Electronic Supplementary Information

Strong dependence of the vertical charge carrier mobility on the π-π stacking distance in molecule/graphene heterojunctions

Wei Hao, [a] *Yishan Wang,* [b] *Hu Zhao,* [c] *Jia Zhu** [b] *and Shuzhou Li** [a]

[a]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[b]College of Chemistry, Key Laboratory of Theoretical & Computational Photochemistry of Ministry of Education, Beijing Normal University, Beijing 100875, P. R. China

[c]Department of Physics, Beijing Normal University, Beijing 100875, P. R. China

*Corresponding author's e-mail: lisz@ntu.edu.sg (S.L.); zhu.jia@bnu.edu.cn (J.Z.)

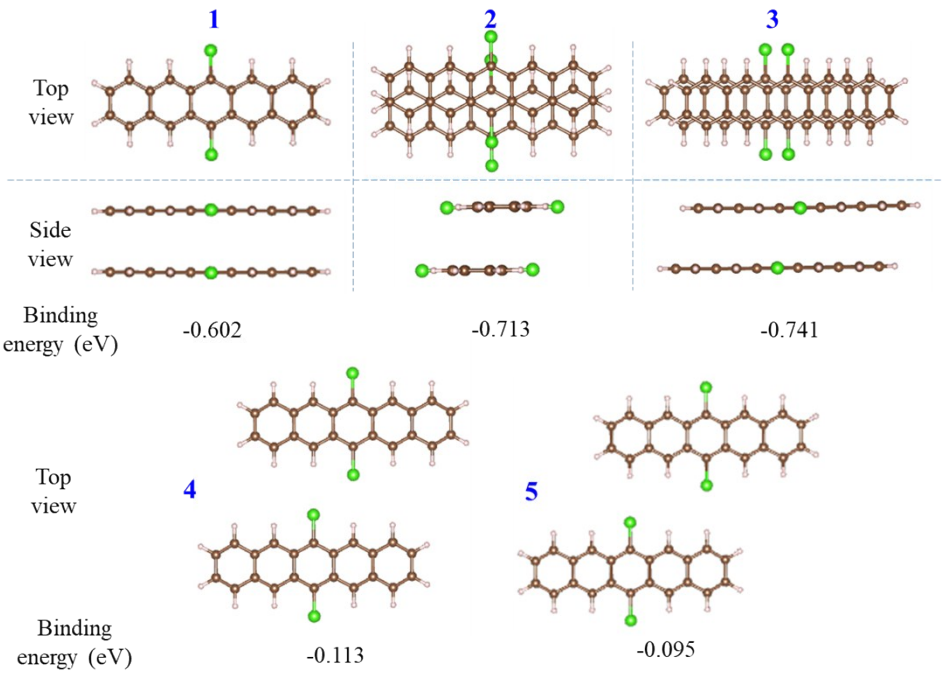


Fig.S1. The side view (a) and top view (b) of DCP dimers in different configurations.

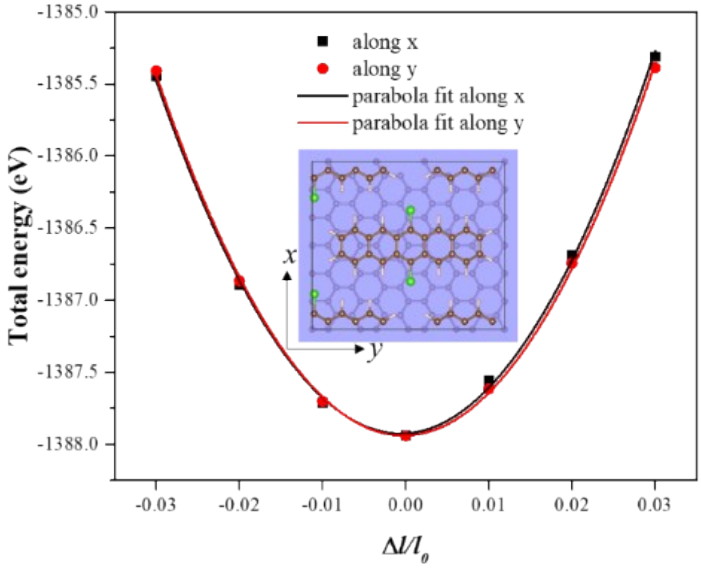


Fig.S2. The total energy changes with dilation ($\Delta l/l_0$) along *x* and *y* direction in DCP1L/G heterojunction.

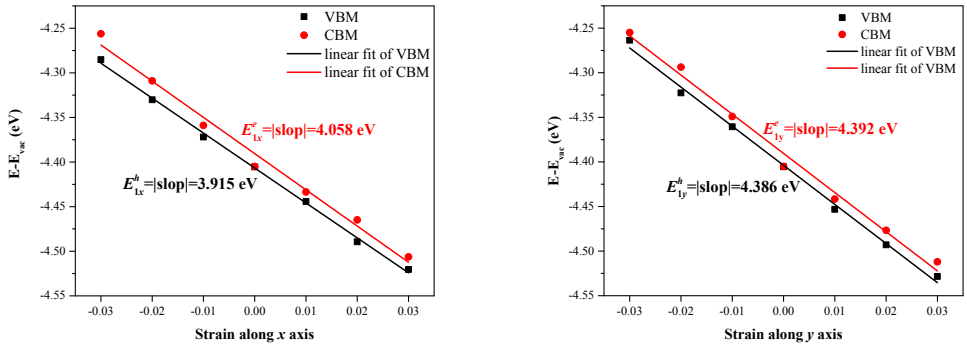


Fig.S3. The linear fitting of CBM and VBM changes with the strain along *x* and *y* direction in DCP1L/G heterojunction.

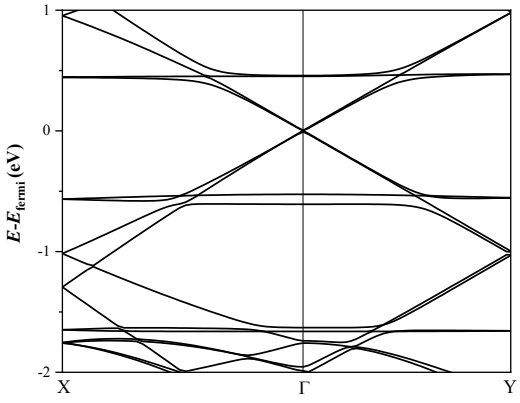


Fig.S4. Then bandstructure of the DCP1L/G heterojunction.

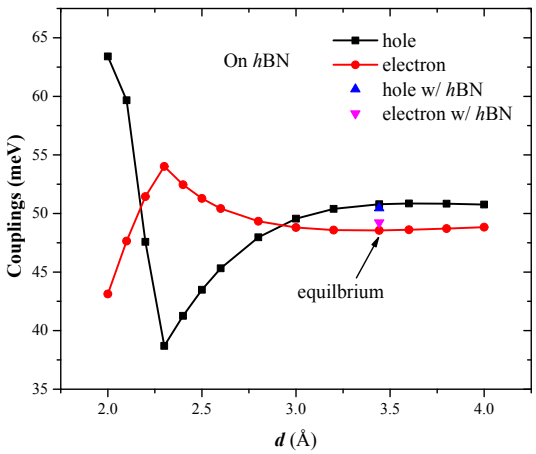


Fig.S5. The dependence of electronic couplings between DCP 1 and 2 in DCP2L/*h*BN heterojunction on the distances between DCP 1 and graphene.

Table S1. The calculated distances (d_0) and binding energies (ΔE_{b0}) between DCP molecule and graphene for different configurations. These sites include the top sites with all or half of the molecular carbon atoms atop of graphene carbon atoms (a and c), the hollow site with all the molecular carbon atoms at hollow sites of graphene rings (b) and the bridges site with half of the molecular carbon atoms atop of the middle site of C-C bonds in graphene (d). Besides, we have also considered the configuration when the molecule is along the armchair direction of graphene (e).

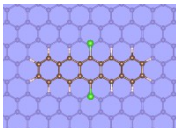
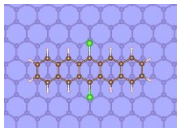
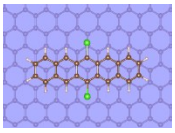
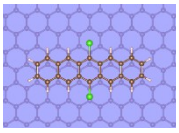
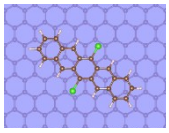
	 (a)	 (b)	 (c)	 (d)	 (e)
d_0 (Å)	3.519	3.483	3.480	3.487	3.518
ΔE_{b0} (eV)	-1.417	-1.476	-1.490	-1.475	-1.450

Table S2. The calculated binding energies (eV/molecule), length of C-H···Cl bond (Å) and inter-distances (Å) between DCP layer and graphene in DCP1L/G composites with different graphene size.

unit cell size	(5×4)	(6×4)	(7×4)
ΔE_{b1} (eV/molecule)	-1.687	-2.016	-1.930
Configuration	unparalleled	paralleled	paralleled
Length of CH···Cl (Å)	2.740	3.319	4.433
d (Å)	--	3.493	3.495

Table S3. The calculated binding energies (eV/molecule) and inter-distances (Å) between PTCDA molecule (layers) and graphene in PTCDA/graphene heterojunctions.

Single PTCDA on G		**PTCDA1L/G**		**PTCDA2L/G**		
ΔE_{b0}	d_0	ΔE_{b1}	d	ΔE_{b2}	d_1	d_2
-1.955	**3.418**	**-2.406**	**3.442**	**-2.062**	**3.423**	**3.448**

Table S4. The calculated binding energies (eV/molecule) and inter-distances (Å) between DCP molecule (layers) and *h*BN in DCP/*h*BN composites.

Single DCP on *h*BN		**DCP1L/*h*BcN**		**DCP2L/*h*BN**		
ΔE_{b0}	d_0	ΔE_{b1}	d	ΔE_{b2}	d_1	d_2
-1.530	**3.515**	**-1.599**	**3.509**	**-1.228**	**3.507**	**3.565**