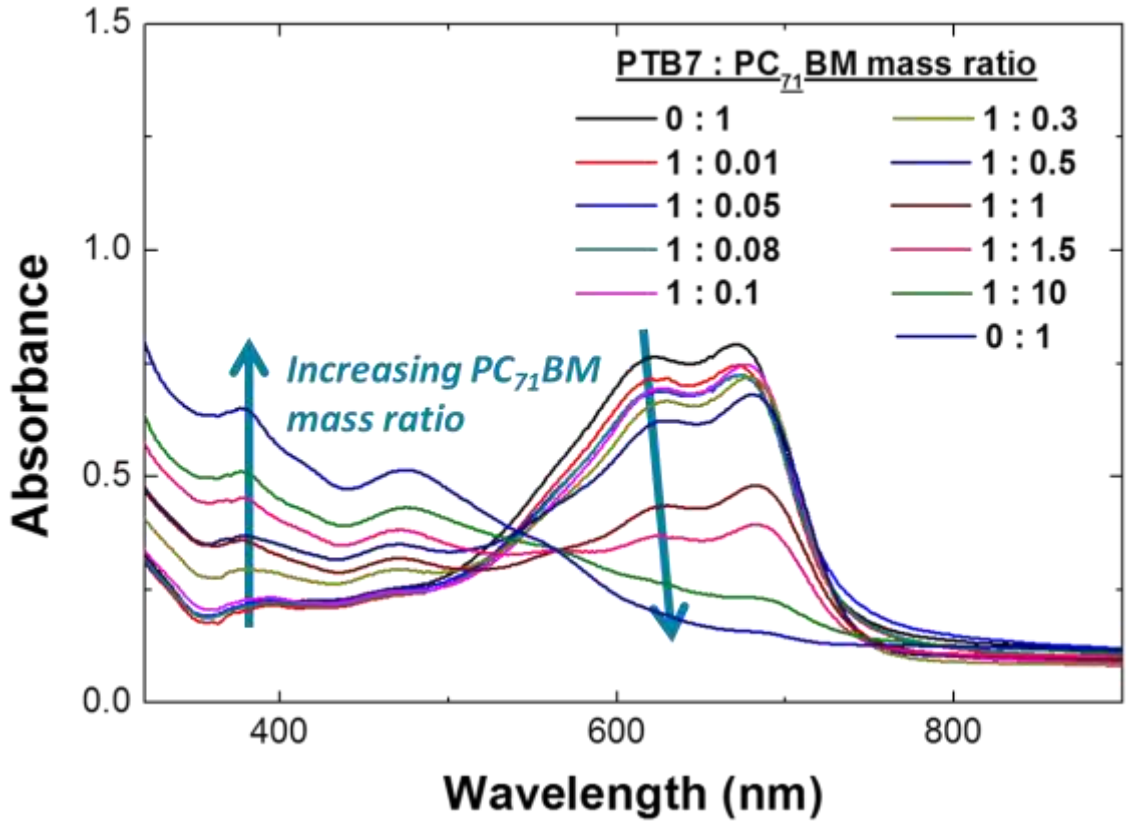
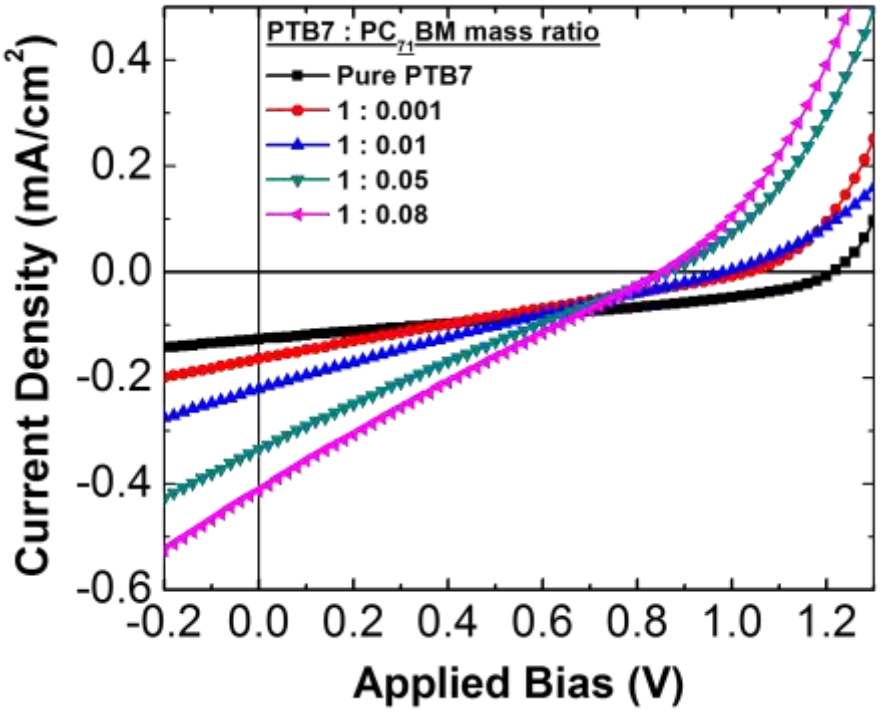
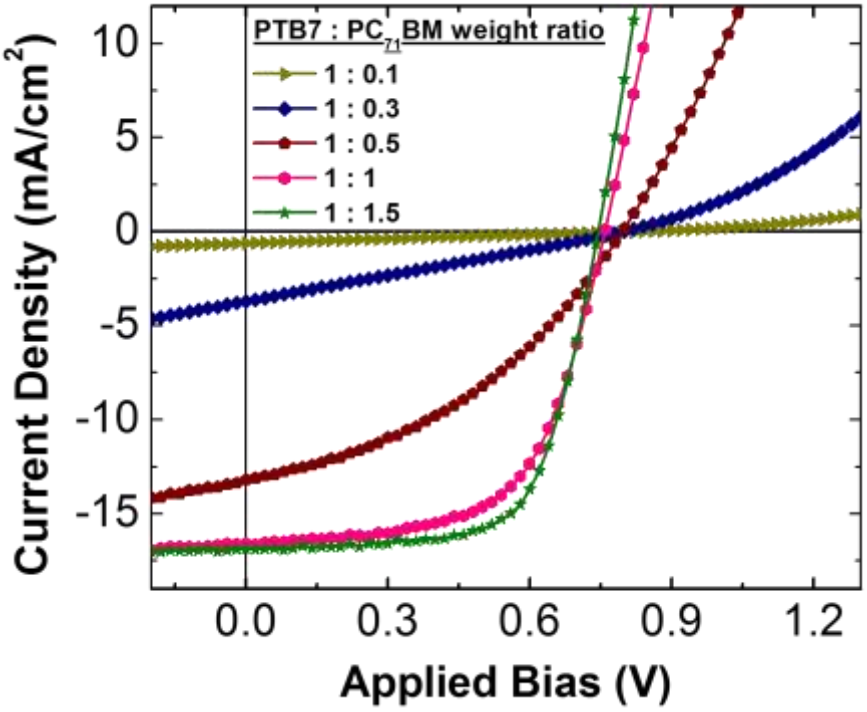


Figure S3. Ultraviolet-visible absorption spectra different D-A ratio, the film thickness were kept around 100nm


PTB7 : PC71BM mass ratio
Pure PTB7
1 : 0.001
1 : 0.01
1 : 0.05
1 : 0.08
Current Density (mA/cm2)
Applied Bias (V)
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2


PTB7 : PC71BM weight ratio
1 : 0.1
1 : 0.3
1 : 0.5
1 : 1
1 : 1.5
Current Density (mA/cm2)
Applied Bias (V)
10
5
0
-5
-10
-15
0.0
0.3
0.6
0.9
1.2

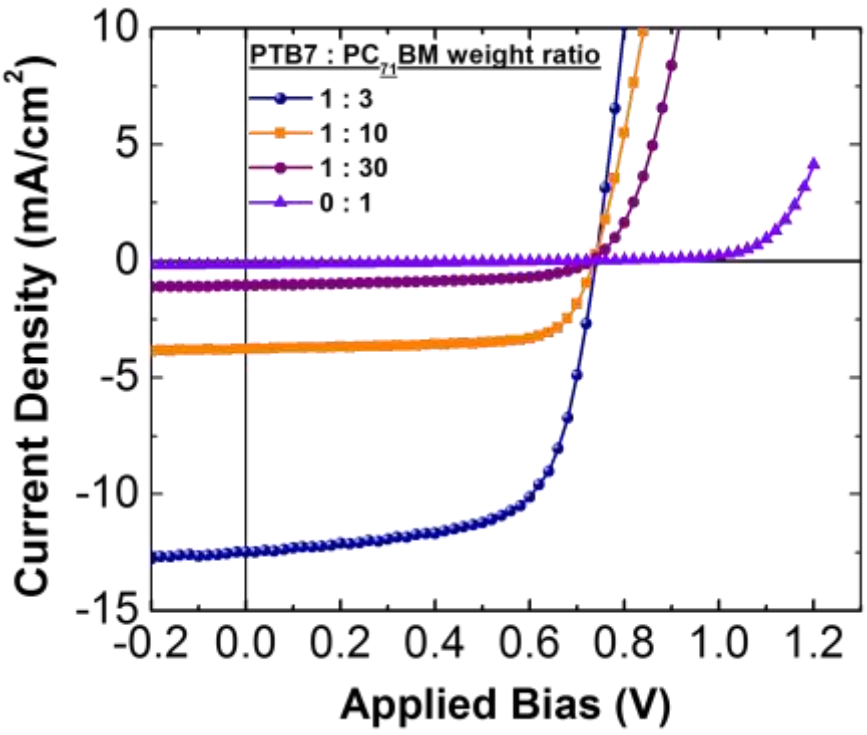


Figure S4. Current-voltage characteristics of OPV devices at different D-A ratios.

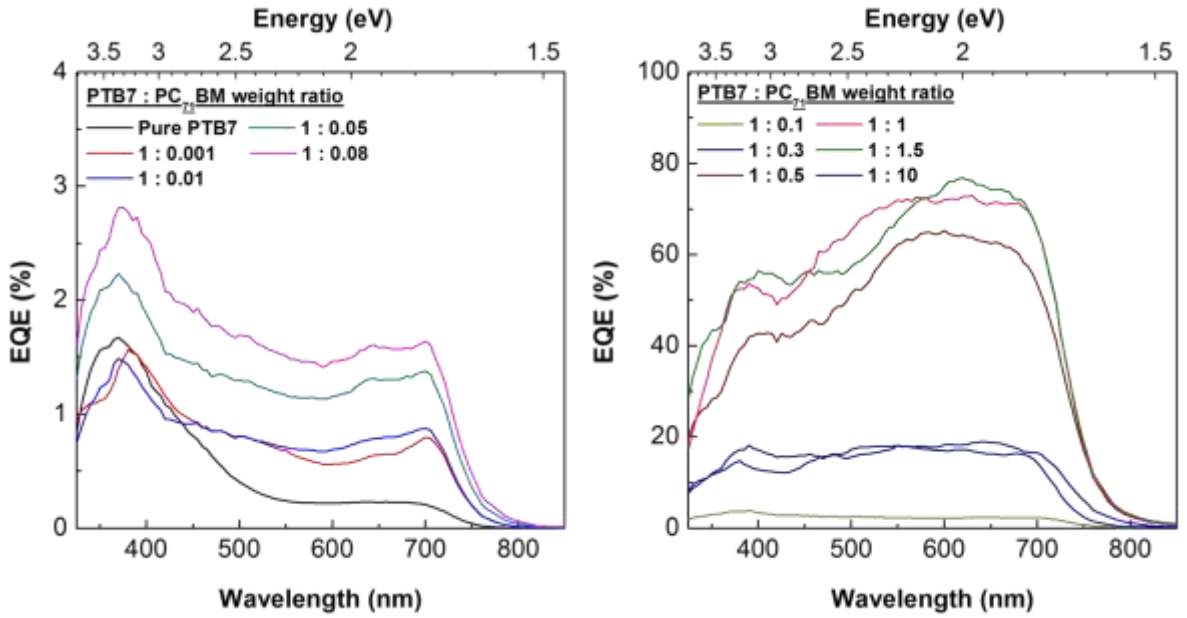


Figure S5. External quantum efficiency curves of OPV devices at different D-A weight ratios.

Donor-Acceptor weight ratio	Electron mobility ($cm^2V^{-1}s^{-1}$)	Energetic Disorder (meV)
1 : 0	9.0×10^{-9}	122
1 : 0.001	2.6×10^{-9}	100
1 : 0.1	1.1×10^{-10}	91
1 : 0.3	2.2×10^{-8}	87
1 : 0.5	4.0×10^{-6}	85
1 : 1	1.9×10^{-5}	88
1 : 1.5	2.2×10^{-4}	81
1 : 10	4.1×10^{-4}	63
0 : 1	9.7×10^{-4}	62

Table S1. Summary of electron mobility and its energetic disorder of PTB7:$PC_{71}BM$ BHJ films at different donor:acceptor weight ratio.

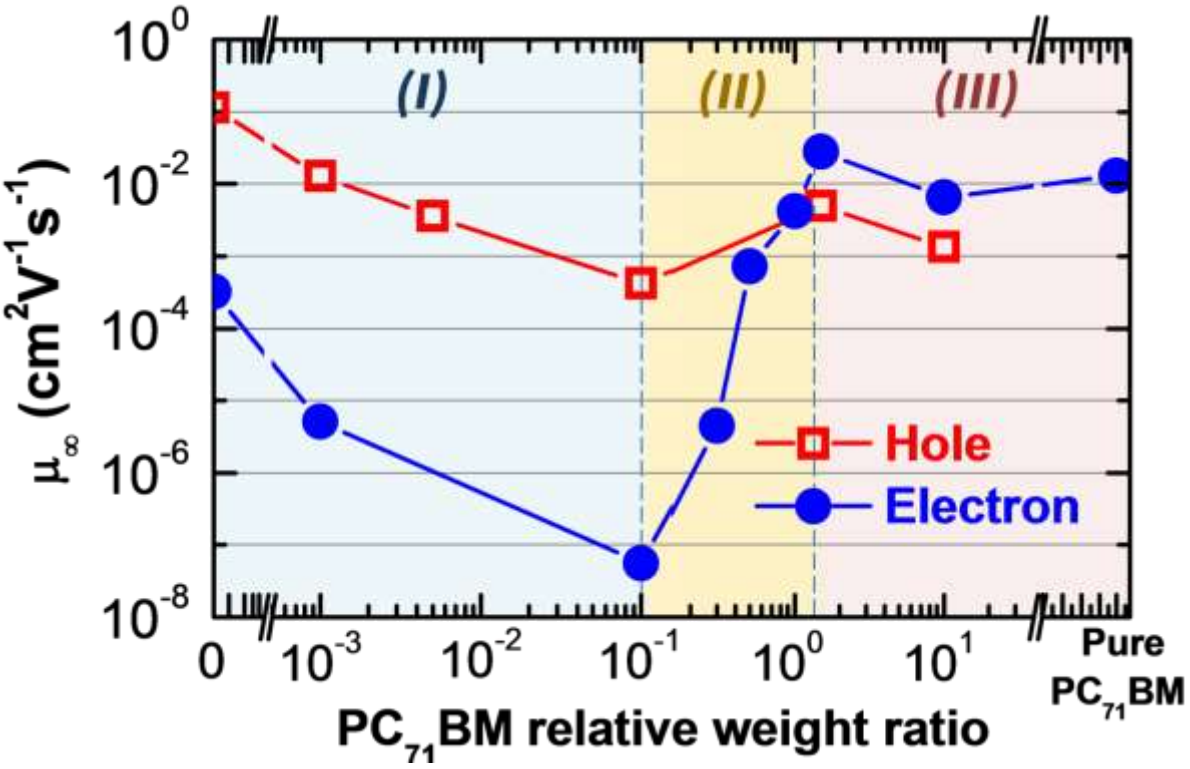


Figure S6. High temperature-limit mobilities of electron and hole at different D-A weight ratios

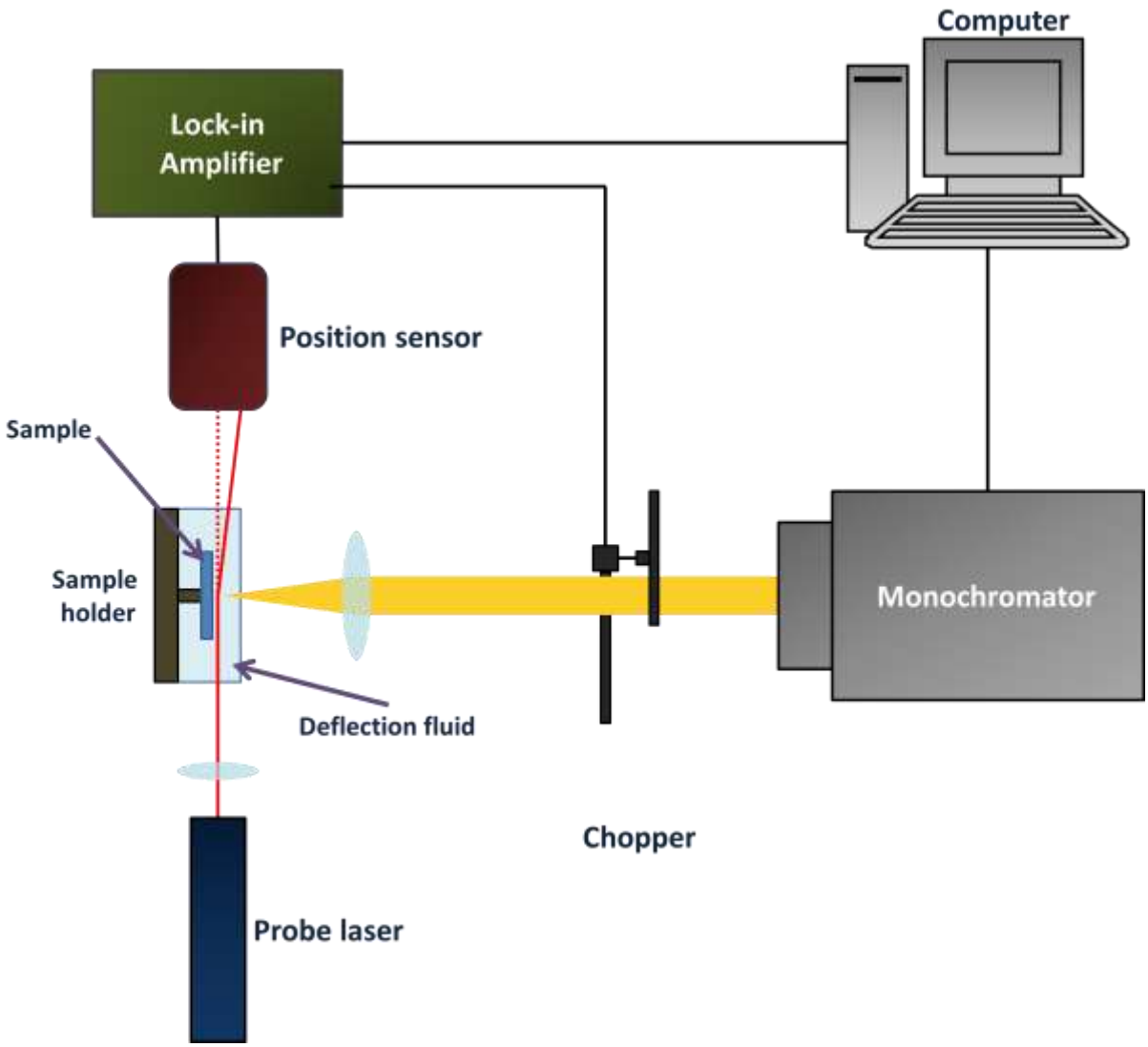


Figure S7. Experimental set-up of photothermal deflection spectroscopy. The sample under investigation was immersed in an inert, temperature sensitive deflection fluid. A mechanically chopped, wavelength tunable light source (pump beam) was shined on the surface of the sample periodically. Once there is heat released from nonradiative relaxation of photo-excited carriers at certain wavelength, the temperature rise results a periodic change in the refractive index of the fluid. A probe laser beam directed parallel to the surface of sample is used to monitor the change of refractive index, and bent proportional to the temperature gradient of the fluid near the sample surface.

Appendix: Trap density to fullerene cluster size

Molecular Density of $PC_{71}BM = 1.44 \times 10^{21}$ $cm^{-3} \approx 1 \times 10^{21}$ cm^{-3}
PTB7 molar mass = 757.11 g/mol

Mass Density of PTB7 = 1.33 g cm^{-3} (The value is from P3HT)
Molecular Density of PTB7 = 1.06×10^{21} $cm^{-3} \approx 1 \times 10^{21}$ cm^{-3}

Trap Density of pure PTB7 = 1.05×10^{18} cm^{-3}
Trap Density at 1 : 0.3 = 2.12×10^{18} cm^{-3}

Assuming

- [Trap Density at 1 : 0.3] = [Trap Density of pure PTB7] + [Trap Density from $PC_{71}BM$ clusters]
  [Trap Density from $PC_{71}BM$ clusters] = 1.07×10^{18} cm^{-3}
- Molecular density of $PC_{71}BM$ in 1 : 0.3 BHJ film $\approx (1 \times 10^{21}$ $cm^{-3}) \times 0.3 = 3 \times 10^{20}$ cm^{-3}
- Say all $PC_{71}BM$ clusters contribute to traps,
  [Number of $PC_{71}BM$ in each cluster]
  = [Molecular density of $PC_{71}BM$] / [Trap Density from $PC_{71}BM$ clusters]
  = $(3 \times 10^{20})/(1.07 \times 10^{18})$
  = 280 ($PC_{71}BM$ per cluster)
- One cluster volume = 5.04×10^{-23} m^3
- Diameter of one cluster ≈ **50 nm**

The order of diameter is in par with that reported by Ade et al.

Reference:
[1] https://www.sesres.com/physicalproperties.asp
[2] B. A. Collins, Z. Li, J. R. Tumbleston, E. Gann, C. R. McNeill, H. Ade, *Adv. Energy Mater.* **2013**, *3*, 65.