Electronic Supplementary Information

Diarylmaleimide-based branched oligomers: strong full-color emission in both solution and solid film

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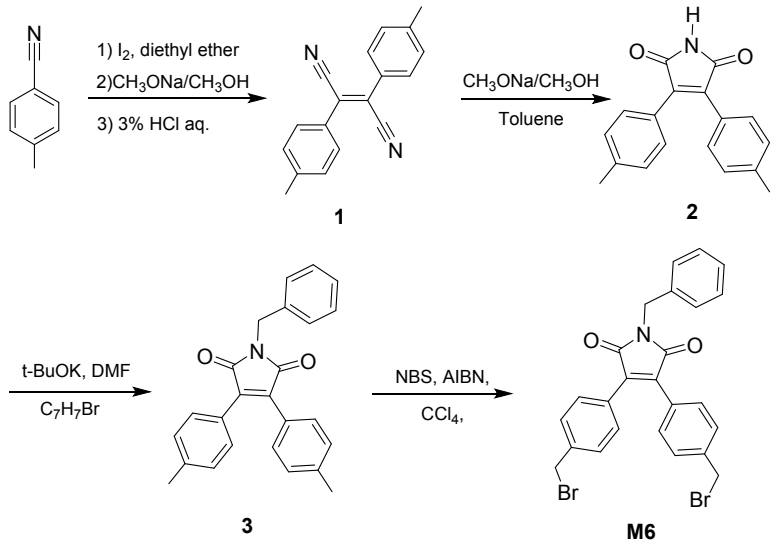
1. Supplemental Schemes, figures and tables



Scheme S1 Synthesis route of **M6**.

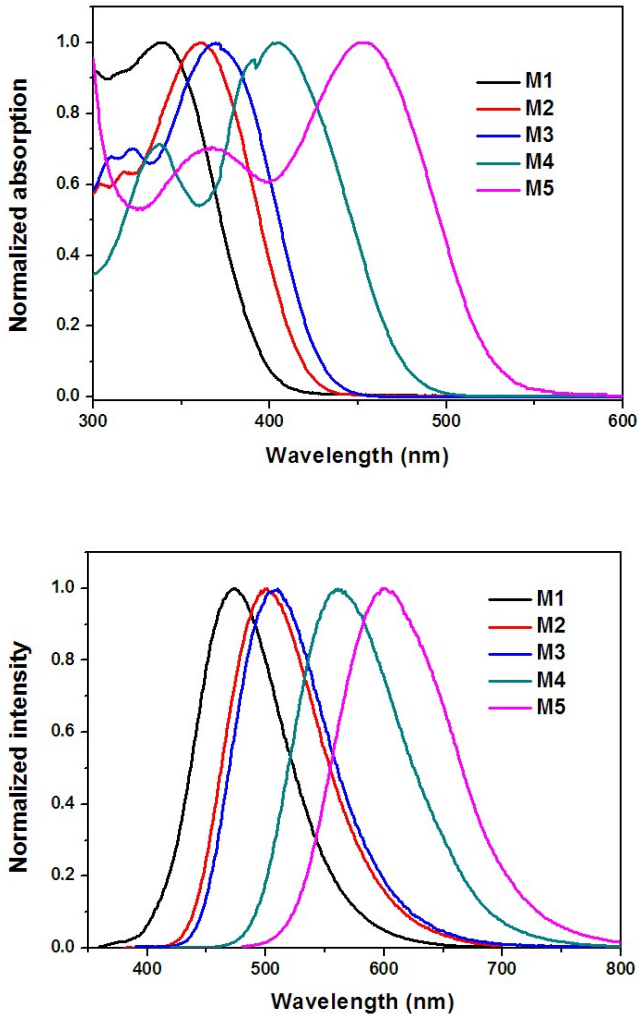


Fig. S1 Normalized absorption (upper) and emission (bottom) spectra of diarylmaleimide fluorophores in solution of chloroform.

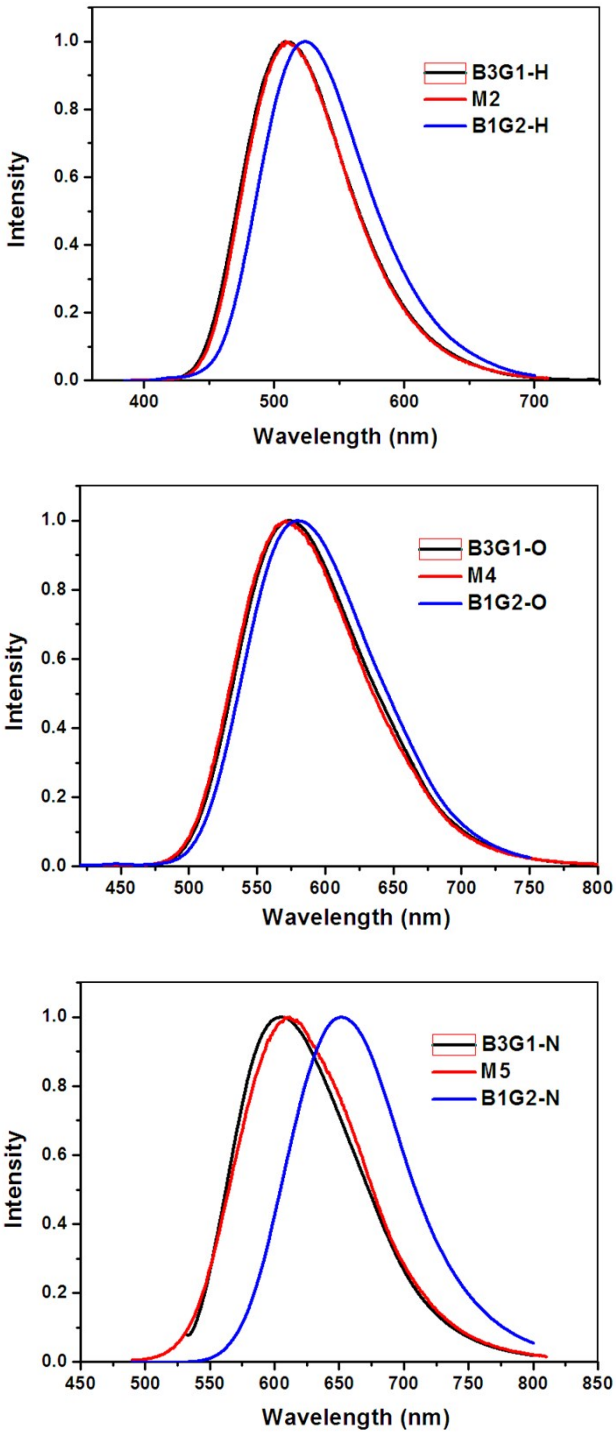


Fig. S2 Comparison of emission spectra of branched oligomers with the corresponding diarylmaleimide fluorophores in chloroform solution.

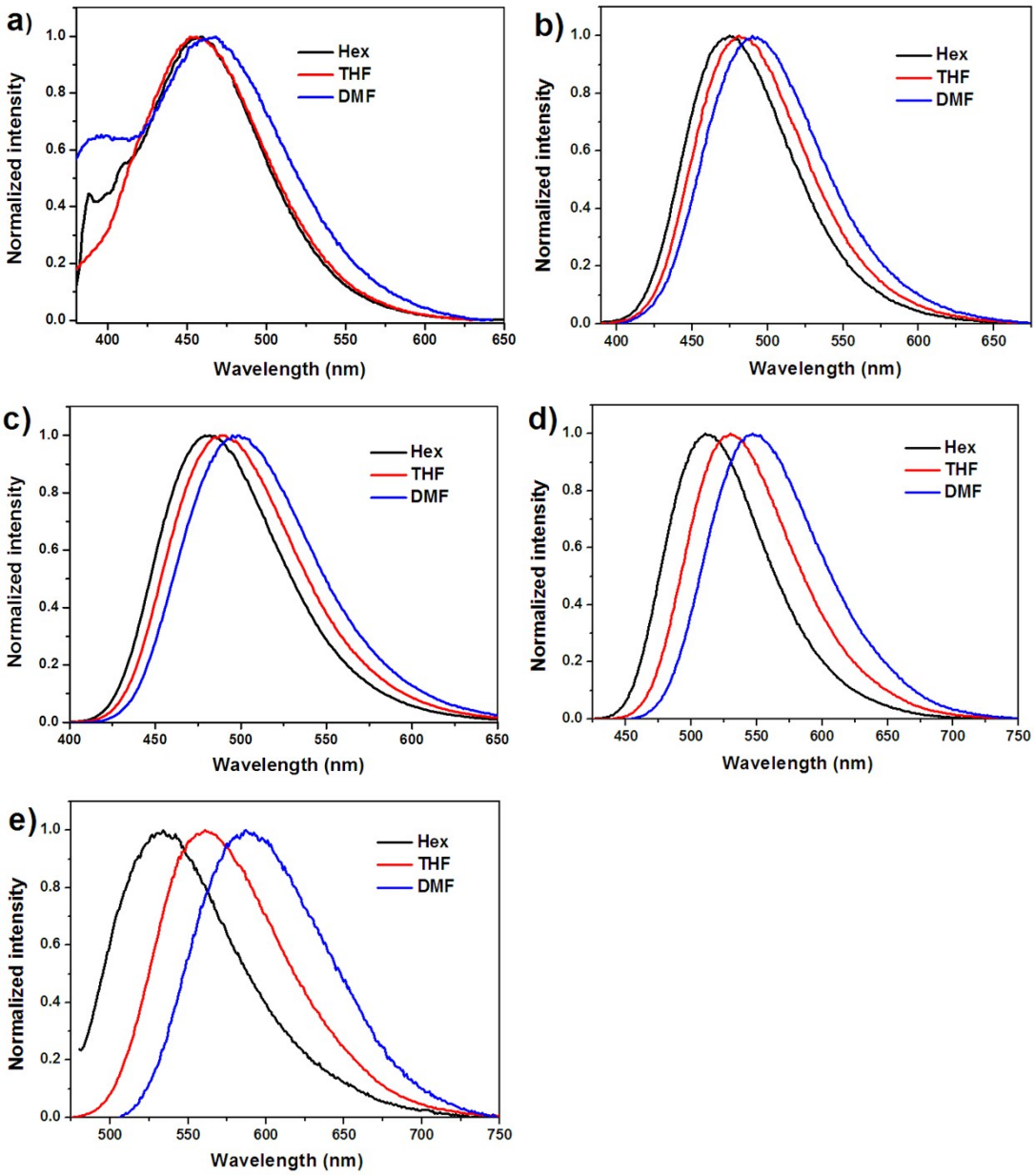


Fig. S3 Emission spectra of M1 (a), M2 (b), M3 (c), M4 (d) and M5 (e) in different solvent.

Table S1 Experimental data of photophysical properties of monomers.

	λ_{abs}, (nm) S / F[a]	λ_{em}, (nm) S / F	Φ_f, (%) S / F
M1	338 / 337	475 / 490	19 / 30
M2	361 / 383	500 / 508	50 / 60
M3	369 / 382	509 / 526	56 / 47
M4	409 / 429	564 / 555	36 / 39
M5	452 / 474	610 / 640	10 / 0.1

[a] S= chloroform solution, F =film.

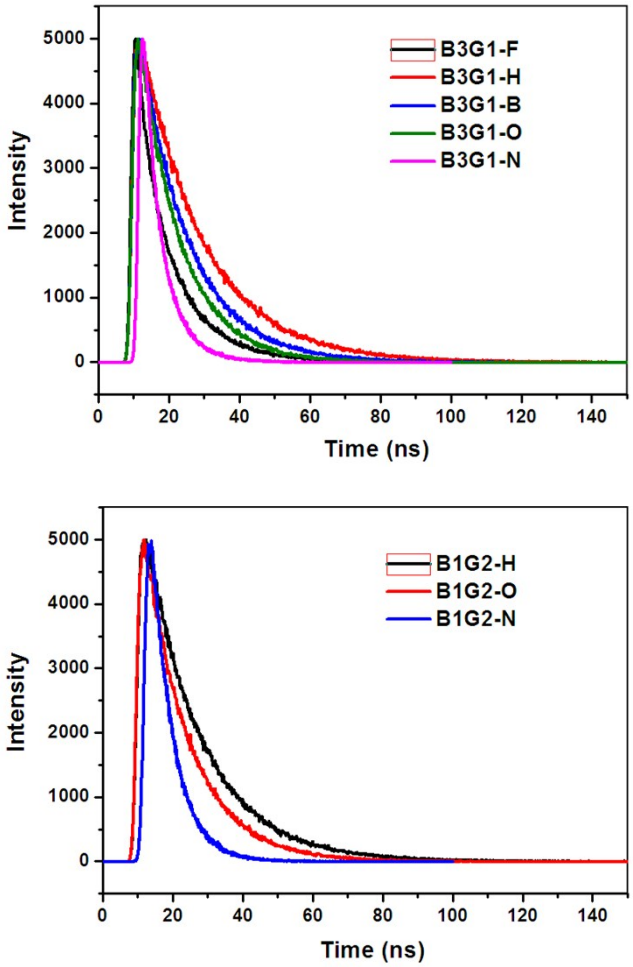


Fig. S4 Transient fluorescence decays of branched oligomers in chloroform solution measured at their maxima emission peak.

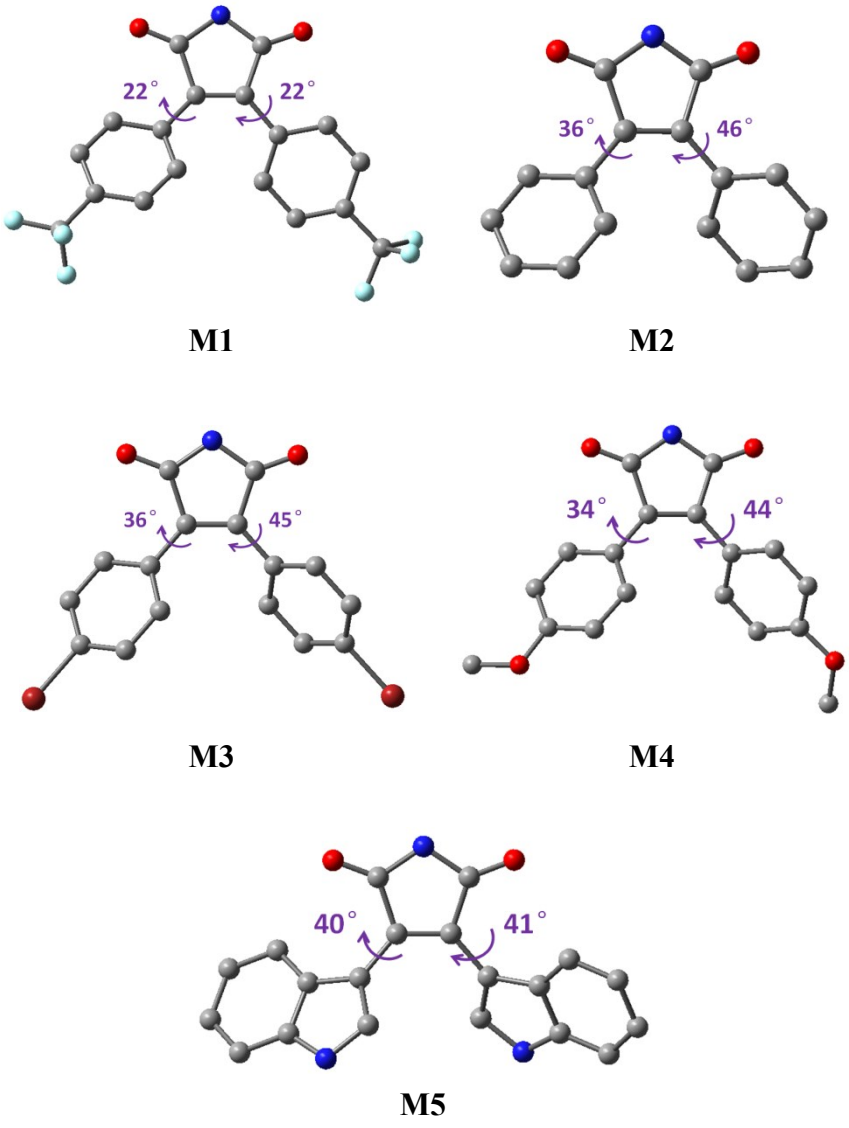


Fig. S5 Optimized geometries of arylmaleimides from B3LYP/6-31G (d) calculation.

Table S2 Calculated absorption photophysics with electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of arylmaleimides.

	Transition	Main orbital transition (CIC)	*E*, eV	λ, nm	*f*
M1	S_1	HOMO-5→LUMO (-0.12) HOMO-4→LUMO (0.16) HOMO→LUMO (0.66)	3.62 (3.67)[a]	342	0.2286
M2	S_1	HOMO-5→LUMO (-0.12) HOMO→LUMO (0.68)	3.53 (3.43)	351	0.2071
M3	S_1	HOMO-7→LUMO (-0.14) HOMO→LUMO (0.68)	3.45 (3.36)	360	0.2979
M4	S_1	HOMO-5→LUMO (0.14) HOMO→LUMO (0.69)	3.20 (3.03)	388	0.2823
M5	S_1	HOMO→LUMO (0.69)	2.86 (2.74)	433	0.1826

[a] The value in brackets is experimental data.

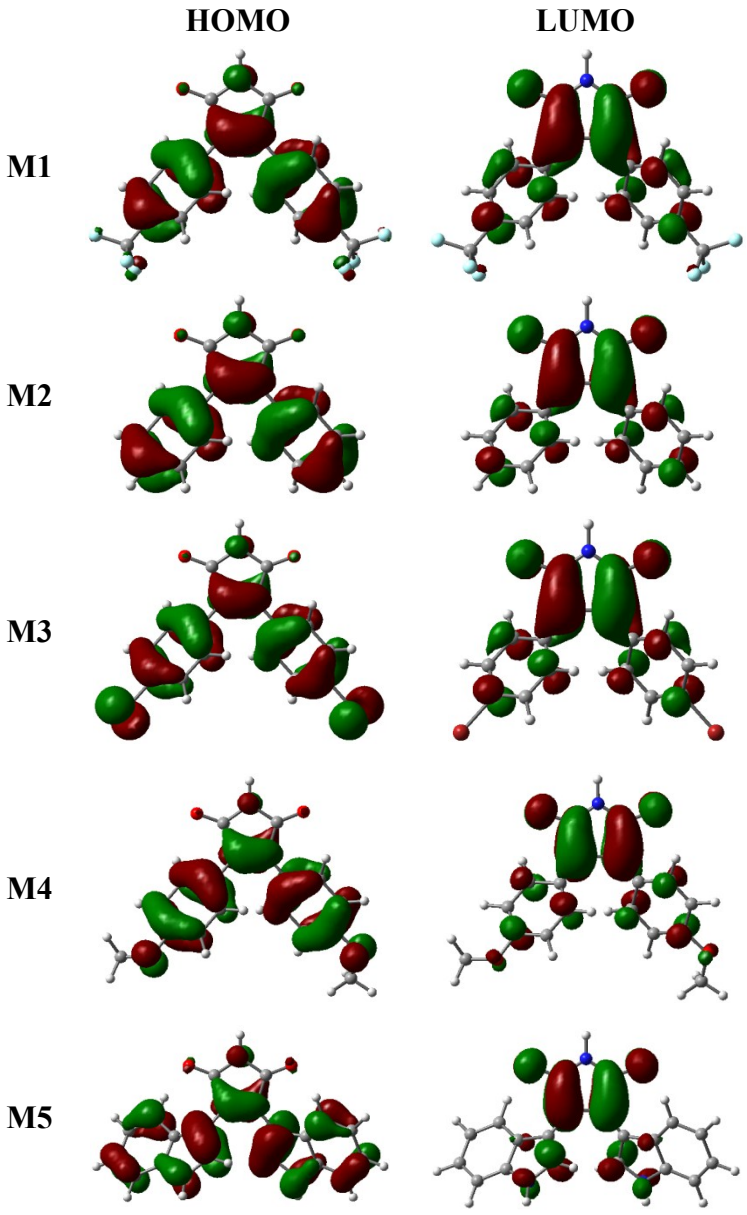


Fig. S6 Electron density distribution of HOMO and LUMO of arylmaleimides.

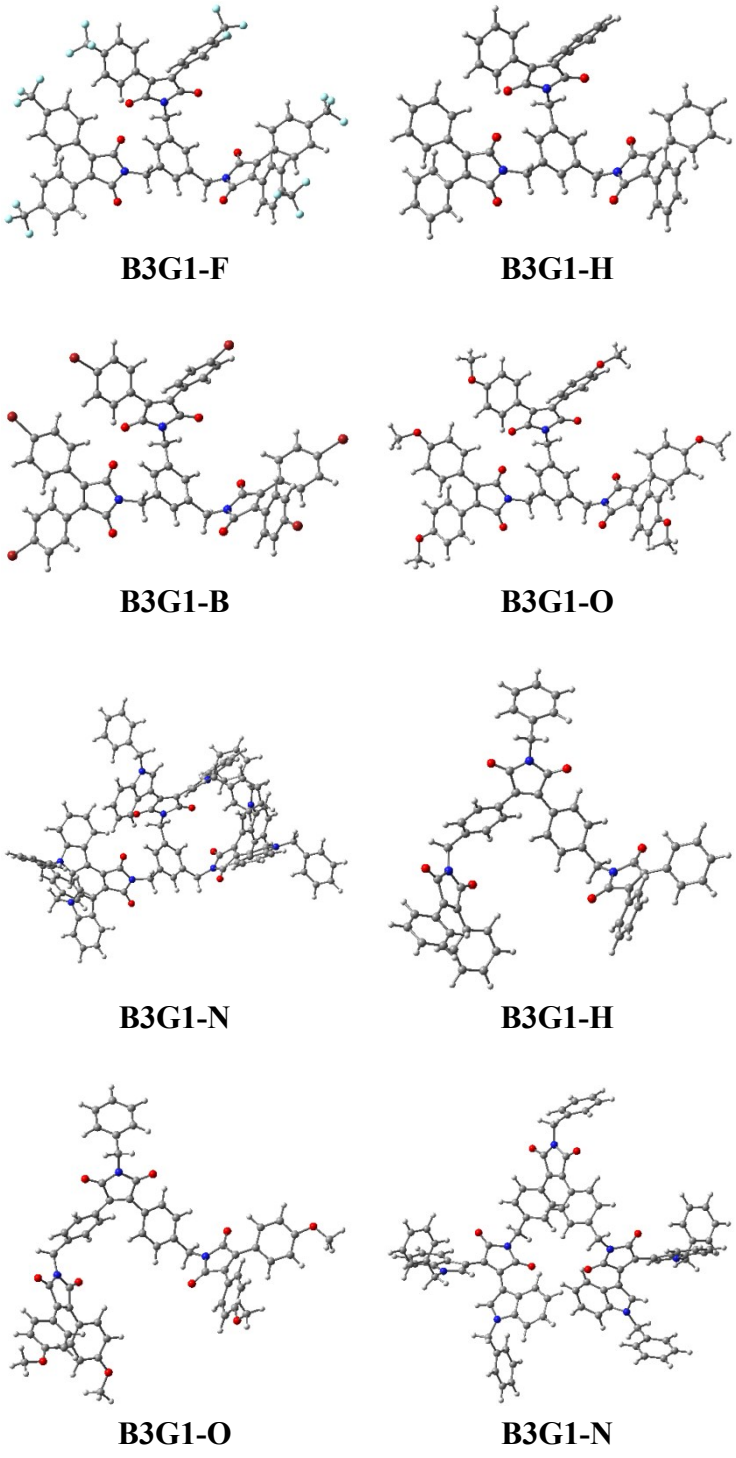


Fig. S7 Optimized geometries of branched oligomers from B3LYP/6-31G (d) calculation.

Table S3. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B3G1-F. HOMO=321; LUMO=322.

Excited State 1:	Singlet-A	3.5223 eV	352.00 nm	f=0.1660
304 -> 324	-0.10959			
321 -> 324	0.66290			
Excited State 2:	Singlet-A	3.5547 eV	348.79 nm	f=0.2753
319 -> 322	-0.33592			
319 -> 323	-0.30426			
320 -> 322	-0.30625			
320 -> 323	0.38417			
Excited State 3:	Singlet-A	3.5776 eV	346.56 nm	f=0.1033
319 -> 322	0.47074			
320 -> 323	0.45189			
Excited State 4:	Singlet-A	3.7697 eV	328.89 nm	f=0.0012
307 -> 324	0.60551			
307 -> 327	-0.14050			
315 -> 324	0.25993			
Excited State 5:	Singlet-A	3.7846 eV	327.60 nm	f=0.0007
305 -> 323	0.12732			
306 -> 322	-0.14505			
306 -> 323	0.57315			
314 -> 323	0.15899			
316 -> 323	0.16395			
Excited State 6:	Singlet-A	3.7881 eV	327.30 nm	f=0.0005
304 -> 322	0.29787			
305 -> 322	-0.48928			
305 -> 323	-0.13644			
306 -> 322	0.13421			
314 -> 322	0.17697			
316 -> 322	-0.14022			

Table S4. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B3G1-H. HOMO=225; LUMO=226.

Excited State 1:	Singlet-A	3.4539 eV	358.97 nm	f=0.1420
208 -> 227	-0.12226			
225 -> 227	0.66700			
Excited State 2:	Singlet-A	3.4758 eV	356.71 nm	f=0.2282
223 -> 226	0.45079			
223 -> 228	0.17732			
224 -> 226	0.19398			
224 -> 228	-0.42230			
Excited State 3:	Singlet-A	3.4981 eV	354.43 nm	f=0.1065
223 -> 226	0.44317			
224 -> 228	0.48481			
Excited State 4:	Singlet-A	3.8039 eV	325.94 nm	f=0.0010
211 -> 227	-0.62063			
211 -> 231	0.13187			
219 -> 227	0.23358			
Excited State 5:	Singlet-A	3.8076 eV	325.62 nm	f=0.0010
210 -> 228	0.60691			
218 -> 228	-0.12687			
220 -> 228	0.17714			
Excited State 6:	Singlet-A	3.8094 eV	325.47 nm	f=0.0007
209 -> 226	0.60588			
210 -> 226	-0.11966			
218 -> 226	0.18350			
220 -> 226	0.11898			

Table S5. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B3G1-B. HOMO=327; LUMO=328.

Excited State 1:	Singlet-A	3.3646 eV	368.49 nm	f=0.2181
312 -> 330	-0.13334			
327 -> 330	0.66350			
Excited State 2:	Singlet-A	3.3912 eV	365.61 nm	f=0.3261
308 -> 329	0.11703			
309 -> 328	-0.11603			
325 -> 328	0.16881			
325 -> 329	0.43171			
326 -> 328	0.44477			
326 -> 329	-0.16764			
Excited State 3:	Singlet-A	3.4169 eV	362.86 nm	f=0.1562
308 -> 328	0.11911			
309 -> 329	-0.10966			
325 -> 328	0.46340			
326 -> 329	0.47217			
Excited State 4:	Singlet-A	3.7899 eV	327.14 nm	f=0.0010
312 -> 330	0.25038			
313 -> 330	-0.55030			
313 -> 334	0.12124			
318 -> 330	0.26643			
Excited State 5:	Singlet-A	3.8016 eV	326.14 nm	f=0.0008
309 -> 328	0.16526			
310 -> 328	-0.25455			
311 -> 328	-0.23435			
311 -> 329	0.45866			
317 -> 329	-0.17624			
319 -> 328	-0.14700			
Excited State 6:	Singlet-A	3.8020 eV	326.11 nm	f=0.0006
309 -> 329	0.16790			
310 -> 328	-0.40148			
310 -> 329	-0.30961			
311 -> 328	0.24231			
311 -> 329	-0.15153			
317 -> 328	-0.17782			
319 -> 329	-0.14494			

Table S6. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B3G1-O. HOMO=273; LUMO=274.

Excited State 1:	Singlet-A	3.1602 eV	392.33 nm	f=0.1966
256 -> 274	-0.10419			
271 -> 274	0.59581			
272 -> 274	-0.29269			
Excited State 2:	Singlet-A	3.1733 eV	390.72 nm	f=0.3152
271 -> 274	0.11996			
271 -> 276	-0.20093			
272 -> 276	-0.42169			
273 -> 275	0.47474			
Excited State 3:	Singlet-A	3.2001 eV	387.44 nm	f=0.1882
271 -> 275	-0.20668			
272 -> 275	-0.42921			
273 -> 276	0.47936			
Excited State 4:	Singlet-A	3.8397 eV	322.90 nm	f=0.0007
257 -> 274	0.53207			
257 -> 282	-0.11624			
258 -> 274	0.28680			
259 -> 274	0.10745			
263 -> 274	-0.25265			
Excited State 5:	Singlet-A	3.8433 eV	322.59 nm	f=0.0007
257 -> 275	-0.18547			
257 -> 276	0.16524			
258 -> 275	0.20717			
258 -> 276	-0.12952			
259 -> 275	0.30644			
259 -> 276	-0.40880			
264 -> 276	-0.14120			
265 -> 275	0.12472			
265 -> 276	-0.10416			
Excited State 6:	Singlet-A	3.8444 eV	322.51 nm	f=0.0004
257 -> 275	-0.11932			
257 -> 276	-0.15436			
258 -> 275	0.32779			
258 -> 276	0.33898	259 -> 275	-0.28718	
259 -> 276	-0.16019	264 -> 275	-0.14290	
265 -> 275	0.10338	265 -> 276	0.12314	

Table S7. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B3G1-N. HOMO=429; LUMO=430.

Excited State 1:	Singlet-A	2.7490 eV	451.01 nm	f=0.1479
427 -> 430	0.41034			
427 -> 431	0.28770			
429 -> 430	0.31317			
429 -> 431	-0.34999			
Excited State 2:	Singlet-A	2.7699 eV	447.61 nm	f=0.2429
427 -> 430	0.45394			
429 -> 431	0.50833			
Excited State 3:	Singlet-A	2.8826 eV	430.11 nm	f=0.1678
428 -> 432	0.68377			
Excited State 4:	Singlet-A	3.7093 eV	334.25 nm	f=0.0587
394 -> 432	0.14140			
424 -> 430	-0.23614			
425 -> 430	-0.13119			
426 -> 432	0.58944			
Excited State 5:	Singlet-A	3.7258 eV	332.77 nm	f=0.1684
423 -> 430	0.14146			
424 -> 430	0.29284			
424 -> 431	0.31761			
425 -> 430	0.32050			
425 -> 431	-0.28332			
426 -> 432	0.19338			
Excited State 6:	Singlet-A	3.7394 eV	331.57 nm	f=0.0299
393 -> 431	0.10559			
423 -> 431	0.10245			
424 -> 430	0.36694			
424 -> 431	-0.16941			
425 -> 431	0.43708			
426 -> 432	0.22138			

Table S8. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B1G2-H. HOMO=225; LUMO=226.

Excited State 1:	Singlet-A	3.4030 eV	364.34 nm	f=0.2095
208 -> 228	-0.14351			
223 -> 228	-0.25575			
225 -> 228	0.62334			
Excited State 2:	Singlet-A	3.4312 eV	361.34 nm	f=0.0863
207 -> 226	-0.10316			
223 -> 226	0.37933			
223 -> 227	-0.17457			
224 -> 226	0.42042			
224 -> 227	0.20837			
225 -> 226	0.23297			
225 -> 227	-0.10192			
Excited State 3:	Singlet-A	3.4338 eV	361.07 nm	f=0.2526
206 -> 227	-0.10119			
223 -> 226	-0.17891			
223 -> 227	-0.36343			
224 -> 226	-0.19340			
224 -> 227	0.44490			
225 -> 226	-0.11035			
225 -> 227	-0.21204			
Excited State 4:	Singlet-A	3.7912 eV	327.03 nm	f=0.0014
206 -> 228	-0.11630			
211 -> 228	-0.60928			
211 -> 229	0.14559			
220 -> 228	-0.23907			
Excited State 5:	Singlet-A	3.8017 eV	326.13 nm	f=0.0017
210 -> 226	0.62645			
218 -> 226	-0.13521			
219 -> 226	0.18886			
Excited State 6:	Singlet-A	3.8045 eV	325.89 nm	f=0.0013
209 -> 227	-0.62572			
209 -> 231	-0.11522			
218 -> 227	0.18628			
219 -> 227	0.14014			

Table S9. Electronic excitation energies (*E*), wavelength (λ) and oscillator strength (*f*) of first 6 calculated singlet excited states for B1G2-O. HOMO=257; LUMO=258.

Excited State 1:	Singlet-A	3.1252 eV	396.72 nm	f=0.1614
256 -> 259	0.22400			
256 -> 260	0.15470			
257 -> 259	0.62182			
Excited State 2:	Singlet-A	3.1296 eV	396.16 nm	f=0.2757
256 -> 260	0.62211			
257 -> 259	-0.15715			
257 -> 260	-0.22388			
Excited State 3:	Singlet-A	3.3873 eV	366.03 nm	f=0.2585
239 -> 258	-0.10347			
255 -> 258	0.66884			
Excited State 4:	Singlet-A	3.7947 eV	326.73 nm	f=0.0016
238 -> 258	0.20245			
242 -> 258	0.20990			
243 -> 258	0.55058			
243 -> 261	-0.14052			
250 -> 258	0.23549			
Excited State 5:	Singlet-A	3.8416 eV	322.74 nm	f=0.0012
241 -> 259	0.62384			
241 -> 266	0.14131			
248 -> 259	0.23633			
Excited State 6:	Singlet-A	3.8420 eV	322.71 nm	f=0.0010
242 -> 260	-0.58236			
242 -> 267	0.10658			
243 -> 260	0.21294			
249 -> 260	-0.23038			

Table S10. Electronic excitation energies (E), wavelength (λ) and oscillator strength (f) of first 6 calculated singlet excited states for B1G2-N. HOMO=361; LUMO=362.

Excited State	1:	Singlet-A	2.6724 eV	463.94 nm	f=0.2418
360 -> 363		0.47989			
360 -> 364		0.19261			
361 -> 363		-0.23506			
361 -> 364		0.39014			
Excited State	2:	Singlet-A	2.6927 eV	460.45 nm	f=0.1541
360 -> 363		-0.40937			
360 -> 364		0.18533			
361 -> 363		0.14694			
361 -> 364		0.50096			
Excited State	3:	Singlet-A	3.3475 eV	370.37 nm	f=0.1810
332 -> 362		-0.12059			
355 -> 362		0.48683			
356 -> 362		0.43828			
357 -> 362		-0.11058			
Excited State	4:	Singlet-A	3.6843 eV	336.52 nm	f=0.0653
331 -> 364		0.11578			
357 -> 364		-0.14280			
358 -> 363		-0.23484			
358 -> 364		0.30312			
359 -> 363		0.10508			
359 -> 364		0.50622			
Excited State	5:	Singlet-A	3.6870 eV	336.28 nm	f=0.1061
330 -> 363		0.11255			
357 -> 363		0.13810			
358 -> 363		0.49435			
358 -> 364		0.15952			
359 -> 363		-0.31552			
359 -> 364		0.19649			
Excited State	6:	Singlet-A	3.7897 eV	327.16 nm	f=0.0013
332 -> 362		-0.12829			
333 -> 362		0.16501			
334 -> 362		0.13814			
335 -> 362		0.39786			
336 -> 362		0.39597			
337 -> 362		0.10721			
350 -> 362		-0.22795			

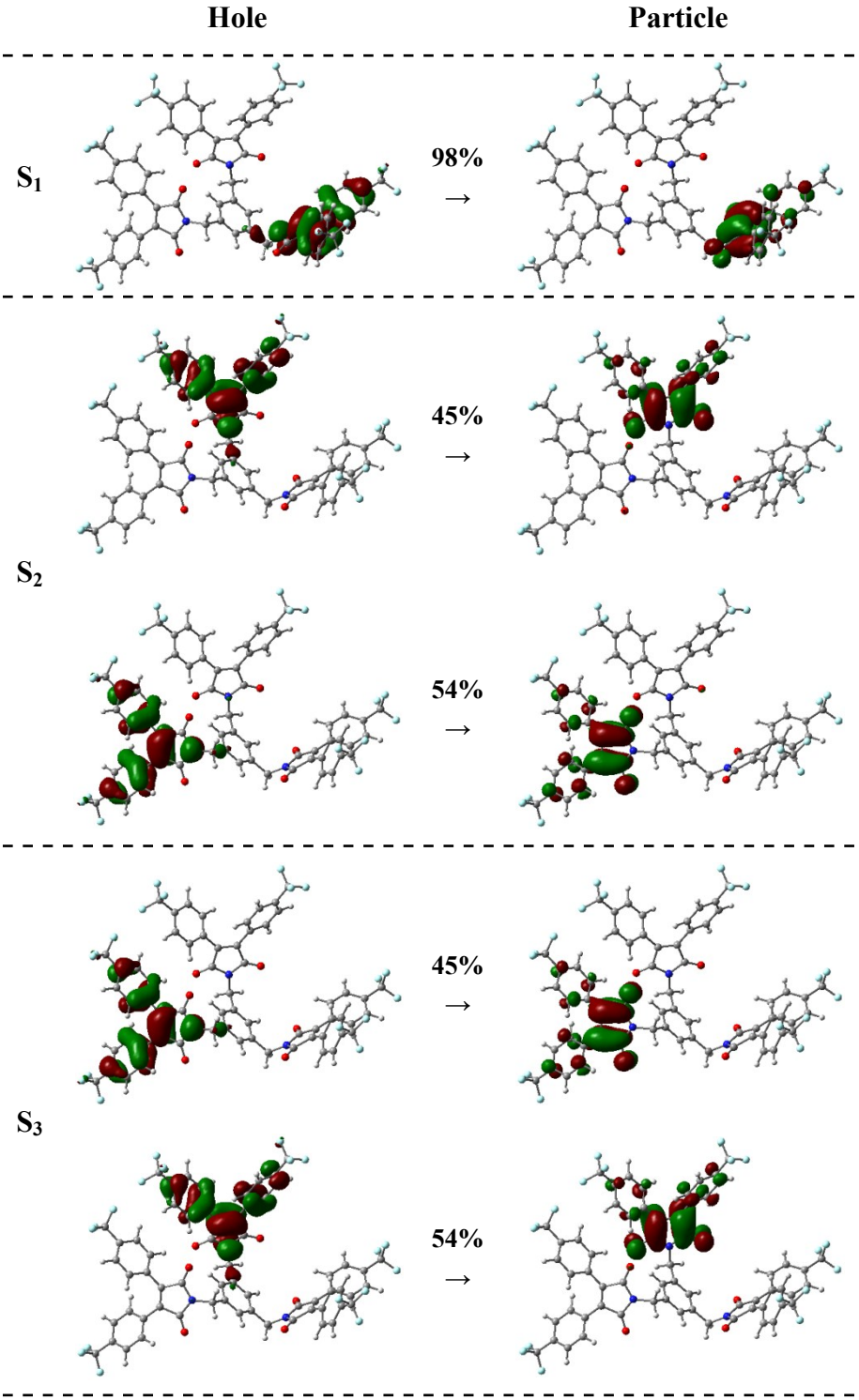


Fig. S8 Natural transition orbital pairs for the first three excited singlet states of B3G1-F.

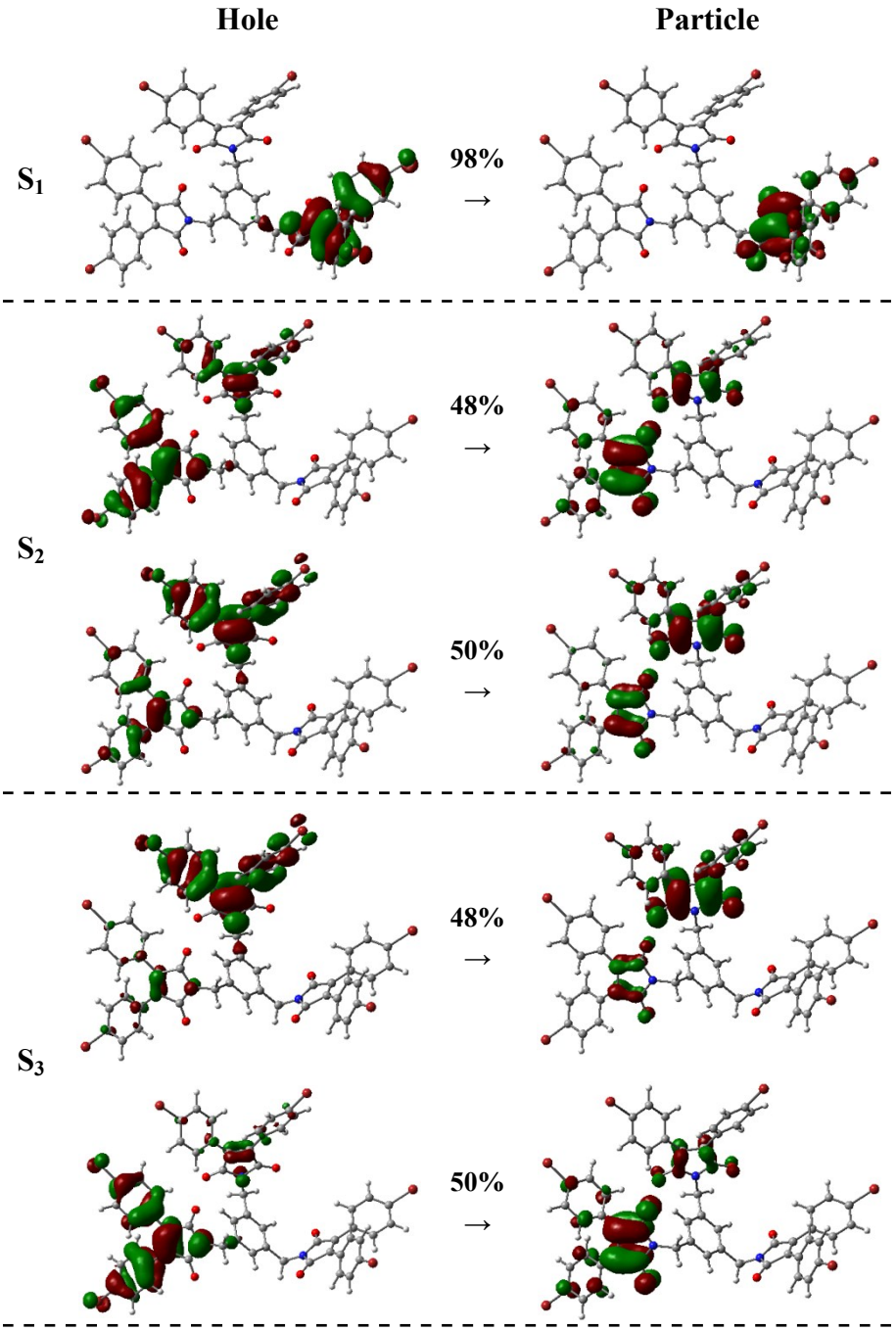


Fig. S9 Natural transition orbital pairs for the first three excited singlet states of B3G1-B.

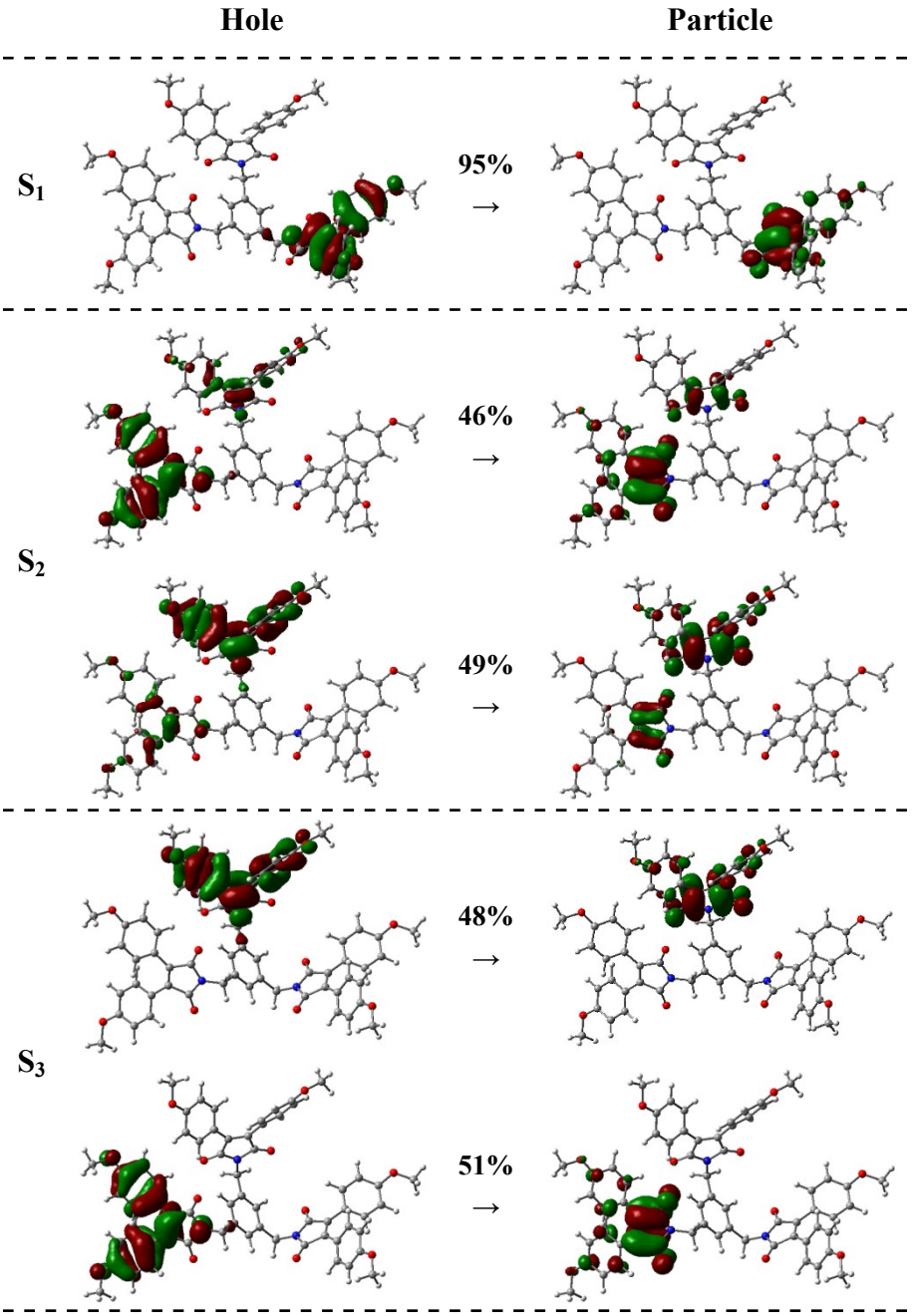


Fig. S10 Natural transition orbital pairs for the first three excited singlet states of B3G1-O.

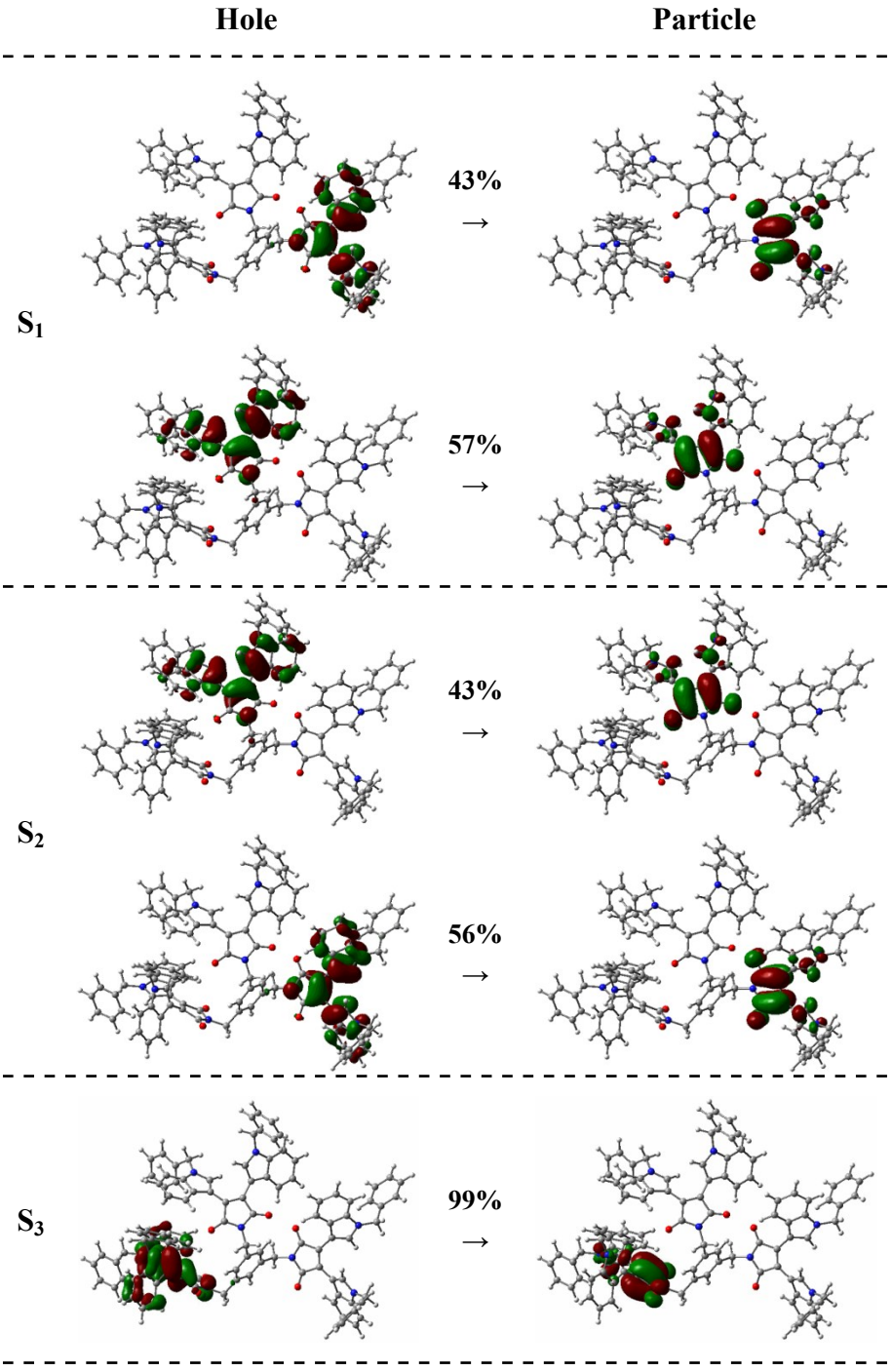


Fig. S11 Natural transition orbital pairs for the first three excited singlet states of B3G1-N.

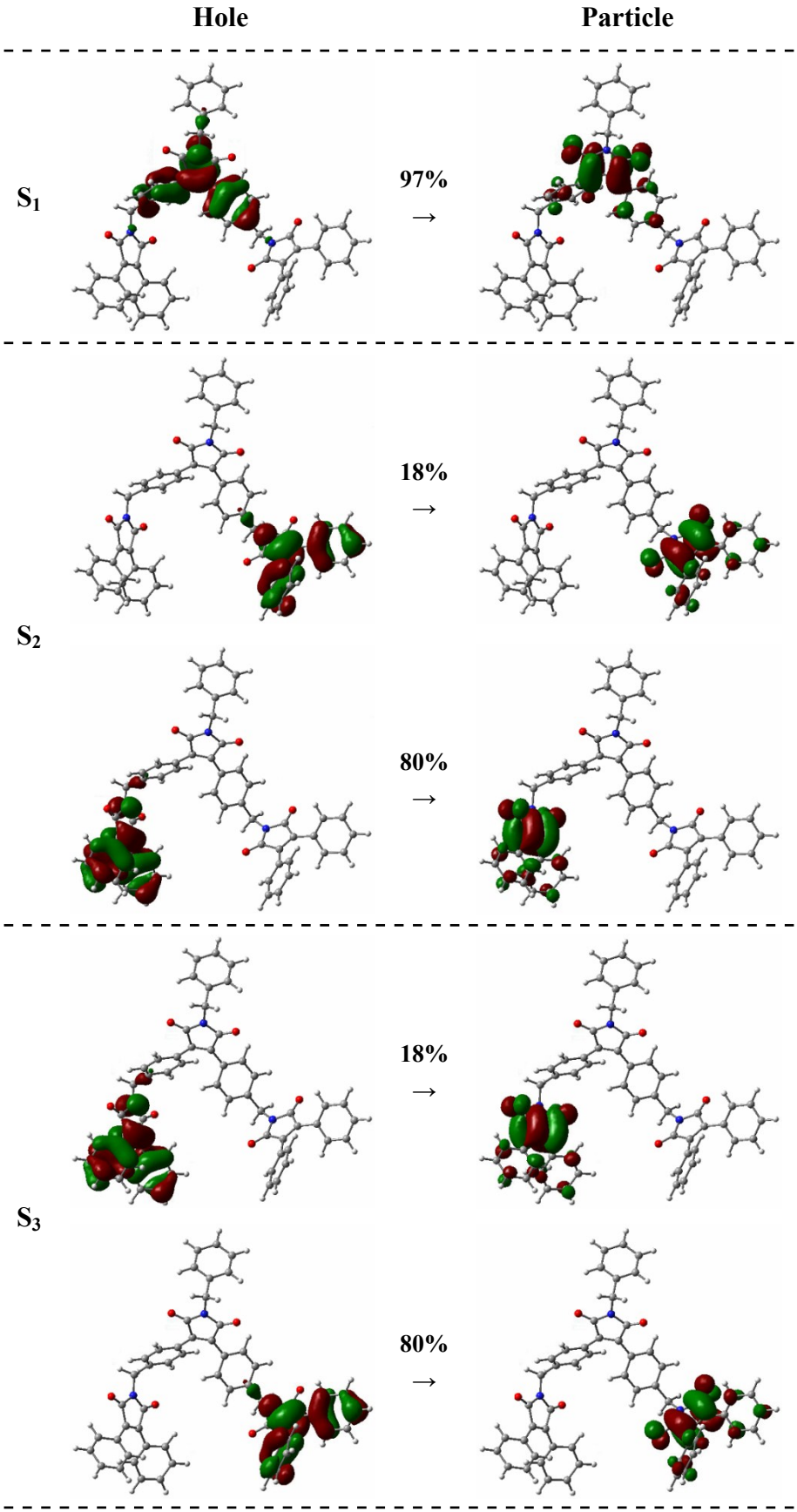


Fig. S12 Natural transition orbital pairs for the first three excited singlet states of B1G2-H.

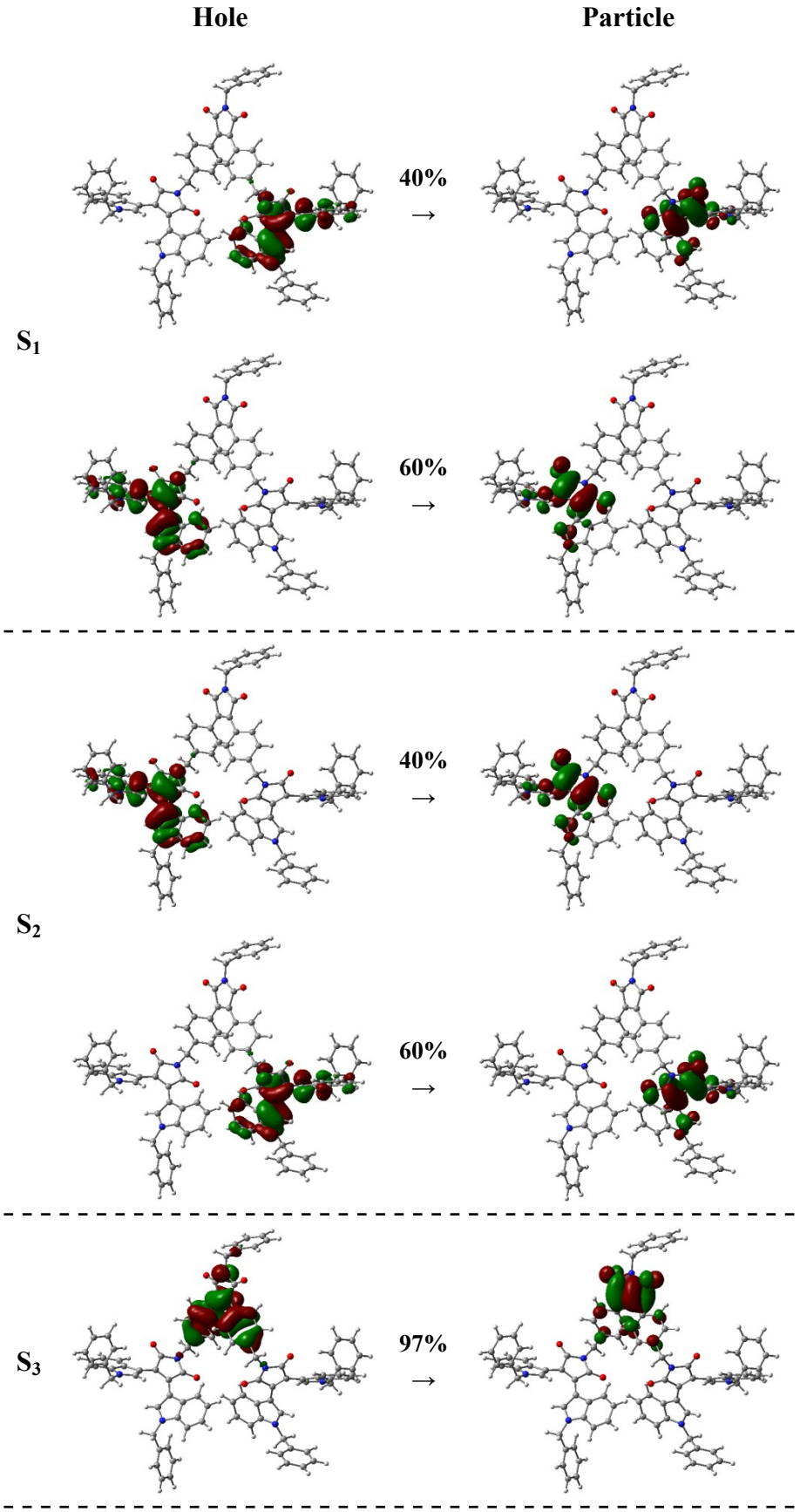


Fig. S13 Natural transition orbital pairs for the first three excited singlet states of B1G2-N.

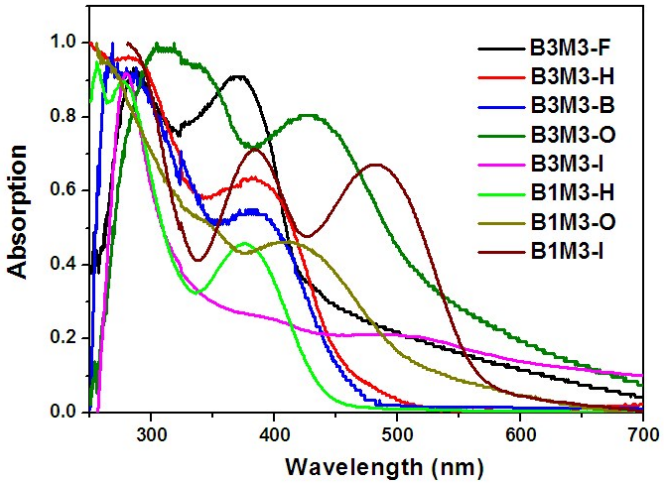


Fig. S14 Absorption spectra of branched oligomers in films.

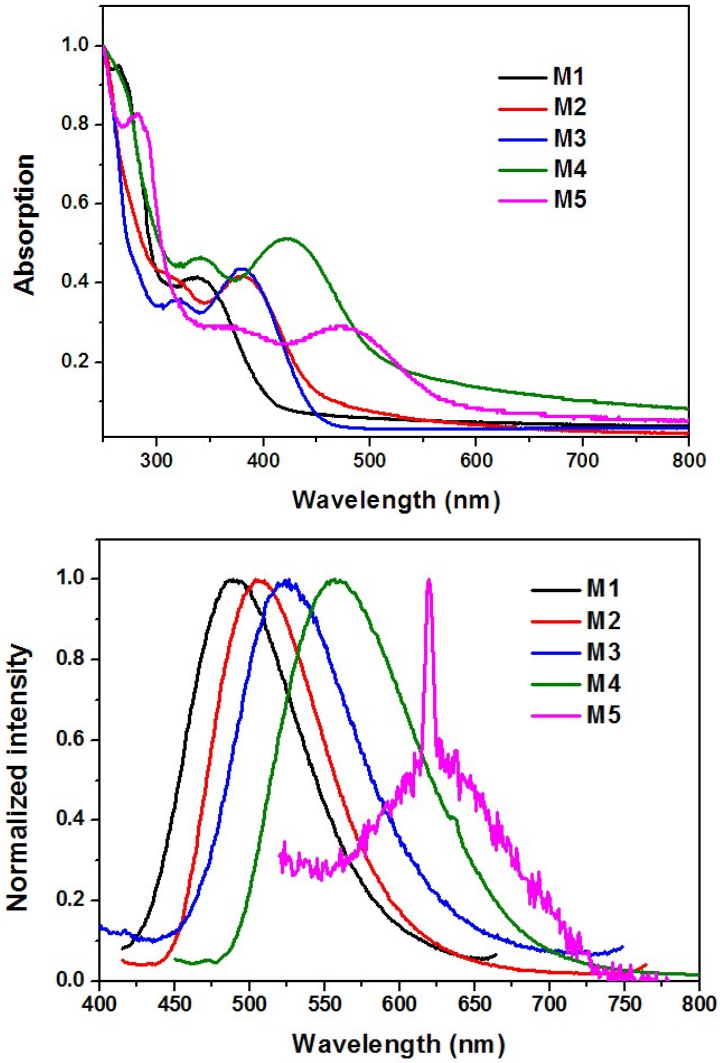


Fig. S15 Absorption (upper) and emission (bottom) spectra of monomers in films.

Table S11. Experimental data of TGA and CV of branched oligomers.

	$T_{5\%}$ (°C)	T_d (°C)	E_{red}^{onset} (v)	λ_{onset} (nm)	E_g^{opt} (ev)	LUMO (-ev)	HOMO (-ev)
B3M1-F	402	440	-0.66	420	2.95	3.74	6.69
B3M1-H	386	452	-0.68	430	2.88	3.72	6.60
B3M1-B	405	402	-0.68	441	2.81	3.72	6.53
B3M1-O	277	302	-0.73	482	2.57	3.67	6.24
B3M1-N	282	421	-0.65	566	2.19	3.75	5.94
B1M2-H	413	434	-0.67	434	2.86	3.73	6.59
B1M2-O	212	417	-0.76	508	2.44	3.64	6.08
B1M2-N	272	433	-0.67	568	2.18	3.73	5.91

2. Experimental Section

Synthesis of bis(4-methylphenyl)fumaronitrile (1)

4-methylbenzylcyanide (5 ml, 0.0377 mol) and iodine (9.57 g, 0.0377 mol) were dissolved in dry diethyl ether (32 mL) under a nitrogen atmosphere. Sodium methoxide methanol solution, which was prepared by adding sodium (1.91 g, 0.083 mol) to dry methanol (ca. 30 mL), was added slowly (over a period of 30 min) into the reaction solution at -78℃. The reaction solution was allowed to warm up by replacing the dry-ice bath with an ice–water bath before the temperature rose above 0 ℃. During this time, more and more light yellow precipitation was formed in the solution. The reaction solution was further stirred for another 3–4 h and then the reaction was quenched with 3–6% hydrochloric acid. The solution was filtered to isolate the solid, which was rinsed with cold methanol–water solution to wash away ionic substances. The resulting solid was further purified via recrystallization from methanol to give compound 1 as white crystals. Yield: 80% (3.95 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 4H), 7.35 (d, J = 7.6 Hz, 4H), 2.46 (s, 6H).

Synthesis of 3,4-bis(4-methylphenyl)maleimide (2)

Bis(4-methylphenyl)fumaronitrile (2.5 g, 0.0097 mmol) was dissolved in dry toluene (50 mL). Sodium methoxide methanol solution, which was prepared by adding sodium (0.69 g, 0.03 mol) to methanol (50 mL), was added to the reaction solution. The solution mixture was then stirred for another 3 h at room temperature. The reaction was quenched with water and then extracted using dichloromethane. It was then dehydrated over anhydrous $MgSO_4$. After removing the solvent, the crude

product was purified by column chromatography with DCM as the eluant, affording compound 2 as yellow solid in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.50 – 7.36 (m, 4H), 7.18 (d, *J* = 6.7 Hz, 4H), 2.38 (d, *J* = 1.5 Hz, 6H).

Synthesis of *N*-benzyl-3,4-bis(4-methylphenyl)maleimide (3)

3,4-Bis(4-methylphenyl)maleimide (550 mg, 2 mmol) was mixed with potassium tert-butoxide (450 mg, 4 mmol) in dried DMF (20 mL) under a nitrogen atmosphere. After the solution was stirred at 0℃ for 1.5 h, benzyl bromide (0.3 mL, 2.5 mmol) was added to the solution. The solution was then stirred at room temperature for about 10 h. The reaction was quenched with water and then extracted using dichloromethane. It was then dehydrated over anhydrous $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography with DCM /petroleum ether (1:5) as the eluant. A green solid was obtained. Yield: 73% (0.54 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.43 – 7.27 (m, 7H), 7.17 (t, *J* = 11.9 Hz, 4H), 4.80 (s, 2H), 2.37 (s, 6H).

Synthesis of M6

To a solution *N*-benzyl-3,4-di-*p*-tolylmaleimide (500 mg, 1.36 mmol) in 12 mL of carbon tetrachloride were added 672 mg (3.78 mmol) of *N*-bromosuccinimide and a small amount of 2,2'-azobis(isobutyronitrile) (AIBN). After 2 h, another portion of AIBN was added. Refluxing was continued for a total of 7 h. The mixture was cooled, water was added and the mixture was extracted with ethyl acetate. The organic extract was washed with brine. It was then dehydrated over anhydrous $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography with

DCM/petroleum ether (1:3) as the eluant, affording white solids of compound M6 in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 6H), 7.41–7.28 (m, 7H), 4.80 (s, 2H), 4.47 (s, 4H).

3. Structural Characterizations

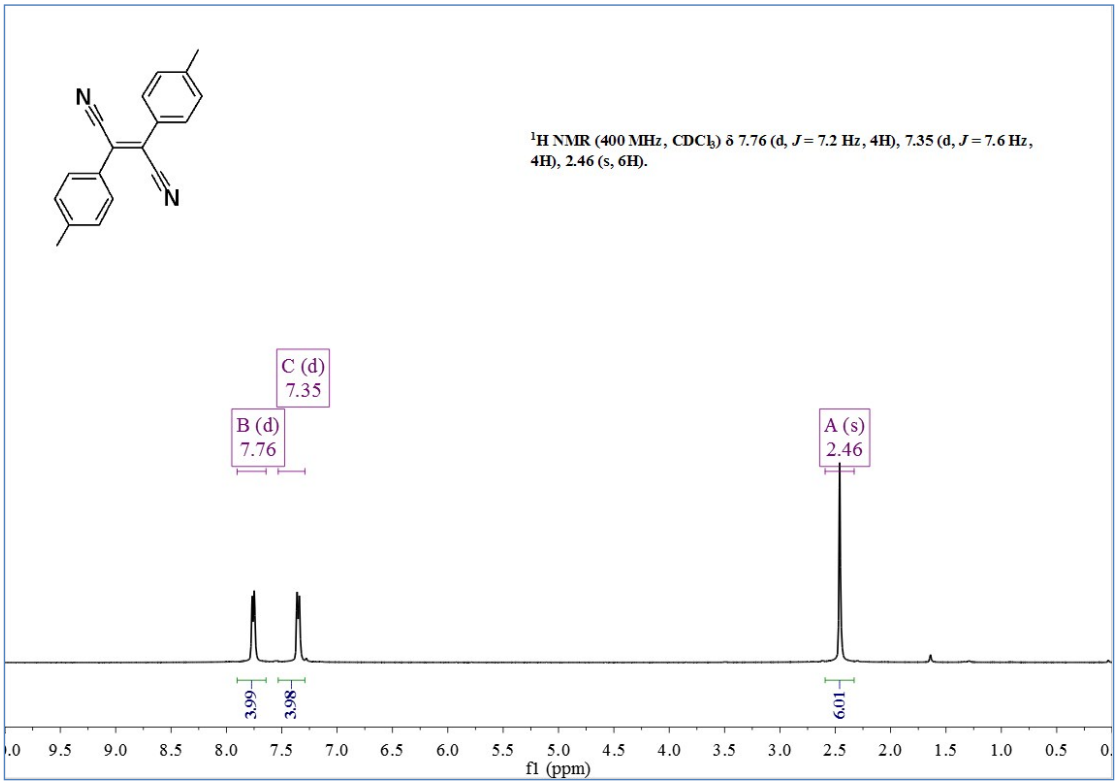


Fig.S16 ^{1}H NMR spectrum of compound 1.

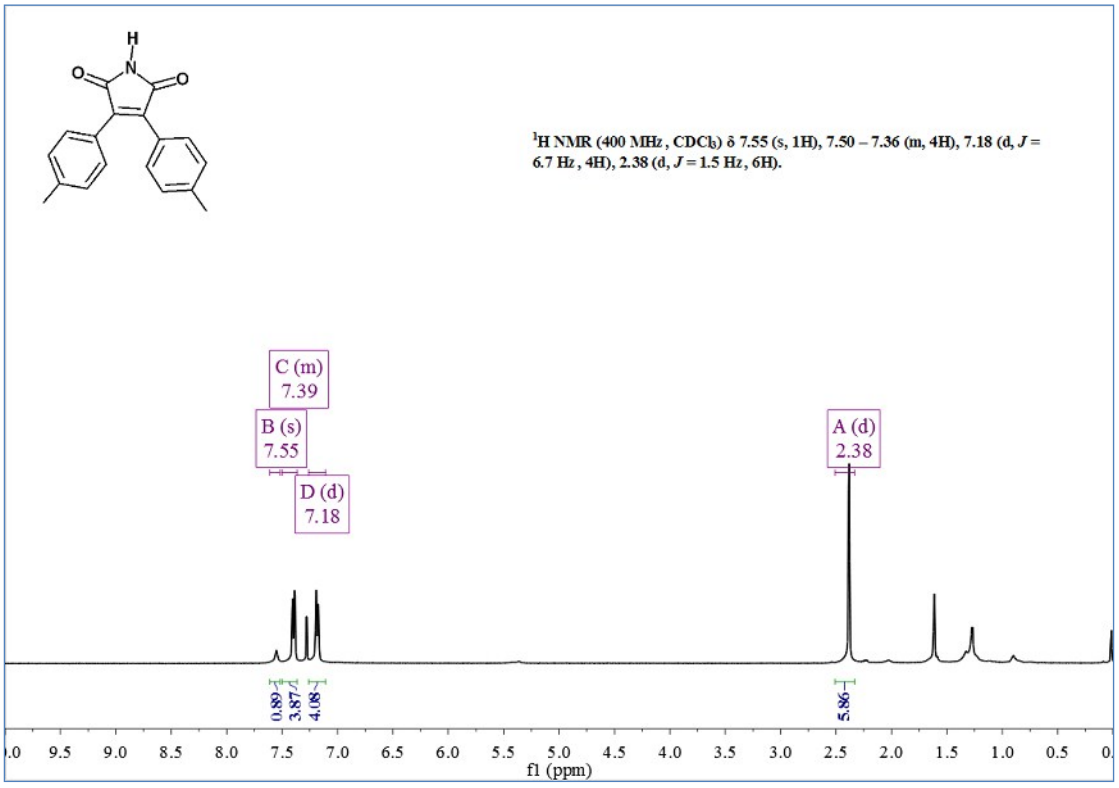


Fig.S17 ^{1}H NMR spectrum of compound 2.

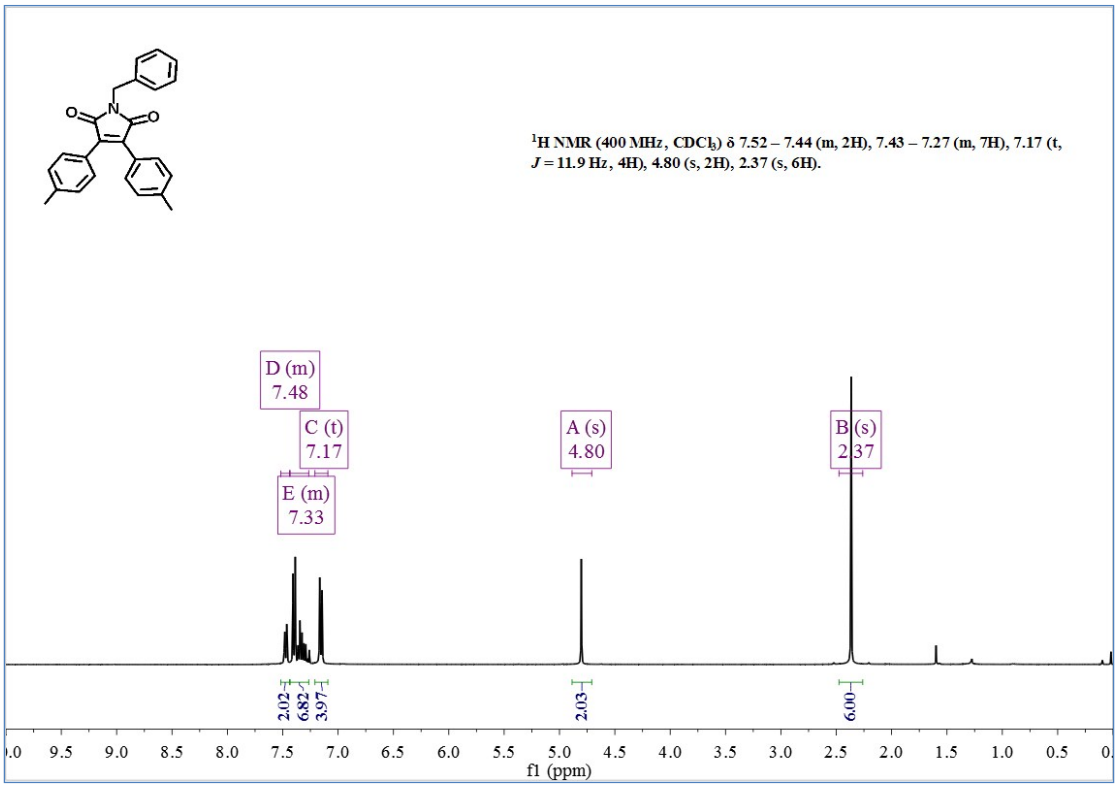


Fig.S18 ^{1}H NMR spectrum of compound 3.

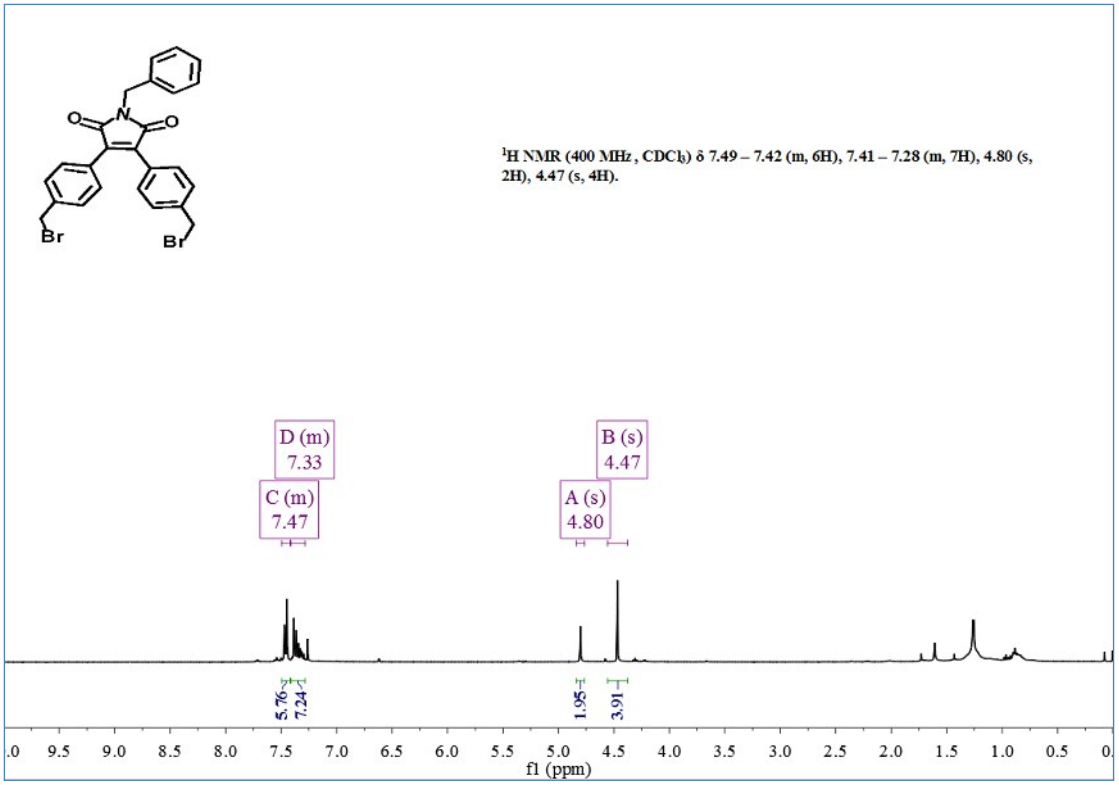


Fig.S19 ^{1}H NMR spectrum of compound M6.

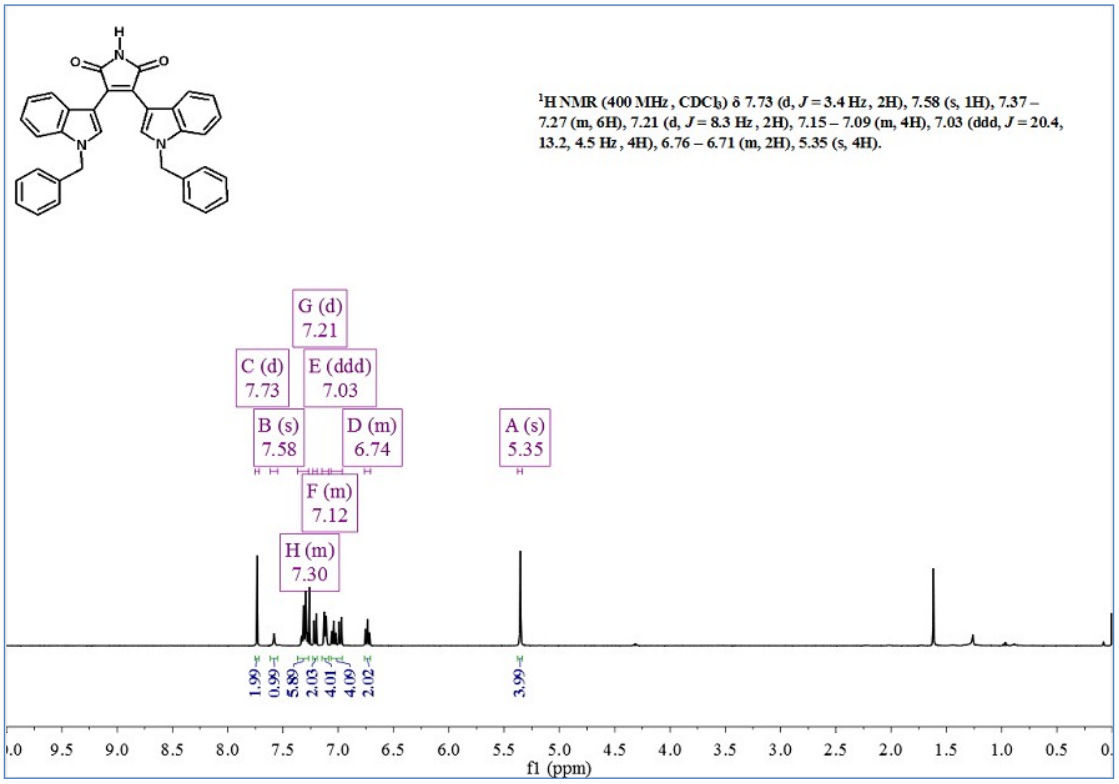


Fig.S20 [1] H NMR spectrum of compound M9.

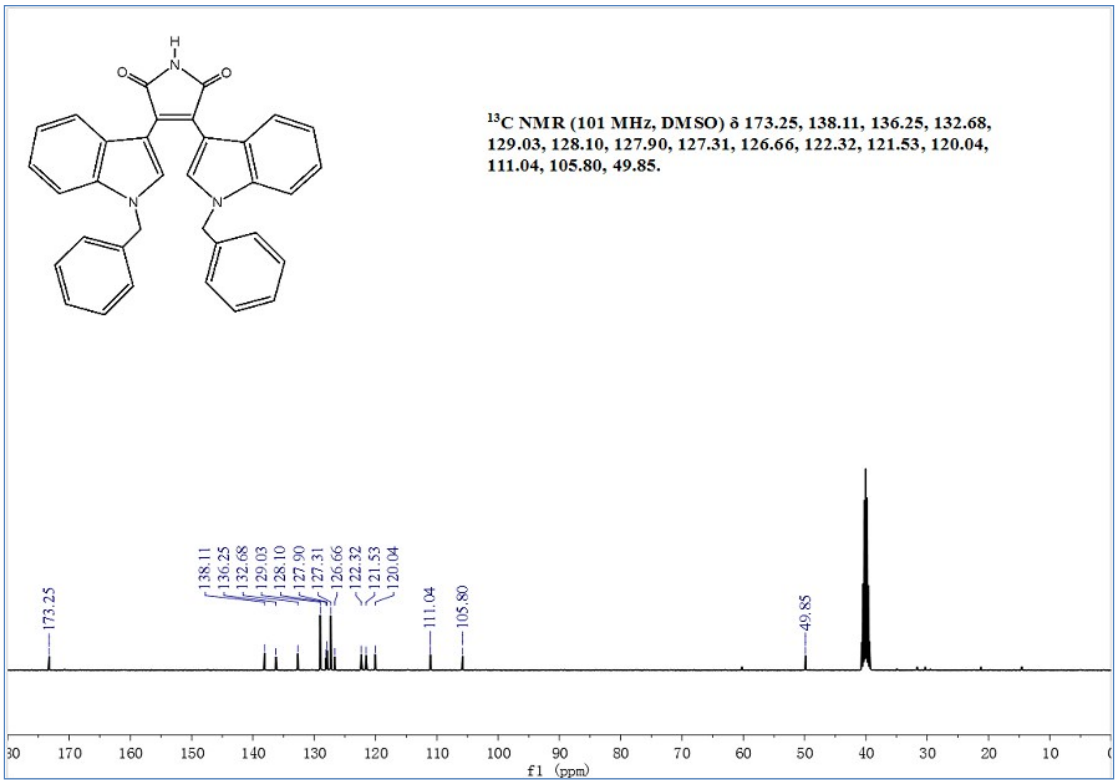


Fig.S21 [13]C NMR spectrum of compound M9.

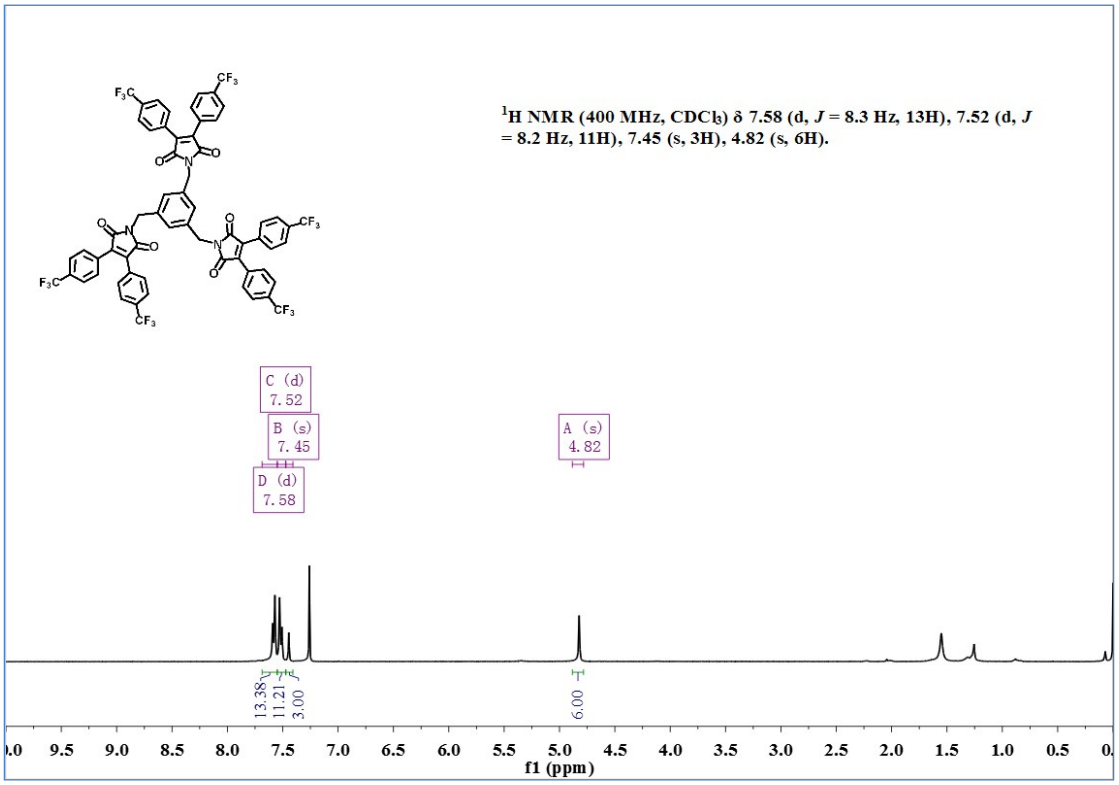


Fig.S22 ^{1}H NMR spectrum of B3G1-F.

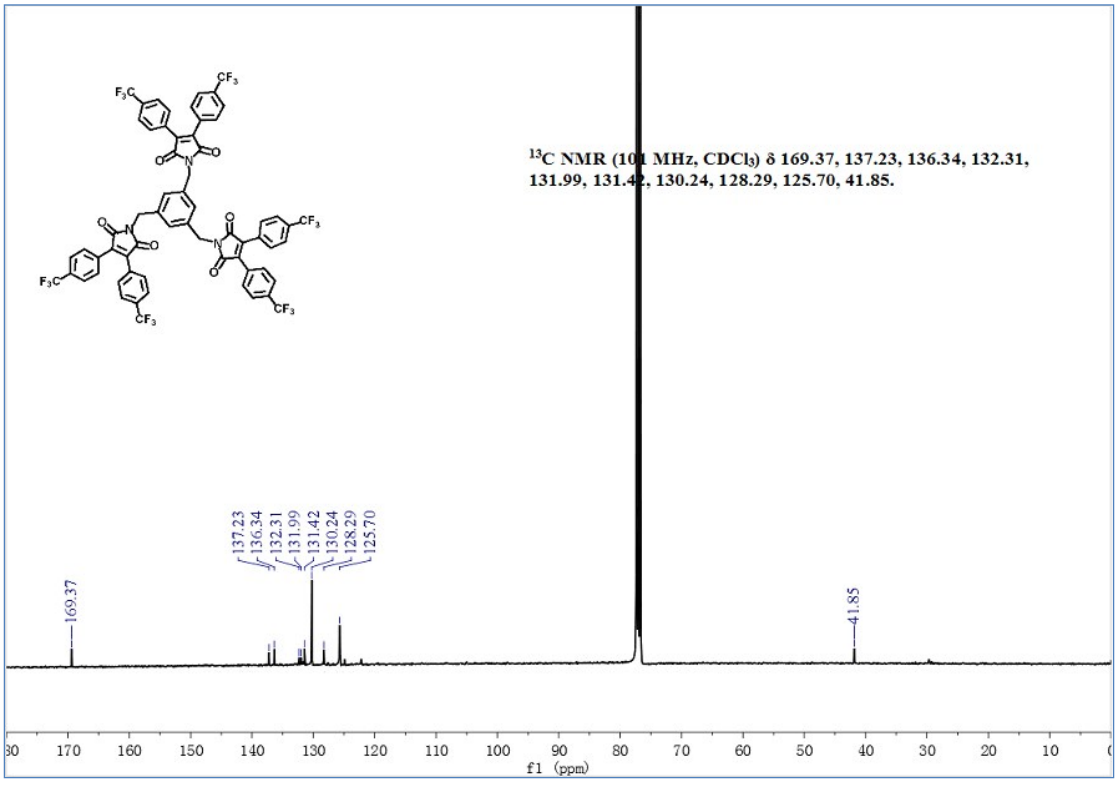


Fig.S23 ^{13}C NMR spectrum of B3G1-F.

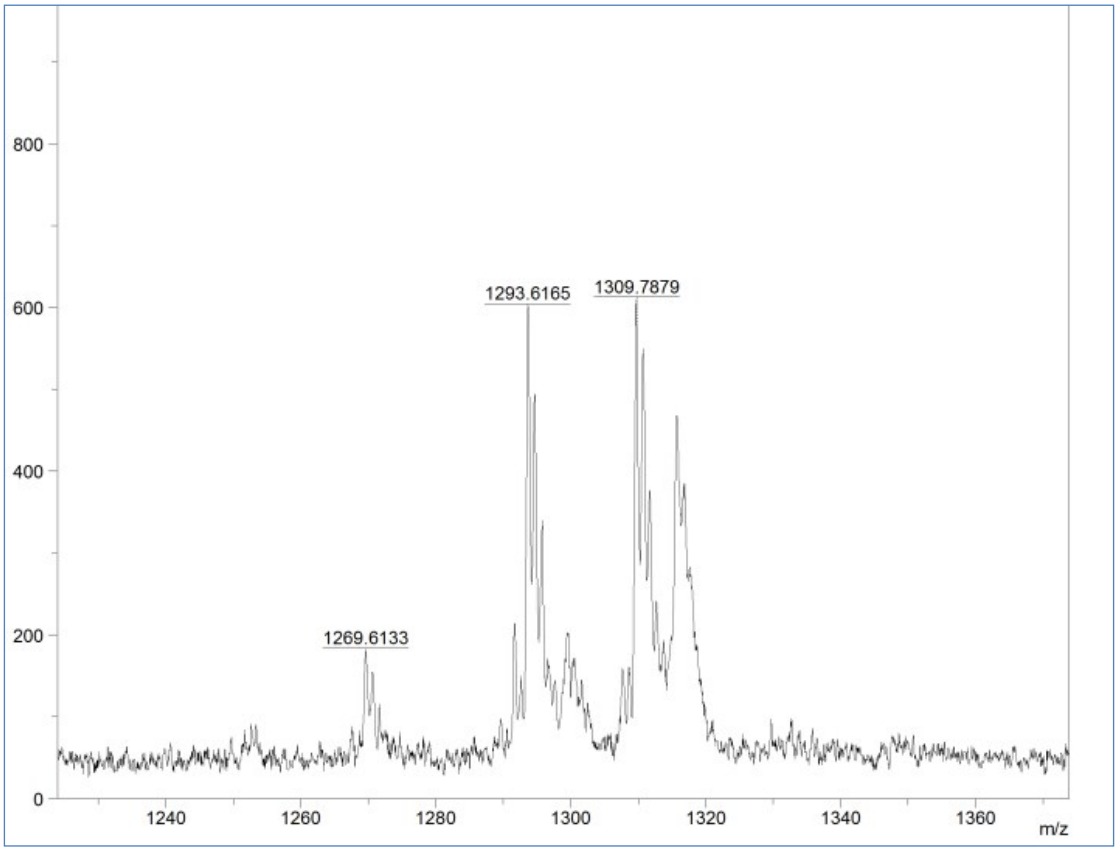


Fig.S24 Mass spectrum of B3G1-F.

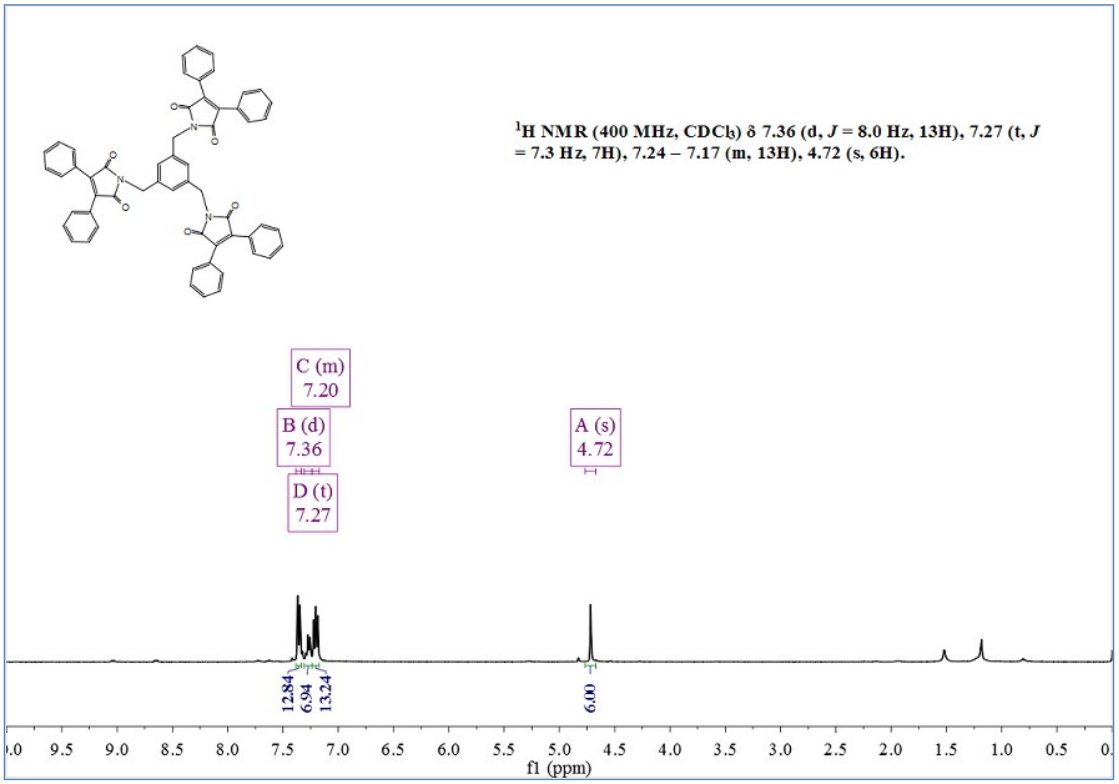


Fig.S25 ^{1}H NMR spectrum of B3G1-H.

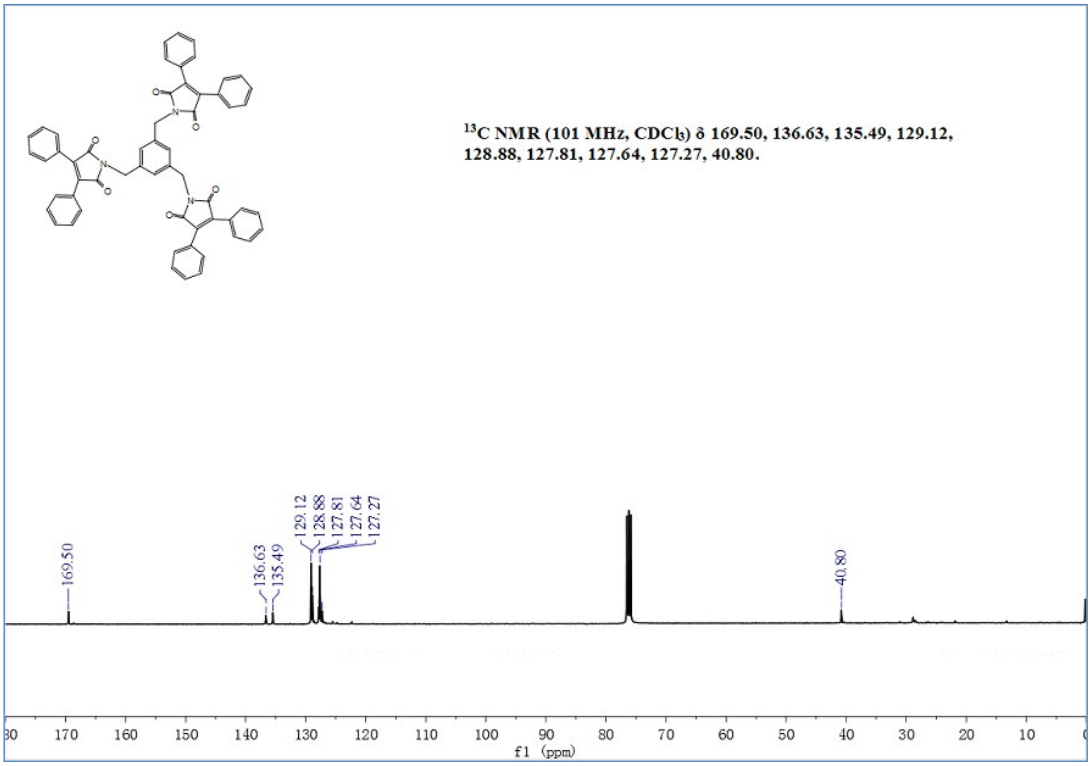


Fig.S26 ^{13}C NMR spectrum of B3G1-H.

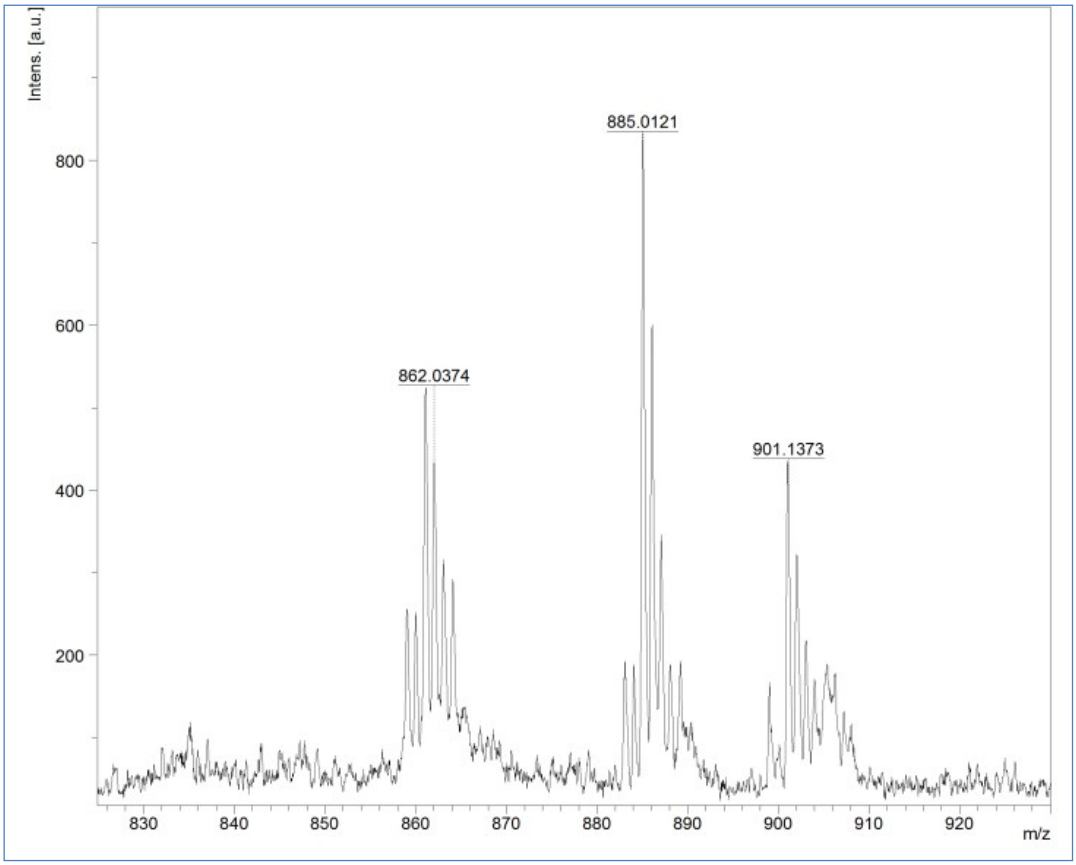


Fig.S27 Mass spectrum of B3G1-H.

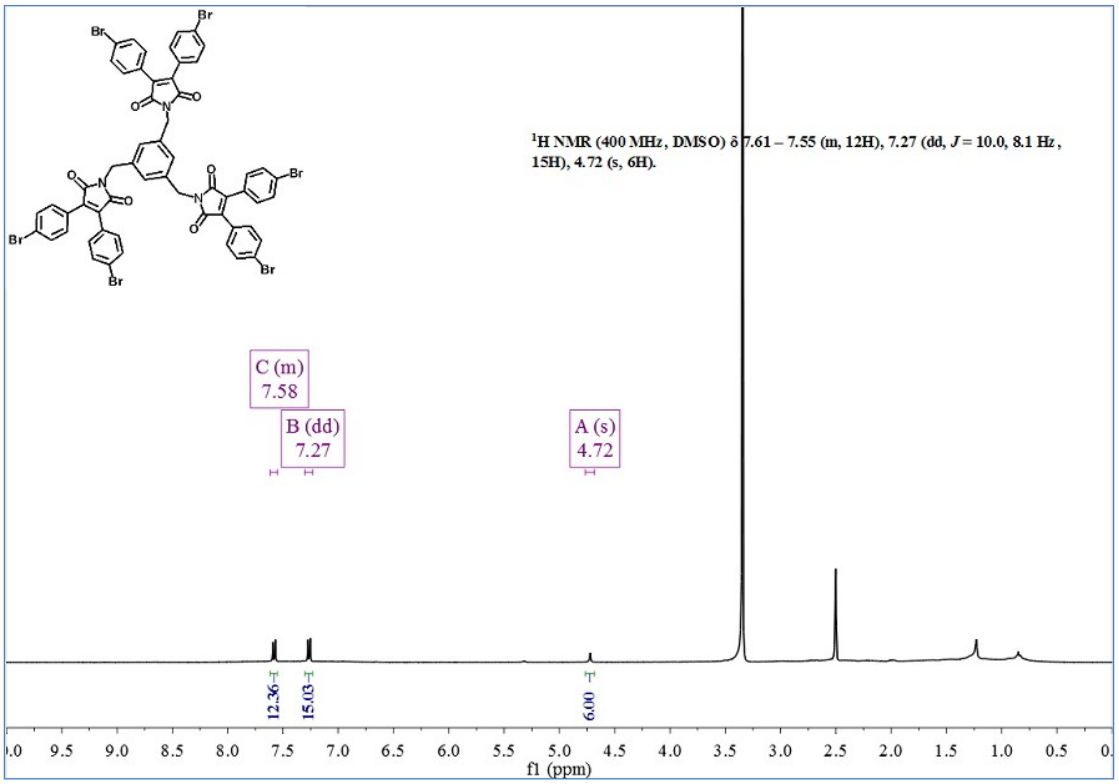


Fig.S28 ^{1}H NMR spectrum of B3G1-B.

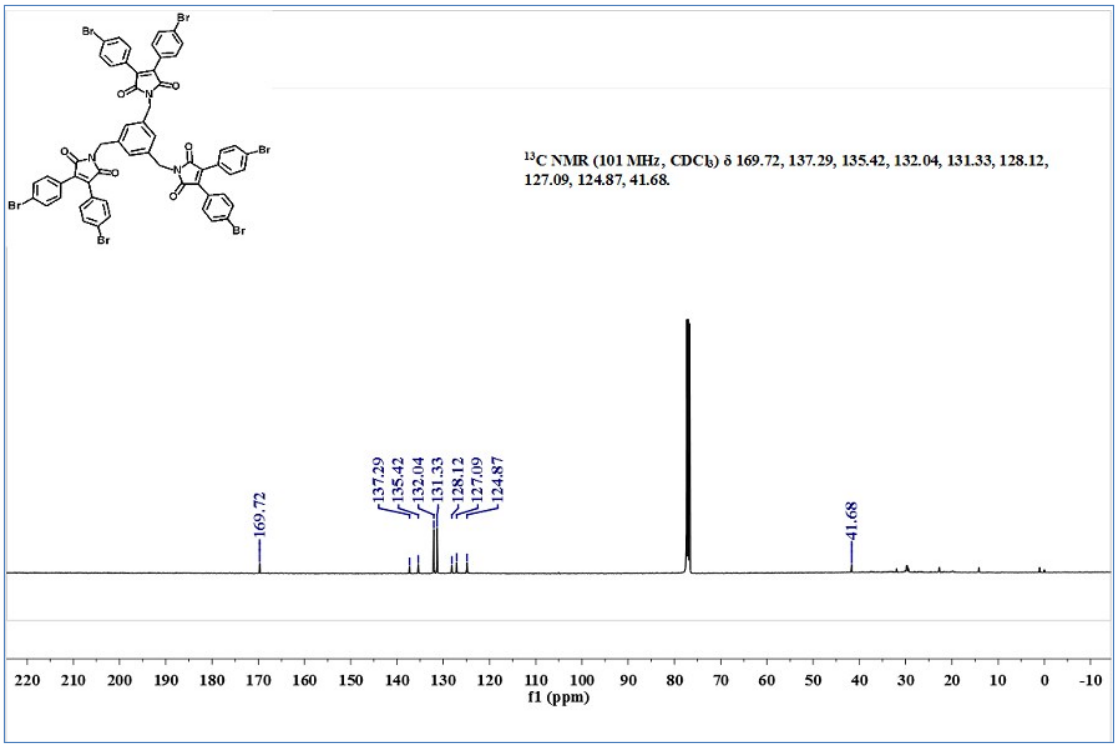


Fig.S29 ^{13}C NMR spectrum of B3G1-B.

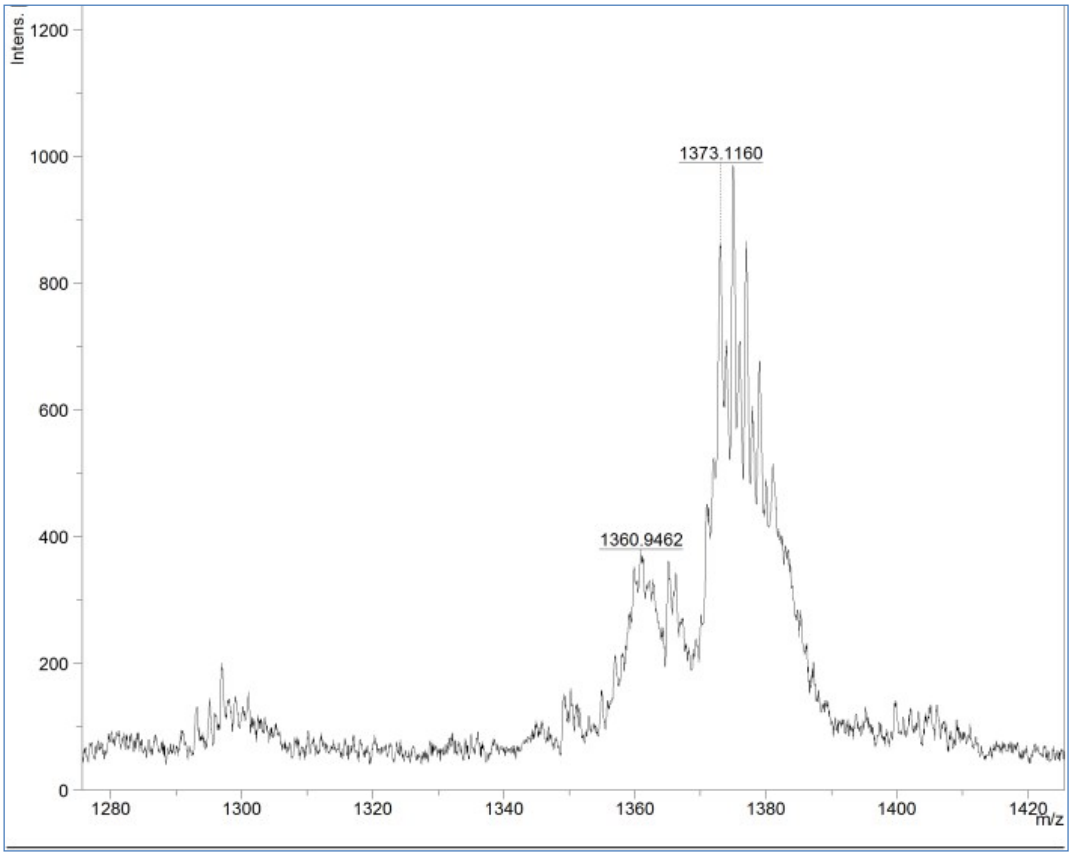


Fig.S30 Mass spectrum of B3G1-B.

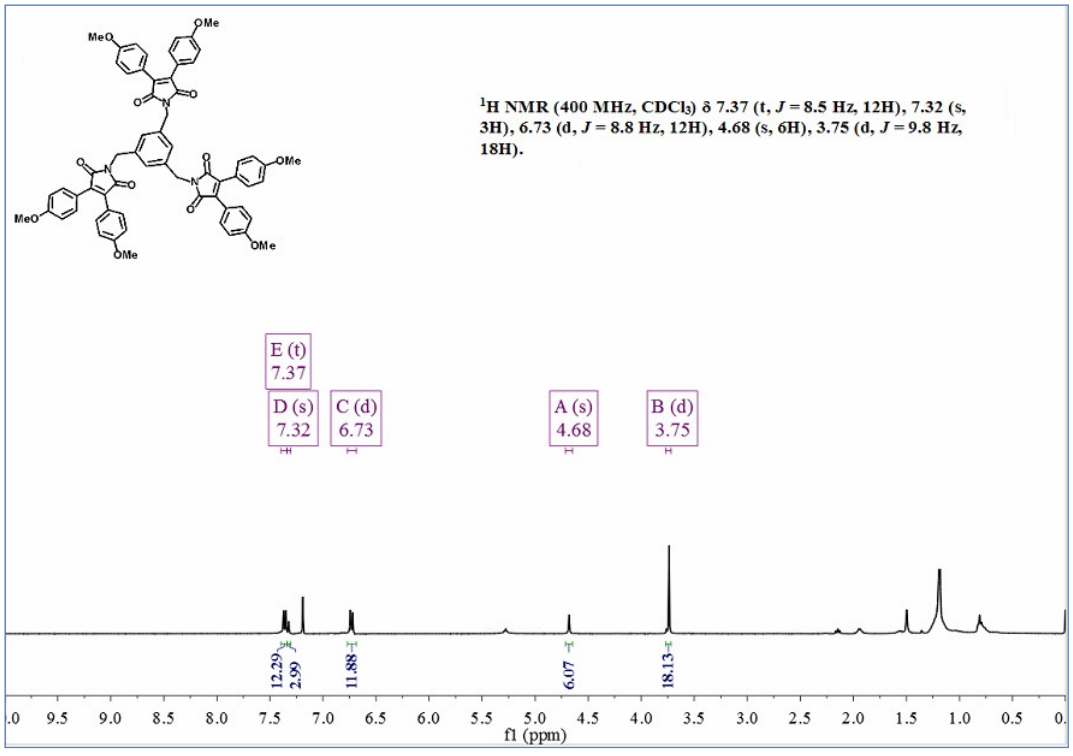


Fig.S31 ^{1}H NMR spectrum of B3G1-O.

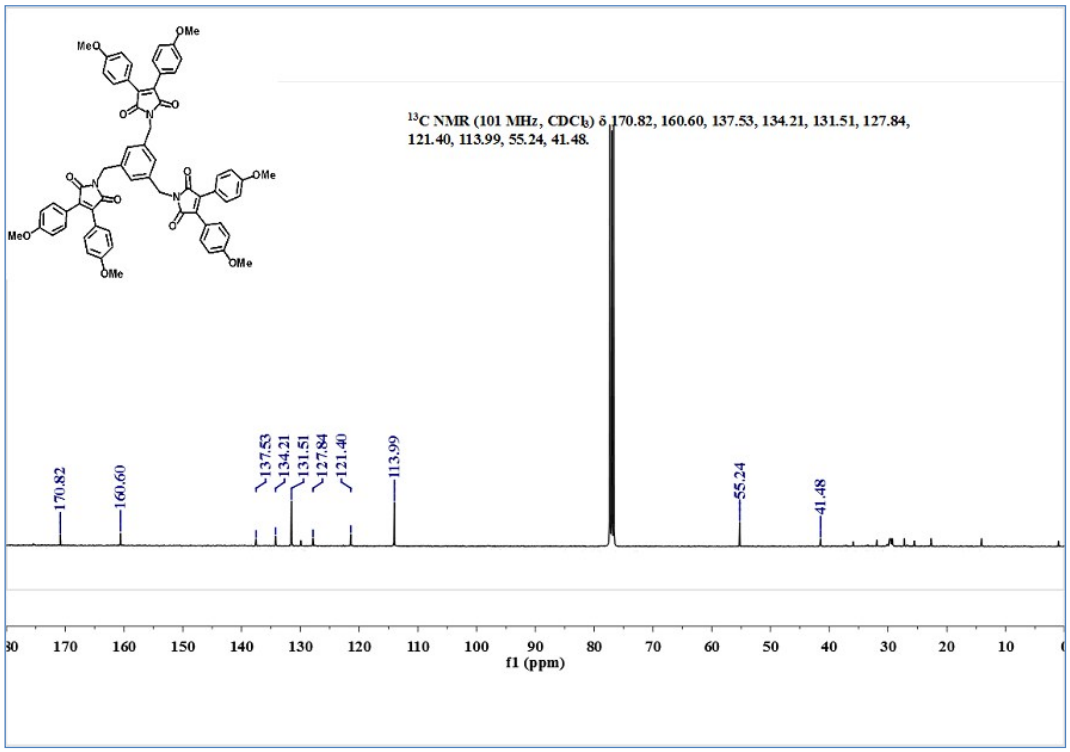


Fig.S32 ^{13}C NMR spectrum of B3G1-O.

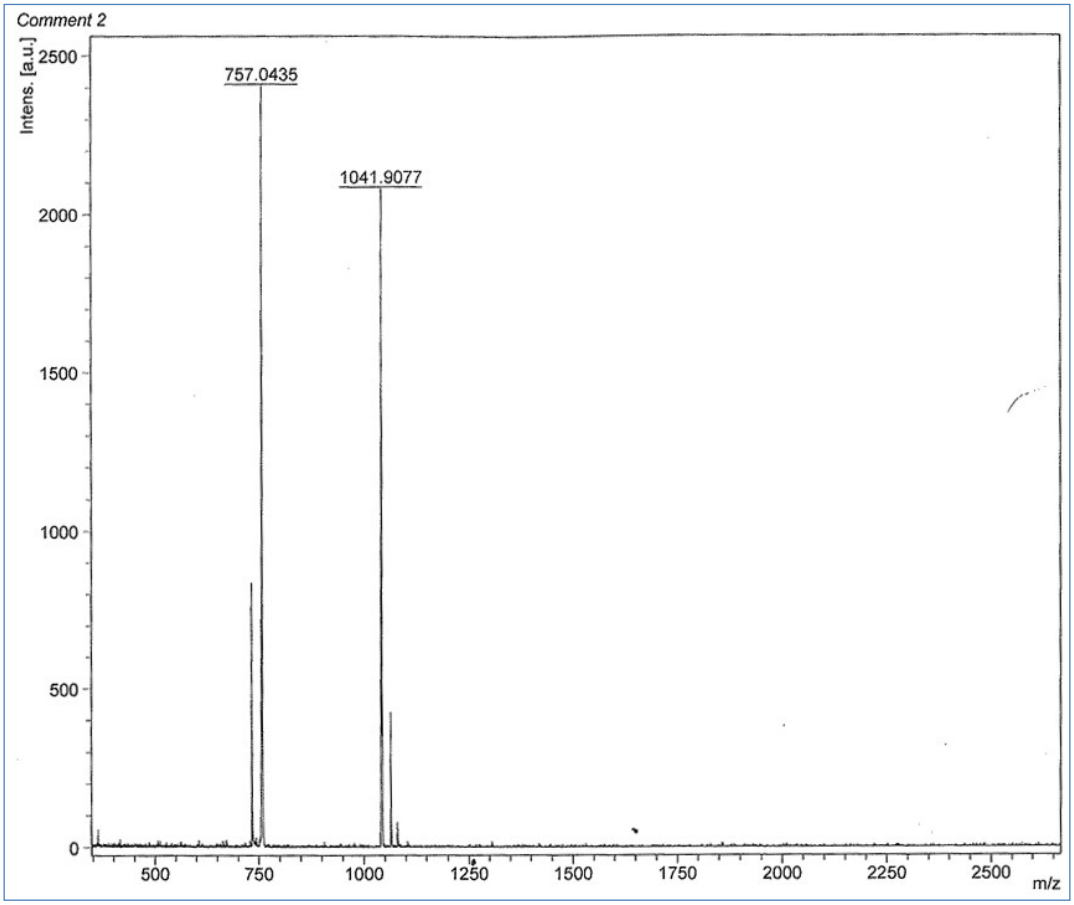


Fig.S33 Mass spectrum of B3G1-O.

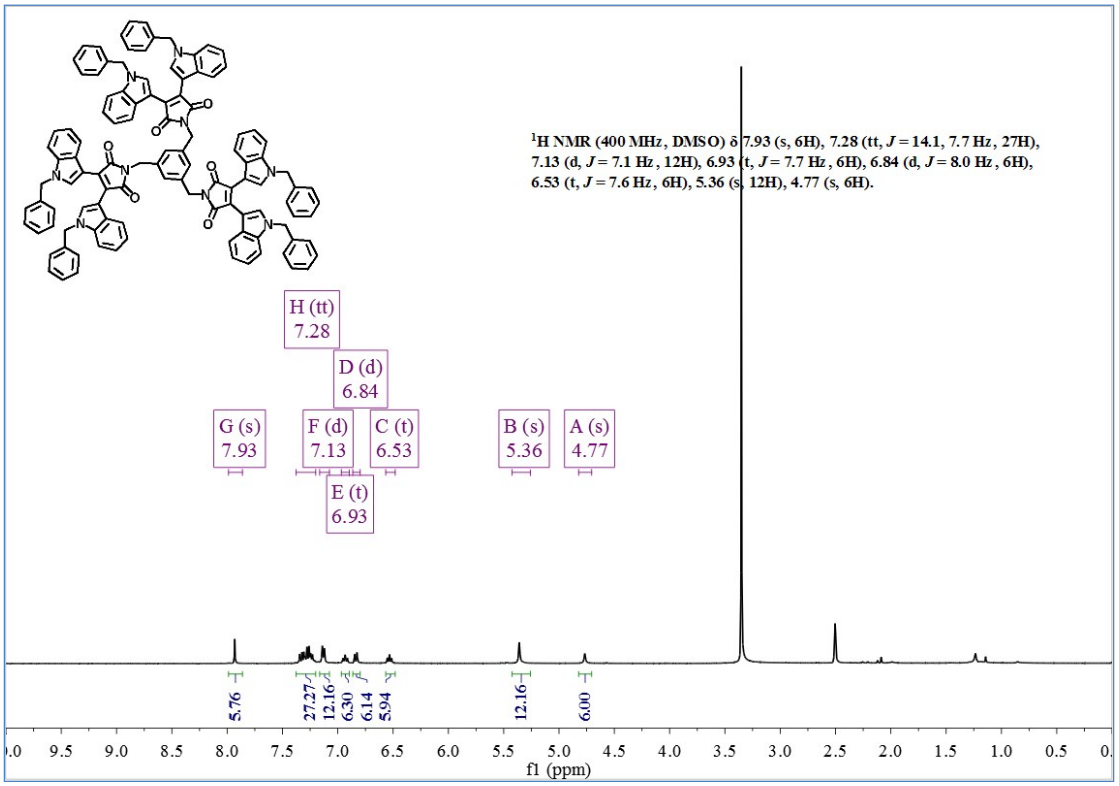


Fig.S34 ^{1}H NMR spectrum of B3G1-N.

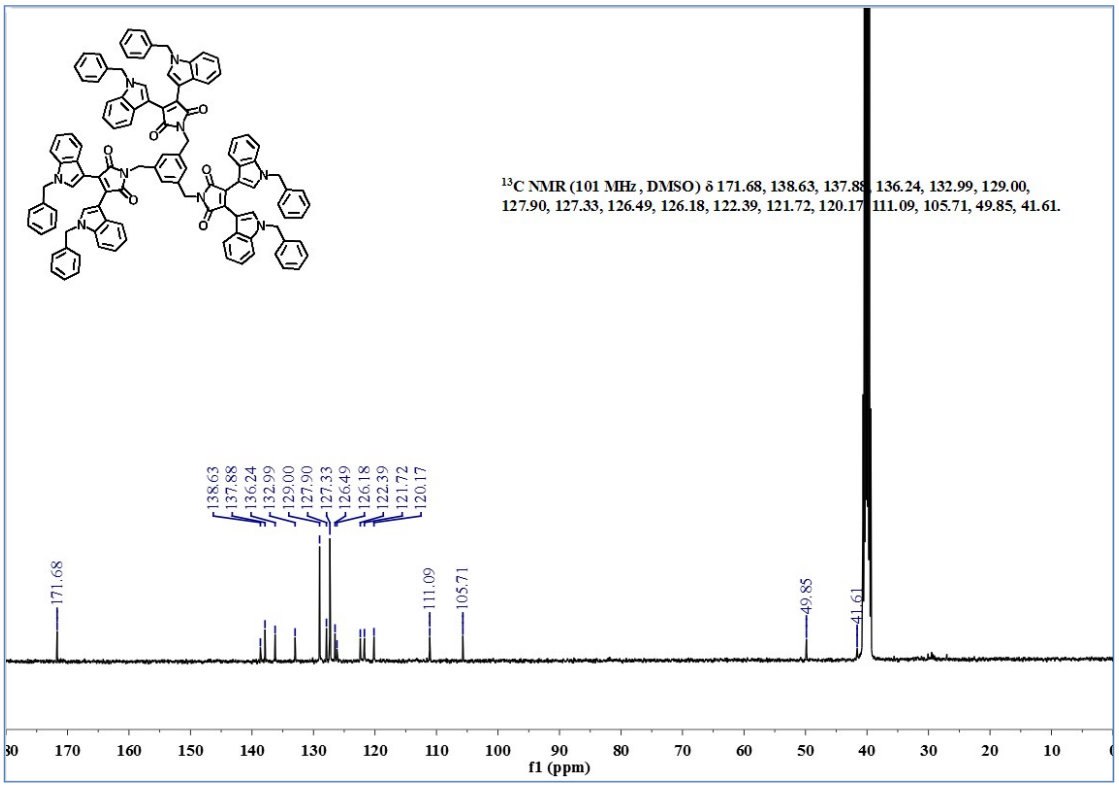


Fig.S35 ^{13}C NMR spectrum of B3G1-N.

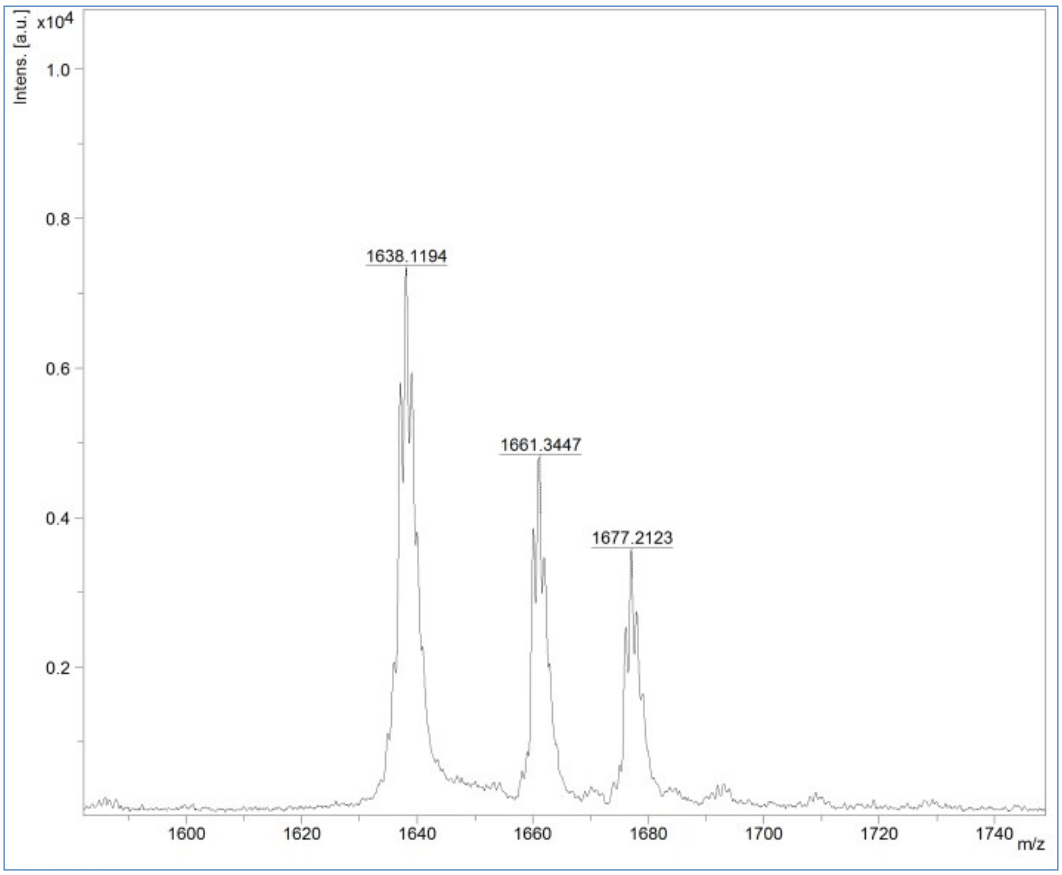


Fig.S36 Mass spectrum of B3G1-N.

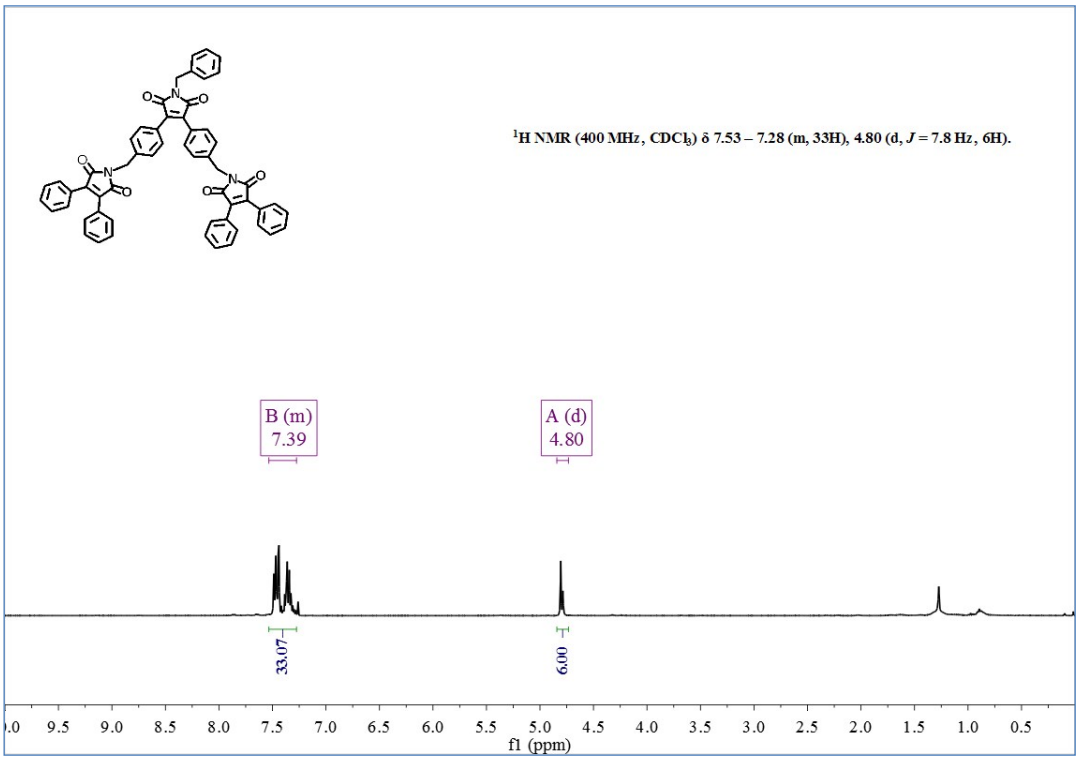


Fig.S37 ^{1}H NMR spectrum of B1G2-H.

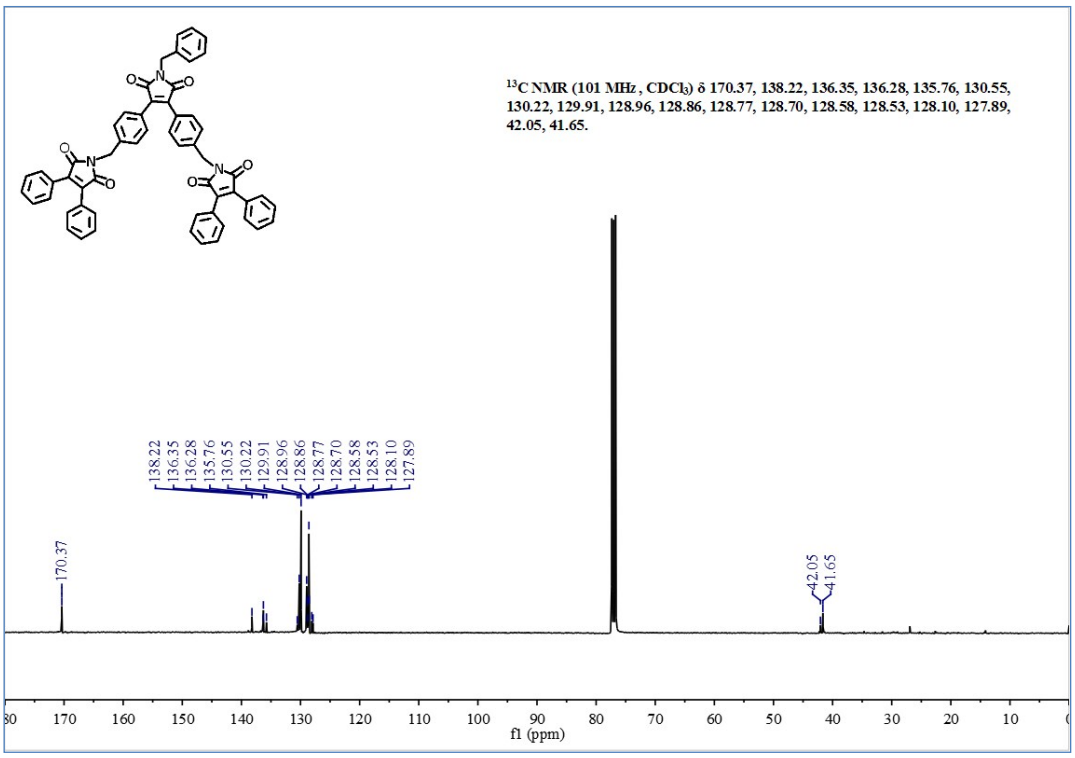


Fig.S38 ^{13}C NMR spectrum of B1G2-H.

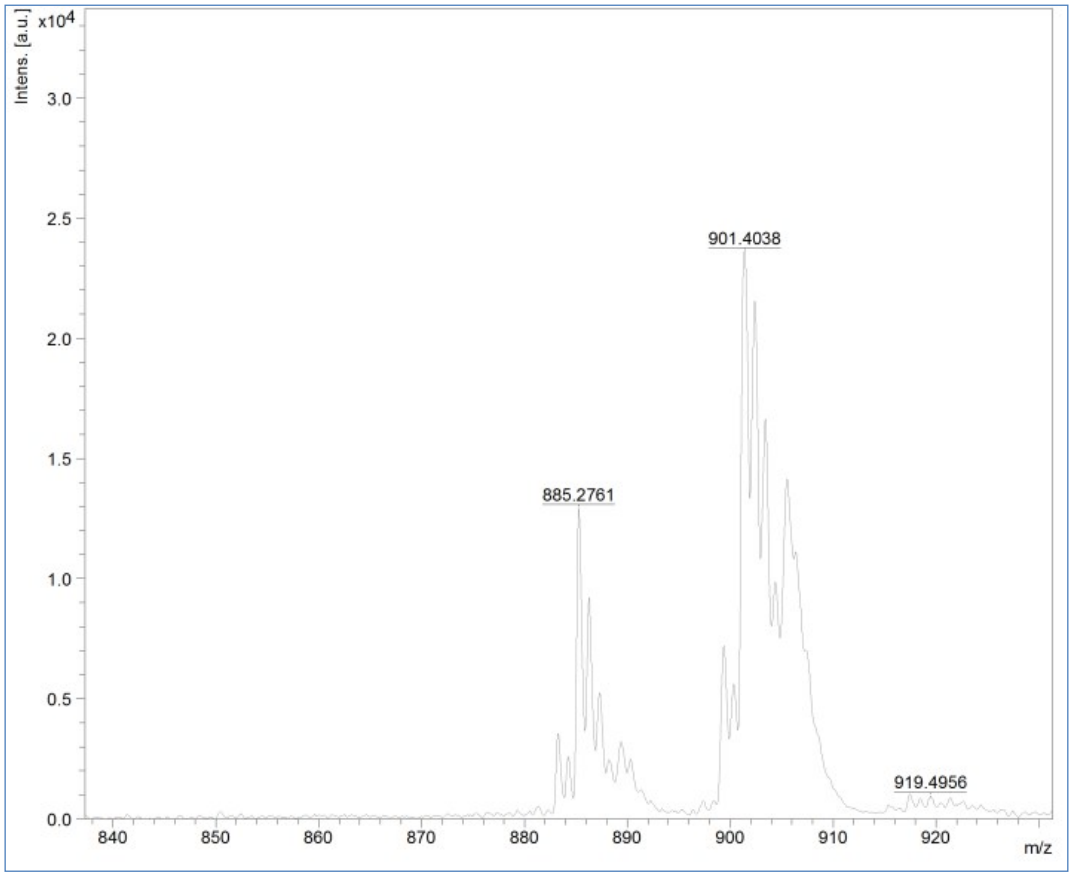


Fig.S39 Mass spectrum of B1G2-H.

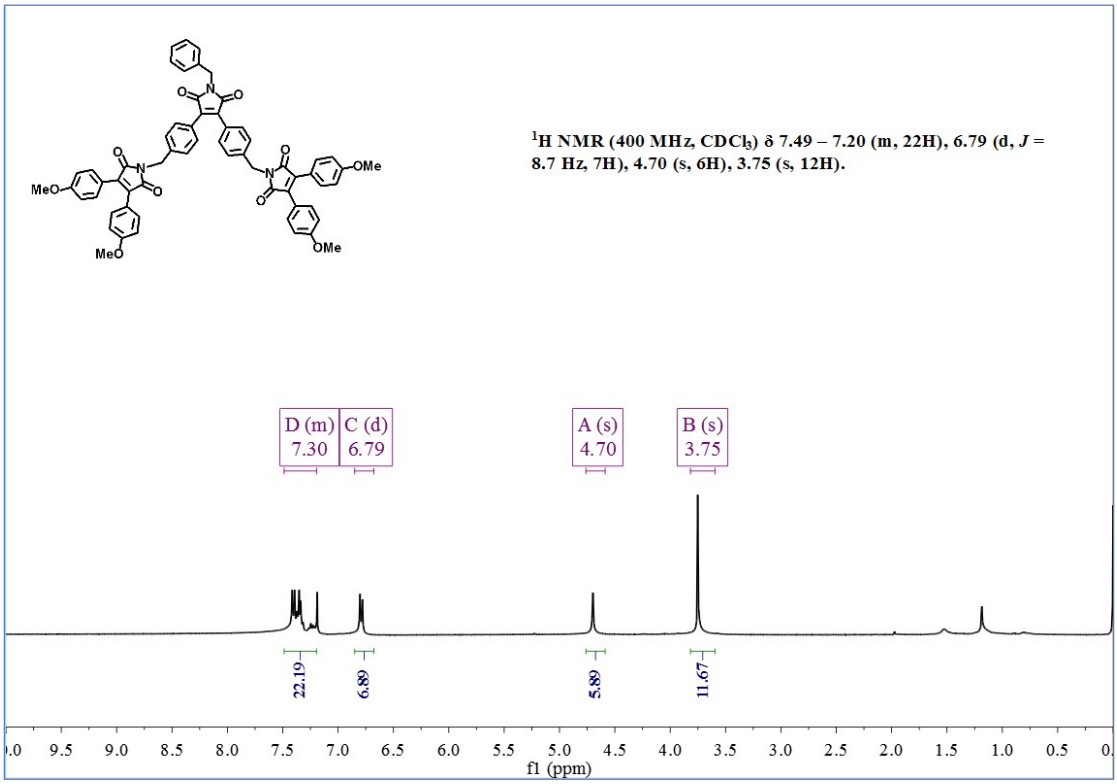


Fig.S40 ^{1}H NMR spectrum of B1G2-O.

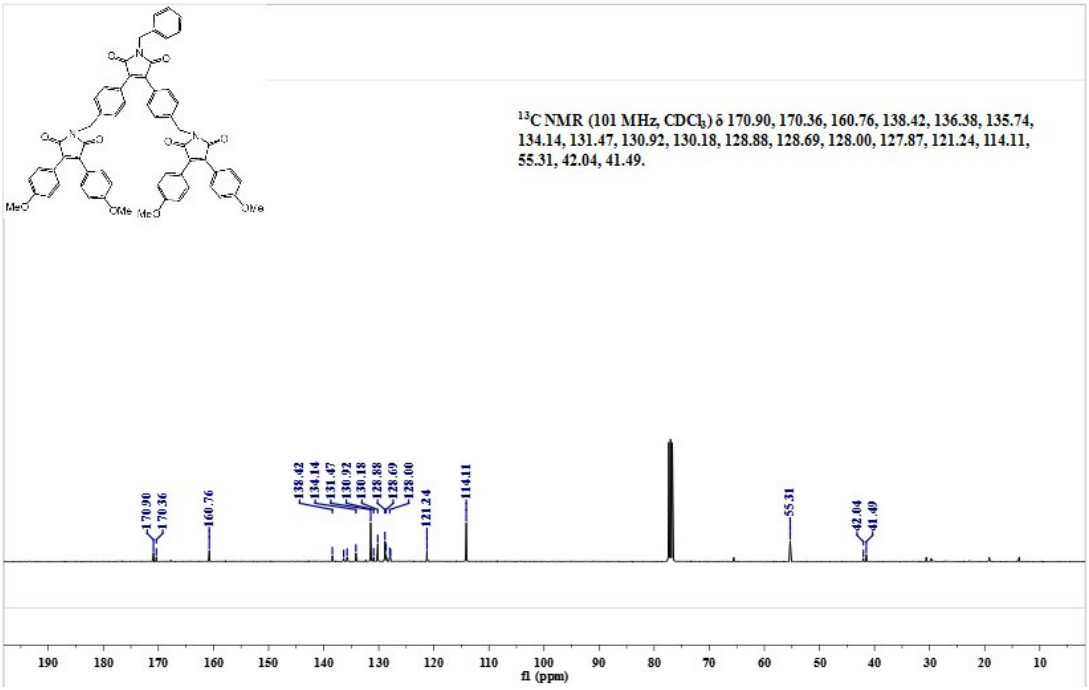


Fig.S41 ^{13}C NMR spectrum of B1G2-O.

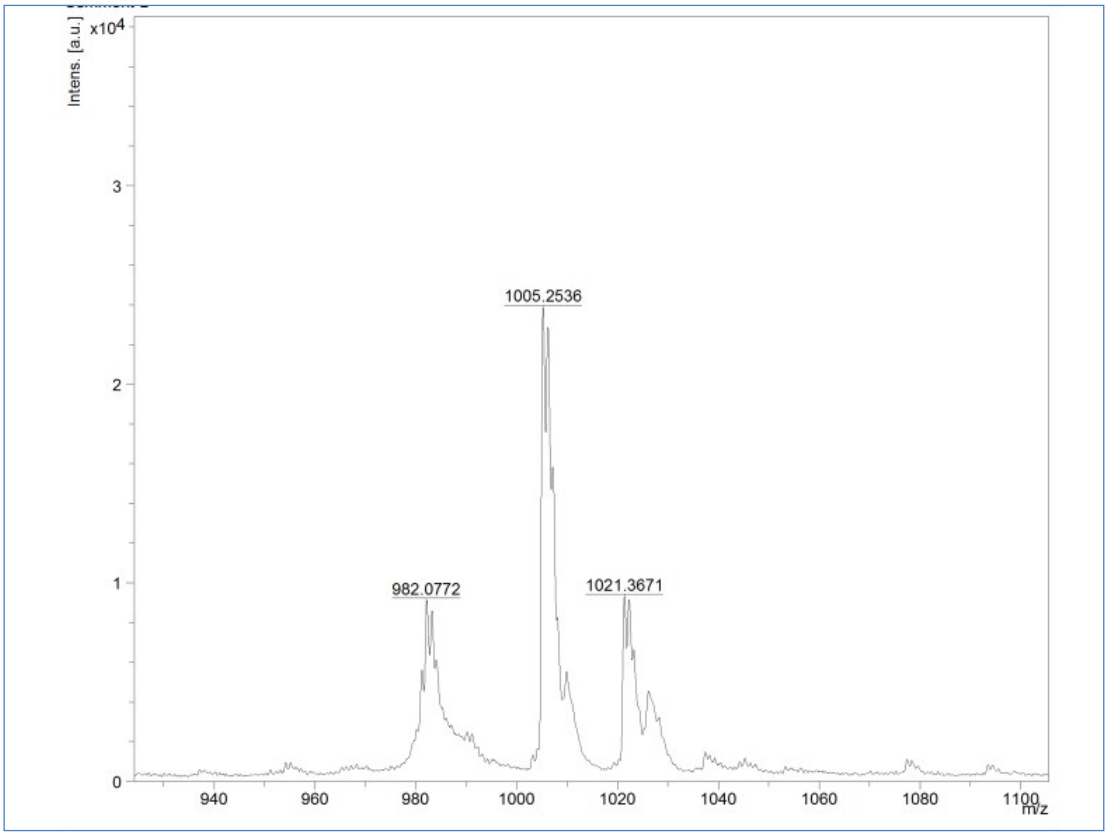


Fig.S42 Mass spectrum of B1G2-O.

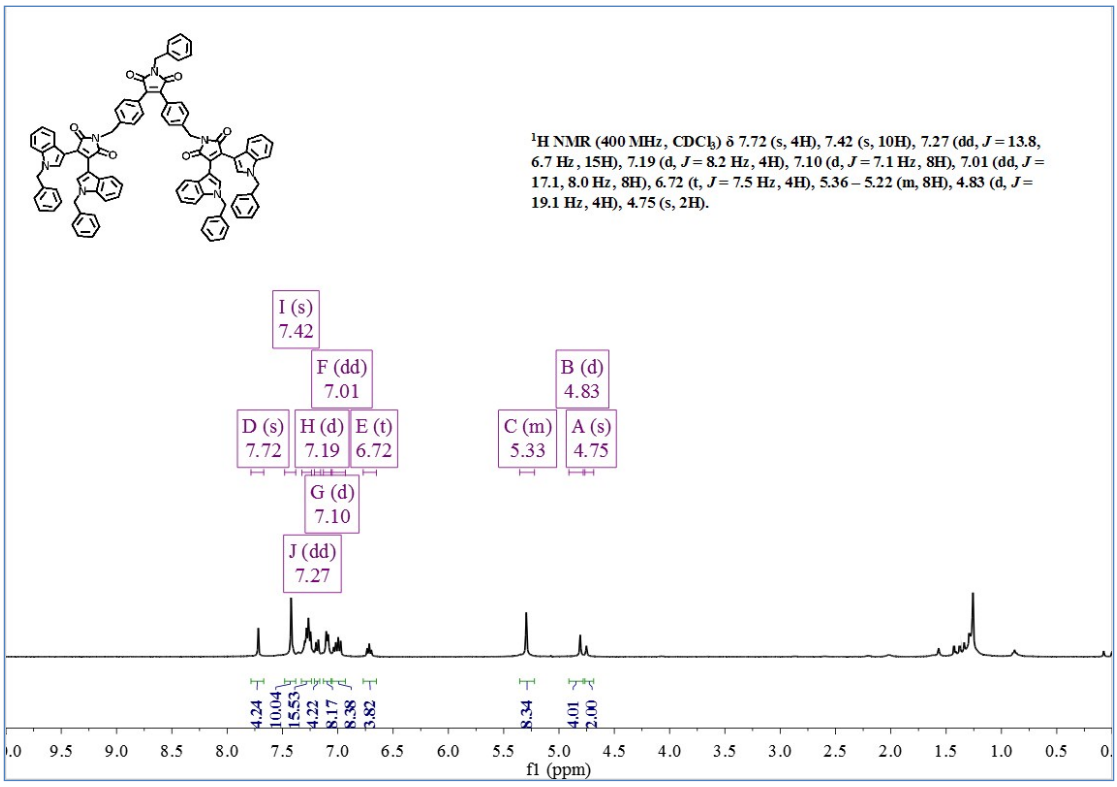


Fig.S43 ^{1}H NMR spectrum of B1G2-N.

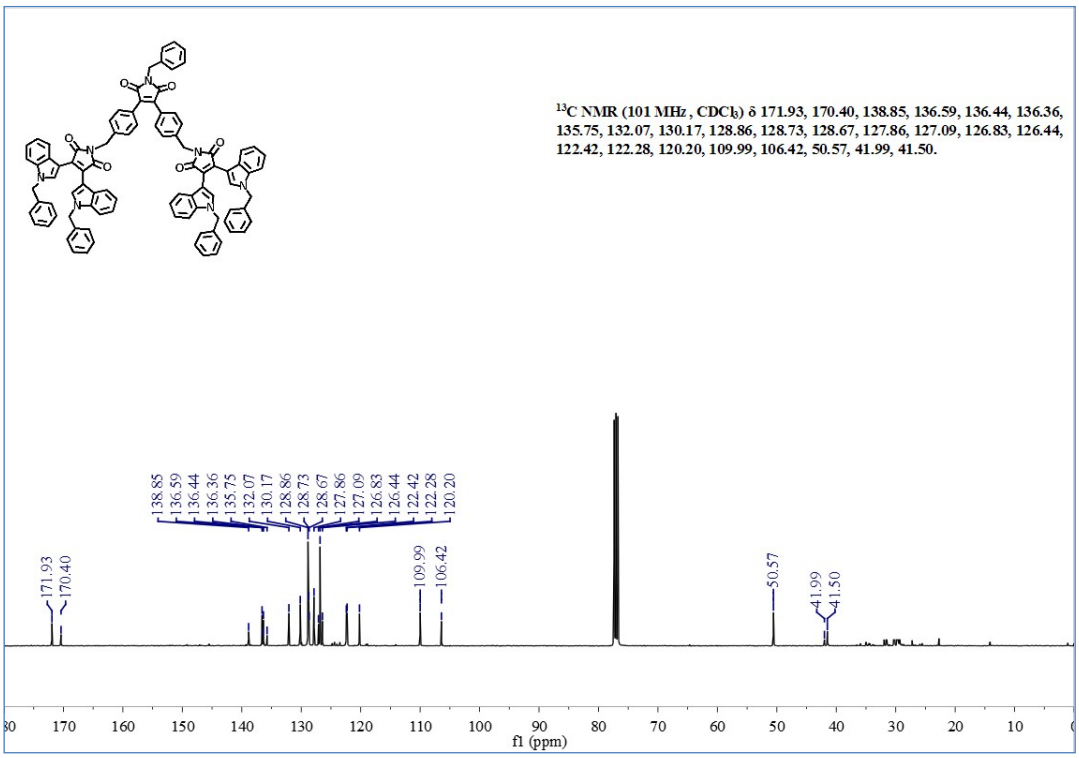


Fig.S44 ^{13}C NMR spectrum of B1G2-N.

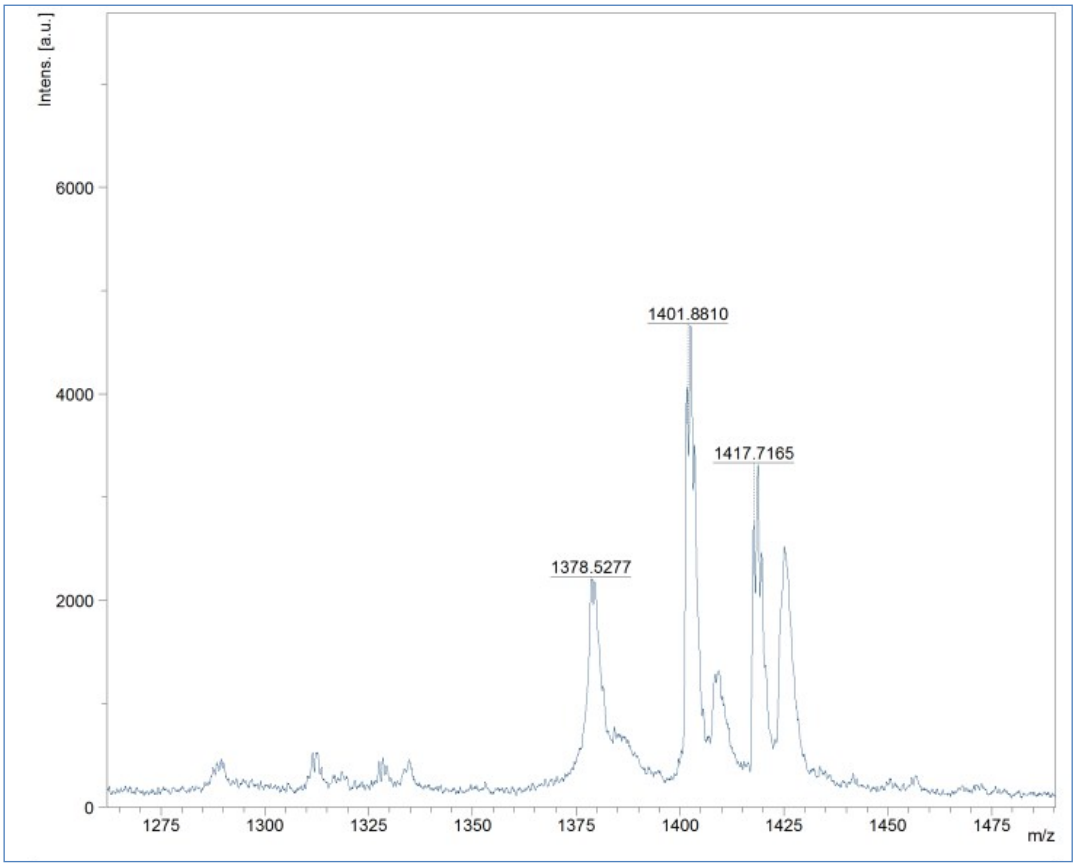


Fig.S45 Mass spectrum of B1G2-N.