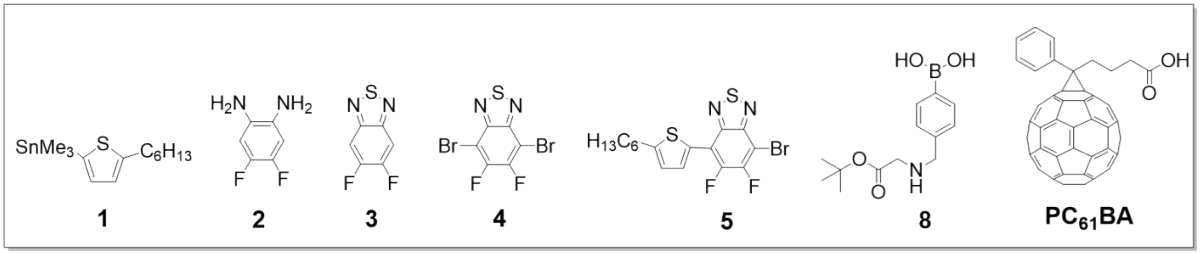
Supporting Information

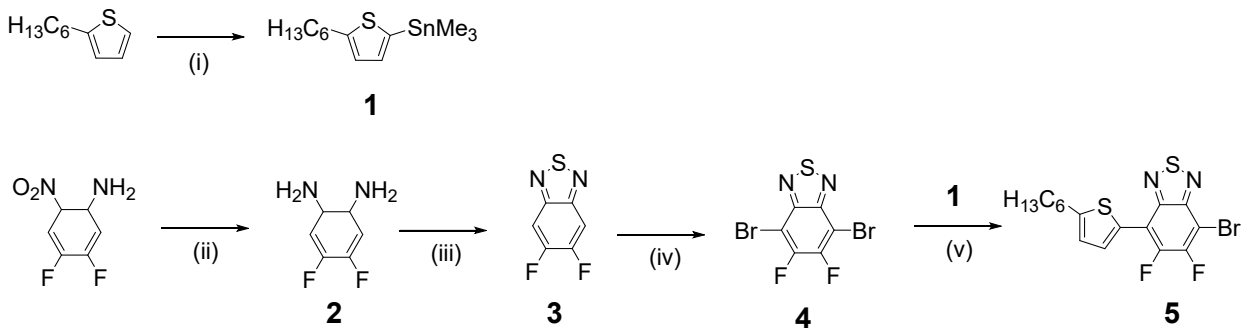
Covalently Linked Benzothiadiazole-Fullerene Adducts for Organic Optoelectronic Devices: Synthesis and Characterization

Divambal Appavoo,[a, b] Komal Bhardwaj,[c, d] Samarendra P. Singh,[e] Emmanuel N. Koukaras,[f] Rachana Kumar,[c, d] and Bimlesh Lochab*[a]

Total 40 pages, Scheme 1, Figures 26, Tables 9

Contents





Scheme S1. Synthesis of **5**, reagents and conditions: (i) a. *n*-BuLi, dry THF, -78 °C, 24 h; b. Me_3SnCl, r.t., 24 h, 100% (ii) $HCOONH_4$, EtOAc, Pd/C, 1 h, 78% (iii) $CHCl_3$, TEA, 0 °C; $SOCl_2$, 0 °C to r.t., 6 h, 71% (iv) a. Fe, 90 °C; b. Br_2, reflux, 2 days, 70% (v) $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, PhMe; b. **1** in PhMe, 16 h, 27%.

(5-Hexylthiophen-2-yl)trimethylstannane, 1 [1]

To a solution of 2-hexylthiophene (1.07 mL, 5.94 mmol) in dry THF (10 mL) at -78 °C was added *n*-butyllithium (8.00 mL, 12.00 mmol, 1.6 M in hexane) under nitrogen. The reaction mixture was allowed to warm to room temperature and stirring continued for 24 h. Trimethyltin chloride (6.50 mL, 6.54 mmol) was added and reaction was left to continue at room temperature for another 24 h. Reaction mixture was then poured into water and diethyl ether was added. Extraction was done

and the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. **1** was obtained as a reddish brown liquid and was used for the next step without further purification (2.05 g, 100%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.04 (d, 1H, *J* = 3.16 Hz, C*H*CSn), 6.90 (d, 1H, *J* = 3.08 Hz, C*H*CC), 2.89 (t, 2H, *J* = 15.12 Hz, CH_2CS), 1.71-1.67 (m, 8H, C$H_{2\text{aliphatic}}$), 0.90 (t, 3H, *J* = 13.52 Hz, CH_2CH_3), 0.37 (s, 9H, Sn(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 152.00, 135.14, 134.78, 125.51, 31.98, 31.76, 30.09, 29.07, 22.73, 14.22, -8.19.

4,5-Difluorobenzene-1,2-diamine, 2[2]

4,5-Difluoro-2-nitroaniline (5.00 g, 28.00 mmol) and ammonium formate (27.08 g, 430.00 mmol) were weighed in a 100 mL 2-neck flask, followed by the addition of ethyl acetate (50 mL). Under an inert atmosphere of nitrogen, Pd/C (0.50 g, 10%) was added and reaction mixture was stirred at room temperature. After 1 h, reaction was stopped, mixture was filtered through celite and rinsed abundantly with ethyl acetate. The filtrate was extracted with water and the organic phase was dried over anhydrous Na_2SO_4 and solvent was evaporated. The dark brown solid obtained was recrystallized from hexane/ethyl acetate (1:2 mixture) to afford **2** as brown crystals (3.16 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 6.51 (t, 2H, *J* = 18.92 Hz, C*H*), 3.30 (broad s, 4H, NH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 145.35, 145.20, 142.98, 142.83, 130.83, 130.73, 105.61, 105.52, 105.47, 105.39.

5,6-Difluorobenzo[c][1,2,5]thiadiazole, 3[3]

To a 2-neck flask containing **2** (3.00 g, 21.00 mmol) was added $CHCl_3$ (30 mL) followed by triethylamine (7.00 mL, 83.00 mmol) and mixture was stirred in an ice bath under nitrogen. At 0 °C, $SOCl_2$ (3.00 mL, 41.00 mmol) was added dropwise to the reaction. After complete addition,

mixture was allowed to warm to room temperature and stirring continued for 6 h. Reaction mixture was poured onto water and extraction was done with $CHCl_3$. The organic phase was dried over anhydrous Na_2SO_4 and the solvent evaporated. The brown residue obtained was purified by silica gel chromatography (eluent 2% ethyl acetate in hexane) giving **3** as a pure white crystalline solid (2.55 g, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.75 (t, 2H, *J* = 17.32 Hz, C*H*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 155.37, 155.17, 152.78, 152.58, 151.05, 151.00, 150.94, 106.39, 106.33, 106.25, 106.18.

4,7-Dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole, 4[4]

3 (2.05 g, 11.00 mmol) and Fe powder (0.19 g, 3.50 mmol) were added to a 100 mL 2-neck flask and heated to 90 °C. Bromine (9.00 mL, 178.00 mmol) was added dropwise, over 1h, to the melt. The reaction was stirred under reflux for two days. After cooling to room temperature, $CHCl_3$ (100 mL) and $Na_2S_2O_3$ aqueous solution (5%, 50 mL) were added to the mixture and stirred for 1h. Extraction was then done with 5% $Na_2S_2O_3$ aqueous solution and water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. Purification of the product was done by silica gel chromatography (eluent 2% ethyl acetate in hexane), followed by recrystallization in ethanol. White crystalline solid of **4** was obtained (2.76 g, 70%). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 153.36, 153.15, 150.76, 150.55, 149.00, 99.62, 99.53, 99.47, 99.39. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): -118.59.

4-Bromo-5,6-difluoro-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole, 5[5]

4 (1.05 g, 3.05 mmol) was added to a 250 mL 2-neck flask that was purged with nitrogen. Degassed toluene (120 mL) was added to the flask followed by $Pd_2(dba)_3$ (0.13 g, 0.15 mmol) and tri(*o*-tolyl) phosphine (0.18 g, 0.60 mmol). A solution of **1** (1.36 g, 3.00 mmol) in toluene (50 mL) was added dropwise, over 2 h, to the above stirring mixture at room temperature. After stirring at room temperature for 16 h, the solvent was evaporated and the residue was purified by silica gel chromatography (eluent 10% CH_2Cl_2 in hexane) resulting in the desired product obtained as a yellow solid (0.35 g, 27 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.07 (d, 1H, J = 3.76 Hz, C*H*CC), 6.93 (d, 1H, J = 3.40 Hz, C*H*CCH_2), 2.91 (t, 2H, J = 15.28 Hz, CH_2CS), 1.42 (quintet, 2H, J = 30.12 Hz, C$H_{2\text{aliphatic}}$), 1.44-1.32 (m, 6H, C$H_{2\text{aliphatic}}$), 0.90 (t, 3H, J = 14.28 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 153.87, 153.67, 151.33, 151.13, 150.98, 150.91, 150.23, 150.04, 150.01, 149.95, 148.02, 147.94, 147.63, 147.44, 131.77, 131.68, 128.33, 128.30, 128.28, 128.24, 124.99, 113.86, 113.74, 96.34, 96.12, 31.69, 31.62, 30.25, 29.84, 28.99, 22.71, 14.21. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): -120.37 (d), -127.72 (d).

$PC_{61}BA$[6]

$PC_{61}BM$ (150 mg, 0.16 mmol) was dissolved in toluene (33 mL) in a 100 mL flask. Concentrated HCl (35%, 16 mL) and glacial acetic acid (33 mL) were added to the flask and reaction was stirred under reflux for 48 h. The reaction mixture was evaporated to dryness and to the brown residue water was added to remove excess acid. After decantation and air drying of the brown solid, the latter was washed several times with CH_2Cl_2, until all unreacted **$PC_{61}BM$** was removed (until the CH_2Cl_2 wash became colourless). **$PC_{61}BA$** was obtained by centrifugation, as a brown solid (135 mg, 95%). ^{1}H NMR ($CDCl_3$, DMSO-d_6, CS_2, 400 MHz, ppm): 7.72 (d, 2H, J = 7.24 Hz, CH_{aromatic}),

7.36-7.28 (m, 3H, C$H_{aromatic}$), 2.75-2.67 (m, 2H, C*H*COOH), 2.28-2.23 (m, 2H, C$H_{2aliphatic}$), 1.99-1.93 (m, 2H, C$H_{2aliphatic}$). IR (cm^{-1}) = 3270 (O-H), 1700 ($\nu_{C=O}$).

(4-(((2-(Tert-butoxy)-2-oxoethyl)amino)methyl)phenyl)boronic acid, 8[7]

4-Aminomethylphenylboronic acid, hydrochloride (200 mg, 1.07 mmol) was dissolved in dry THF (5 mL) in a 10 mL flask and kept under nitrogen. Triethylamine (1.07 mL, 2.13 mmol) was added to the above and stirring was done in an ice bath. At 0 °C, a THF solution of *tert*-butyl-2-bromoacetate (0.18 mL, 0.71 mmol in 3 mL THF) was added dropwise to the above stirring mixture over two hours. The reaction was allowed to continue at room temperature for 18 h, after which the solvent was evaporated. Ethyl acetate was added to the residue and extraction was done with distilled water, followed by brine. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The product was used for the next step without further purification (crude yield = 126 mg, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.69 (d, 2H, J = 7.84 Hz), 7.43 (d, 2H, J = 7.84 Hz), 3.92 (s, 2H), 3.41 (s, 2H), 1.48 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 170.76, 13378, 128.91, 55.32, 27.97.

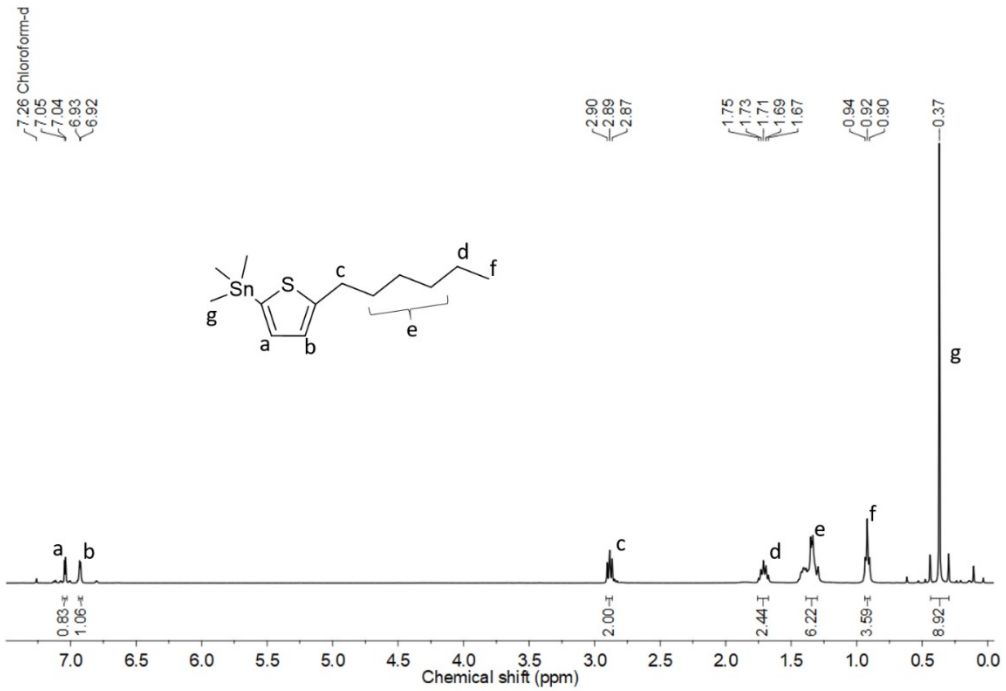


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

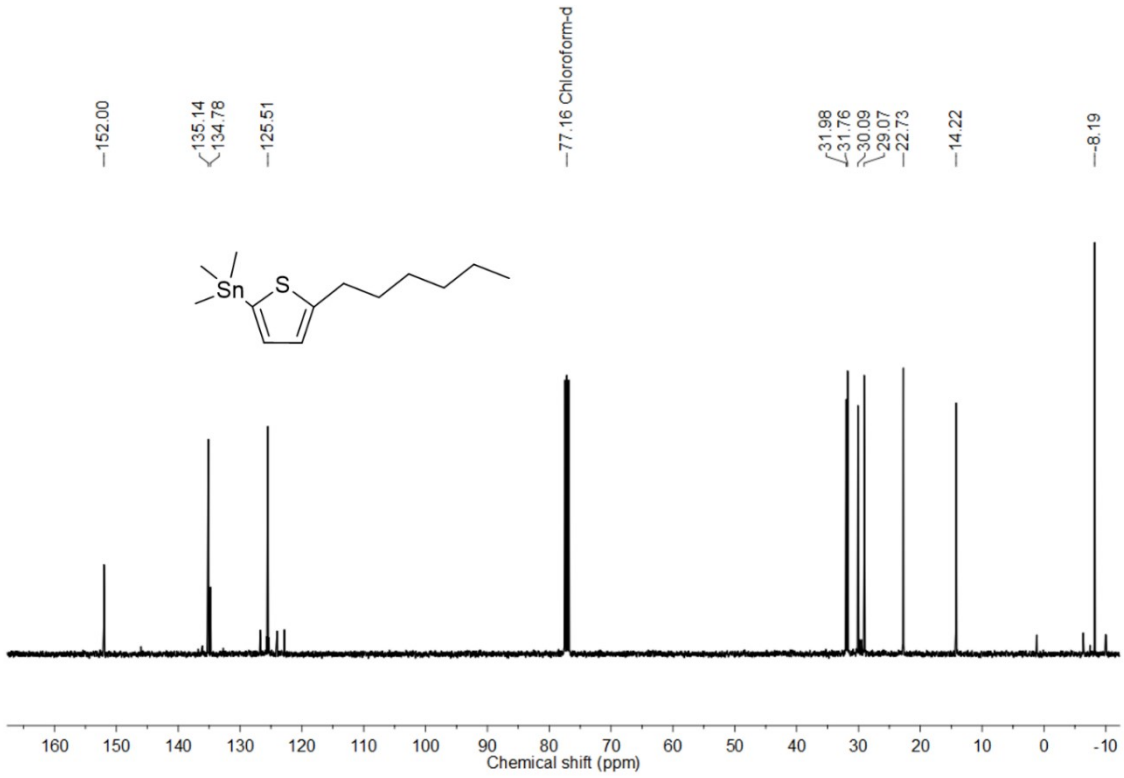


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

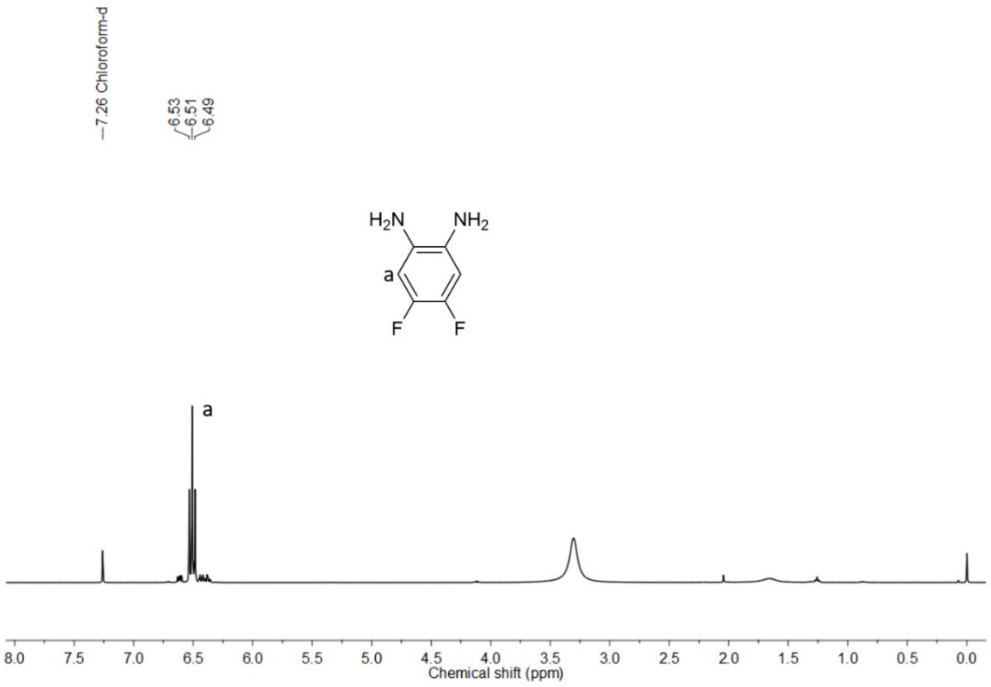


Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$.

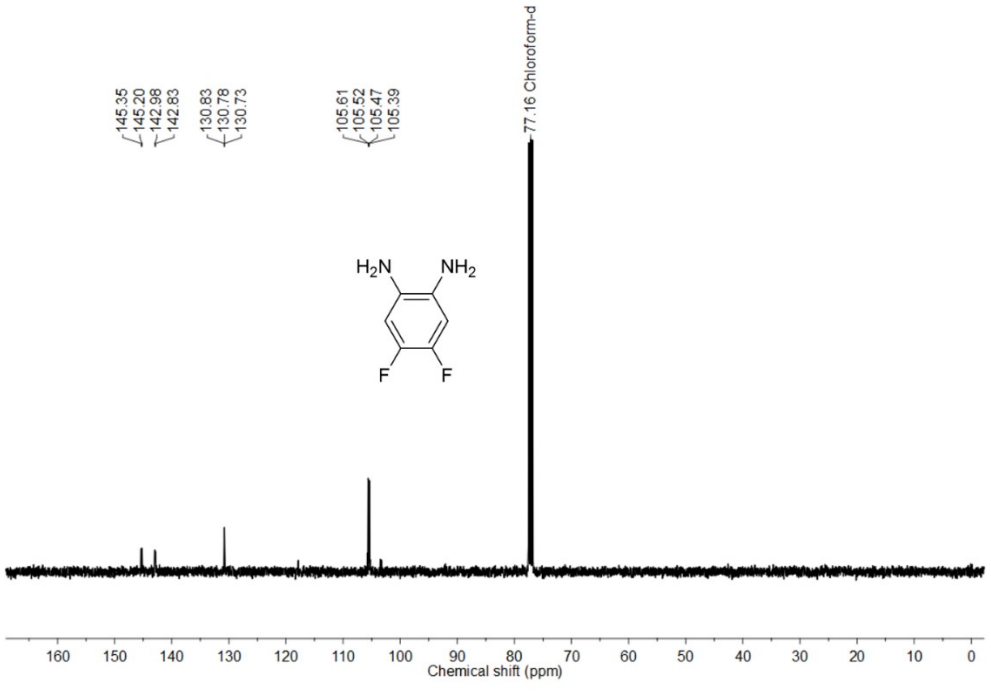


Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$.

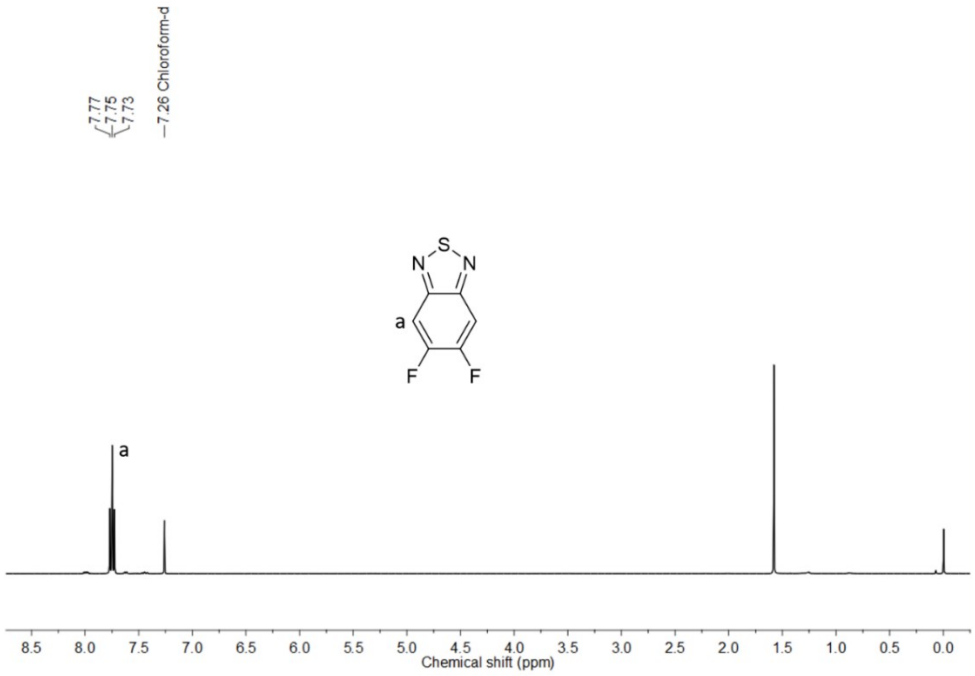


Figure S5. ^{1}H NMR spectrum of **3** in $CDCl_3$.

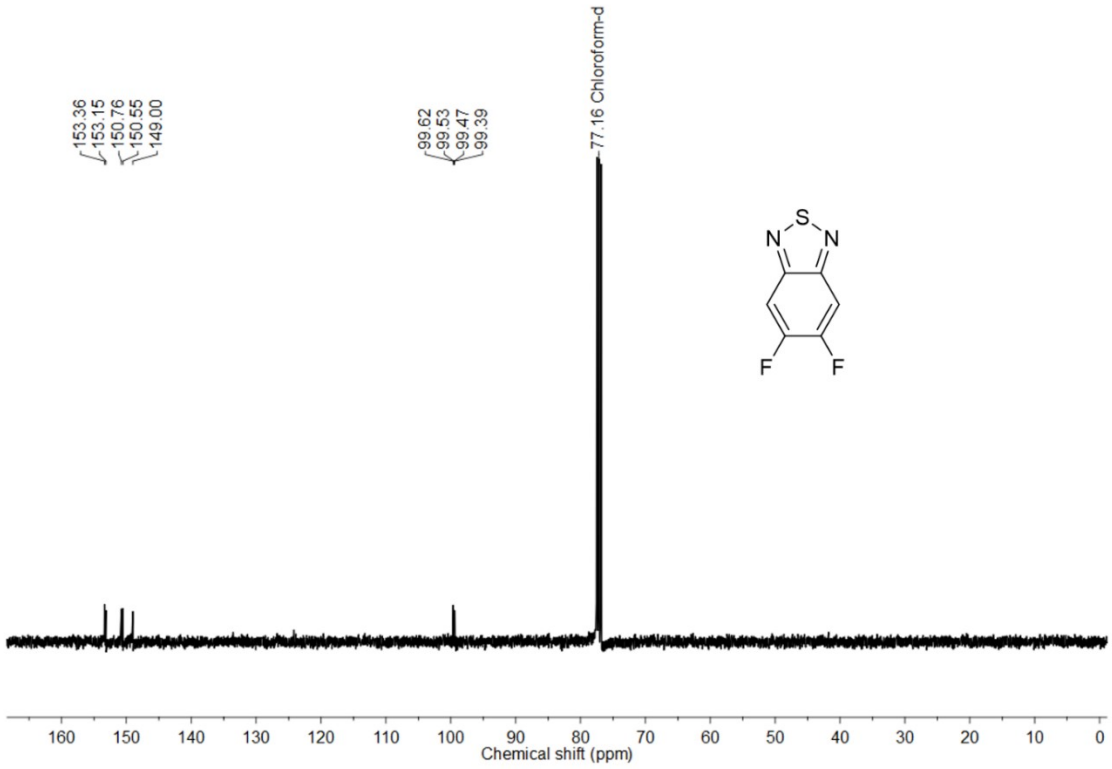


Figure S6. ^{13}C NMR spectrum of **3** in $CDCl_3$.

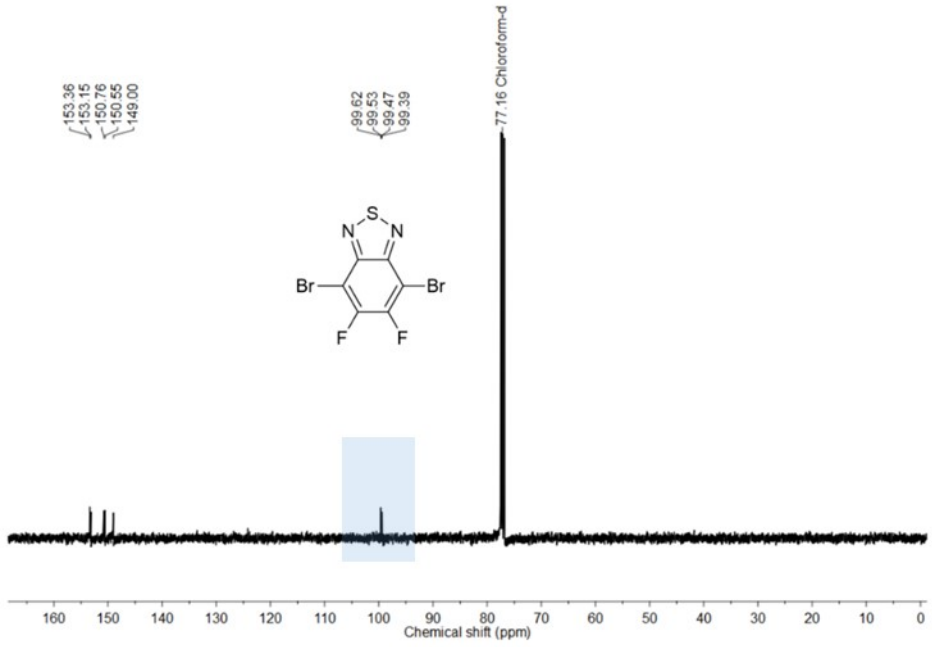


Figure S7. ^{13}C NMR spectrum of **4** in $CDCl_3$.

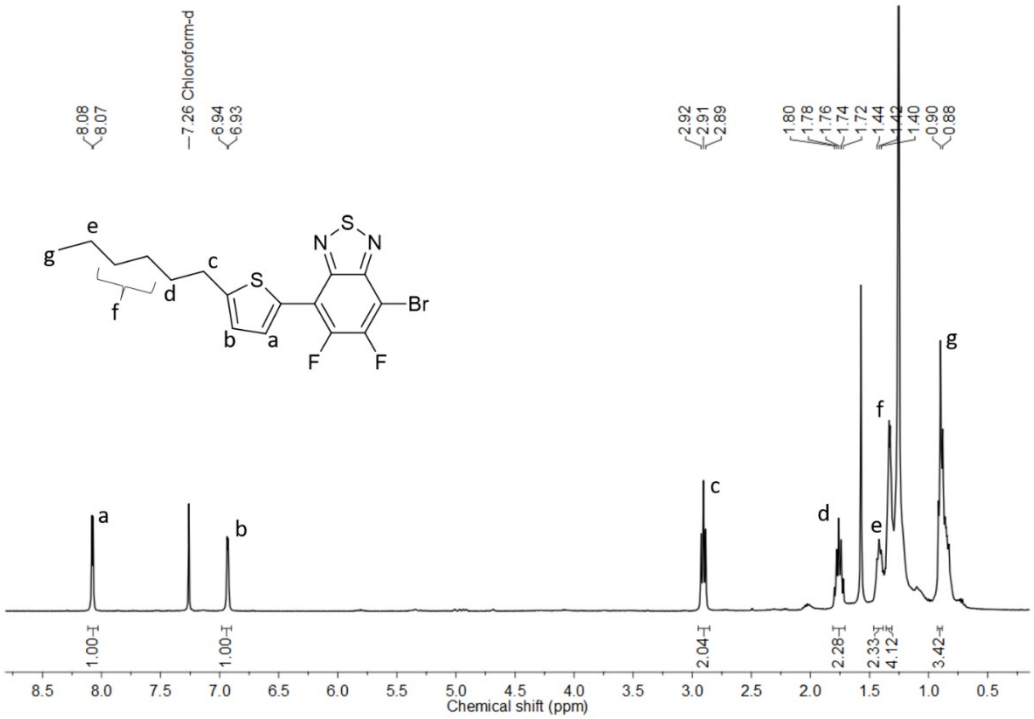


Figure S8. ^{1}H NMR spectrum of **5** in $CDCl_3$.

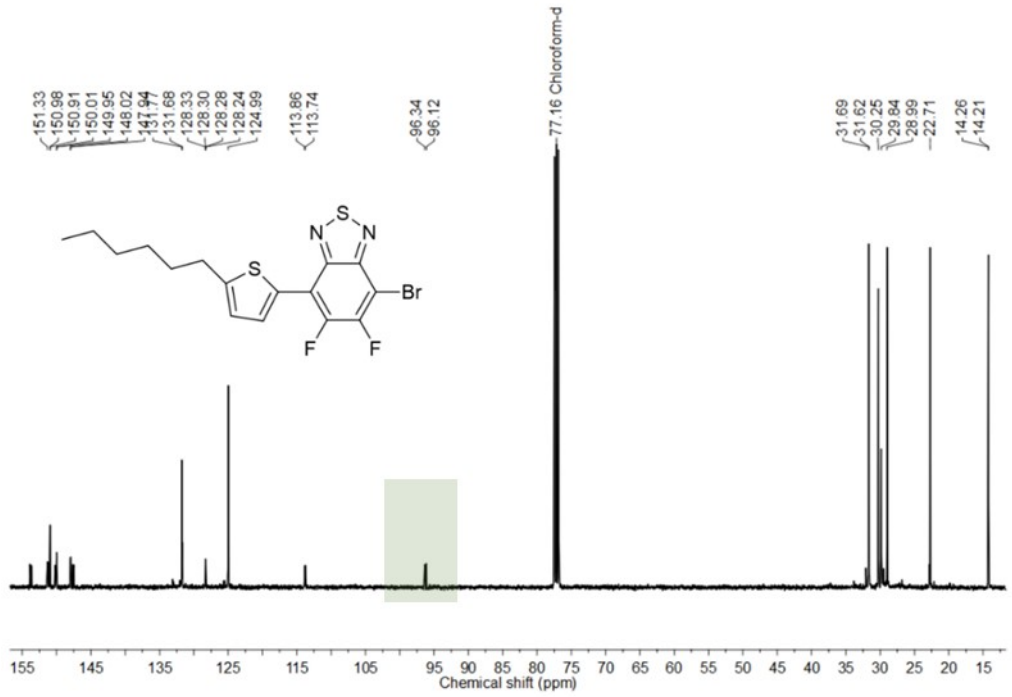


Figure S9. ^{13}C NMR spectrum of **5** in $CDCl_3$.

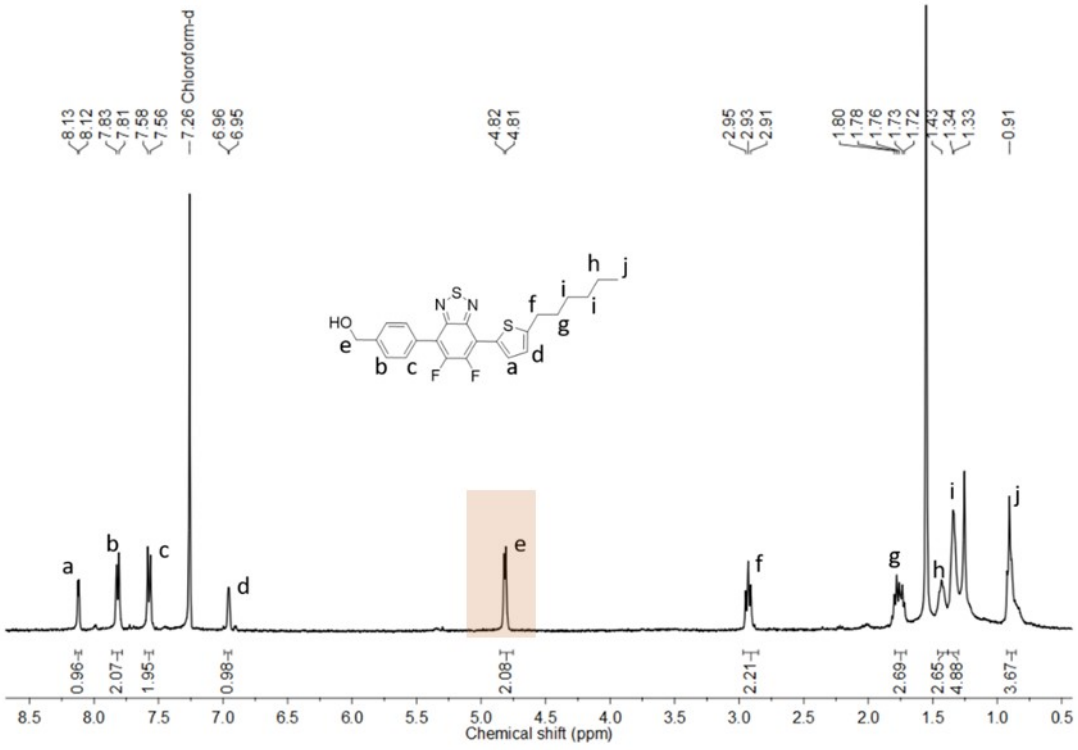


Figure S10. ^{1}H NMR of **6** in $CDCl_3$.

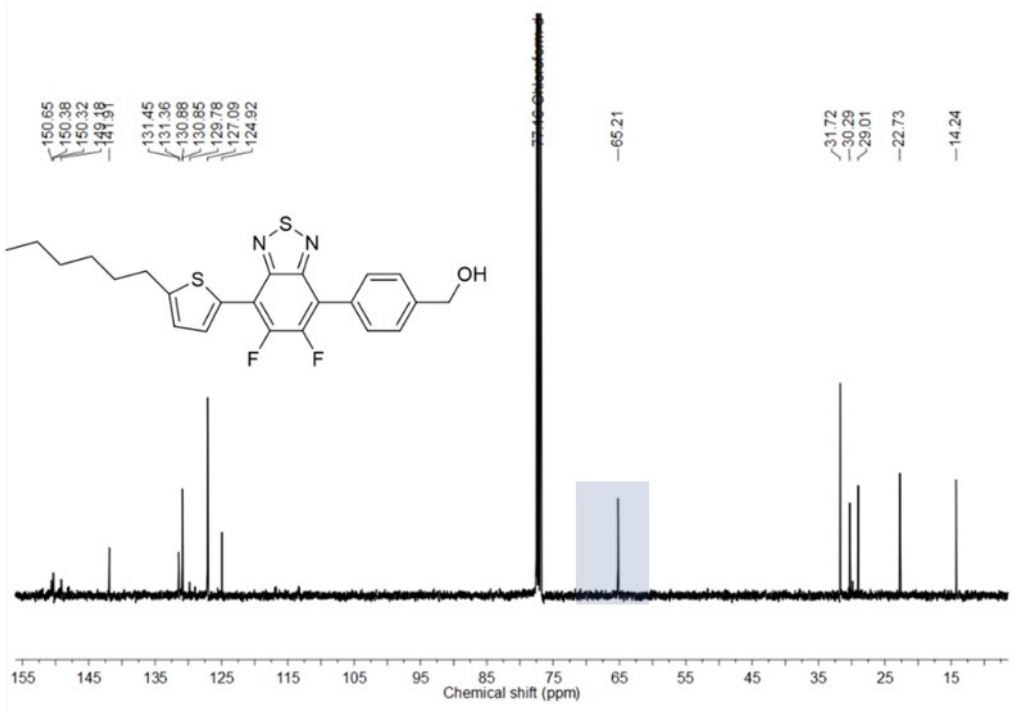


Figure S11. ^{13}C NMR spectrum of **6** in $CDCl_3$.

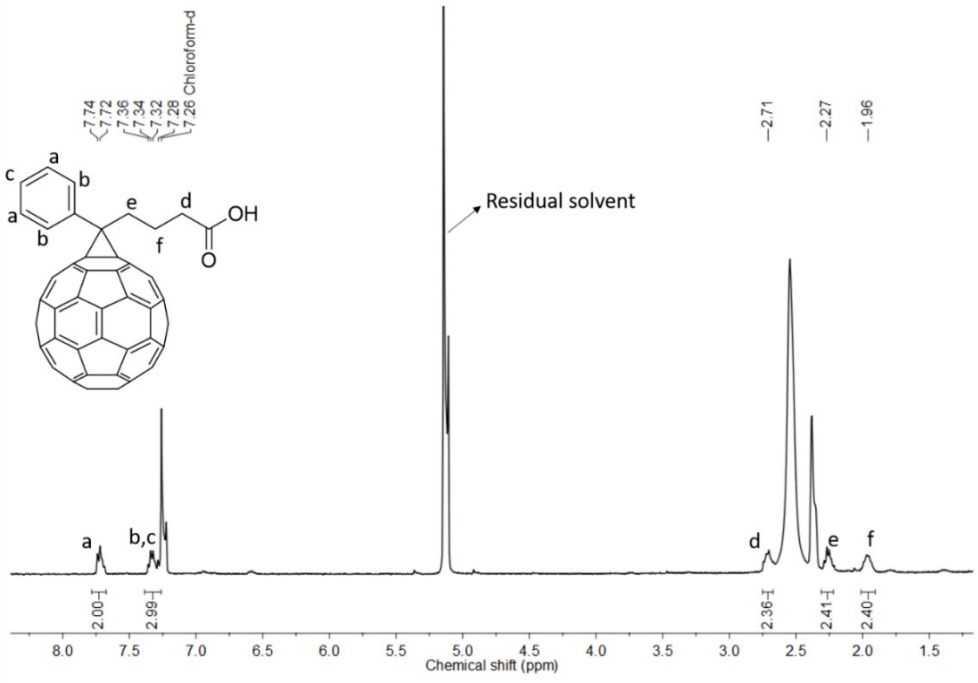


Figure S12. ^{1}H NMR of $PC_{61}BA$ in $CDCl_3$ with some DMSO-d_6 and CS_2.

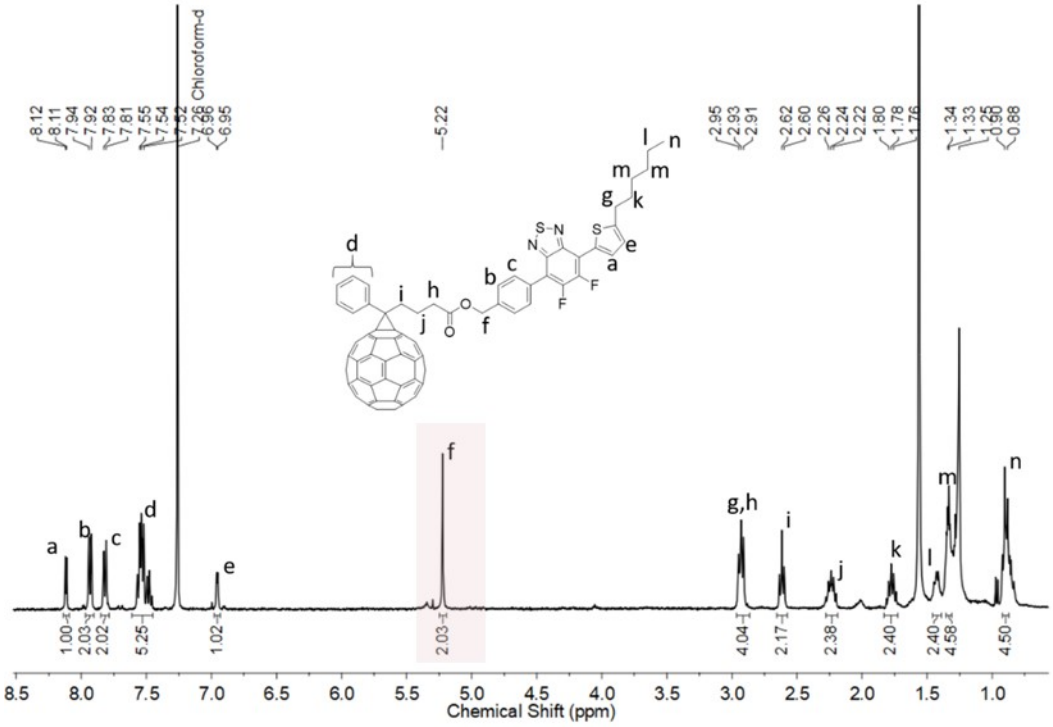


Figure S13. ^{1}H NMR of **7** in $CDCl_3$.

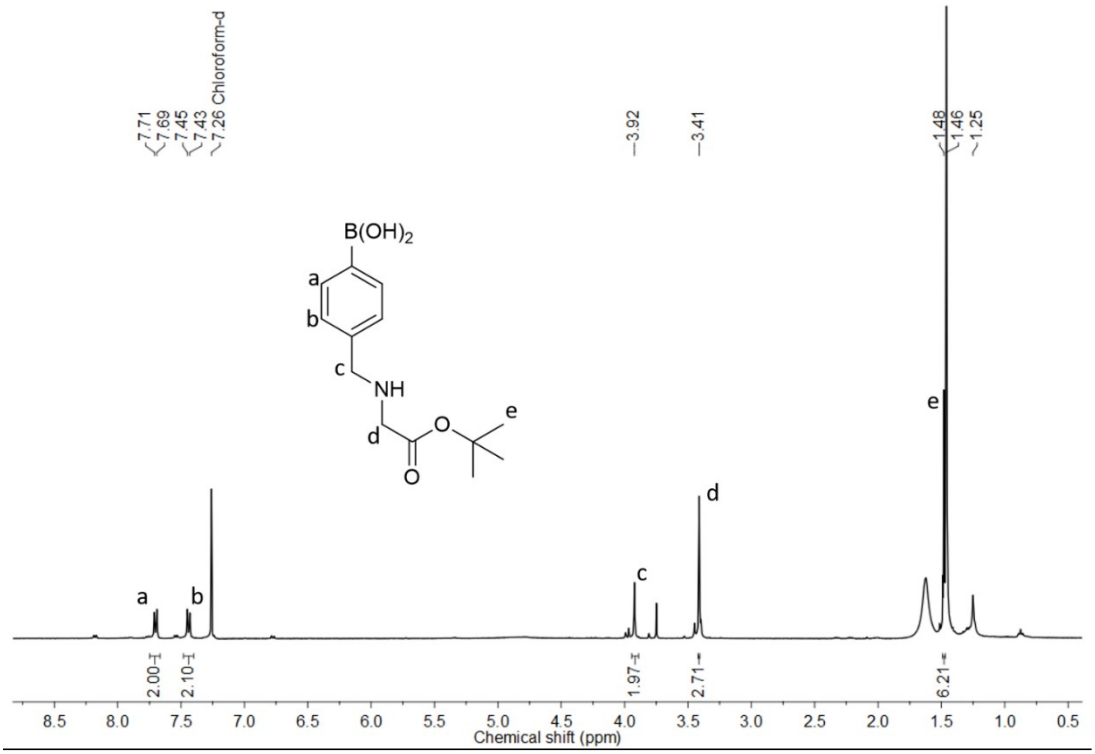


Figure S14. ^{1}H NMR spectrum of **8** in $CDCl_3$.

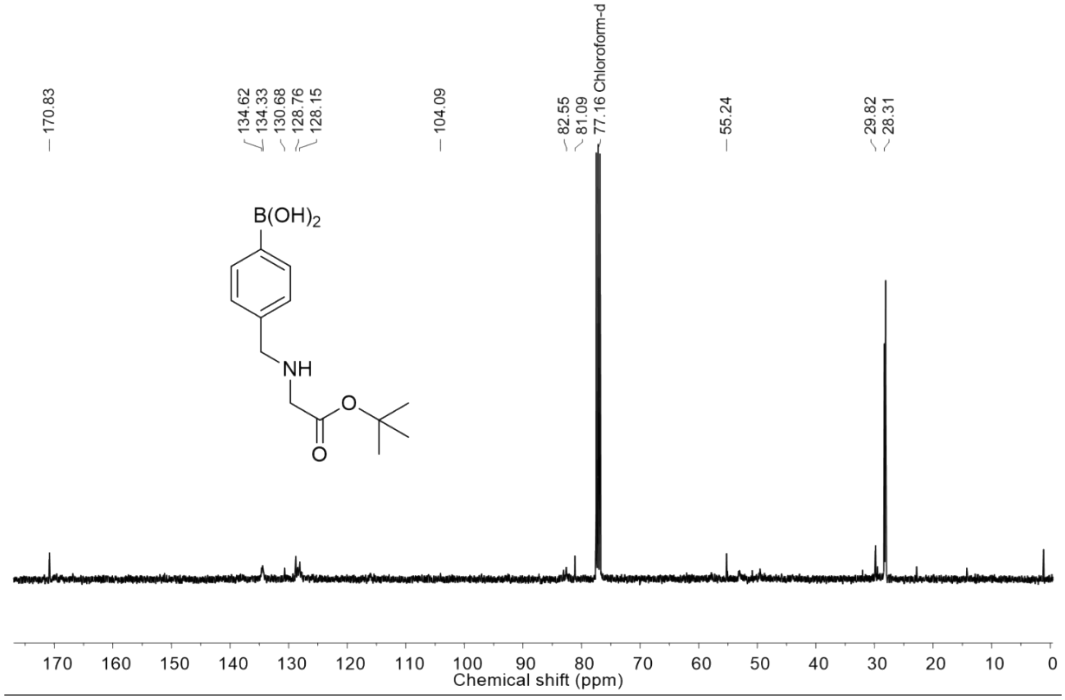


Figure S15. ^{13}C NMR spectrum of **8** in $CDCl_3$.

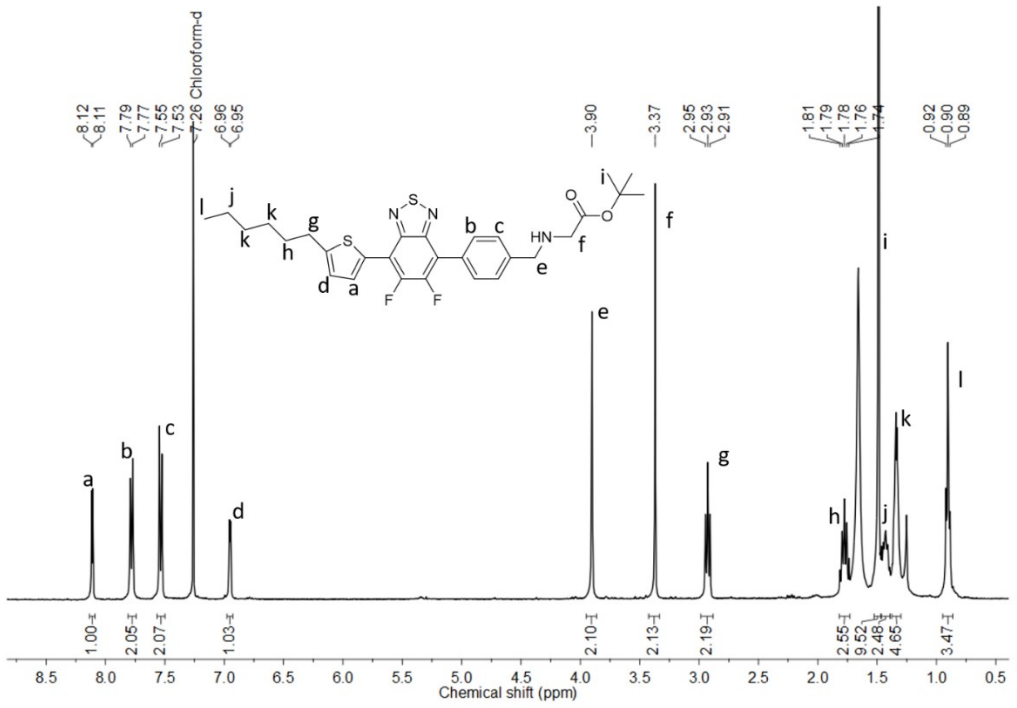


Figure S16. ^{1}H NMR of **9** in $CDCl_3$.

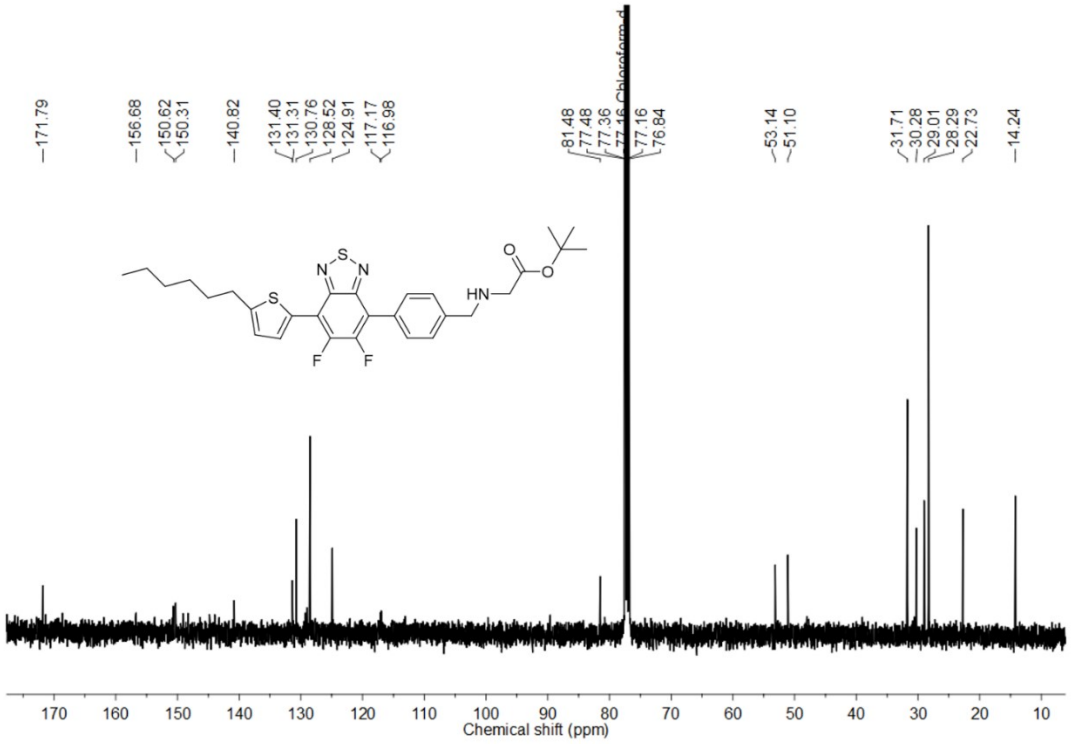


Figure S17. ^{13}C NMR of **9** in $CDCl_3$.

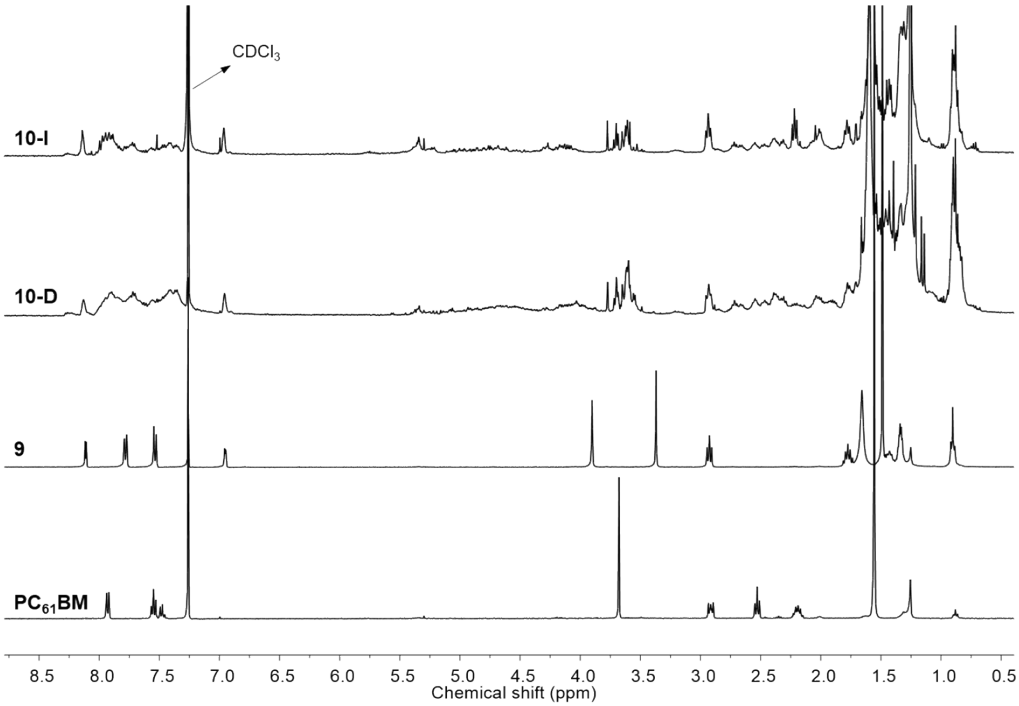


Figure S18. Stacked ^{1}H NMR spectra of $PC_{61}BM$, **9**, **10-D** and **10-I** in $CDCl_3$.

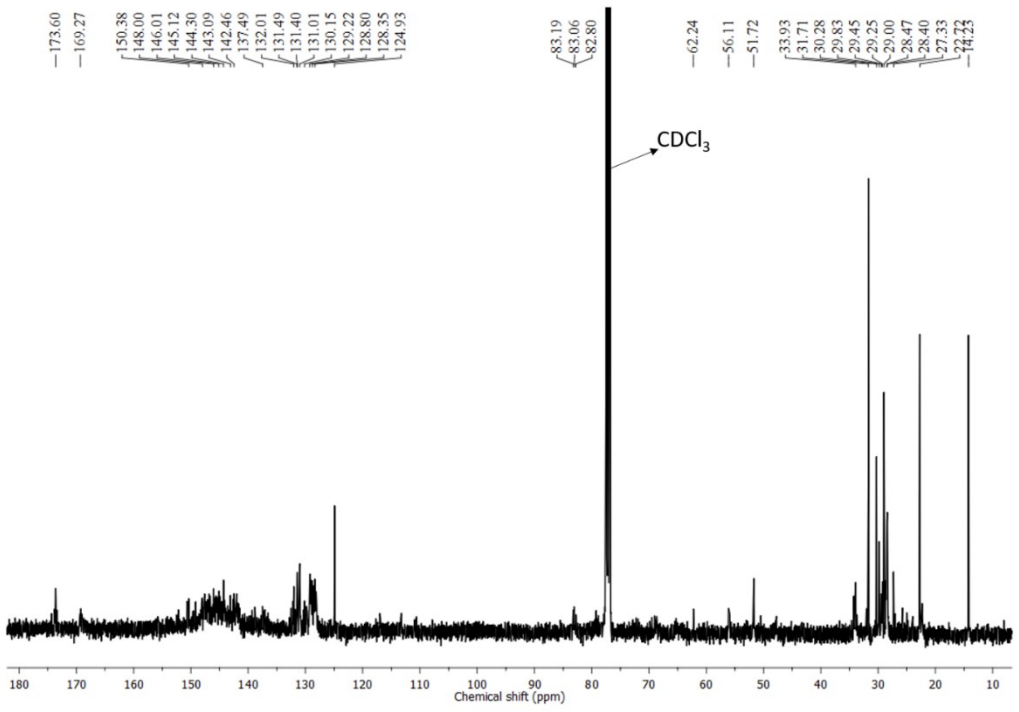


Figure S19. ^{13}C NMR spectrum of **10-I** in $CDCl_3$.

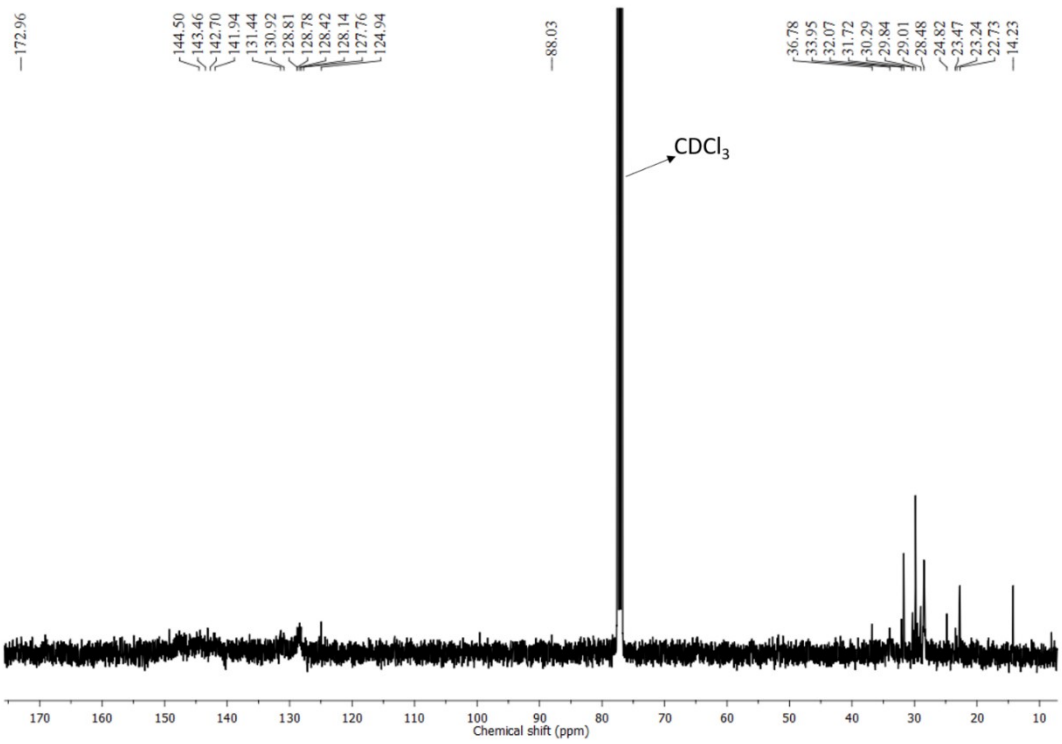


Figure S20. ^{13}C NMR spectrum of **10-D** in $CDCl_3$.

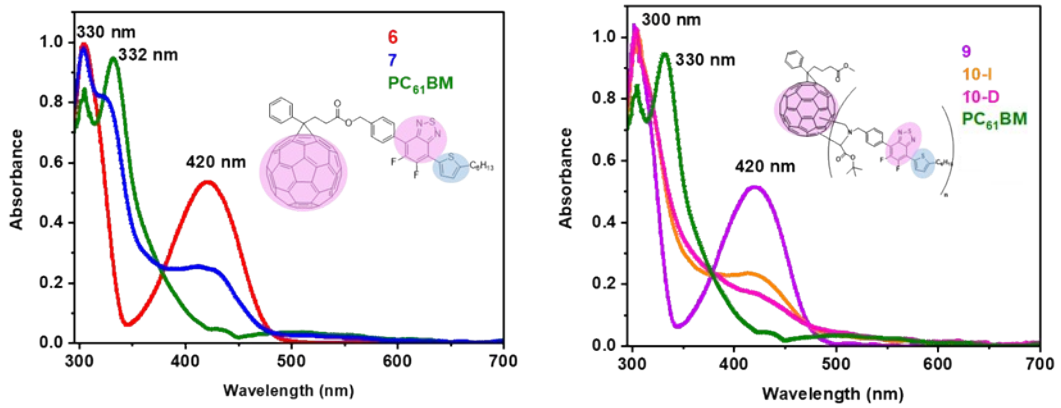


Figure S21. UV-visible spectra of (A) **6**, **7**, and $PC_{61}BM$ and (B) **9**, **10-I**, **10-D**, and $PC_{61}BM$ in ODCB (concentrations of 10^{-5} M).

Details of the Calculations

The initial geometry optimization calculations were performed employing the gradient corrected functional PBE[8] of Perdew, Burke and Ernzerhof. The def-SVP basis set[9] was used for all of the calculations. At this stage of the calculations, to increase the computational efficiency (without loss in accuracy), the resolution of the identity method[10] was used for the treatment of the two-electron integrals. The final geometry optimizations were further performed using Truhlar's meta-hybrid exchange–correlation functional M06,[11] and the same basis set. Tight convergence criteria were placed for the SCF energy (up to 10^{-7} Eh) and the one-electron density (rms of the density matrix up to 10^{-8}) as well as for the norm of the Cartesian gradient (residual forces both average and maximum smaller than 1.5×10^{-5} a.u.) and residual displacements (both average and maximum smaller than 6×10^{-5} a.u.). The UV-visible spectra have been produced by convoluting Gaussian functions with HWHM = 0.1 eV centered at the excitation wavenumbers.

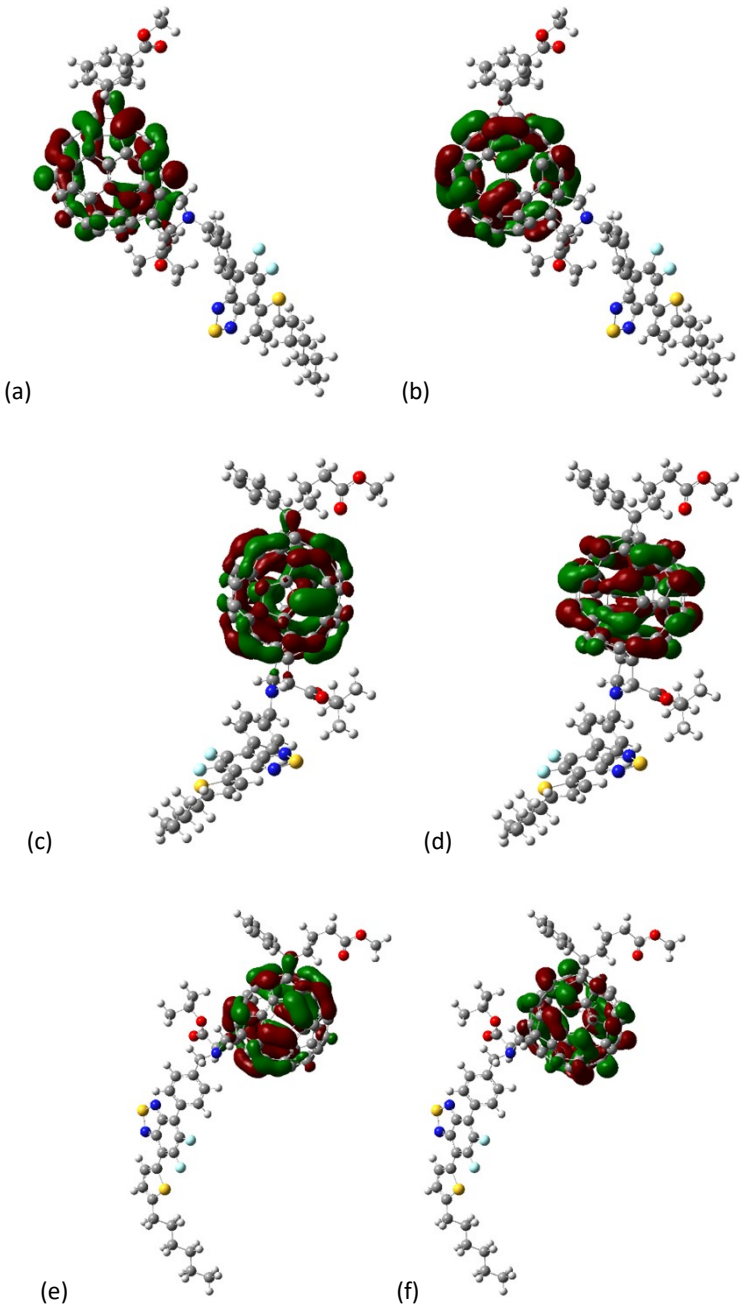


Figure S22. Isosurface of the **10-I** as different regio-isomers: (a) HOMO and (b) LUMO of **$PC_{61}BM$-1xBTF_2**, the (c) HOMO and (d) LUMO of **$PC_{61}BM$-1xBTF_2-*para*** structure, as well as the (e) HOMO and (f) LUMO of **$PC_{61}BM$-1xBTF_2@conf3** structure. Computed at the M06/def2-SVP level of theory.

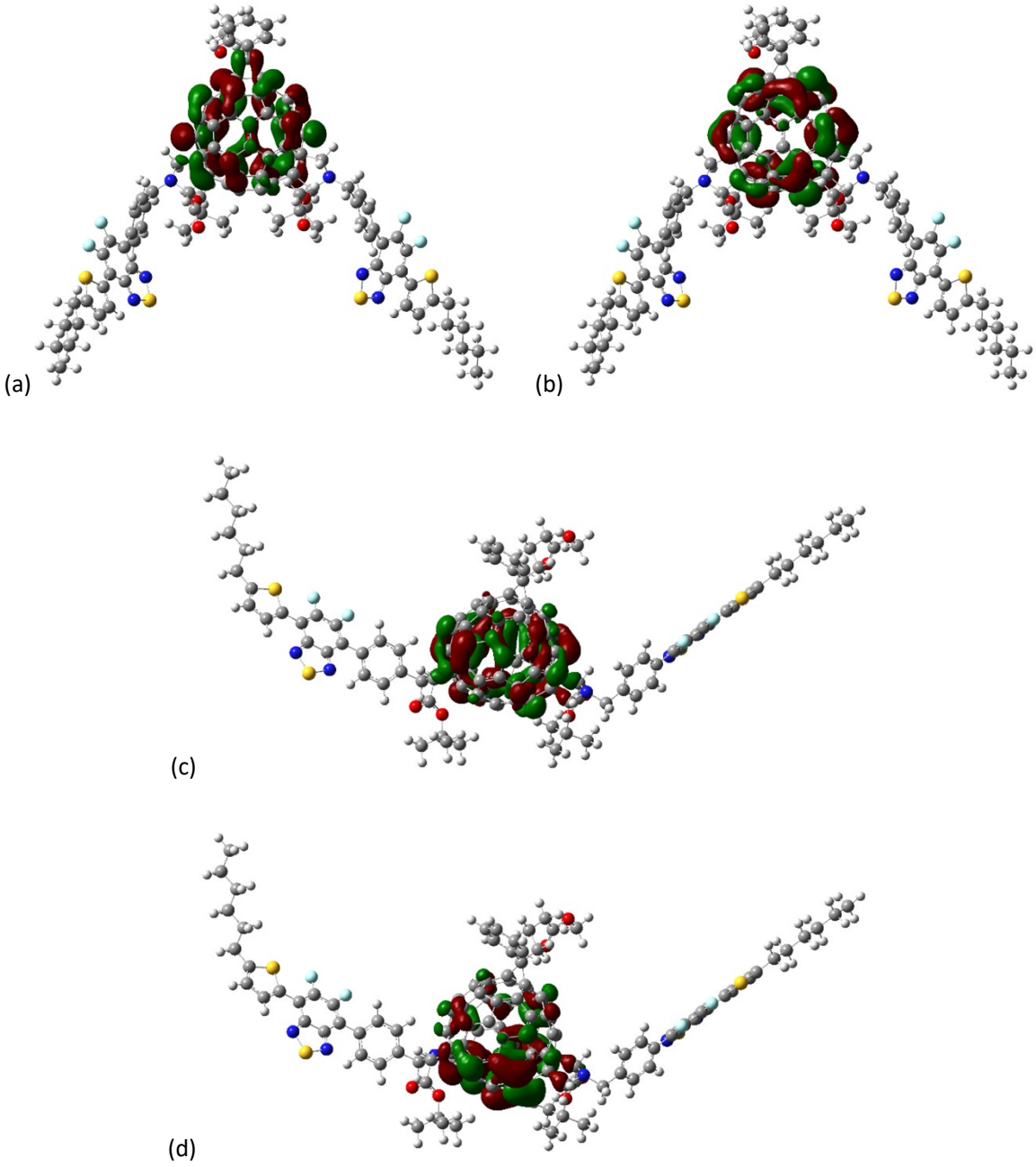


Figure S23. Isosurfaces of the **10-D** as different regio-isomers of doubly functionalized: (a) HOMO and (b) LUMO of **$PC_{61}BM$-2xBTF_2** and (c) HOMO and (d) LUMO of **$PC_{61}BM$-2xBTF_2@conf3**. Computed at the M06/def2-SVP level of theory.

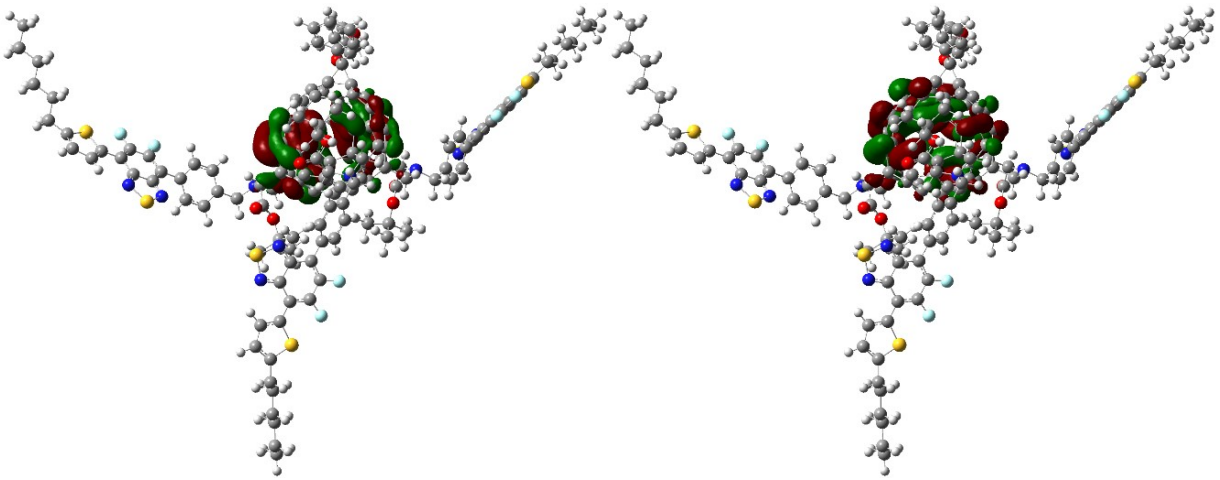


Figure S24. Isosurfaces of the **10-D** as different regio-isomers of triply functionalized: (left) HOMO and (right) LUMO of **$PC_{61}BM$-3xBTF_2**. Computed at the M06/def2-SVP level of theory.

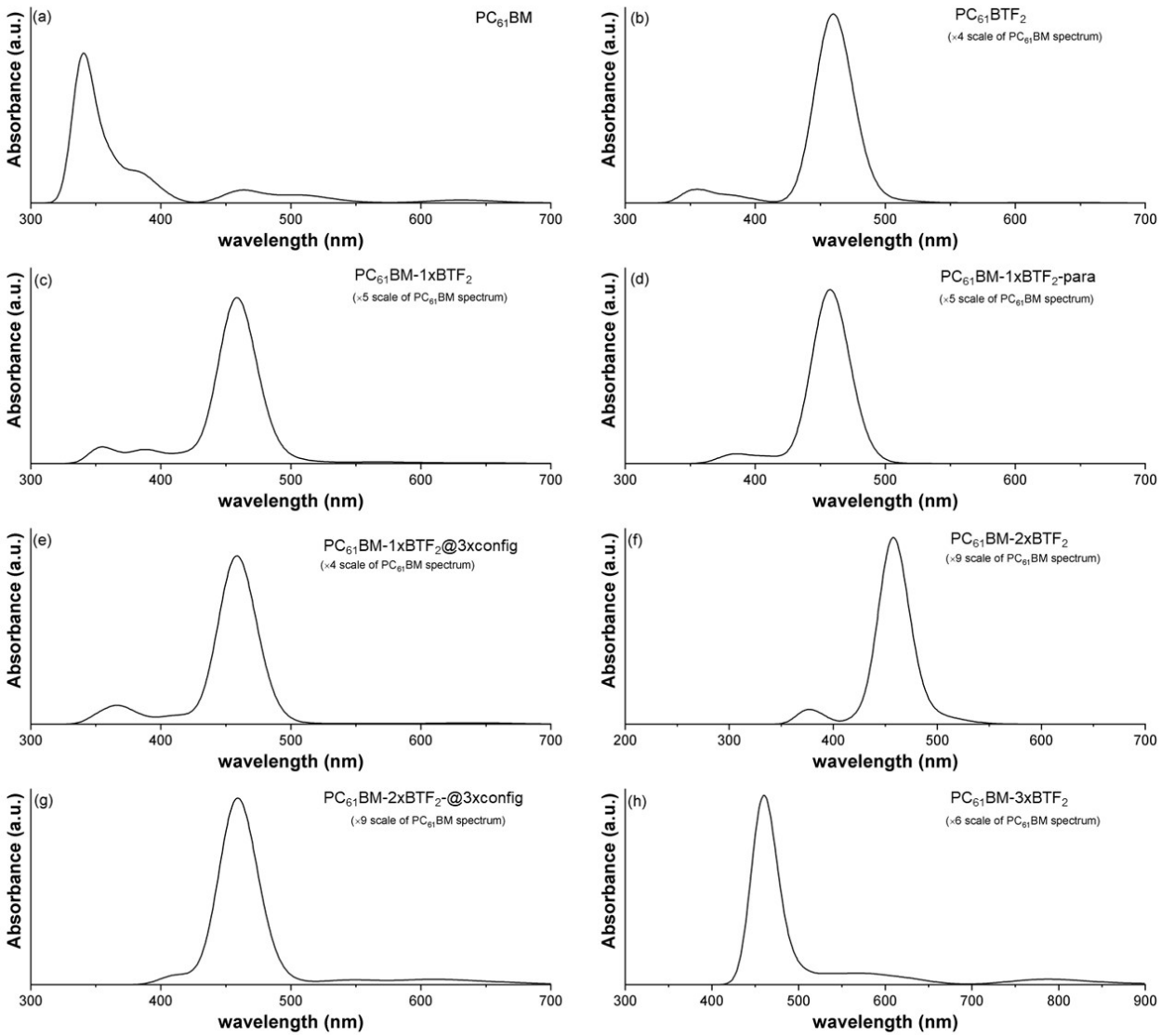


Figure S25. Theoretical UV-visible spectra of the reference structures (a) $PC_{61}BM$ and (b) **$PC_{61}BTF_2$**, as well as the functionalized $PC_{61}BM$ structures **10-I**: (c) **$PC_{61}BM\text{-}1xBTF_2$**, (d) **$PC_{61}BM\text{-}1xBTF_2$-*para*** and (e) **$PC_{61}BM\text{-}1xBTF_2$@config3**, the doubly functionalized structures **10-D**: (f) **$PC_{61}BM\text{-}2xBTF_2$** and (g) **$PC_{61}BM\text{-}2xBTF_2$@config3** and the triply-functionalized structure (h) **$PC_{61}BM\text{-}3xBTF_2$** (notice the wider x-axis scale). Computed at the M06/def2-SVP level of theory.

Excited States Results

In **Tables S1a-h** shows the computed quantities on the excited states of various fullerene adducts. For all structures 40 excited states were computed except for the largest structure, **$PC_{61}BM$-3xBTF_2**, for which 30 excited states were computed to reduce the computational cost. Along with the main contributions to the excitation, for each transition, the charge density as well as the change in charge density on each group is provided. Each structure is separated in the following groups (if they exist), **fullerene cage**, **$PC_{61}BM$**, **BTF_2** (all included). Excitations that result in considerable charge transfer are denoted as bold.

Table S1a. Characteristics details of the excited states of $PC_{61}BM$.

Excitation No.	Wavelength (nm)	*f*	Main Contributions	fullerene	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	631	0.0017	HOMO->LUMO (96%)	97-->100 (3)	3-->0 (-3)	0.484	5.519
2	619	0.0000	HOMO->L+1 (88%)	97-->100 (3)	3-->0 (-3)	0.036	5.503
3	590	0.0000	H-1->LUMO (95%)	100-->100 (0)	0-->0 (0)	0.036	5.498
4	589	0.0000	H-2->LUMO (95%)	100-->100 (0)	0-->0 (0)	0.000	5.503
5	565	0.0000	H-3->L+1 (49%), H-2->L+1 (37%), H-1->L+1 (13%)	100-->100 (0)	0-->0 (0)	0.051	5.503
6	555	0.0003	H-4->LUMO (10%), H-2->L+1 (15%), H-1->L+1 (51%), HOMO->L+2 (22%)	99-->99 (0)	1-->1 (0)	0.183	5.325
7	544	0.0000	H-3->LUMO (75%), H-1->L+2 (14%)	99-->99 (0)	1-->1 (0)	0.000	5.498
8	536	0.0002	H-3->L+1 (46%), H-2->L+1 (38%)	99-->100 (1)	1-->0 (-1)	0.137	5.536
9	515	0.0020	H-4->L+1 (16%), H-1->L+1 (16%), HOMO->L+2 (56%)	98-->99 (1)	2-->1 (-1)	0.465	5.922
10	514	0.0008	H-4->L+1 (57%), H-2->L+2 (15%), HOMO->L+2 (15%)	98-->99 (1)	2-->1 (-1)	0.295	5.767
11	504	0.0000	H-3->LUMO (15%), H-2->L+2 (15%), H-1->L+2 (66%)	100-->99 (-1)	0-->1 (1)	0.025	5.480
12	502	0.0014	H-3->L+2 (80%), H-2->L+2 (10%)	99-->98 (-1)	1-->2 (1)	0.388	5.482
13	490	0.0001	H-4->LUMO (87%)	97-->100 (3)	3-->0 (-3)	0.114	5.409

14	481	0.0014	H-4->L+1 (18%), H-3->L+2 (18%), H-2->L+2 (49%), H-1->L+2 (11%)	99-->99 (0)	1-->1 (0)	0.374	5.563
15	461	0.0066	H-4->L+2 (94%)	97-->98 (1)	3-->2 (-1)	0.804	5.559
16	402	0.0000	H-5->L+1 (61%), HOMO->L+4 (32%)	91-->100 (9)	9-->0 (-9)	0.057	5.514
17	398	0.0057	H-5->LUMO (66%), H-1->L+3 (15%)	91-->100 (9)	9-->0 (-9)	0.694	5.570
18	382	0.0118	HOMO->L+3 (75%)	95-->100 (5)	5-->0 (-5)	0.980	5.845
19	381	0.0019	H-5->L+2 (13%), H-3->L+3 (30%), H-2->L+3 (14%)	97-->99 (2)	3-->1 (-2)	0.397	5.901
20	377	0.0001	H-10->LUMO (20%), H-2->L+4 (28%), H-1->L+4 (14%)	98-->99 (1)	2-->1 (-1)	0.095	5.468
21	376	0.0002	H-5->L+1 (26%), HOMO->L+4 (43%)	92-->100 (8)	8-->0 (-8)	0.119	5.513
22	376	0.0001	H-12->LUMO (16%), H-3->L+3 (10%), H-1->L+4 (21%), HOMO->L+5 (15%)	94-->99 (5)	6-->1 (-5)	0.088	5.438
23	374	0.0008	H-3->L+3 (17%), H-2->L+3 (26%)	93-->100 (7)	7-->0 (-7)	0.252	5.737
24	365	0.0003	H-9->LUMO (54%), H-7->LUMO (12%), H-1->L+5 (19%)	89-->99 (10)	11-->1 (-10)	0.144	5.519
25	363	0.0051	H-6->LUMO (44%)	66-->99 (33)	34-->1 (-33)	0.627	5.645
26	361	0.0127	H-5->LUMO (20%), H-3->L+4 (13%), H-1->L+3 (33%)	92-->100 (8)	8-->0 (-8)	0.987	5.583
27	357	0.0023	H-8->LUMO (13%), H-6->L+1 (27%), H-5->L+2 (36%)	74-->99 (25)	26-->1 (-25)	0.415	5.105
28	353	0.0003	H-6->LUMO (11%), H-6->L+1 (25%), H-5->L+2 (12%), H-4->L+4 (11%)	70-->99 (29)	30-->1 (-29)	0.155	5.442
29	352	0.0009	H-6->L+2 (11%), H-4->L+3 (51%)	86-->99 (13)	14-->1 (-13)	0.254	5.536
30	349	0.0115	H-9->L+1 (12%), H-3->L+4 (17%), H-2->L+4 (15%), H-1->L+3 (10%)	93-->99 (6)	7-->1 (-6)	0.924	5.601
31	347	0.0001	H-14->LUMO (20%), H-10->L+1 (16%), H-7->LUMO (24%)	75-->99 (24)	25-->1 (-24)	0.084	5.499
32	347	0.0058	H-13->L+1 (10%), H-8->L+1 (11%), H-6->L+1 (13%), HOMO->L+3 (10%)	83-->99 (16)	17-->1 (-16)	0.655	5.452

33	344	0.0008	H-13->LUMO (10%), H-12->L+1 (11%), H-6->LUMO (19%)	80-->99 (19)	20-->1 (-19)	0.240	5.715
34	342	0.0010	H-11->L+1 (10%), H-10->L+1 (25%), H-7->LUMO (17%)	80-->100 (20)	20-->0 (-20)	0.268	5.492
35	341	0.0075	H-8->L+1 (31%)	95-->99 (4)	5-->1 (-4)	0.738	4.832
36	340	0.0316	H-10->LUMO (13%), H-9->L+1 (15%), H-3->L+4 (29%)	97-->99 (2)	3-->1 (-2)	1.512	5.678
37	339	0.0058	H-12->LUMO (17%), H-11->LUMO (10%), H-11->L+1 (13%), HOMO->L+5 (14%)	99-->99 (0)	1-->1 (0)	0.649	6.090
38	338	0.0158	H-8->LUMO (12%), H-8->L+1 (15%), H-1->L+4 (22%), HOMO->L+5 (17%)	97-->99 (2)	3-->1 (-2)	1.065	6.373
39	337	0.0101	H-12->LUMO (21%), H-11->L+1 (17%)	95-->99 (4)	5-->1 (-4)	0.852	4.882
40	335	0.0023	H-10->LUMO (11%), H-9->L+1 (43%), H-2->L+4 (20%)	97-->100 (3)	3-->0 (-3)	0.406	5.284

Table S1b. Characteristics details of the excited states of $PC_{61}BTF_2$.

Excitation No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	μ_{ge} (D)	μ_e (D)
1	628	0.0017	H-1->LUMO (95%)	97-->100 (3)	3-->0 (-3)	0.479	5.619
2	617	0.0000	H-1->L+1 (87%)	97-->100 (3)	3-->0 (-3)	0.025	5.527
3	591	0.0000	H-2->LUMO (96%)	100-->100 (0)	0-->0 (0)	0.036	5.527
4	588	0.0000	H-3->LUMO (94%)	100-->100 (0)	0-->0 (0)	0.000	5.523
5	565	0.0000	H-4->L+1 (46%), H-3->L+1 (52%)	100-->100 (0)	0-->0 (0)	0.051	5.537
6	555	0.0002	H-5->LUMO (10%), H-2->L+1 (69%), H-1->L+2 (19%)	99-->99 (0)	1-->1 (0)	0.161	5.691
7	543	0.0000	H-4->LUMO (71%), H-2->L+2 (17%)	99-->99 (0)	1-->1 (0)	0.036	5.508
8	535	0.0002	H-4->L+1 (48%), H-3->L+1 (41%)	99-->100 (1)	1-->0 (-1)	0.132	5.493
9	514	0.0014	H-5->L+1 (51%), H-3->L+2 (17%), H-1->L+2 (21%)	98-->99 (1)	2-->1 (-1)	0.390	5.814
10	513	0.0024	H-5->L+1 (25%), H-2->L+1 (17%), H-1->L+2 (50%)	98-->99 (1)	2-->1 (-1)	0.507	6.039
11	504	0.0000	H-4->LUMO (16%), H-2->L+2 (80%)	100-->99 (-1)	0-->1 (1)	0.025	5.520
12	501	0.0015	H-4->L+2 (79%), H-3->L+2 (11%)	99-->98 (-1)	1-->2 (1)	0.393	5.656

13	492	0.0000	HOMO->LUMO (99%)	1-->100 (99)	99-->0 (-99)	0.025	5.567
14	490	0.0002	H-5->LUMO (84%)	97-->100 (3)	3-->0 (-3)	0.157	5.384
15	480	0.0012	H-5->L+1 (15%), H-4->L+2 (15%), H-3->L+2 (56%)	90-->99 (9)	10-->1 (-9)	0.353	5.528
16	480	0.0001	HOMO->L+1 (91%)	9-->100 (91)	91-->0 (-91)	0.111	5.537
17	461	0.0058	H-5->L+2 (94%)	97-->98 (1)	3-->2 (-1)	0.756	5.605
18	460	0.4244	HOMO->L+3 (98%)	0-->0 (0)	100-->100 (0)	6.443	2.789
19	438	0.0000	HOMO->L+2 (100%)	0-->98 (98)	100-->2 (-98)	0.000	5.545
20	403	0.0001	H-8->L+1 (59%), H-1->L+5 (31%)	84-->100 (16)	16-->0 (-16)	0.080	5.569
21	398	0.0056	H-8->LUMO (63%), H-2->L+4 (18%)	84-->100 (16)	16-->0 (-16)	0.687	5.457
22	382	0.0107	H-1->L+4 (68%)	94-->100 (6)	6-->0 (-6)	0.934	5.232
23	381	0.0025	H-15->L+1 (15%), H-8->L+2 (12%), H-4->L+4 (25%), H-3->L+4 (18%)	94-->99 (5)	6-->1 (-5)	0.446	5.828
24	377	0.0000	H-17->LUMO (27%), H-3->L+5 (47%)	96-->99 (3)	4-->1 (-3)	0.062	5.511
25	377	0.0001	H-8->L+1 (24%), H-1->L+5 (41%)	92-->100 (8)	8-->0 (-8)	0.098	5.563
26	376	0.0002	H-16->LUMO (20%), H-2->L+5 (28%), H-1->L+6 (10%)	94-->99 (5)	6-->1 (-5)	0.132	5.669
27	374	0.0005	H-4->L+4 (21%), H-3->L+4 (28%), H-2->L+5 (10%)	89-->100 (11)	11-->0 (-11)	0.208	5.711
28	373	0.0000	H-1->L+3 (100%)	97-->0 (-97)	3-->100 (97)	0.000	5.530
29	365	0.0054	H-13->LUMO (13%), H-9->LUMO (28%), H-8->LUMO (10%)	73-->99 (26)	27-->1 (-26)	0.645	5.841
30	365	0.0016	H-13->LUMO (44%), H-9->LUMO (16%), H-2->L+6 (17%)	84-->99 (15)	16-->1 (-15)	0.349	5.403
31	361	0.0116	H-8->LUMO (15%), H-4->L+5 (13%), H-2->L+4 (39%)	87-->100 (13)	13-->0 (-13)	0.945	5.741
32	359	0.0015	H-9->L+1 (46%), H-8->L+2 (15%)	61-->99 (38)	39-->1 (-38)	0.343	5.251
33	355	0.0000	H-2->L+3 (99%)	100-->0 (-100)	0-->100 (100)	0.000	5.540
34	355	0.0014	H-9->L+1 (12%), H-8->L+2 (26%)	80-->99 (19)	20-->1 (-19)	0.323	5.243

35	355	0.0000	H-3->L+3 (99%)	100-->0 (-100)	0-->100 (100)	0.000	5.553
36	352	0.0013	H-9->L+2 (12%), H-5->L+4 (47%)	83-->99 (16)	17-->1 (-16)	0.307	5.494
37	349	0.0083	H-13->L+1 (14%), H-4->L+5 (14%), H-3->L+5 (14%)	90-->99 (9)	10-->1 (-9)	0.785	5.589
38	349	0.0002	H-4->L+3 (97%)	99-->3 (-96)	1-->97 (96)	0.119	5.470
39	349	0.0069	H-15->LUMO (11%), H-9->LUMO (15%)	78-->97 (19)	22-->3 (-19)	0.715	5.974
40	347	0.0038	H-19->LUMO (19%), H-17->L+1 (17%), H-11->LUMO (23%)	67-->99 (32)	33-->1 (-32)	0.532	5.645

Table S1c. Characteristics details of the excited states of $PC_{61}BM$-1xBTF_2.

Excit. No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	644	0.0020	HOMO->LUMO (97%)	97-->99 (2)	2-->0 (-2)	1-->0 (-1)	0.526	6.002
2	583	0.0014	H-3->LUMO (40%), HOMO->L+1 (45%)	98-->99 (1)	1-->1 (0)	1-->0 (-1)	0.409	5.900
3	567	0.0023	H-2->LUMO (62%), HOMO->L+1 (25%)	98-->99 (1)	1-->0 (-1)	1-->0 (-1)	0.525	5.259
4	566	0.0013	H-3->LUMO (49%), H-2->LUMO (19%), HOMO->L+1 (21%)	98-->99 (1)	1-->0 (-1)	1-->0 (-1)	0.394	5.914
5	533	0.0007	H-2->L+1 (82%)	98-->99 (1)	1-->1 (0)	1-->1 (0)	0.290	5.658
6	522	0.0003	H-3->L+1 (76%)	99-->99 (0)	1-->1 (0)	1-->1 (0)	0.194	5.356
7	515	0.0031	H-4->LUMO (73%)	96-->99 (3)	2-->1 (-1)	2-->0 (-2)	0.578	5.714
8	493	0.0081	HOMO->L+2 (75%)	97-->97 (0)	2-->2 (0)	2-->1 (-1)	0.919	6.077
9	485	0.0010	H-5->LUMO (15%), H-1->LUMO (77%)	21-->99 (78)	0-->0 (0)	79-->0 (-79)	0.319	5.375
10	484	0.0015	H-5->LUMO (54%), H-1->LUMO (22%)	76-->99 (23)	1-->1 (0)	23-->0 (-23)	0.394	5.691
11	479	0.0022	H-4->L+1 (62%)	96-->99 (3)	2-->1 (-1)	2-->1 (-1)	0.469	5.951
12	465	0.0025	H-5->L+1 (40%), H-3->L+2 (13%), H-2->L+2 (36%)	97-->98 (1)	1-->1 (0)	2-->1 (-1)	0.494	5.408
13	459	0.4527	H-1->L+3 (95%)	3-->3 (0)	0-->0 (0)	97-->97 (0)	6.645	3.408
14	457	0.0113	H-5->L+1 (25%), H-2->L+2 (46%)	92-->95 (3)	1-->1 (0)	7-->3 (-4)	1.046	6.333

15	455	0.0001	H-1->L+1 (96%)	4-->99 (95)	0-->1 (1)	96-->1 (-95)	0.092	5.600
16	450	0.0038	H-5->L+1 (18%), H-3->L+2 (69%)	98-->97 (-1)	1-->2 (1)	1-->1 (0)	0.601	5.650
17	425	0.0070	H-4->L+2 (91%)	95-->97 (2)	2-->2 (0)	3-->1 (-2)	0.793	4.961
18	***422***	***0.0153***	***H-6->LUMO (92%)***	***9-->99 (90)***	***0-->0 (0)***	***90-->1 (-89)***	***1.171***	***4.678***
19	408	0.0089	H-5->L+2 (83%)	93-->97 (4)	2-->2 (0)	5-->1 (-4)	0.880	5.803
20	406	0.0002	H-1->L+2 (95%)	1-->97 (96)	0-->2 (2)	99-->1 (-98)	0.144	5.678
21	405	0.0000	HOMO->L+3 (99%)	97-->0 (-97)	2-->0 (-2)	2-->100 (98)	0.000	5.540
22	403	0.0018	H-6->L+1 (83%)	14-->99 (85)	1-->1 (0)	86-->1 (-85)	0.390	5.715
23	394	0.0084	H-8->LUMO (54%), H-3->L+4 (18%)	79-->99 (20)	12-->0 (-12)	9-->1 (-8)	0.840	4.898
24	388	0.0211	HOMO->L+4 (74%)	94-->99 (5)	3-->0 (-3)	3-->0 (-3)	1.321	6.077
25	384	0.0062	H-11->LUMO (16%), H-2->L+4 (13%), HOMO->L+5 (41%)	93-->99 (6)	3-->1 (-2)	4-->1 (-3)	0.712	5.591
26	379	0.0001	H-2->L+3 (99%)	98-->1 (-97)	1-->0 (-1)	1-->99 (98)	0.062	5.593
27	377	0.0032	H-8->LUMO (16%), H-8->L+1 (51%), H-3->L+4 (10%)	82-->98 (16)	12-->1 (-11)	6-->1 (-5)	0.506	5.385
28	374	0.0000	H-3->L+3 (99%)	99-->1 (-98)	0-->0 (0)	1-->99 (98)	0.025	5.514
29	369	0.0080	H-17->LUMO (10%), H-3->L+5 (18%), H-2->L+4 (45%), HOMO->L+5 (11%)	95-->99 (4)	2-->1 (-1)	3-->1 (-2)	0.792	5.115
30	368	0.0030	HOMO->L+6 (42%)	88-->97 (9)	8-->1 (-7)	4-->3 (-1)	0.485	5.253
31	365	0.0005	H-6->L+2 (88%)	14-->97 (83)	0-->2 (2)	86-->1 (-85)	0.195	5.355
32	363	0.0021	H-15->LUMO (17%)	86-->98 (12)	10-->1 (-9)	4-->1 (-3)	0.407	5.671
33	361	0.0023	H-11->LUMO (30%), HOMO->L+5 (12%), HOMO->L+6 (23%)	86-->98 (12)	9-->1 (-8)	6-->2 (-4)	0.416	5.255
34	358	0.0074	H-14->LUMO (12%), H-4->L+4 (17%)	89-->99 (10)	7-->1 (-6)	4-->1 (-3)	0.751	4.864
35	355	0.0133	H-4->L+4 (25%)	82-->98 (16)	14-->1 (-13)	4-->2 (-2)	1.003	5.995
36	355	0.0004	H-4->L+3 (93%)	91-->2 (-89)	2-->0 (-2)	7-->98 (91)	0.167	5.652
37	353	0.0044	H-14->LUMO (10%), H-11->L+1 (15%), H-10->LUMO (14%), H-3->L+6 (20%)	82-->98 (16)	14-->1 (-13)	4-->2 (-2)	0.576	5.975

38	350	0.0104	H-11->L+1 (12%), H-8->L+1 (12%), H-3->L+4 (15%), H-2->L+5 (11%)	90-->99 (9)	6-->1 (-5)	4-->1 (-3)	0.878	6.171
39	349	0.0062	H-10->LUMO (10%), H-3->L+6 (10%), H-2->L+6 (23%)	83-->97 (14)	12-->1 (-11)	4-->2 (-2)	0.676	5.762
40	348	0.0025	H-11->L+1 (27%), H-10->LUMO (13%), H-4->L+4 (12%)	80-->99 (19)	15-->1 (-14)	5-->1 (-4)	0.431	5.644

Table S1d. Characteristics details of the excited states of $PC_{61}BM$-1xBTF_2-*para*.

Excit. No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	671	0.0000	HOMO->LUMO (98%)	98-->99 (1)	1-->0 (-1)	1-->0 (-1)	0.076	5.552
2	619	0.0000	H-3->LUMO (10%), H-2->LUMO (14%), HOMO->L+1 (68%)	98-->99 (1)	1-->0 (-1)	1-->1 (0)	0.025	5.536
3	608	0.0000	H-2->LUMO (73%), HOMO->L+1 (19%)	99-->99 (0)	0-->0 (0)	1-->0 (-1)	0.036	5.540
4	606	0.0000	H-3->LUMO (83%), H-2->LUMO (12%)	99-->99 (0)	0-->0 (0)	1-->0 (-1)	0.025	5.528
5	543	0.0001	H-4->LUMO (21%), H-4->L+1 (33%), H-3->L+1 (16%), H-2->L+1 (26%)	99-->99 (0)	0-->0 (0)	0-->1 (1)	0.088	5.514
6	539	0.0000	H-4->LUMO (67%), H-2->L+1 (12%)	99-->99 (0)	1-->0 (-1)	0-->0 (0)	0.051	5.542
7	532	0.0002	H-3->L+1 (51%), H-2->L+1 (42%)	99-->99 (0)	0-->0 (0)	1-->1 (0)	0.130	5.422
8	519	0.0000	H-4->L+1 (58%), H-3->L+1 (24%), H-2->L+1 (15%)	99-->99 (0)	1-->0 (-1)	1-->1 (0)	0.025	5.544
9	486	0.0005	H-1->LUMO (99%)	1-->99 (98)	0-->0 (0)	99-->0 (-99)	0.223	5.319
10	***458***	***0.1797***	***H-6->LUMO (33%), H-5->LUMO (38%), H-1->L+2 (22%)***	***40-->77 (37)***	***3-->0 (-3)***	***57-->22 (-35)***	***4.183***	***3.845***
11	458	0.3139	H-6->LUMO (10%), H-5->LUMO (10%), H-1->L+2 (76%)	12-->22 (10)	1-->0 (-1)	88-->78 (-10)	5.527	2.493
12	454	0.0002	H-1->L+1 (95%)	2-->99 (97)	0-->0 (0)	98-->1 (-97)	0.127	5.604
13	448	0.0006	H-6->L+1 (46%), H-5->L+1 (43%)	49-->99 (50)	3-->0 (-3)	47-->1 (-46)	0.246	5.498
14	439	0.0014	HOMO->L+3 (88%)	95-->96 (1)	2-->3 (1)	3-->1 (-2)	0.359	5.295
15	431	0.0022	H-6->LUMO (48%), H-5->LUMO (45%)	51-->99 (48)	3-->0 (-3)	46-->0 (-46)	0.450	5.483

16	425	0.0001	H-3->L+3 (38%), H-2->L+3 (59%)	99-->96 (-3)	0-->3 (3)	1-->1 (0)	0.076	5.539
17	413	0.0001	HOMO->L+2 (98%)	97-->1 (-96)	1-->0 (-1)	1-->99 (98)	0.098	5.621
18	412	0.0088	H-7->L+1 (12%), H-6->L+1 (26%), H-5->L+1 (27%), H-3->L+3 (18%), H-2->L+3 (10%)	68-->97 (29)	4-->1 (-3)	28-->2 (-26)	0.880	6.203
19	409	0.0064	H-6->L+1 (17%), H-5->L+1 (18%), H-4->L+3 (15%), H-3->L+3 (25%), H-2->L+3 (16%)	78-->98 (20)	2-->2 (0)	20-->1 (-19)	0.748	6.214
20	406	0.0018	H-4->L+3 (79%)	95-->97 (2)	2-->2 (0)	3-->1 (-2)	0.393	5.234
21	405	0.0004	H-7->LUMO (87%)	83-->99 (16)	13-->1 (-12)	3-->0 (-3)	0.178	5.526
22	397	0.0026	H-7->L+1 (59%), HOMO->L+4 (18%)	87-->99 (12)	10-->1 (-9)	3-->1 (-2)	0.465	5.107
23	387	0.0167	H-7->L+1 (15%), HOMO->L+4 (59%)	93-->93 (0)	5-->0 (-5)	2-->7 (5)	1.171	4.978
24	387	0.0011	H-2->L+2 (92%)	99-->6 (-93)	0-->0 (0)	1-->94 (93)	0.306	5.390
25	384	0.0000	H-3->L+2 (97%)	99-->1 (-98)	0-->0 (0)	1-->99 (98)	0.025	5.527
26	384	0.0006	HOMO->L+5 (63%)	94-->96 (2)	3-->1 (-2)	2-->4 (2)	0.219	5.595
27	381	0.0005	H-17->LUMO (15%), HOMO->L+6 (52%)	97-->97 (0)	2-->1 (-1)	2-->2 (0)	0.200	5.535
28	379	0.0023	H-15->L+1 (11%), H-4->L+4 (32%), H-3->L+4 (13%), H-2->L+4 (14%)	92-->99 (7)	3-->1 (-2)	5-->0 (-5)	0.435	5.240
29	374	0.0080	H-4->L+4 (27%), H-3->L+4 (22%), H-2->L+4 (14%)	92-->99 (7)	4-->0 (-4)	4-->1 (-3)	0.797	4.967
30	373	0.0002	H-16->LUMO (36%), HOMO->L+7 (12%)	95-->98 (3)	4-->1 (-3)	1-->1 (0)	0.130	5.659

Table S1e. Characteristics details of the excited states of $PC_{61}BM$-1xBTF_2@conf3.

Excit. No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	649	0.0016	HOMO->LUMO (72%), HOMO->L+1 (25%)	97-->99 (2)	2-->0 (-2)	1-->0 (-1)	0.465	5.830
2	638	0.0017	HOMO->LUMO (25%), HOMO->L+1 (70%)	97-->99 (2)	2-->0 (-2)	1-->1 (0)	0.483	5.710
3	594	0.0006	H-2->LUMO (92%)	99-->99 (0)	1-->0 (-1)	1-->0 (-1)	0.268	5.799
4	570	0.0013	H-3->LUMO (21%), H-2->L+1 (72%)	99-->99 (0)	1-->0 (-1)	1-->1 (0)	0.395	5.435

5	544	0.0000	H-4->LUMO (51%), H-3->LUMO (29%)	98-->99 (1)	1-->0 (-1)	1-->0 (-1)	0.072	5.511
6	532	0.0006	H-4->LUMO (11%), H-3->LUMO (32%), H-3->L+1 (33%), H-2->L+1 (19%)	99-->99 (0)	1-->0 (-1)	1-->1 (0)	0.260	5.436
7	530	0.0005	H-4->LUMO (33%), H-3->LUMO (12%), H-3->L+1 (44%)	98-->99 (1)	1-->0 (-1)	1-->1 (0)	0.248	5.332
8	510	0.0006	H-4->L+1 (83%)	96-->99 (3)	1-->0 (-1)	3-->1 (-2)	0.264	5.593
9	485	0.0042	HOMO->L+3 (86%)	97-->98 (1)	2-->1 (-1)	1-->1 (0)	0.656	6.152
10	475	0.0005	H-1->LUMO (99%)	0-->99 (99)	0-->0 (0)	100-->0 (-100)	0.226	5.320
11	464	0.0007	H-1->L+1 (98%)	0-->99 (99)	0-->0 (0)	100-->1 (-99)	0.255	5.779
12	***460***	***0.0586***	***H-6->L+1 (11%), H-5->L+1 (51%), H-2->L+3 (15%), H-1->L+2 (11%)***	***64-->87 (23)***	***1-->0 (-1)***	***35-->12 (-23)***	***2.395***	***7.857***
13	459	0.4073	H-1->L+2 (86%)	8-->12 (4)	0-->0 (0)	92-->88 (-4)	6.303	11.755
14	454	0.0045	H-5->LUMO (48%), H-5->L+1 (15%), H-2->L+3 (16%)	74-->99 (25)	1-->1 (0)	25-->1 (-24)	0.657	5.012
15	449	0.0011	H-3->L+3 (82%)	98-->98 (0)	1-->1 (0)	2-->1 (-1)	0.329	5.375
16	442	0.0111	H-5->LUMO (24%), H-2->L+3 (48%)	88-->98 (10)	1-->1 (0)	11-->1 (-10)	1.021	5.632
17	425	0.0067	H-4->L+3 (85%)	96-->98 (2)	2-->1 (-1)	2-->1 (-1)	0.778	5.995
18	416	0.0000	HOMO->L+2 (99%)	97-->0 (-97)	2-->0 (-2)	1-->100 (99)	0.051	5.500
19	415	0.0009	H-6->LUMO (81%), H-5->LUMO (13%)	36-->99 (63)	1-->0 (-1)	63-->0 (-63)	0.277	5.527
20	***411***	***0.0159***	***H-6->L+1 (75%), H-5->L+1 (19%)***	***39-->99 (60)***	***1-->0 (-1)***	***61-->1 (-60)***	***1.178***	***6.325***
21	405	0.0022	H-7->LUMO (13%), H-7->L+1 (31%), HOMO->L+4 (32%)	92-->98 (6)	5-->1 (-4)	4-->1 (-3)	0.439	5.734
22	396	0.0026	H-7->LUMO (47%), HOMO->L+5 (10%)	87-->98 (11)	5-->1 (-4)	8-->1 (-7)	0.469	5.282
23	390	0.0005	H-1->L+3 (83%)	11-->98 (87)	0-->1 (1)	88-->1 (-87)	0.199	5.354
24	389	0.0050	H-5->L+3 (47%), H-1->L+3 (16%)	61-->98 (37)	3-->1 (-2)	36-->1 (-35)	0.641	4.961
25	387	0.0000	H-2->L+2 (99%)	99-->0 (-99)	1-->0 (-1)	1-->100 (99)	0.000	5.542
26	384	0.0022	H-10->LUMO (10%), H-10->L+1 (15%), HOMO->L+4 (10%), HOMO->L+5 (23%)	89-->97 (8)	6-->1 (-5)	5-->2 (-3)	0.428	5.515

27	380	0.0080	H-10->LUMO (17%), H-10->L+1 (11%), H-7->L+1 (10%)	89-->98 (9)	9-->1 (-8)	2-->1 (-1)	0.806	5.766
28	375	0.0000	H-3->L+2 (99%)	99-->0 (-99)	0-->0 (0)	1-->100 (99)	0.025	5.540
29	373	0.0147	H-10->L+1 (32%), H-7->LUMO (12%), HOMO->L+4 (18%), HOMO->L+5 (16%)	91-->98 (7)	7-->1 (-6)	2-->1 (-1)	1.081	4.469
30	370	0.0043	H-7->L+1 (16%), H-2->L+4 (26%), HOMO->L+5 (24%)	94-->97 (3)	5-->1 (-4)	2-->2 (0)	0.584	5.417
31	369	0.0035	H-7->L+1 (18%), H-2->L+4 (24%), HOMO->L+4 (18%)	92-->98 (6)	6-->1 (-5)	2-->1 (-1)	0.522	5.735
32	366	0.0000	H-4->L+2 (99%)	98-->0 (-98)	1-->0 (-1)	1-->100 (99)	0.025	5.511
33	365	0.0164	H-15->LUMO (10%), HOMO->L+6 (41%)	91-->98 (7)	7-->1 (-6)	2-->1 (-1)	1.127	6.565
34	363	0.0014	H-2->L+5 (42%), HOMO->L+7 (12%)	93-->97 (4)	5-->1 (-4)	1-->2 (1)	0.332	5.533
35	360	0.0090	H-11->LUMO (32%), HOMO->L+6 (12%)	75-->98 (23)	24-->1 (-23)	1-->1 (0)	0.829	6.225
36	358	0.0028	H-14->LUMO (13%), H-4->L+4 (10%), H-3->L+4 (16%)	90-->98 (8)	9-->1 (-8)	1-->1 (0)	0.464	5.699
37	352	0.0136	H-10->LUMO (22%), H-2->L+5 (20%), H-2->L+6 (13%)	92-->97 (5)	6-->1 (-5)	2-->1 (-1)	1.006	6.039
38	350	0.0008	H-3->L+4 (14%), H-3->L+5 (21%)	84-->97 (13)	8-->1 (-7)	8-->2 (-6)	0.238	5.554
39	348	0.0007	H-6->L+3 (65%), H-5->L+3 (14%)	46-->95 (49)	1-->1 (0)	53-->4 (-49)	0.224	5.361
40	347	0.0025	H-6->L+2 (54%), H-5->L+2 (38%)	45-->3 (-42)	1-->0 (-1)	54-->97 (43)	0.425	5.132

Table S1f. Characteristics details of the excited states of $PC_{61}BM$-2xBTF_2.

Excit. No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	566	0.0001	HOMO->LUMO (87%)	96-->94 (-2)	2-->1 (-1)	1-->5 (4)	0.084	5.526
2	564	0.0003	H-1->LUMO (90%)	97-->96 (-1)	1-->1 (0)	2-->3 (1)	0.195	5.530
3	519	0.0109	HOMO->L+1 (52%), HOMO->L+2 (13%), HOMO->L+3 (24%)	96-->47 (-49)	2-->1 (-1)	1-->52 (51)	1.096	5.833
4	509	0.0118	H-1->L+1 (53%), H-1->L+2 (13%), H-1->L+3 (24%)	97-->47 (-50)	1-->1 (0)	2-->52 (50)	1.133	5.167
5	493	0.0092	H-4->LUMO (19%), HOMO->L+4 (77%)	96-->97 (1)	2-->0 (-2)	1-->2 (1)	0.981	4.643

6	488	0.0134	H-5->LUMO (10%), H-1->L+4 (84%)	97-->97 (0)	1-->0 (-1)	2-->2 (0)	1.181	5.894
7	483	0.0137	H-4->LUMO (72%), HOMO->L+4 (15%)	97-->95 (-2)	1-->1 (0)	2-->5 (3)	1.187	4.607
8	477	0.0047	H-5->LUMO (83%)	96-->98 (2)	1-->1 (0)	3-->2 (-1)	0.687	5.341
9	***463***	***0.0326***	***H-4->L+1 (53%), H-4->L+2 (13%), H-4->L+3 (24%)***	***95-->45 (-50)***	***1-->1 (0)***	***4-->54 (50)***	***1.790***	***3.837***
10	***458***	***0.6000***	***H-3->L+1 (17%), H-3->L+2 (26%), H-2->L+2 (14%), H-2->L+3 (30%)***	***3-->28 (25)***	***0-->1 (1)***	***97-->71 (-26)***	***7.644***	***13.146***
11	***457***	***0.3092***	***H-3->L+1 (16%), H-3->L+2 (30%), H-2->L+2 (12%), H-2->L+3 (32%)***	***1-->28 (27)***	***0-->1 (1)***	***99-->72 (-27)***	***5.481***	***7.256***
12	445	0.0070	H-5->L+1 (43%), H-5->L+2 (11%), H-5->L+3 (20%), H-4->L+4 (18%)	96-->55 (-41)	1-->1 (0)	3-->44 (41)	0.812	5.696
13	436	0.0015	H-6->LUMO (90%)	88-->98 (10)	1-->1 (0)	11-->2 (-9)	0.374	5.893
14	430	0.0218	H-5->L+1 (11%), H-4->L+4 (74%)	96-->87 (-9)	1-->1 (0)	3-->12 (9)	1.411	5.527
15	426	0.0157	H-5->L+4 (83%)	95-->93 (-2)	1-->0 (-1)	4-->6 (2)	1.193	5.441
16	425	0.0000	H-1->L+3 (22%), HOMO->L+2 (17%), HOMO->L+3 (42%)	97-->26 (-71)	2-->1 (-1)	2-->74 (72)	0.062	5.499
17	424	0.0000	H-1->L+1 (21%), H-1->L+2 (37%), HOMO->L+1 (12%), HOMO->L+2 (21%)	97-->29 (-68)	1-->1 (0)	2-->70 (68)	0.044	5.504
18	422	0.0000	H-1->L+1 (12%), H-1->L+2 (21%), HOMO->L+1 (21%), HOMO->L+2 (37%)	97-->29 (-68)	2-->1 (-1)	2-->70 (68)	0.044	5.504
19	421	0.0000	H-1->L+2 (17%), H-1->L+3 (43%), HOMO->L+3 (22%)	97-->26 (-71)	1-->1 (0)	2-->74 (72)	0.051	5.506
20	420	0.0001	H-2->LUMO (98%)	0-->98 (98)	0-->1 (1)	100-->2 (-98)	0.111	5.564
21	418	0.0001	H-3->LUMO (98%)	0-->98 (98)	0-->1 (1)	100-->2 (-98)	0.098	5.505
22	403	0.0002	H-6->L+1 (50%), H-6->L+2 (13%), H-6->L+3 (23%)	89-->48 (-41)	1-->1 (0)	10-->51 (41)	0.116	5.610
23	396	0.0002	H-2->L+1 (60%), H-2->L+2 (12%), H-2->L+3 (27%)	0-->43 (43)	0-->1 (1)	100-->56 (-44)	0.142	5.612
24	395	0.0003	H-3->L+1 (58%), H-3->L+2 (17%),	0-->42 (42)	0-->1 (1)	100-->57 (-43)	0.148	5.435

			H-3->L+3 (24%)					
25	390	0.0014	H-6->L+4 (69%)	83-->97 (14)	2-->0 (-2)	15-->2 (-13)	0.342	5.635
26	***387***	***0.0166***	***H-7->LUMO (77%)***	***22-->97 (75)***	***0-->1 (1)***	***77-->2 (-75)***	***1.171***	***5.962***
27	***385***	***0.0209***	***H-8->LUMO (68%)***	***31-->97 (66)***	***1-->1 (0)***	***68-->2 (-66)***	***1.310***	***4.976***
28	385	0.0000	H-2->L+1 (30%), H-2->L+2 (60%)	1-->28 (27)	0-->1 (1)	99-->71 (-28)	0.000	5.542
29	384	0.0000	H-4->L+2 (27%), H-4->L+3 (64%)	96-->25 (-71)	1-->1 (0)	2-->74 (72)	0.000	5.546
30	384	0.0000	H-4->L+1 (33%), H-4->L+2 (57%)	96-->29 (-67)	1-->1 (0)	3-->70 (67)	0.025	5.554
31	384	0.0000	H-3->L+2 (25%), H-3->L+3 (67%)	0-->26 (26)	0-->1 (1)	100-->74 (-26)	0.000	5.543
32	383	0.0008	H-8->LUMO (19%), H-1->L+5 (12%), HOMO->L+5 (10%), HOMO->L+6 (26%)	65-->96 (31)	2-->1 (-1)	33-->3 (-30)	0.263	5.654
33	382	0.0000	H-2->L+4 (95%)	2-->98 (96)	0-->0 (0)	98-->2 (-96)	0.062	5.581
34	381	0.0001	H-3->L+4 (94%)	3-->98 (95)	0-->0 (0)	97-->2 (-95)	0.084	5.612
35	380	0.0019	HOMO->L+5 (66%), HOMO->L+6 (11%)	93-->94 (1)	3-->1 (-2)	5-->6 (1)	0.394	5.422
36	374	0.0000	H-5->L+2 (35%), H-5->L+3 (59%)	96-->24 (-72)	1-->1 (0)	3-->76 (73)	0.036	5.545
37	374	0.0000	H-5->L+1 (36%), H-5->L+2 (50%), H-5->L+3 (13%)	96-->31 (-65)	1-->1 (0)	3-->68 (65)	0.025	5.531
38	373	0.0188	H-1->L+5 (64%), HOMO->L+6 (15%)	96-->95 (-1)	2-->1 (-1)	3-->5 (2)	1.223	5.582
39	372	0.0276	H-1->L+6 (78%)	95-->96 (1)	1-->1 (0)	4-->3 (-1)	1.478	4.298
40	368	0.0085	H-4->L+6 (15%), H-1->L+8 (11%), HOMO->L+7 (43%)	87-->91 (4)	3-->1 (-2)	10-->8 (-2)	0.814	5.463

Table S1g. Characteristics details of the excited states of $PC_{61}BM$-2xBTF_2@conf3.

Excit. No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	1063	0.0024	HOMO->LUMO (86%)	97-->97 (0)	0-->0 (0)	3-->3 (0)	0.731	5.219
2	1044	0.0040	HOMO->L+1 (90%)	97-->97 (0)	0-->0 (0)	3-->2 (-1)	0.940	6.472
3	956	0.0005	H-1->LUMO (78%), HOMO->LUMO (12%)	97-->97 (0)	0-->0 (0)	2-->3 (1)	0.319	5.324
4	868	0.0071	H-1->L+1 (86%)	97-->97 (0)	0-->0 (0)	2-->2 (0)	1.143	6.041
5	660	0.0063	H-4->LUMO (76%), H-4->L+1 (11%)	95-->97 (2)	3-->0 (-3)	3-->3 (0)	0.941	5.981
6	655	0.0028	H-4->LUMO (15%), H-4->L+1 (77%)	95-->97 (2)	3-->0 (-3)	3-->2 (-1)	0.619	5.713

7	623	0.0062	H-5->LUMO (77%), HOMO->L+2 (11%)	94-->97 (3)	2-->0 (-2)	4-->3 (-1)	0.908	4.931
8	607	0.0150	H-5->L+1 (36%), HOMO->L+2 (41%)	95-->96 (1)	1-->0 (-1)	4-->3 (-1)	1.389	6.664
9	599	0.0031	H-5->L+1 (50%), HOMO->L+2 (39%)	95-->96 (1)	1-->0 (-1)	4-->3 (-1)	0.629	5.180
10	589	0.0014	H-1->L+2 (87%)	97-->96 (-1)	0-->1 (1)	2-->4 (2)	0.412	5.205
11	555	0.0123	H-6->LUMO (65%), H-6->L+1 (21%)	64-->97 (33)	3-->0 (-3)	34-->3 (-31)	1.204	4.769
12	545	0.0006	H-6->LUMO (14%), H-2->LUMO (40%), H-2->L+1 (33%)	16-->97 (81)	1-->0 (-1)	84-->3 (-81)	0.267	5.538
13	542	0.0065	H-6->L+1 (54%), H-2->LUMO (23%)	48-->97 (49)	2-->0 (-2)	50-->3 (-47)	0.865	4.982
14	541	0.0026	H-3->LUMO (86%)	4-->97 (93)	0-->0 (0)	95-->3 (-92)	0.551	6.047
15	537	0.0011	H-2->LUMO (29%), H-2->L+1 (59%)	6-->97 (91)	0-->0 (0)	93-->2 (-91)	0.353	5.279
16	519	0.0000	H-3->L+1 (97%)	1-->97 (96)	0-->0 (0)	99-->2 (-97)	0.072	5.603
17	513	0.0038	H-8->LUMO (14%), H-7->LUMO (73%)	13-->97 (84)	0-->0 (0)	87-->3 (-84)	0.648	4.913
18	508	0.0031	H-8->LUMO (32%), H-8->L+1 (40%), H-7->L+1 (17%)	26-->97 (71)	1-->0 (-1)	72-->3 (-69)	0.576	5.303
19	494	0.0008	HOMO->L+3 (97%)	97-->2 (-95)	0-->0 (0)	3-->98 (95)	0.295	5.821
20	484	0.0005	HOMO->L+4 (92%)	97-->1 (-96)	0-->0 (0)	3-->99 (96)	0.233	5.332
21	481	0.0097	H-9->L+1 (12%), H-8->LUMO (26%), H-8->L+1 (17%), H-7->LUMO (14%), HOMO->L+5 (11%)	50-->96 (46)	2-->1 (-1)	48-->3 (-45)	0.996	6.381
22	480	0.0008	H-4->L+2 (74%)	88-->95 (7)	3-->1 (-2)	10-->4 (-6)	0.291	5.759
23	***475***	***0.0139***	***H-9->L+1 (23%), H-8->LUMO (12%), H-7->L+1 (28%), H-4->L+2 (11%)***	***58-->97 (39)***	***2-->1 (-1)***	***40-->3 (-37)***	***1.187***	***4.811***
24	468	0.0033	H-9->LUMO (59%), H-8->L+1 (11%), H-7->L+1 (11%)	75-->97 (22)	2-->0 (-2)	23-->3 (-20)	0.576	5.802
25	468	0.0045	H-1->L+3 (96%)	97-->2 (-95)	0-->0 (0)	3-->98 (95)	0.671	4.915
26	462	0.0002	H-1->L+4 (93%)	98-->0 (-98)	0-->0 (0)	2-->100 (98)	0.137	5.443
27	460	0.5189	H-3->L+3 (66%), H-2->L+4 (11%)	14-->22 (8)	0-->0 (0)	85-->78 (-7)	7.123	12.577
28	459	0.1518	H-9->LUMO (12%), H-3->L+3 (11%), HOMO->L+5 (46%)	69-->77 (8)	1-->2 (1)	31-->21 (-10)	3.851	9.340
29	458	0.2521	H-3->L+3 (17%), H-2->L+4 (78%)	2-->3 (1)	0-->0 (0)	98-->97 (-1)	4.954	5.277
30	456	0.0070	H-9->L+1 (35%), H-7->L+1 (30%)	58-->95 (37)	2-->1 (-1)	41-->5 (-36)	0.823	5.016

31	446	0.0074	H-10->LUMO (25%), H-1->L+5 (48%)	92-->96 (4)	2-->2 (0)	6-->3 (-3)	0.838	6.130
32	441	0.0033	H-10->LUMO (14%), H-5->L+2 (27%), H-1->L+5 (26%)	93-->96 (3)	2-->1 (-1)	5-->3 (-2)	0.553	5.952
33	435	0.0025	H-10->L+1 (66%)	87-->97 (10)	3-->0 (-3)	10-->2 (-8)	0.486	5.127
34	434	0.0088	H-10->LUMO (11%), H-5->L+2 (40%), HOMO->L+6 (13%)	91-->96 (5)	3-->1 (-2)	6-->3 (-3)	0.899	6.268
35	425	0.0084	H-10->LUMO (30%), HOMO->L+6 (29%)	88-->97 (9)	5-->1 (-4)	7-->2 (-5)	0.872	5.443
36	422	0.0010	H-13->LUMO (39%)	72-->97 (25)	13-->0 (-13)	15-->3 (-12)	0.300	5.668
37	413	0.0100	H-6->L+2 (63%)	70-->96 (26)	4-->1 (-3)	26-->3 (-23)	0.936	5.310
38	410	0.0271	H-1->L+6 (48%)	85-->98 (13)	10-->1 (-9)	5-->2 (-3)	1.537	6.094
39	407	0.0052	H-13->L+1 (46%), HOMO->L+6 (20%)	73-->97 (24)	13-->0 (-13)	14-->2 (-12)	0.670	5.502
40	402	0.0000	H-2->L+2 (96%)	1-->95 (94)	0-->1 (1)	99-->4 (-95)	0.025	5.556

Table S1h. Characteristics details of the excited states of $PC_{61}BM$-3xBTF_2.

Excit. No.	Wavelength (nm)	f	Main Contributions	fullerene	BTF_2	$PC_{61}BM$	μ_{ge} (D)	μ_e (D)
1	1030	0.0050	HOMO->LUMO (98%)	97-->97 (0)	0-->0 (0)	3-->3 (0)	1.045	4.858
2	910	0.0016	H-1->LUMO (91%)	96-->97 (1)	0-->0 (0)	4-->3 (-1)	0.550	5.962
3	813	0.0050	HOMO->L+1 (96%)	97-->95 (-2)	0-->0 (0)	3-->4 (1)	0.928	5.656
4	780	0.0142	H-1->L+1 (88%)	95-->96 (1)	0-->0 (0)	4-->4 (0)	1.535	6.155
5	627	0.0124	H-5->LUMO (10%), H-4->LUMO (74%)	69-->97 (28)	2-->0 (-2)	29-->3 (-26)	1.287	6.476
6	616	0.0049	HOMO->L+5 (86%)	95-->96 (1)	0-->0 (0)	5-->4 (-1)	0.804	4.768
7	597	0.0077	H-4->L+1 (11%), H-1->L+5 (77%)	91-->96 (5)	1-->0 (-1)	8-->4 (-4)	0.988	5.351
8	572	0.0271	H-4->L+1 (61%), H-1->L+5 (14%)	72-->96 (24)	2-->0 (-2)	25-->4 (-21)	1.816	7.188
9	557	0.0003	H-7->LUMO (30%), H-6->LUMO (61%)	80-->97 (17)	2-->0 (-2)	19-->3 (-16)	0.194	5.666
10	536	0.0242	H-7->LUMO (53%), H-6->LUMO (28%)	69-->97 (28)	1-->0 (-1)	30-->3 (-27)	1.661	4.745
11	521	0.0026	H-2->LUMO (87%)	6-->97 (91)	0-->0 (0)	94-->3 (-91)	0.540	5.666
12	506	0.0001	HOMO->L+2 (100%)	97-->0 (-	0-->0	3-->100	0.095	5.466

				97)	(0)	(97)		
13	504	0.0007	HOMO->L+3 (91%)	97-->0 (-97)	0-->0 (0)	3-->100 (97)	0.270	5.787
14	503	0.0161	H-6->L+1 (77%)	80-->96 (16)	2-->0 (-2)	19-->4 (-15)	1.315	4.568
15	503	0.0001	H-3->LUMO (89%)	10-->97 (87)	0-->0 (0)	90-->3 (-87)	0.116	5.517
16	499	0.0003	HOMO->L+4 (94%)	96-->2 (-94)	0-->0 (0)	4-->98 (94)	0.167	5.671
17	498	0.0001	H-5->LUMO (85%), H-4->LUMO (11%)	21-->96 (75)	1-->0 (-1)	79-->4 (-75)	0.095	5.594
18	497	0.0076	H-8->L+1 (10%), H-7->L+1 (75%)	63-->95 (32)	2-->0 (-2)	35-->4 (-31)	0.895	6.087
19	491	0.0058	H-8->LUMO (53%), H-6->L+1 (10%)	45-->96 (51)	1-->0 (-1)	54-->4 (-50)	0.778	5.348
20	491	0.0000	H-1->L+2 (99%)	96-->1 (-95)	0-->0 (0)	4-->99 (95)	0.044	5.519
21	489	0.0013	H-1->L+3 (91%)	96-->0 (-96)	0-->0 (0)	3-->100 (97)	0.362	5.220
22	***479***	***0.0450***	***H-11->LUMO (57%)***	***70-->96 (26)***	***2-->0 (-2)***	***28-->3 (-25)***	***2.140***	***3.581***
23	476	0.0050	H-12->LUMO (11%), H-9->LUMO (27%), H-9->L+1 (27%), H-3->L+1 (16%)	25-->96 (71)	0-->0 (0)	75-->4 (-71)	0.709	5.971
24	475	0.0004	H-1->L+4 (95%)	96-->1 (-95)	0-->0 (0)	3-->99 (96)	0.194	5.401
25	472	0.0007	H-2->L+1 (96%)	1-->95 (94)	0-->0 (0)	99-->4 (-95)	0.267	5.801
26	471	0.0022	H-12->LUMO (20%), H-3->L+1 (43%)	42-->96 (54)	1-->1 (0)	57-->4 (-53)	0.465	5.884
27	467	0.0029	H-5->L+1 (87%), H-4->L+1 (11%)	19-->95 (76)	1-->0 (-1)	80-->5 (-75)	0.536	5.983
28	464	0.0065	H-9->L+1 (16%), H-4->L+5 (26%), H-3->L+1 (25%)	39-->95 (56)	1-->0 (-1)	60-->4 (-56)	0.799	6.261
29	461	0.0073	H-9->L+1 (10%), H-4->L+5 (45%), HOMO->L+6 (11%)	61-->95 (34)	2-->1 (-1)	37-->5 (-32)	0.849	4.756
30	459	0.6036	H-3->L+3 (13%), H-2->L+4 (80%)	3-->2 (-1)	0-->0 (0)	97-->98 (1)	7.677	12.331

Table S2. Dipole moments of all the structures. μ_g, ground state dipole moment, μ_e, excited state dipole moment, $\Delta\mu_{ge}$, difference between the ground state and excited state (that corresponds to

the ones listed **Table 3**) dipole moments. The transition electric dipole moment is computed from $\mu_{ge} = \left[(\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2\right]^{1/2}$, while $\Delta\mu_{ge}$is the scalar difference computed as $\Delta\mu_{ge} = \mu_e - \mu_g$.

Structure	**μ_g (D)**	**μ_e (D)**	**$\Delta\mu_{ge}$ (D)**	**μ_{ge} (D)**
$PC_{61}BM$	5.504	5.519	0.0148	0.484
$PC_{61}BTF_2$, 7	5.537	5.619	0.0819	0.479
$PC_{61}BM$-1xBTF_2-*para*, 10-I	2.863	3.849	0.9818	4.182
$PC_{61}BM$-1xBTF_2, 10-I	3.4279	6.002	2.5744	0.526
$PC_{61}BM$-1xBTF_2@conf3, 10-I	5.704	5.830	0.1258	0.464
$PC_{61}BM$-2xBTF_2, 10-D	1.2777	5.526	4.2485	0.084
$PC_{61}BM$-2xBTF_2@conf3, 10-D	2.7153	5.219	2.5039	0.731
$PC_{61}BM$-3xBTF_2, 10-D	2.1667	5.656	3.4892	0.928

References

1. J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei and D. F. Perepichka, *Chem. Mater.*, 2008, **20**, 2484-2494.
2. S. Ram and R. E. Ehrenkaufer, *Tetrahedron Lett.*, 1984, **25**, 3415-3418.
3. H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angewandte Chemie International Edition*, 2011, **50**, 2995-2998.
4. *WO Pat.,* WO 2012/169605 A1, 2012.
5. J.-L. Wang, Z.-F. Chang, X.-X. Song, K.-K. Liu and L.-M. Jing, *J. Mater. Chem. C*, 2015, **3**, 9849-9858.
6. R. Kumar, S. Khan, N. Gupta, S. Naqvi, K. Gaurav, C. Sharma, M. Kumar, P. Kumar and S. Chand, *Carbon*, 2016, **107**, 765-773.
7. S. Manku, F. Wang and D. G. Hall, *J. Comb. Chem.*, 2003, **5**, 379-391.
8. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

9. A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571-2577.
10. K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283-290.
11. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.