Electronic Supplementary Information

A Designed Bithiopheneimide-Based Conjugated Polymer for Organic Photovoltaic with Ultrafast Charge Transfer at Donor/$PC_{71}BM$ Interface: Theoretical Study and Characterization

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Table S1. The first singlet excitation energies E and the corresponding (maximum) absorption wavelength E_λ of **1** (n=2) calculated by different functionals PBE0 and CAM-B3LYP with the 6-31G(d) basis set compared with the experimental value.

	PBE0	CAM-B3LYP	Exp.
E/eV	2.03	2.40	1.75
E_λ/nm	610	517	603

Table S2. The HOMO energy (eV) of **1** (n=1) calculated by different functionals B3LYP, PBE0, and BHandHLYP with the 6-31G(d) basis set compared with its experimental value.

	B3LYP	PBE0	BHandHLYP	Exp.
HOMO	-5.21	-5.47	-6.15	-5.43

Table S3. Calculated the excitation energies (E) and oscillator strengths (f) for **1/PC$_{71}$BM** and **4/PC$_{71}$BM** (n=1) heterojunctions at TD-CAM-B3LYP/6-31G(d) level.

	1/PC$_{71}$BM		**4/PC$_{71}$BM**	
	E/eV (nm)	f	E/eV (nm)	f
S_1	2.26 (550)	0.0083	2.26 (549)	0.0079
S_2	2.43 (511)	0.0410	2.35 (527)	0.2969
S_3	2.59 (479)	0.0496	2.43 (511)	0.0511
S_4	2.65 (468)	0.0345	2.59 (479)	0.0489
S_5	2.70 (460)	0.0795	2.65 (468)	0.0358
S_6	2.70 (458)	0.0363	2.70 (460)	0.0790
S_7	2.71 (457)	0.0220	2.71 (458)	0.0824
S_8	2.79 (444)	0.0024	2.71 (457)	0.0196
S_9	2.80 (444)	0.0014	2.79 (444)	0.0015
S_{10}	2.82 (440)	1.0833	2.80 (443)	0.0031
S_{11}	2.84 (436)	0.0026	2.85 (435)	0.0003
S_{12}	2.97 (417)	0.0022	2.97 (417)	0.0016
S_{13}	2.98 (415)	0.0014	2.99 (414)	0.0048
S_{14}	3.00 (413)	0.0067	3.01 (412)	0.0085
S_{15}	3.03 (409)	0.0092	3.03 (410)	0.7813
S_{16}	3.05 (407)	0.0058	3.05 (404)	0.0102
S_{17}	3.08 (403)	0.0002	3.08 (403)	0.0005
S_{18}	3.09 (401)	0.0015	3.09 (401)	0.0014
S_{19}	3.12 (397)	0.0040	3.12 (397)	0.0034
S_{20}	3.15 (394)	0.0057	3.14 (395)	0.0023

Table S4. Calculated V_{DA} (eV) of inter-CT excited states for **1/PC$_{71}$BM** and **4/PC$_{71}$BM** (n=1).

	$S_{1\leftarrow0}$	$S_{2\leftarrow0}$	$S_{3\leftarrow0}$	$S_{4\leftarrow0}$	$S_{13\leftarrow0}$	$S_{14\leftarrow0}$	$S_{15\leftarrow0}$	$S_{16\leftarrow0}$	$S_{19\leftarrow0}$	$S_{20\leftarrow0}$
1/PC$_{71}$BM					0.019	1.074	0.595	0.820	1.475	1.439
4/PC$_{71}$BM	0.679		0.998	0.515					0.550	0.130

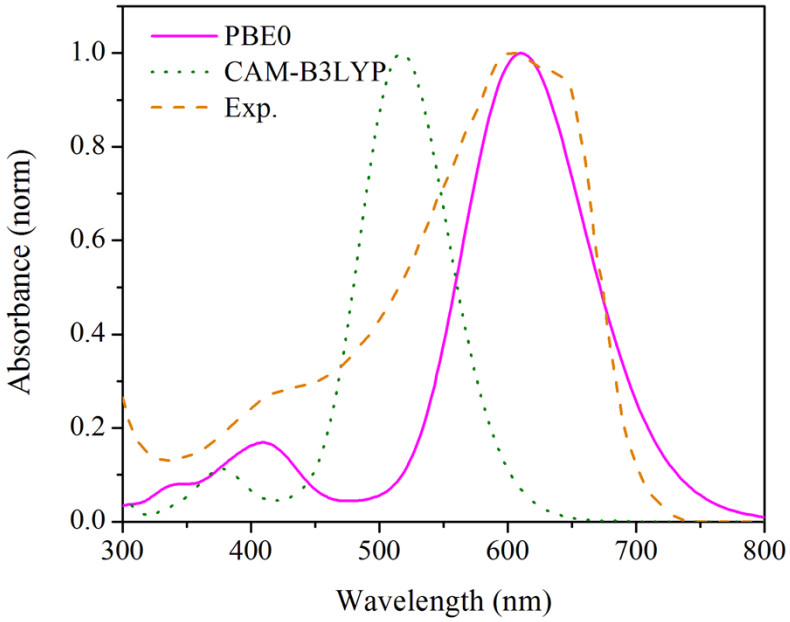

Figure S1. The absorption spectra for **1** (n=2) calculated by two different functionals with its experimental absorption spectrum.

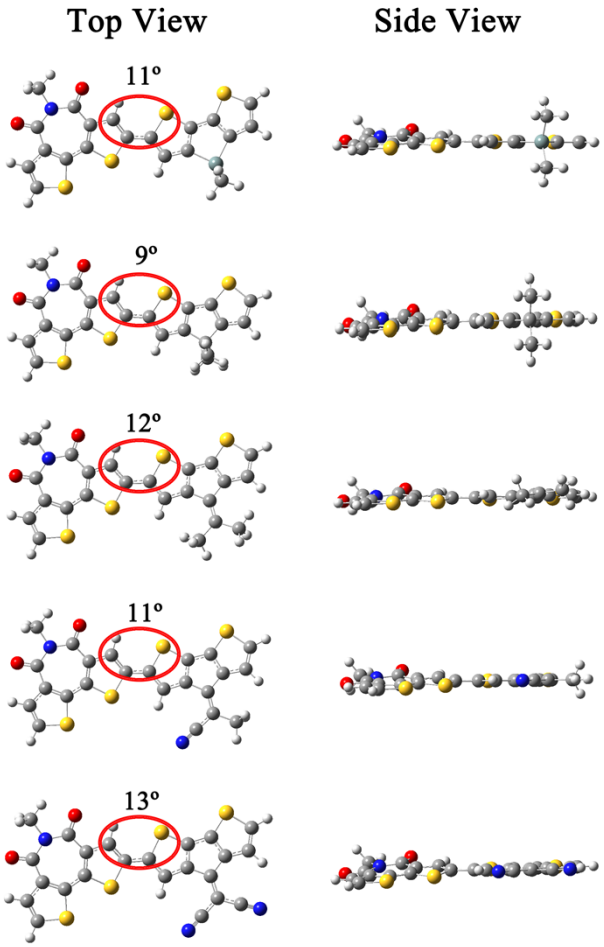

Figure S2. Optimized geometries for **1-5** (n=1) calculated at the PBE0/6-31G(d) level with the dihedral angles between D and A moieties marked with red circles.

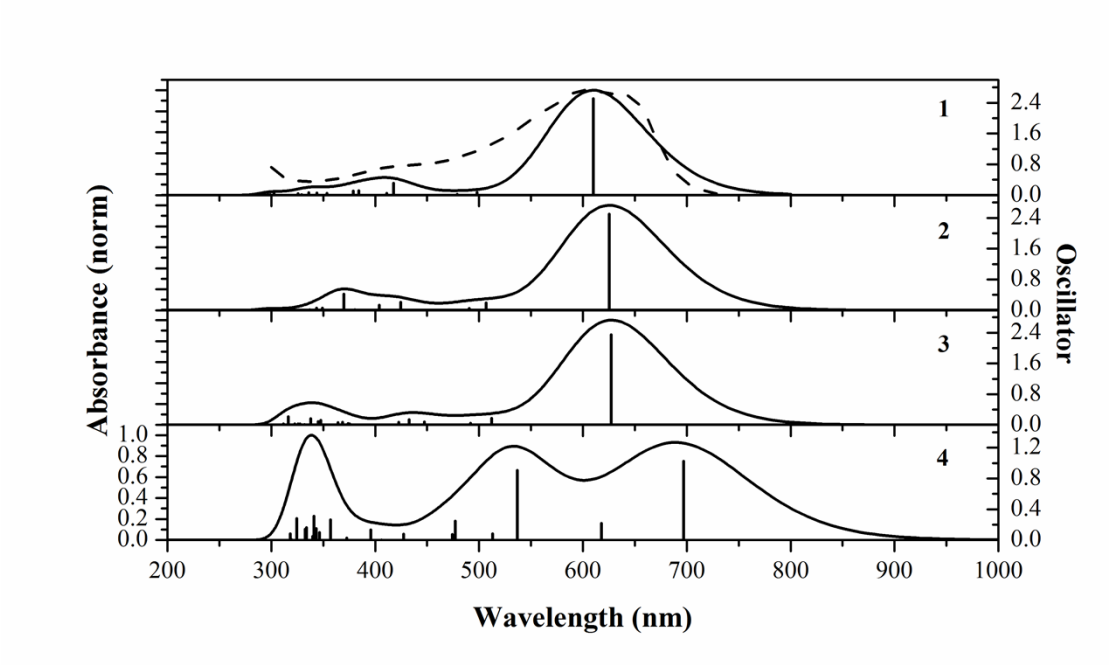

Figure S3. Simulated absorption spectra and related oscillator strengths of **1**-**4** (n=2, the dotted line represents the experimental value of **1** in the top part).

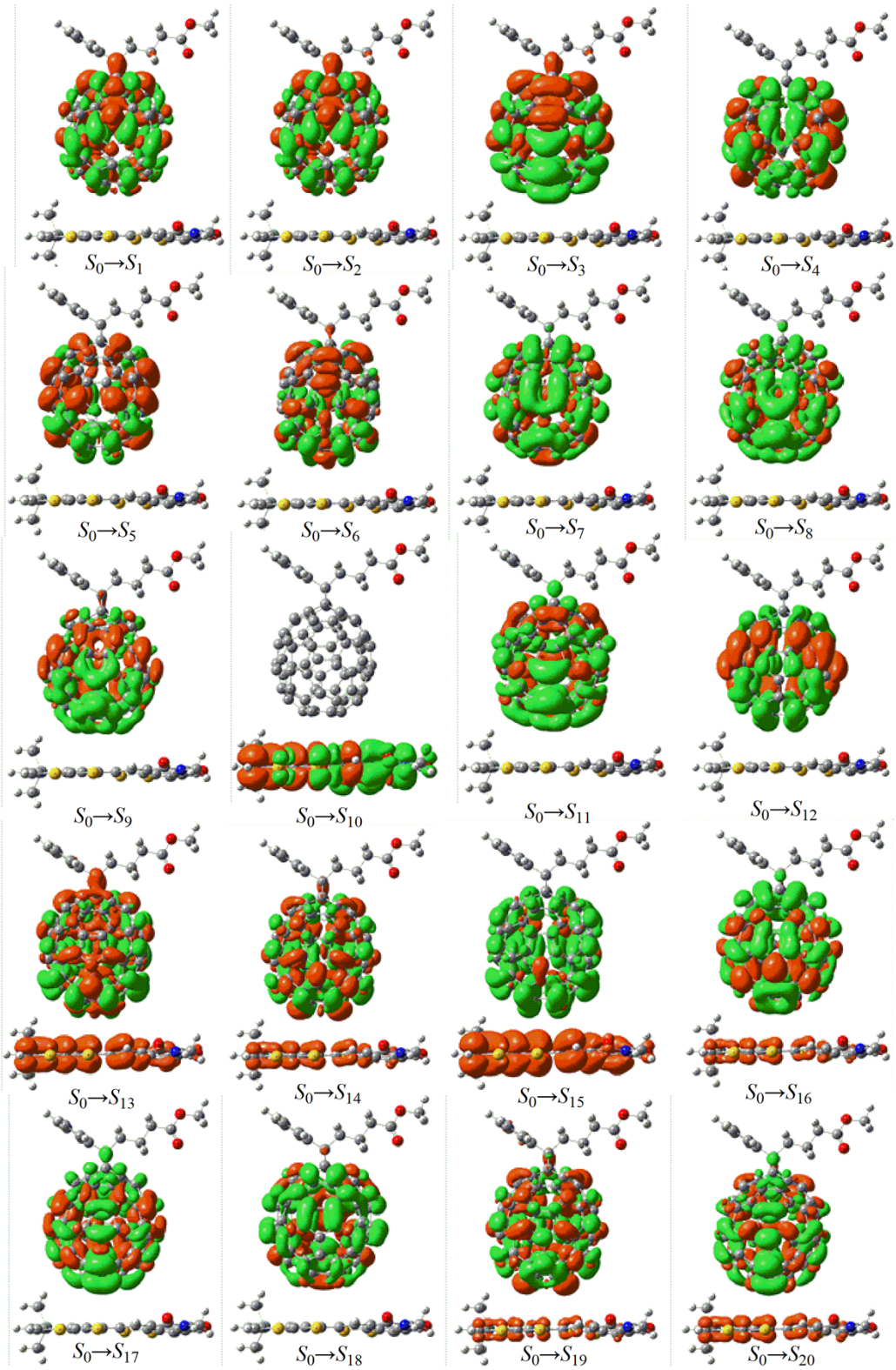

Figure S4. Charge density difference maps for **1/PC$_{71}$BM** heterojunction at the TD-CAM-B3LYP/ 6-31G(d)//B3LYP/6-31G(d) level, where the orange and green colors correspond to the decrease and increase in electron density, respectively.

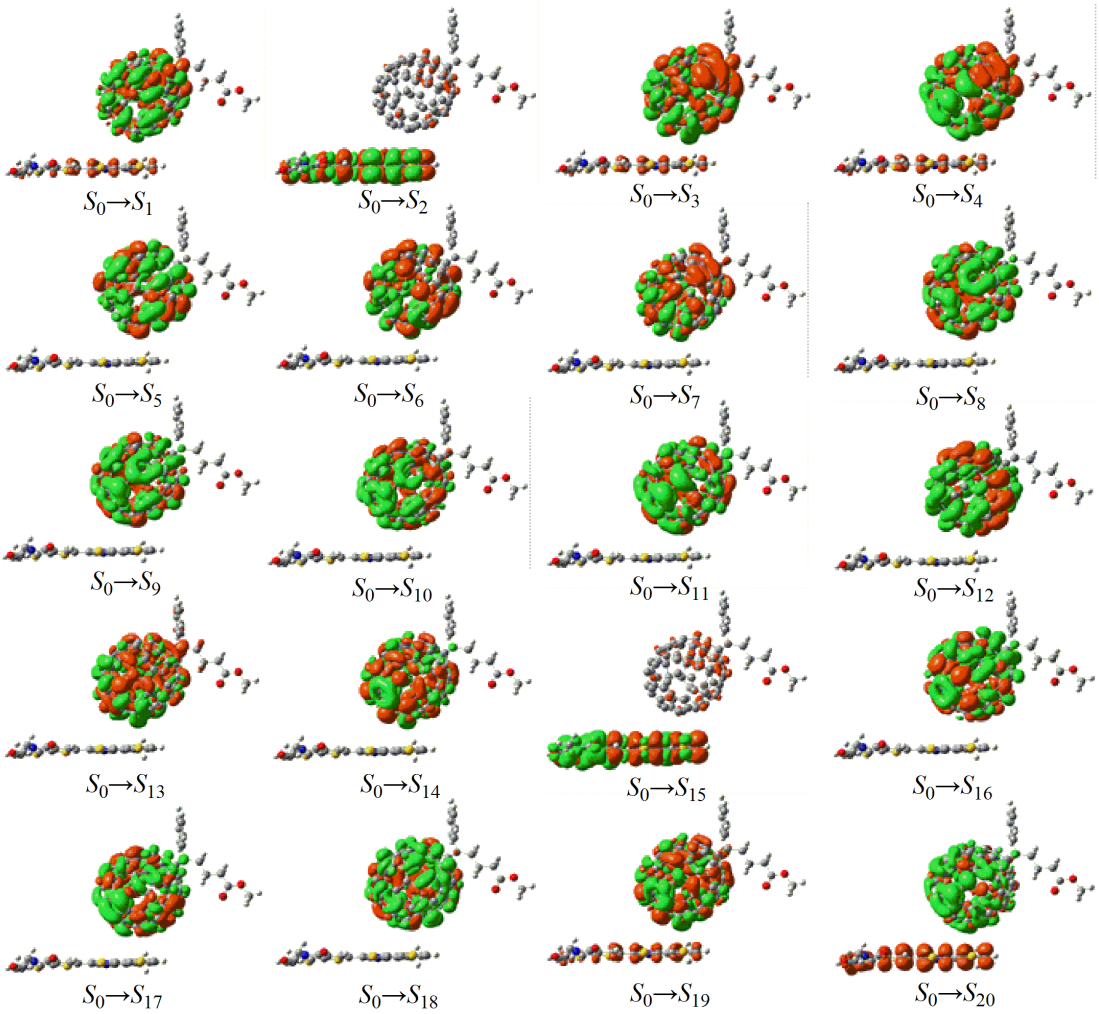

Figure S5. Charge density difference maps for **4/PC$_{71}$BM** heterojunction at the TD-CAM-B3LYP/ 6-31G(d)//B3LYP/6-31G(d) level, where the orange and green colors correspond to the decrease and increase in electron density, respectively.