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Exploring the effects of axial halogen substitutions of boron subphthalocyanines on their performance in BsubPC/C60 organic solar cells: A DFT/TDDFT-based computational study

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Table S1. The binding energies of X-BsubPC/C60 bi-molecular systems obtained with PCM and the BSSE corrections in gas phase. Unit: kJ/mol

System	With BSSE	BSSE	Without BSSE
F(B)	31.31	15.82	47.13
Cl(B)	33.09	11.96	45.04
Br(B)	33.14	23.88	57.03
F(U)	75.21	28.42	103.63
Cl(U)	75.40	27.56	102.96
Br(U)	75.50	27.42	102.92

Table S2. The binding energies of X-BsubPC/60 bi-molecular systems in gas phase or with PCM, U=Umbrella, B=Bed.

	B3LYP+GD3/6-31g*//Gas Phase				B3LYP+GD3/6-31g*//Condensed Phase			
BsubPC	E(BsubPC) (a.u)	E(C60) (a.u)	E(Dimer) (a.u)	Binding Energy (kJ/mol)	E(BsubPC) (a.u)	E(C60) (a.u)	E(Dimer) (a.u)	Binding Energy (kJ/mol)
F(B)	-1375.22	-2286.29	-3661.53	-49.39	-1375.23	-2286.29	-3661.53	-47.13
Cl(B)	-1735.57	-2286.29	-4021.87	-47.80	-1735.57	-2286.29	-4021.88	-45.04
Br(B)	-3847.07	-2286.29	-6133.38	-59.98	-3847.08	-2286.29	-6133.39	-57.03
F(U)	-1375.22	-2286.29	-3661.55	-104.82	-1375.23	-2286.29	-3661.55	-103.63
Cl(U)	-1735.57	-2286.29	-4021.89	-104.97	-1735.57	-2286.29	-4021.90	-102.96
Br(U)	-3847.07	-2286.29	-6133.40	-104.74	-3847.08	-2286.29	-6133.40	-102.92

Table S3. The dipole moment, Mulliken charge and B-X bond length of X-BsubPC monomers and shortest distance between X atom and C60 in bed configurations with B3LYP+GD3/6-31G*/PCM. Unit: Debye for dipole moment, Å for length and distance.

	Dipole Moment	Mulliken Charges of X Atom	B-X Bond Length	Shortest Distance between X and C60
F-BsubPC	4.2243	-0.2774	1.39	3.16
Cl-BsubPC	5.8717	-0.2726	1.89	3.70
Br-BsubPC	6.0881	-0.3482	2.06	3.62

Table S4. The HOMO, LUMO, and gap energies of X-BsubPC/C60 configurations corrected with Equation 3-4, U=Umbrella, B=Bed.

	ωB97XD			LC-ωPBE			CAM-B3LYP		
	HOMO(eV)	LUMO(eV)	Gap(eV)	HOMO(eV)	LUMO(eV)	Gap(eV)	HOMO(eV)	LUMO(eV)	Gap(eV)
F-BsubPC/C60(U)	-5.88	-2.61	3.27	-6.25	-2.50	3.75	-5.31	-3.05	2.26
Cl-BsubPC/C60(U)	-5.97	-2.65	3.32	-6.35	-2.55	3.80	-5.41	-3.09	2.31
Br-BsubPC/C60(U)	-6.00	-2.66	3.34	-6.37	-2.56	3.81	-5.43	-3.10	2.33
F-BsubPC/C60(B)	-5.85	-2.50	3.35	-6.22	-2.40	3.82	-5.29	-2.94	2.35
Cl-BsubPC/C60(B)	-5.94	-2.53	3.42	-6.32	-2.43	3.89	-5.38	-2.96	2.42
Br-BsubPC/C60(B)	-5.97	-2.51	3.46	-6.35	-2.42	3.93	-5.41	-2.95	2.46

Table S5. The HOMO, LUMO, and gap energies of X-BsubPC/C60 configuration in gas phase, U=Umbrella, B=Bed.

	ωB97XD			LC-ωPBE			CAM-B3LYP		
	HOMO(eV)	LUMO(eV)	Gap(eV)	HOMO(eV)	LUMO(eV)	Gap(eV)	HOMO(eV)	LUMO(eV)	Gap(eV)
F-BsubPC/C60(U)	-6.73	-1.76	4.97	-7.1	-1.65	5.45	-6.17	-2.20	3.97
Cl-BsubPC/C60(U)	-6.81	-1.80	5.01	-7.19	-1.7	5.49	-6.26	-2.25	4.01
Br-BsubPC/C60(U)	-6.83	-1.81	5.02	-7.21	-1.71	5.50	-6.27	-2.25	4.02
F-BsubPC/C60(B)	-6.70	-1.65	5.05	-7.07	-1.56	5.51	-6.14	-2.09	4.05
Cl-BsubPC/C60(B)	-6.79	-1.69	5.10	-7.16	-1.59	5.57	-6.23	-2.12	4.11
Br-BsubPC/C60(B)	-6.81	-1.67	5.14	-7.19	-1.57	5.62	-6.25	-2.11	4.14

Table S6. The CT state energies of X-BsubPC/C60 bi-molecular systems. Unit: eV.

	Gas Phase			Condensed Phase		
	ωB97XD	LC-ωPBE	CAM-BL3YP	ωB97XD	LC-ωPBE	CAM-BL3YP
F-BsubPC/C60(U)	2.65	3.05	2.45	2.65	3.05	2.45
Cl-BsubPC/C60(U)	2.70	3.12	2.46	2.70	3.12	2.46
Br-BsubPC/C60(U)	2.70	3.13	2.54	2.71	3.46	2.55
F-BsubPC/C60(B)	3.19	3.62	2.51	3.19	3.62	2.52
Cl-BsubPC/C60(B)	3.29	3.71	2.54	3.31	3.73	2.54
Br-BsubPC/C60(B)	3.32	3.73	2.53	3.34	3.73	2.53

Table S7. The V_{OC}s of X-BsubPC/C60 configurations calculated in gas phase and experiment. Unit: eV for energy; V for V_{oc}.

Configurations		F-U	Cl-U	Br-U	F-B	Cl-B	Br-B
ωB97XD	HOMO	-6.73	-6.81	-6.83	-6.70	-6.79	-6.81
	LUMO	-1.76	-1.80	-1.81	-1.65	-1.69	-1.67
	1/R	3.29	3.26	3.27	2.56	2.46	2.46
	Voc	1.68	1.74	1.75	2.49	2.64	2.67
LC-ωPBE	HOMO	-7.10	-7.19	-7.21	-7.07	-7.16	-7.19
	LUMO	-1.65	-1.70	-1.71	-1.56	-1.59	-1.57
	1/R	3.29	3.26	3.27	2.56	2.46	2.46
	Voc	2.16	2.22	2.23	2.96	3.12	3.15
CAM-B3LYP	HOMO	-6.17	-6.26	-6.27	-6.14	-6.23	-6.25
	LUMO	-2.20	-2.25	-2.25	-2.09	-2.12	-2.11
	1/R	3.29	3.26	3.27	2.56	2.46	2.46
	Voc	0.68	0.75	0.75	1.49	1.65	1.68
Experiment[1]	Voc	1.00 (F-BsubPC/C60), 1.06 (Cl-BsubPC/C60)					

Table S8. The experimental Voc results from other papers.

Experimental Results	
Device Composition	Voc (V)
ITO/MoO3(5nm)/Cl-BsubPC(13nm)/C60(32Nm)/BCP(7nm)/Ag[2]	1.0
ITO/MoO3 (15 nm)/ Cl-BsubPC (10 nm)/C60 (30 nm)/ BCP:C60/Al (120 nm).[3]	1.05±0.04
ITO/MoO3 (10 nm)/Cl-BsubPC(9nm)/C60(30 nm)/Bathocuproine (BCP) (10 nm)/Ag (100 nm)[4]	1.00±0.01
ITO/MoO3(5nm)/F-BsubPC(13nm)/C60(36nm)/BCP(10nm)/Al(100 nm)[1]	1.00±0.019
ITO/MoO3(5nm)/Cl-BsubPC(13nm)/C60(36nm)/BCP(10nm)/Al(100 nm)[1]	1.06±0.002
ITO/MoOx (5 nm)/Cl-BsubPC (15 nm)/C60 (40 nm)/BPhen (6 nm)/Al (100 nm)[5]	1.05±0.02

Table S9. The surface area of monomers and X-BsubPC/C60 configurations. Unit: Å^2

System	Surface Area
F-BsubPC	385.98
Cl-BsubPC	399.78
Br-BsubPC	405.20
F-BsubPC/C60 (U)	653.09
Cl-BsubPC/C60 (U)	669.51
Br-BsubPC/C60 (U)	673.54
F-BsubPC/C60 (B)	732.34
Cl-BsubPC/C60 (B)	736.68
Br-BsubPC/C60 (B)	737.64

Table S10. Absorption π→π* excited state energy and oscillator strength of monomers and X-BsubPC/C60 bi-molecular systems with three LRC density functionals. Unit: nm (λ_{ave}), eV (Energy)

	System	Excited State	Strength	Energy (eV)	Wavelength (nm)
ωB97XD	F-BsubPC	1	0.3527	2.56	484.43
		2	0.3527	2.56	484.39
		Average	0.7054	2.56	484.41
	Cl-BsubPC	1	0.3421	2.54	488.15
		2	0.3421	2.54	488.06
		Average	0.6842	2.54	488.11
	Br-BsubPC	1	0.3364	2.54	488.84
		2	0.3364	2.54	488.78
		Average	0.6728	2.54	488.81
LC-ωPBE	F-BsubPC	1	0.3595	2.49	497.68
		2	0.3595	2.49	497.61
		Average	0.719	2.49	497.65
	Cl-BsubPC	1	0.3491	2.47	501.96
		2	0.3491	2.47	501.85
		Average	0.6982	2.47	501.91
	Br-BsubPC	1	0.3436	2.47	502.71
		2	0.3436	2.47	502.65
		Average	0.6872	2.47	502.68
CAM-B3LYP	F-BsubPC	1	0.3521	2.56	483.41
		2	0.3521	2.56	483.36
		Average	0.7042	2.56	483.39
	Cl-BsubPC	1	0.3415	2.55	487.06
		2	0.3415	2.55	486.97
		Average	0.6830	2.55	487.02
	Br-BsubPC	1	0.3364	2.54	488.84
		2	0.3364	2.54	488.78
		Average	0.6728	2.54	488.81

ωB97XD	F-BsubPC/C60(U)	1	0.2589	2.54	488.10
		2	0.2621	2.54	487.70
		Average	0.521	2.54	487.90
	F-BsubPC/C60(B)	1	0.3942	2.50	496.40
		2	0.2721	2.54	489.00
		Average	0.6663	2.52	493.38
	Cl-BsubPC/C60(U)	1	0.2085	2.48	500.40
		2	0.2092	2.49	498.10
		Average	0.4177	2.49	499.25
	Cl-BsubPC/C60(B)	1	0.4271	2.49	498.20
		2	0.2617	2.52	491.40
		Average	0.6888	2.50	495.62
	Br-BsubPC/C60(U)	1	0.2019	2.47	501.80
		2	0.2107	2.49	498.20
		Average	0.4126	2.48	499.96
	Br-BsubPC/C60(B)	1	0.4123	2.49	498.90
		2	0.2584	2.52	492.10
		Average	0.6707	2.50	496.28
LC-ωPBE	F-BsubPC/C60(U)	1	0.2304	2.43	509.50
		2	0.2344	2.45	506.00
		Average	0.4648	2.44	507.73
	F-BsubPC/C60(B)	1	0.4074	2.45	507.00
		2	0.2827	2.47	501.10
		Average	0.6901	2.46	504.58
	Cl-BsubPC/C60(U)	1	0.2251	2.41	513.60
		2	0.2269	2.43	510.50
		Average	0.452	2.42	512.04
	Cl-BsubPC/C60(B)	1	0.4311	2.43	510.60
		2	0.2719	2.46	504.20
		Average	0.703	2.44	508.12
	Br-BsubPC/C60(U)	1	0.2205	2.41	514.40
		2	0.2238	2.43	511.30
		Average	0.4443	2.42	512.84
	Br-BsubPC/C60(B)	1	0.4166	2.42	511.40
		2	0.2684	2.46	505.00
		Average	0.685	2.44	508.89
CAM-B3LYP	F-BsubPC/C60(U)	1	0.0604	2.45	506.11
		2	0.0681	2.48	500.00
		3	0.1643	2.52	491.40
		4	0.0291	2.53	489.20
		5	0.0089	2.54	487.30
		6	0.0579	2.55	487.10

	7	0.0566	2.56	484.60
	Average	0.4453	2.51	493.06
F-BsubPC/C60(B)	1	0.3436	2.48	500.10
	2	0.0768	2.52	492.90
	3	0.1398	2.54	487.80
	4	0.0589	2.55	486.80
	5	0.0212	2.55	486.00
	Average	0.6403	2.51	494.86
Cl-BsubPC/C60(U)	1	0.1367	2.46	503.30
	2	0.1668	2.48	500.30
	3	0.0231	2.54	488.90
	4	0.011	2.54	487.50
	5	0.0193	2.55	486.60
	6	0.0163	2.55	485.30
	Average	0.3732	2.48	498.95
Cl-BsubPC/C60(B)	1	0.4154	2.48	499.70
	2	0.1772	2.52	491.90
	3	0.0722	2.54	489.00
	4	0.0092	2.55	486.50
	5	0.0042	2.55	485.70
	Average	0.6782	2.50	496.26
Br-BsubPC/C60(U)	1	0.153	2.46	504.20
	2	0.1727	2.48	499.00
	3	0.0093	2.53	489.40
	4	0.0136	2.54	487.50
	5	0.0032	2.55	486.30
	Average	0.3518	2.48	500.45
Br-BsubPC/C60(B)	1	0.4018	2.48	500.00
	2	0.1772	2.52	492.60
	3	0.0712	2.53	489.70
	4	0.0076	2.55	486.40
	5	0.0022	2.55	485.80
	Average	0.66	2.50	496.70

Table S11. The ground to excited state transition electric dipole moment of X-BsubPC/C60 configurations (X=F, Cl and Br) with different functionals.

	State	ωB97XD	LC-ωPBE	CAM-B3LYP
F(U)	G→1	4.1602	3.6510	1.0051
	G→2	4.2084	3.9041	1.1207
Cl(U)	G→1	3.4354	3.8055	2.2650
	G→2	3.4304	3.8131	2.7471
Br(U)	G→1	3.3354	3.7347	2.5396
	G→2	3.4555	3.7668	2.8378
F(B)	G→1	6.4423	6.7999	5.6571
	G→2	4.9809	4.6640	1.2468
Cl(B)	G→1	7.0045	7.2460	6.8338
	G→2	4.2337	4.5129	2.8695
Br(B)	G→1	6.7718	7.0141	6.6140
	G→2	4.1866	4.4618	2.8734

Table S12. The average wavelength of both X-BsubPC/C60 (X=F, Cl, Br) U and B configurations. Unit: nm.

	ωB97XD	LC-ωPBE	CAM-B3LYP
F-BsubPC/C60(U)	487.9	507.7	493.1
F-BsubPC/C60(B)	493.4	504.6	494.9
Cl-BsubPC/C60(U)	499.3	512.0	499.0
Cl-BsubPC/C60(B)	495.6	508.1	496.3
Br-BsubPC/C60(U)	500.0	512.8	500.5
Br-BsubPC/C60(B)	496.3	508.9	496.7

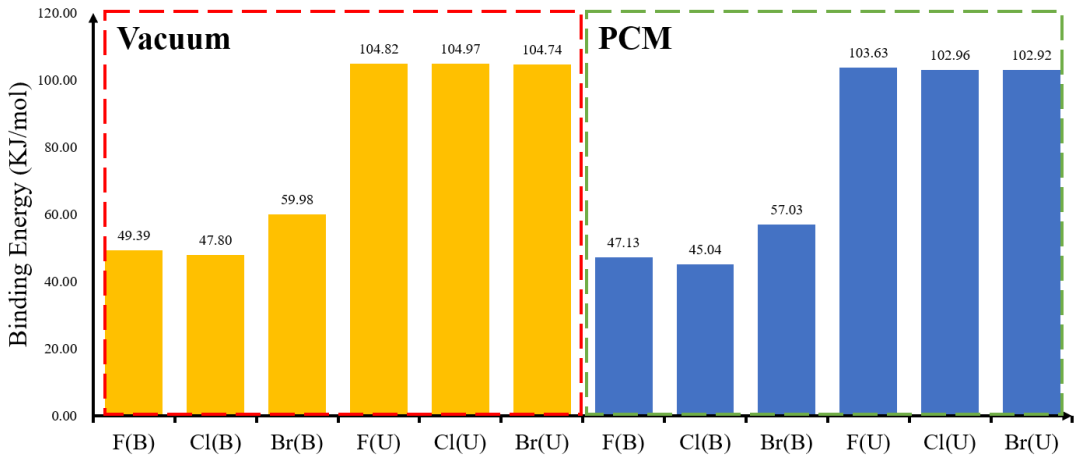

Figure S1. The binding energies of X-BsubPC/C60 configurations in gas phase and condensed phase, U=Umbrella, B=Bed.

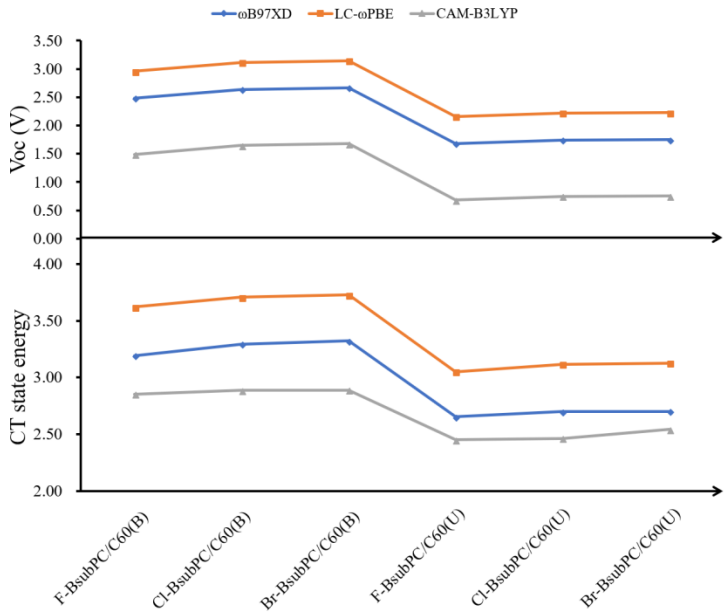

Figure S2. The calculated Voc and CT energies of X-BsubPC/C60 configurations in gas phase.

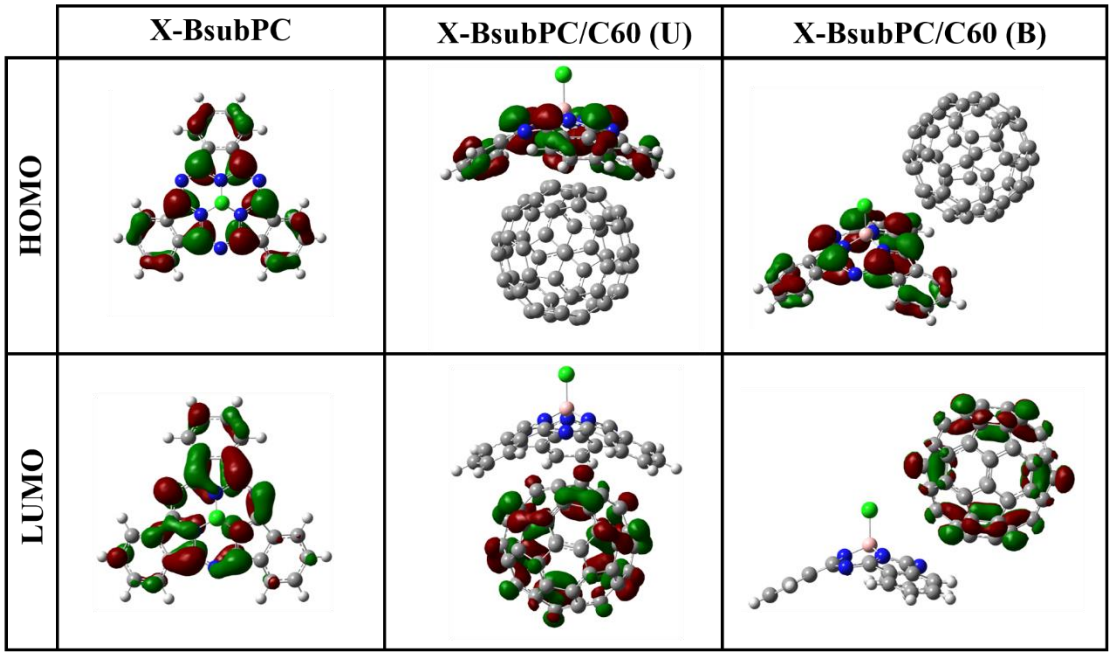

Figure S3. Schematic representations of frontier molecular orbitals of monomer and X-BsubPC/C60 bi-molecular systems (X=F, Cl, Br). (iso-surface value=0.03 a.u, density=0.0004).

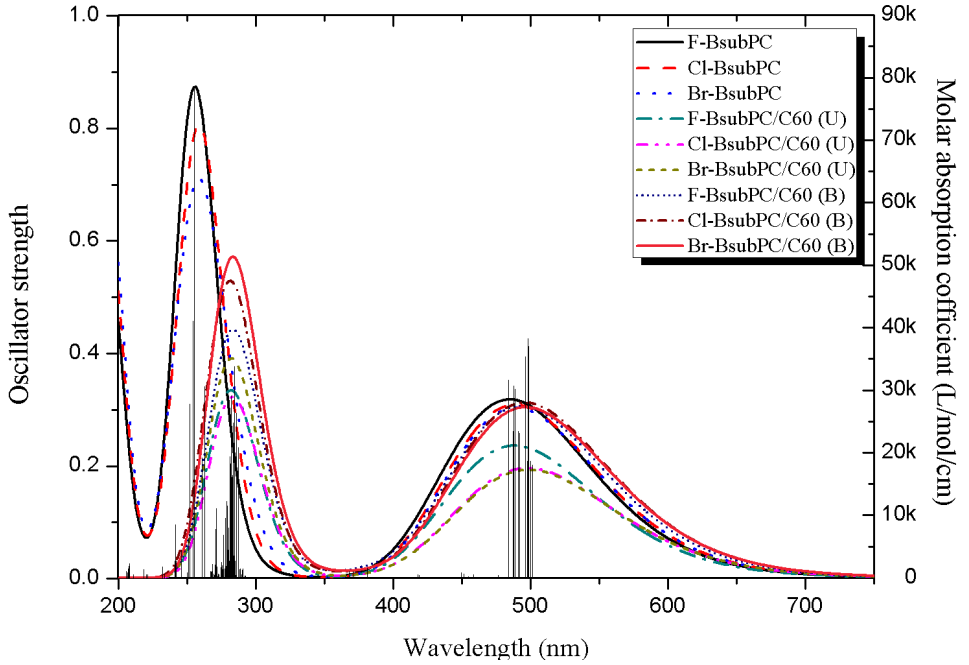

Figure S4. The absorption spectra of X-BsubPC monomers and X-BsubPC/C60 bi-molecular systems obtained with ωB97XD functional.

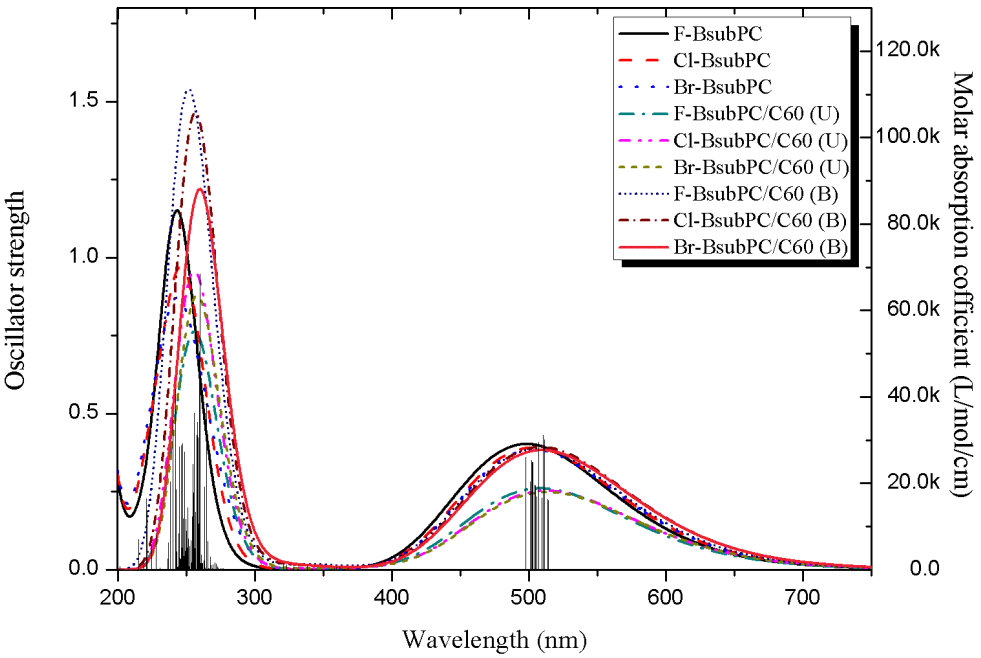

Figure S5. The absorption spectra of X-BsubPC monomers and X-BsubPC/C60 bi-molecular systems obtained with LC-ωPBE functional.

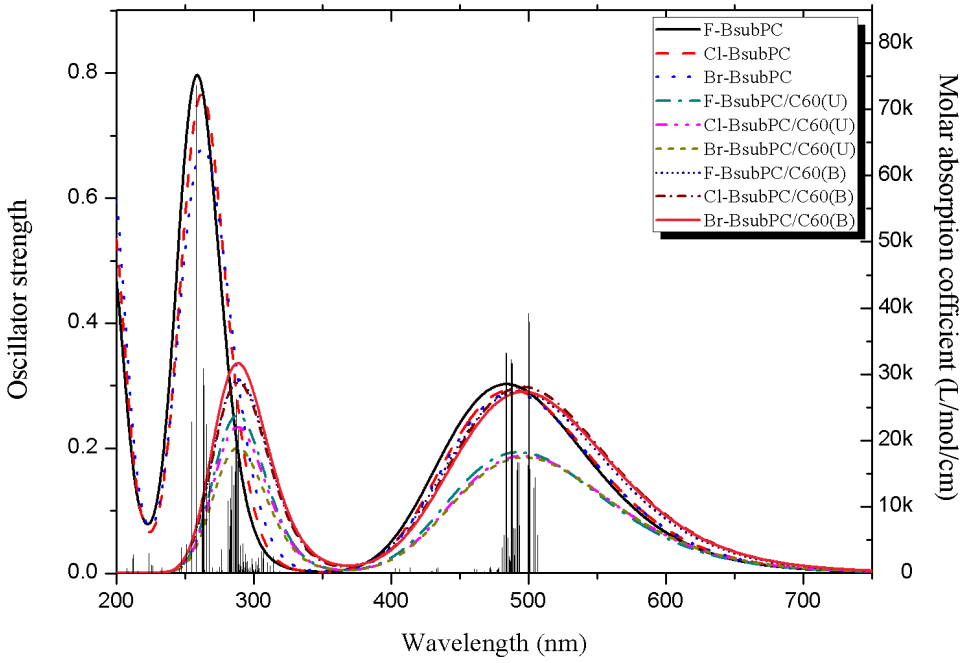

Figure S6. The absorption spectra of X-BsubPC monomers and X-BsubPC/C60 bi-molecular systems obtained with CAM-B3LYP functional.

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