Electronic supplementary information of:

Photon-absorbing charge-bridging states in organic bulk heterojunctions consisting of diketopyrrolopyrrole derivatives and PCBM

Mikiya Fujii,[a,b] Woong Shin,[c] Takuma Yasuda,[c,d] and Koichi Yamashita[a,b,*]

[a]Department of Chemical System Engineering, School of Engineering, the University of Tokyo, Tokyo, 113-8656, Japan.

[b]CREST, JST, 113-8656 Japan.

[c]INAMORI Frontier Research Center, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

[d]PRESTO, JST, 819-0395, Japan.

*E-mail: yamasita@chemsys.t.u-tokyo.ac.jp

Table of contents

S1: PM3 analyses of excited states of PCBM/D1 – PCBM/D5

Table S1-1: PM3/CIS coefficients, C, of the corresponding slater determinants which are first three main configurations of photo absorbing excited states of supermolecules of each DPP derivative and PCBM. The indices of occupied and virtual molecular orbitals are shown in the parenthesis.

	State index (wavelength /nm)	1st configuration C (occ -> vir)	2nd configuration C (occ -> vir)	3rd configuration C (occ -> vir)
PCBM/D1	1st (572)	0.858 (265 -> 270)	-0.293 (264 -> 273)	-0.200 (265 -> 275)
PCBM/D2	1st (550)	0.905 (245 -> 251)	0.219 (243 -> 254)	-0.156 (245 -> 262)
PCBM/D3	3rd (494)	0.733 (245 -> 252)	-0.368 (243 -> 246)	0.243 (239 -> 247)
PCBM/D4	2nd (500)	-0.798(273 -> 280)	0.232 (272 -> 282)	0.228 (269 -> 274)
PCBM/D5	3rd (492)	-0.836(263 -> 270)	-0.206 (260 -> 264)	0.203(263 -> 278)

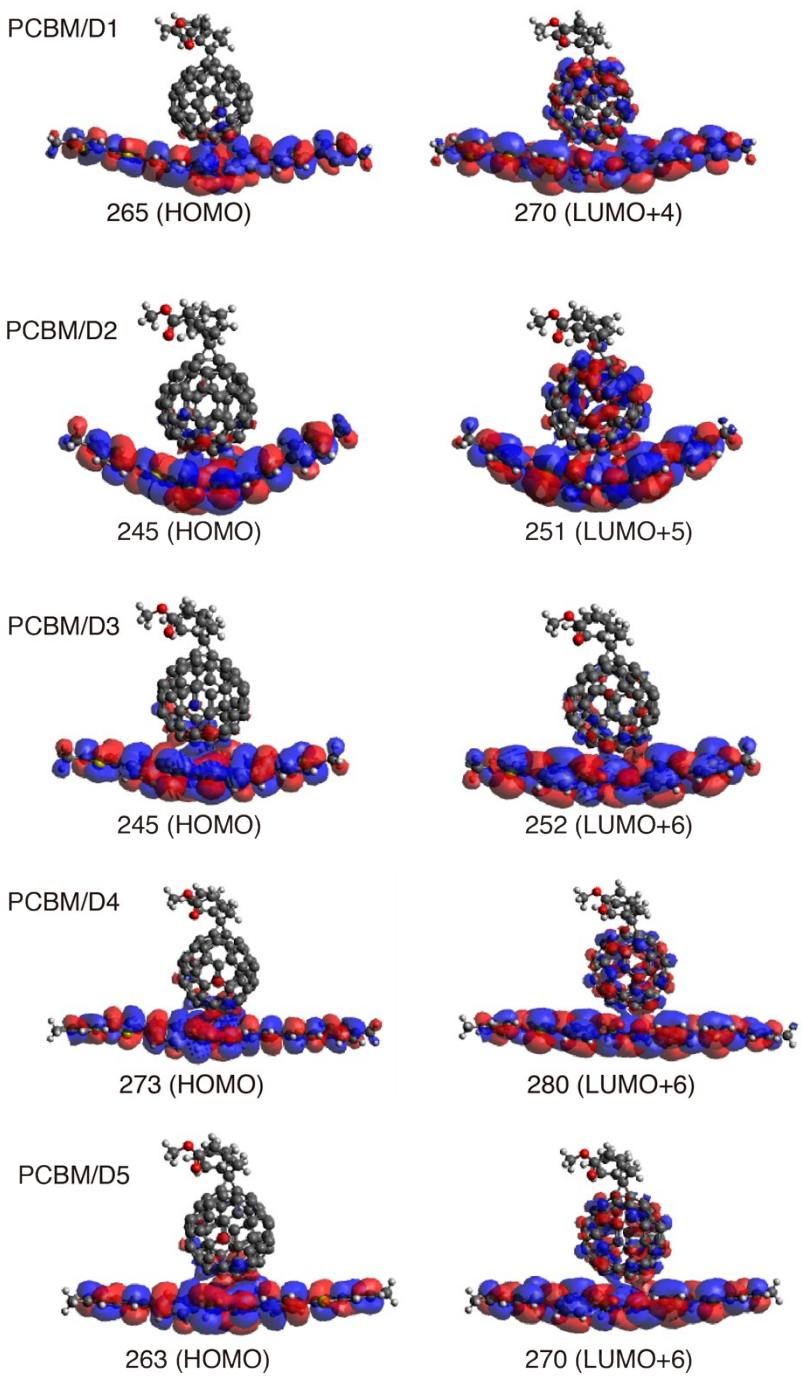

Figure S1-1: Molecular orbitals of PM3, which mainly contribute to the photo absorbing excited states of supermolecules of each DPP derivative and PCBM. (iso value = -0.002)

S2: DFT analyses of ionization potential of D2 and electron affinity of PCBM with CAM-B3LYP/6-31+G*

We calculated energies of charge transfer states of D2/PCBM as the differences between ionization potential (I_P) of D2 and electron affinity (E_A) of PCBM, where these ionization potential and electron affinity were calculated by the delta SCF method. Then, by comparing the energy of the charge transfer state by DFT/CAM-B3LYP/6-31+G* with one by DFT/CAM-B3LYP/6-31G*, we estimated numerical correction to the TDDFT/CAM-B3LYP/6-31G* results by adopting larger basis function, 6-31+G*, because TDDFT/CAM-B3LYP/6-31+G* calculations demand extremely large computer resources. Even in DFT/CAM-B3LYP/6-31+G* calculations, it was not accomplished to satisfy the convergence criterion of SCF for systems consisting of more than 100 atoms like D2/PCBM. The results are summarized in Table S2-1 and then we estimated the numerical correction as 0.19 eV even for the charge transfer state.

Table S2-1: Ionization potential (I_P) of D2, electron affinity (E_A) of PCBM, and difference of them. Both DFT/CAM-B3LYP/6-31G* and DFT/CAM-B3LYP/6-31+G* are adopted to calculated I_P and E_A

	I_P of D2 /eV	E_A of PCBM /eV	I_P - E_A /eV
DFT/CAM-B3LYP/6-31G*	6.07	1.67	4.40
DFT/CAM-B3LYP/6-31+G*	6.32	2.11	4.21

S3: TDDFT analyses of excited states of PCBM/D1 – PCBM/D5 with CAM-B3LYP/6-31G*

Table S3-1: TDDFT coefficients, C, of the corresponding slater determinants which are first three main configurations of photo absorbing excited states of supermolecules of each DPP derivative and PCBM. The indices of occupied and virtual molecular orbitals are shown in the parenthesis.

	State index (wavelength /nm)	1st configuration C (occ -> vir)	2nd configuration C (occ -> vir)	3rd configuration C (occ -> vir)
PCBM/D1	1st (526)	-0.81 (408 -> 411)	0.31 (408 -> 409)	0.25 (408 -> 412)
PCBM/D2	5th (480)	0.60 (364 -> 367)	0.45 (362 -> 365)	0.40 (364 -> 368) -0.39 (364 -> 365)
PCBM/D3	10th (442)	-0.84(364 -> 368)	0.23 (361 -> 366)	0.22 (360 -> 365)
PCBM/D4	10th (441)	0.69 (404 -> 408)	-0.32 (400 -> 406)	-0.30 (404 -> 407)
PCBM/D5	11th (432)	-0.63 (390 -> 394)	0.55 (390 -> 391)	-0.23 (387 -> 392)

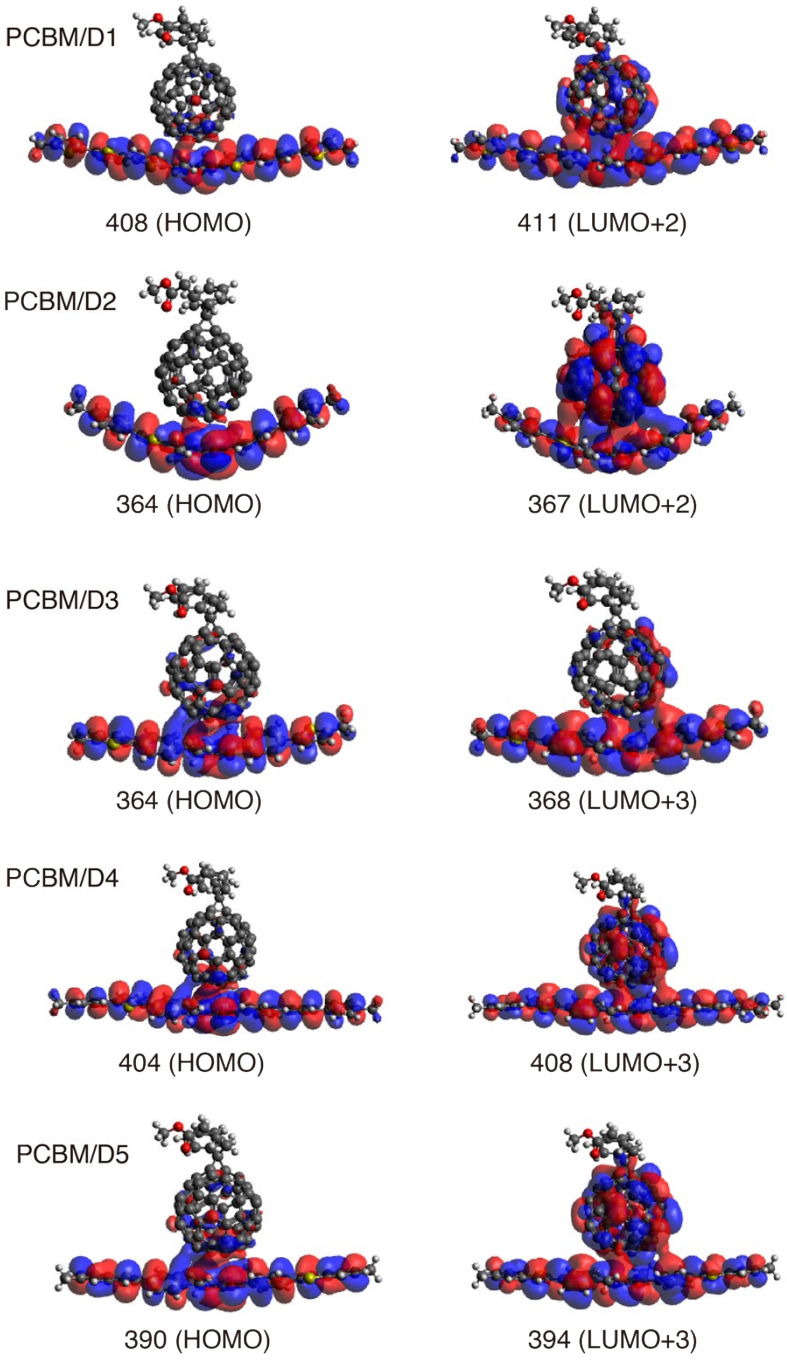

Figure S3-1: Molecular (Kohn-Sham) orbitals of DFT/Cam-B3LYP/6-31G*, which mainly contribute to the photo absorbing excited states of supermolecules of each DPP derivative and PCBM. (iso value = -0.005)