Electronic Supplementary Information:

Insights into Photoinduced Carrier Dynamics and Hydrogen Evolution Reaction of Organic PM6/PCBM Heterojunctions

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Contents

Excitonic Effects in the PCBM@PM6 Heterojunction.....S2

Supplementary Figures.....S3

Supplementary Tables.....S6

References S7

Excitonic Effects in the PCBM@PM6 Heterojunction

Excitonic effects are generally important in organic materials. However, high-level electronic structure methods such as LR-TDDFT and GW/BSE that take the excitonic effects into consideration are very expensive for NAMD simulations.[1-3] Previous explorations have also proved that some dynamical processes are less influenced by excitonic effects and DFT-based NAMD simulations still can provide reliable description.[4-8]

To assess excitonic effects for our studied system, the energy gaps of CBM-VBM or LUMO-HOMO obtained by DFT calculations and the excitation energies from the S_0 to S_1 states by LR-TDDFT calculations are compared. The results of 10 structures randomly extracted from the NVE trajectory are listed in Table S1. In Fig. S2, the dashed lines are linearly fitted from these data. Note that the transitions between (a) CBM-VBM and (b) HOMO-LUMO make major contribution to the $S_0 \rightarrow S_1$ excitation in PM6 and PCBM, respectively. It is clear that the energy difference between LR-TDDFT and DFT calculations for PM6 and PCBM are less than 0.06 eV and 0.2 eV, respectively. The energy gaps from DFT calculations also exhibit the linear dependence, suggesting DFT-based NAMD method can be regarded as a practical theoretical method to obtain valuable insights into photoinduced carrier dynamics in PCBM@PM6 heterojunctions.

Supplementary Figures

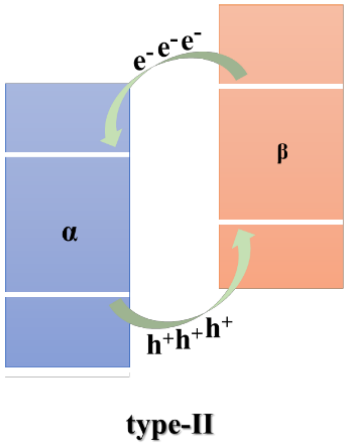

Fig. S1 Schematic diagram of type-II heterojunction widely used in the discipline of condensed matter.

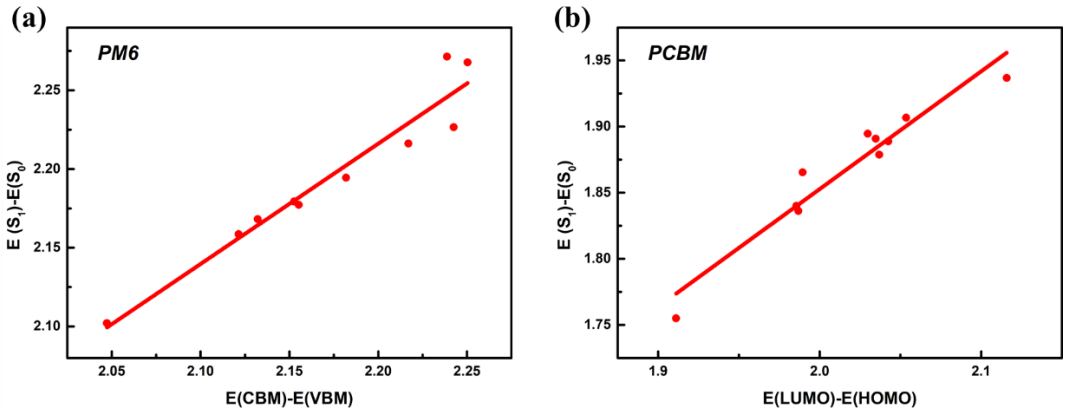

Fig. S2 The comparison between excitation energies from the S_0 to S_1 states by LR-TDDFT calculations and energy gaps of CBM-VBM in PM6 (a) or LUMO-HOMO in PCBM (b) obtained by DFT calculations.

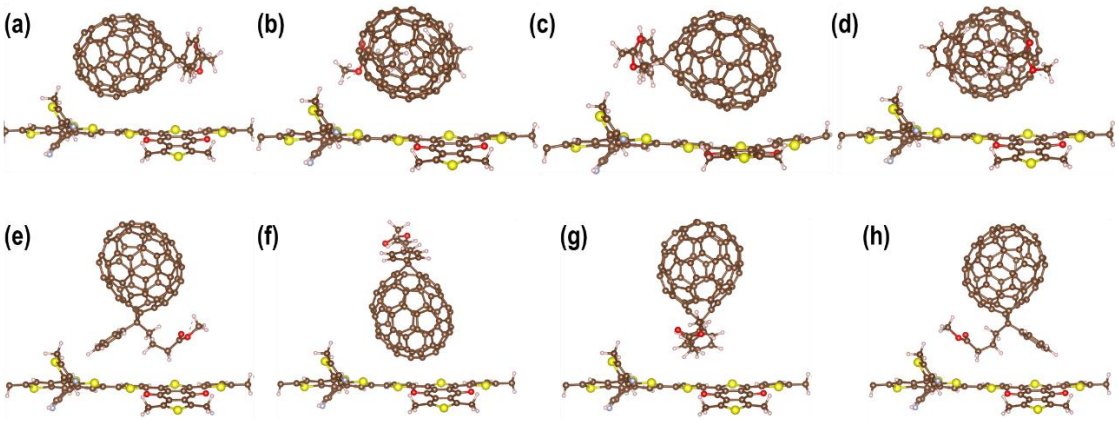

Fig. S3 The PBE+D3 optimized PM6/PCBM structures with different stacking patterns. In (a)-(d), the nanocomposite is constructed with a "lying" PCBM on the PM6 surface; in (e)-(h), the nanocomposite is constructed with a "standing" PCBM on the PM6 surface.

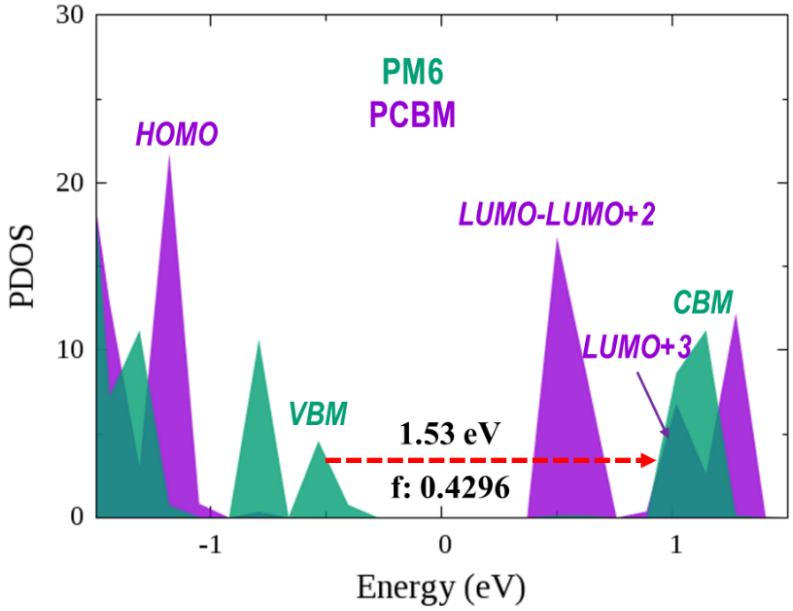

Fig. S4 The PDOS of PCBM@PM6 calculated at the PBE+D3 level.

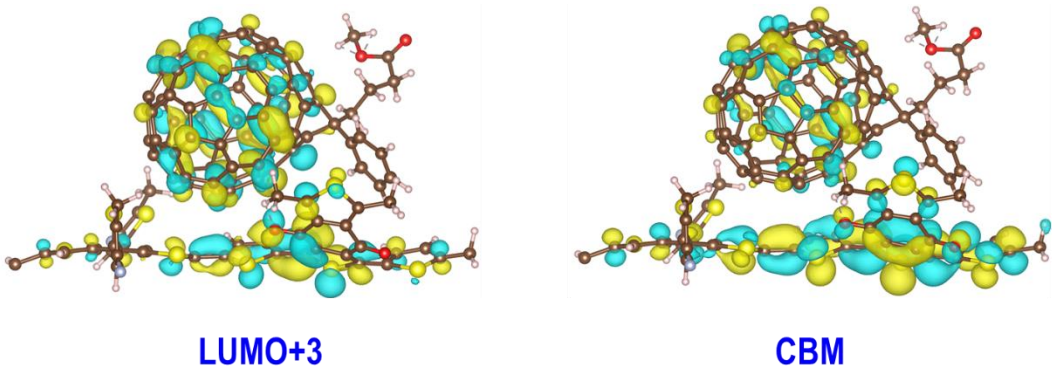

Fig. S5 HSE06+D3 calculated spatial distributions of LUMO+3 and CBM states in the molecular dynamics.

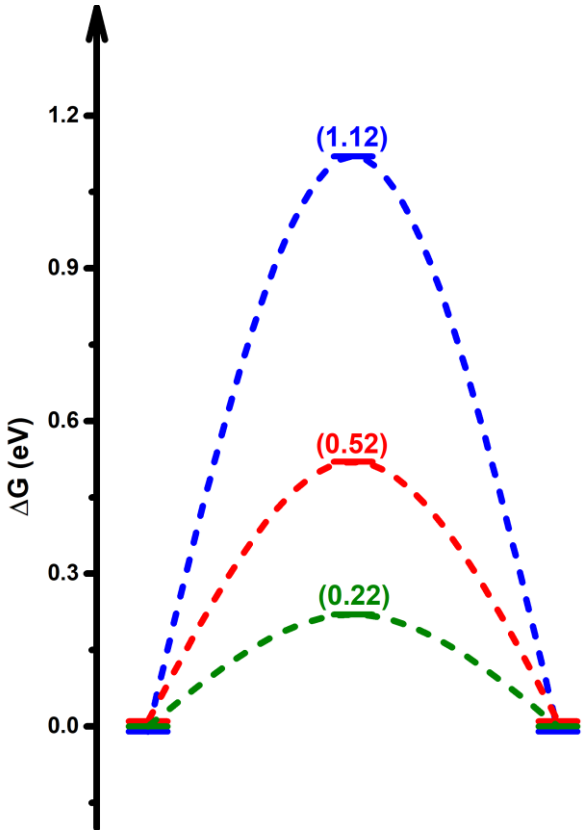

Fig. S6 Gibbs free energy profiles for hydrogen evolution at C666 site (blue), C665 site (red), and C666 site with adjacent C665 site pre-hydrogenated (green) calculated at thePBE+D3 level.

Supplementary Tables

Table S1 The energy gaps of CBM-VBM in PM6 or LUMO-HOMO in PCBM obtained by DFT calculations and excitation energies from the S_0 to S_1 states by LR-TDDFT calculations.

	PM6		PCBM	
	E(CBM)-E(VBM)	$E(S_1)-E(S_0)$	E(HOMO)-E(LUMO)	$E(S_1)-E(S_0)$
point1	2.25032	2.26777	1.98686	1.83627
point2	2.2387	2.27141	2.11581	1.93681
point3	2.12142	2.15855	1.9895	1.86543
point4	2.04731	2.10207	1.91115	1.75499
point5	2.1527	2.17948	2.05363	1.90675
point6	2.21697	2.2162	1.98554	1.83998
point7	2.15526	2.17733	2.03694	1.8788
point8	2.24252	2.22663	2.02982	1.89468
point9	2.18195	2.1945	2.03471	1.89085
point10	2.13223	2.16819	2.0426	1.88881

Table S2 The PBE+D3 calculated adsorption energies (eV) of PM6/PCBM with different stacking patterns in Fig. S3.

structure	E_{ads}
a	0.55
b	0.61
c	0.55
d	0.49
e	0.42
f	0.41
g	0.38
h	0.39

Table S3 The HSE06+D3 calculated excitation energies (eV) and oscillation strength of different transitions in PM6/PCBM.

transition	energy	oscillation strength
VBM->LUMO	1.56	0.00249
VBM->LUMO+1	1.60	0.00278
VBM->LUMO+2	1.65	0.00460
VBM->LUMO+3	2.12	0.00060
VBM->CBM	2.16	0.51053

References

1. X. Jiang, Q. Zheng, Z. Lan, W. A. Saidi, X. Ren and J. Zhao, *Sci. Adv*, 2021, **7**, eabf3759.
2. X. Zhang, G. Lu, R. Baer, E. Rabani and D. Neuhauser, *J. Chem. Theory Comput.*, 2020, **16**, 1064-1072.
3. J. Liu, Z. Li, X. Zhang and G. Lu, *npj Computational Materials*, 2021, **7**.
4. R. Long and O. V. Prezhdo, *Nano Lett.*, 2014, **14**, 3335-3341.
5. R. Sarkar, M. Habib, S. Pal and O. V. Prezhdo, *Nanoscale*, 2018, **10**, 12683-12694.
6. J.-J. Yang, Z.-W. Li, X.-Y. Liu, W.-H. Fang and G. L. Cui, *Phys. Chem. Chem. Phys.*, 2020, **22**, 19542-19548.
7. X.-Y. Xie, J.-J. Yang, X.-Y. Liu, Q. Fang, W.-H. Fang and G. L. Cui, *Phys. Chem. Chem. Phys.*, 2021, **23**, 13503-13511.
8. Y. Lei, Z. Zheng, L. Vasquez, J. Zhao, J. Ma and H. Ma, *J. Phys. Chem. Lett.*, 2022, **13**, 4840-4848.