Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

o-Carborane based fluorophores as efficient luminescent systems both as solids and as water-dispersible nanoparticles

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1. Experimental section:

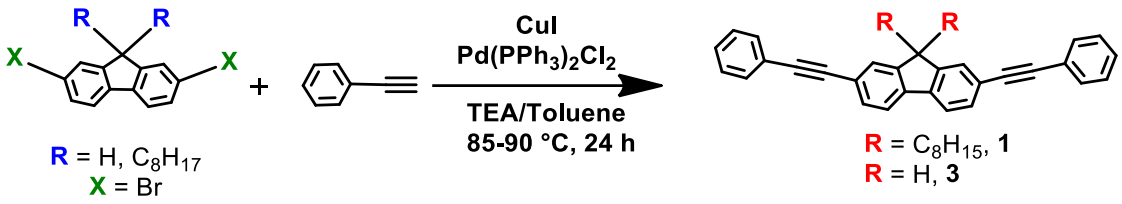
Instrumentation. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. ATR-IR spectra were recorded on JASCO FT/IR-4700 spectrometer on a high-resolution. ^{1}H NMR, ^{11}B NMR, $^{11}B\{^{1}H\}$ NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a NMR-FT Bruker 400 MHz spectrometer using deuterated acetonitrile (CD_3CN) at 25 ºC. Chemical shifts are reported in ppm and referenced to the residual solvent peak for ^{1}H and $^{13}C\{^{1}H\}$ NMR or to $BF_3{\cdot}OEt_2$ as an external standard for ^{11}B and $^{11}B\{^{1}H\}$ NMR. Chemical shifts are reported in ppm and coupling constants in Hertz. Multiplets nomenclature is as follows: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet.

The UV-Vis spectra were recorded on a JASCO V-780 UV-Visible/NIR spectrophotometers, using spectroscopic grade THF (Sigma-Aldrich), in normal quartz cuvette having 1 cm path length, for different solutions for each compound in the range 10^{-4} to 10^{-5} M in order to calculate the molar extinction coefficients (Φ) were run on a with a quartz cell having a path length of 1 cm in the range of 190-600 nm. Solid-state electronic spectra were run on a JASCO V-780 UV-Visible/NIR spectrophotometer equipped with a 60 mm integrating sphere model ISN-901i/A001461872. The fluorescence emission and excitation spectra for all samples in solution were recorded in a VARIANT Cary Eclipse Fluorescence spectrometer. No fluorescent contaminants were detected on excitation in the wavelength region of experimental interest. The fluorescence quantum yields were determined by the "single point method" and repeated three times with similar optical density for reproducibility, against quinine sulfate in 0.5 M aqueous sulfuric acid with $\Phi_F = 0.54$ as a standard. For the aggregates in THF/water (1/99, v/v) the refractive index was assumed to be that of pure water (1.33). Thin films were prepared by spin coating solutions of **2** and **4** in THF at a concentration of 15 $mg{\cdot}mL^{-1}$ on Spectrosil B quartz substrates at 3200 rpm Solid state emission and excitation spectra were run on a Nanologt Horib Jobin Yvon IHR320 fluorimeter. Quantum yields for compounds **1**–**6** in the solid state were measured on a Hammatsu Absolute PL Quantum Yield Spectometer C9920-O2G. Images of nanoparticles were obtained from a Transmission Electron Microscope (TEM) 120 KV JEOL 1210, using ultrathin carbon film on lacey carbon support film, 400 mesh, Copper. Fluorescence images were obtained using an inverted Olympus IX70 microscope coupled with a TRITC filter cube. Particle size distribution were determined using a Zetasizer Nano ZS; Malvern Instruments.

Materials. All reactions were performed under atmosphere of nitrogen employing standard Schlenk techniques. Toluene was purchased from Merck and distilled from sodium benzophenone prior to use. Commercial grade diethyl ether, hexane, petroleum ether, *n*-heptane, chloroform and dichloromethane were used without further purification. $B_{10}H_{14}$ was supplied from KatChem Ltd. (Prague) and used as received. Di-bromo-fluorene was purchased from TCI chemicals, diiodothiophene, phenylacetylene, bis(triphenylphosphine) palladium(II)dichloride ($Pd(PPh_3)_2Cl_2$), CuI, triethyl amine, trimethylsilylacetylene were purchased from Sigma-Aldrich, diethyl sulfide and 4-butylphenylacetylene were purchased from Alfa Aesar.

General synthesis of acetylene precursors for fluorene derivatives:

The acetylene precursors for fluorene derivatives were prepared with the appropriate stoichiometric amounts of starting materials. A dry 10ml round-bottomed flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with a mixture of di-bromo fluorene derivatives, $Pd(PPh_3)_2Cl_2$ and copper iodide, toluene and TEA (v/v 1/9) were added at room temperature. The reaction mixture was allowed to stir for 30 minutes then 1.2 equivalent of 4-butylphenylacetylene was added to the resulting dark brown slurry. After the reaction was refluxed for 24 h, the volatiles were removed with rotary evaporator. The dark brown residue was washed with MeOH followed by hexane, the resultant solids were finally purified by preparative thin layer chromatography (preparative TLC), obtaining the corresponding acetylene precursors.



Synthesis of 9,9-dioctyl-2,7-bis(phenylethynyl)-9H-fluorene (1)

2,7-dibromo-9,9-dioctylfluorene (270 mg, 0.49 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), CuI (6 mg, 0.032 mmol) and phenylacetylene (131 mg, 1.28 mmol) afford compound **1** as pale white solid after purification with preparative TLC (hexane/dichloromethane, 1:1). Yield: 61%. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, J = 8 Hz, 2H), 7.65 (d, J = 8 Hz, 4H), 7.59 (d, J = 8 Hz, 5H), 7.41 (m, 7H), 2.05 (t, J = 16 Hz, 4H), 1.2 (m, 22 H), 0.89 (t, J = 18 MHz, 6H). ^{13}C NMR ($CDCL_3$): δ151.07, 140.70, 131.77, 130.77, 128.45, 126.12, 123.04, 122.03, 120.27, 90.68, 89.88, 55.42, 40.04, 31.25, 30.27, 29.33, 23.87, 22.50, 14.13. FT-IR: 2924 (str, C_{aryl}-H). Elemental analysis calcd. (%) for $C_{45}H_{50}$: C, 91.47; H, 8.52. Found: C, 90.98; H, 8.16.

Synthesis of 2,7-bis(phenylethynyl)-9H-fluorene (3)

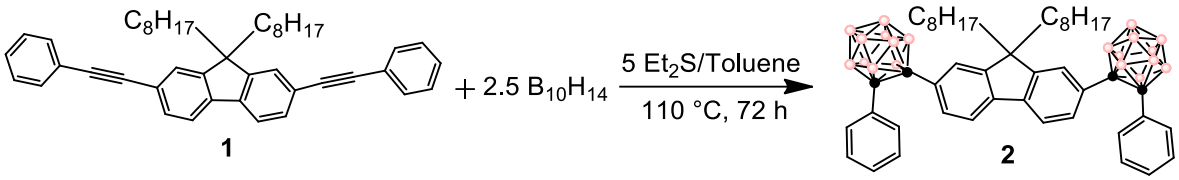
2, 7-dibromofluorene (100 mg, 0.48 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), copper iodide (6mg, 0.032 mmol) and phenylacetylene (90.4 mg, 0.57 mmol) afford compound **3** as pale white solid after purification with preparative TLC (eluent used 1:1 hexane and dichloromethane). Yield: 64%. ^{1}H NMR ($CDCl_3$) δ 7.78 (d, J = 8 Hz, 2H), 7.74 (s, 2H), 7.61 (s, 1H), 7.58 (d, J = 8 Hz, 4H), 7.38 (m, 5H), 3.95 (s, 2H). ^{13}C NMR ($CDCL_3$): δ 143.46, 141.14, 131.57, 130.49, 128.47, 123.32, 121.76, 120.33, 29.88, 89.59, 36.61. FT-IR: **3**056 (str, C_{aryl}-H). Elemental analysis calcd. (%) for $C_{29}H_{18}$: C, 95.05; H, 4.95. Found: C, 94.98; H, 4.86.

General Synthesis of *o*-carborane- functionalized fluorene derivatives:

The fluorene derivatives containing two *o*-carborane clusters were afforded in two steps, first adding an excess amount of diethyl sulfide (Et_2S, 5 equiv per acetylene precursor) to a toluene solution (6-8ml) of decaborane ($B_{10}H_{14}$) and a second step by adding the corresponding acetylene precursors (**1** and **3**) at room temperature. The reaction mixture was heated to reflux and the further stirred for 3 days.

Synthesis of [9,9-dioctyl-2,7-bis(phenyl)-1-o-carboran-1-yl]-9H-fluorene (2)

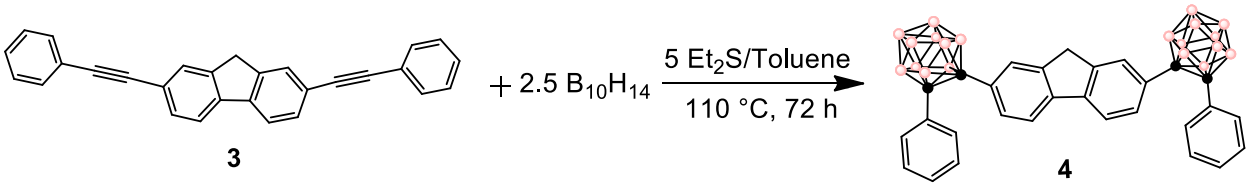
Decaborane (0.59 g, 4.8 mmol), Et_2S (1.2 mL, 11 mmol) and precursor **1** (1.03 g, 2.2 mmol) in toluene afforded compound **3** as a white solid. Yield: 34%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.45 (d, J = 8Hz, 6H), 7.37 (d, J = 8Hz, 2H), 7.32 (s, 2H), 7.17 (t, J = 18Hz, 2H), 7.09 (t, J = 18 Hz, 4H), 1.72 (m, 4H), 1.22 (m, 12 H), 0.97 (m, 6H), 0.90 (t, J = 18 Hz, 6H). ^{11}B NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$), δ (ppm): -3.14 (br s, 2H), -10.79 (br s, 8H). ^{11}B{^{1}H} NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$), δ (ppm): -2.62 (br s, 2H), -10.30 (br s, 8H) ^{13}C NMR ($CDCl_3$): δ 151.14, 141.30, 130.55, 130.12, 130.07, 128.14, 125.00, 119.91, 85.84, 85.49, 55.19. FT-IR: 3210 (str, C_{aryl}-H), 2576 (str, B-H). Elemental analysis calcd. (%) for $C_{40}B_{20}H_{70}$: C, 65.33; H, 8.53. Found: C, 65.31; H, 8.59.



1 2

Synthesis of [2,7-bis(phenyl)-1-o-carboran-1-yl]-9H-fluorene (4)

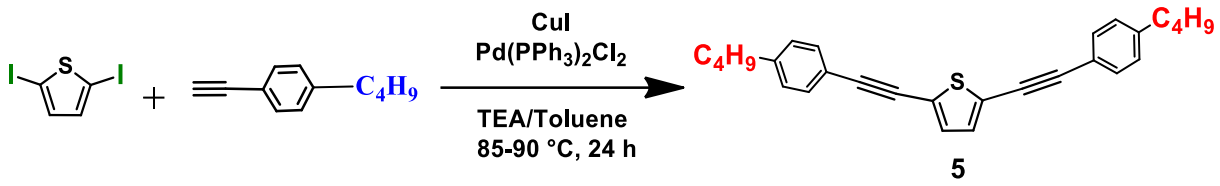
Decaborane (0.59 g, 4.8 mmol), Et_2S (1.2 mL, 11 mmol), and precursor **3** (1.03 g, 2.2 mmol) in toluene afforded compound 4 as a white solid. Yield: 38%. ^{1}H NMR ($CDCl_3$) δ 7.59 (s, 2H), 7.45 (m, 8H), 7.21 (t, J = 18 Hz, 2H), 7.13 (t, J = 18 Hz, 3H), 3.65 (s, 2H). ^{11}B NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$), δ (ppm): 1.76 (br s, 2H), -9.80 (br s, 8H). ^{11}B{^{1}H} NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$), δ (ppm): -2.65 (br s, 2H), -10.68 (br s, 8H). ^{13}C NMR δ 143.63, 141.96, 130.63, 129.76, 128.30, 119.97, 85.84, 85.50, 36.62, FT-IR: 2952 (str, C_{aryl}-H), 2590 (str, B-H). Elemental analysis calcd. (%) for $C_{29}B_{20}H_{38}$: C, 57.78; H, 6.35. Found: C, 57.72; H, 6.31.



3 4

General Synthesis of acetylene precursors for thiophene derivatives:

The acetylene precursors for thiophene derivatives were prepared with the proper stoichiometric amounts of starting materials respectively. A dry 10ml round-bottomed flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with a mixture of mono-iodo or di-iodo thiophene compounds, $Pd(PPh_3)_2Cl_2$ and copper iodide, toluene and triethylamine (TEA) (v/v 1/99) at room temperature. The reaction mixture was allowed to stir for 30 minutes, then 1.3 to 2.3 equivalents of the 4-butylphenylacetylene derivatives was added to the resulting dark brown slurry containing mono-iodo or di-iodo thiophene, respectively. After, the reaction was refluxed for 24 h, the volatiles were removed with rotary evaporator. The dark brown residue was washed with MeOH followed by hexane, the resultant solids were finally purified by preparative thin layer chromatography (preparative TLC), obtaining the corresponding acetylene precursors.

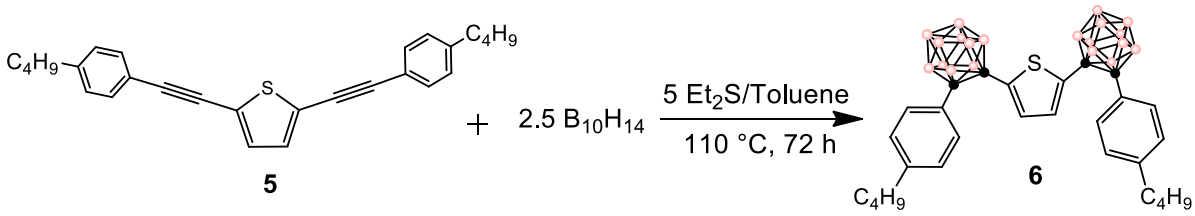


Synthesis of 2,5-bis((4-butylphenyl)ethynyl)thiophene (5)

2,5-diiodothiophene (200 mg, 0.595 mmol), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.026 mmol), copper iodide (12 mg, 0.063 mmol) and 4-butylphenylacetylene (222 mg, 1.403 mmol) in 5ml toluene/TEA mixture afforded compound **9** as pale white solid after purification with preparative TLC (eluent used 1:1 hexane and dichloromethane). Yield: 62%. ^{1}H NMR (CDCl3): δ 7.48 (d, J= 8 Hz, 4H), 7.21 (d, J = 8Hz, 4H), 7.17 (s, 2H), 2.67 (t, J = 8Hz, 4H), 1.65 (m, 4H), 1.405 (m, 4H), 0.98 (t, J = 4Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 144.52, 144.07, 94.11, 81.22, 35.71, 33.27, 22.44, 13.87. FT-IR: 2956 (str, C_{aryl}-H). Elemental analysis calcd. (%) for $C_{28}H_{28}S$: C, 84.79; H, 7.12. Found: C, 84.75; H, 7.16.

Synthesis of 2,5-bis((4-butylphenyl)-*o*-carboran-1-yl)thiophene (6).

To a toluene (5 mL) solution of $B_{10}H_{14}$ (200 mg, 1.636 mmol), an excess amount (Et_2S, 5 equiv per acetylene precursor, 0.4 mL, 3.725 mmol), and precursor **5** (296 mg, 0.745 mmol) at room temperature. The reaction mixture was refluxed for 3 days to afford compound **6** as white solid. Yield: 46% ^{1}H NMR ($CDCl_3$): δ ^{1}H NMR (CDCl3): δ 7.29 (d, J = 8 Hz, 4H), 7.02 (d, J = 8 Hz, 4H), 6.59 (s, 2H), 2.59 (t, J = 8Hz, 4H), 1.57 (m, 5H), 1.31 (m, 4H), 0.93 (t, J = 8Hz, 6H). ^{11}B NMR ($CDCl_3$): δ -1.88 (s, 2H), -9.78 (s, 8H). ^{11}B {^{1}H} NMR ($CDCl_3$): δ -2.46 (s, 2H), -10.34 (s, 8H). **^{13}C NMR ($CDCl_3$):** δ 145.98, 137.77, 130.86, 128.43, 127.47, 85.95, 85.94, 35.10, 35.17, 22.23, 13.91 **FT-IR:** 3191 (str, C_{aryl}-H), 2514 (str, B-H). Elemental analysis calcd. (%) for $C_{28}B_{20}H_{48}S$: C, 53.13; H, 7.64. Found: C, 53.22; H, 7.16.



2. NMR Spectra

9,9-dioctyl-2,7-bis(phenylethynyl)-9H-fluorene (1)

Figure S1. **^{1}H NMR** (400 MHz, $CDCl_3$) of **1**

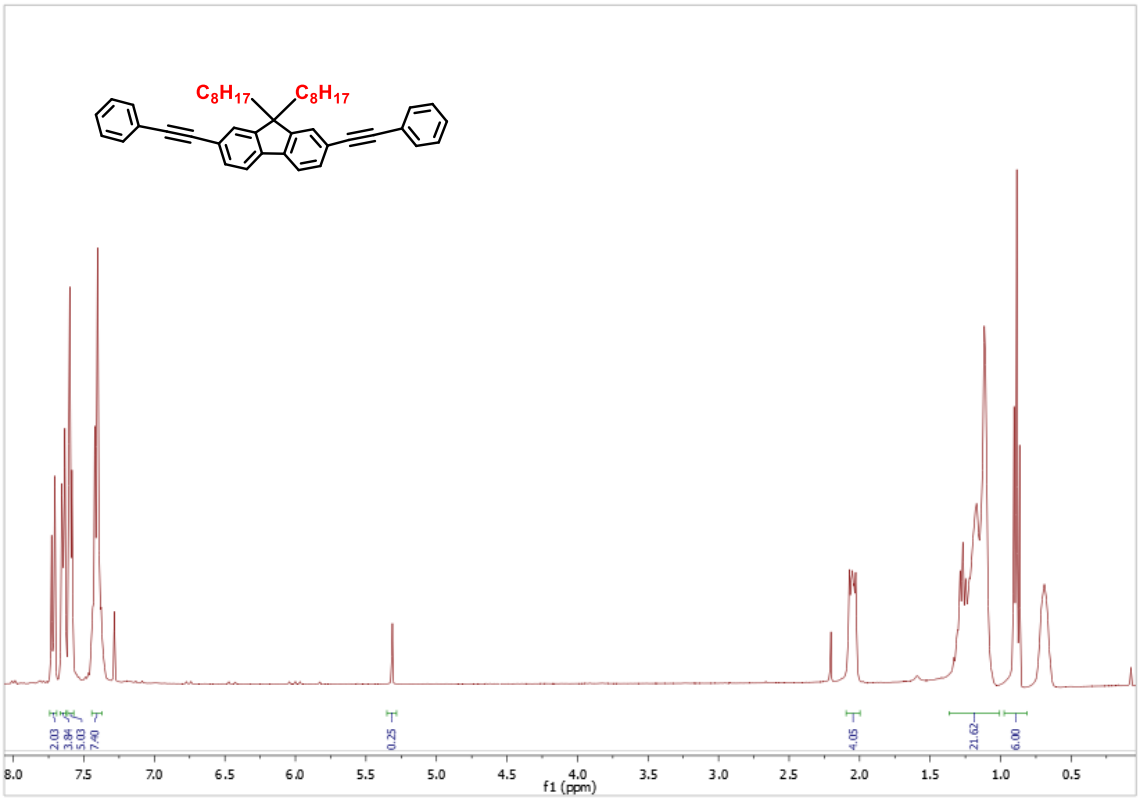
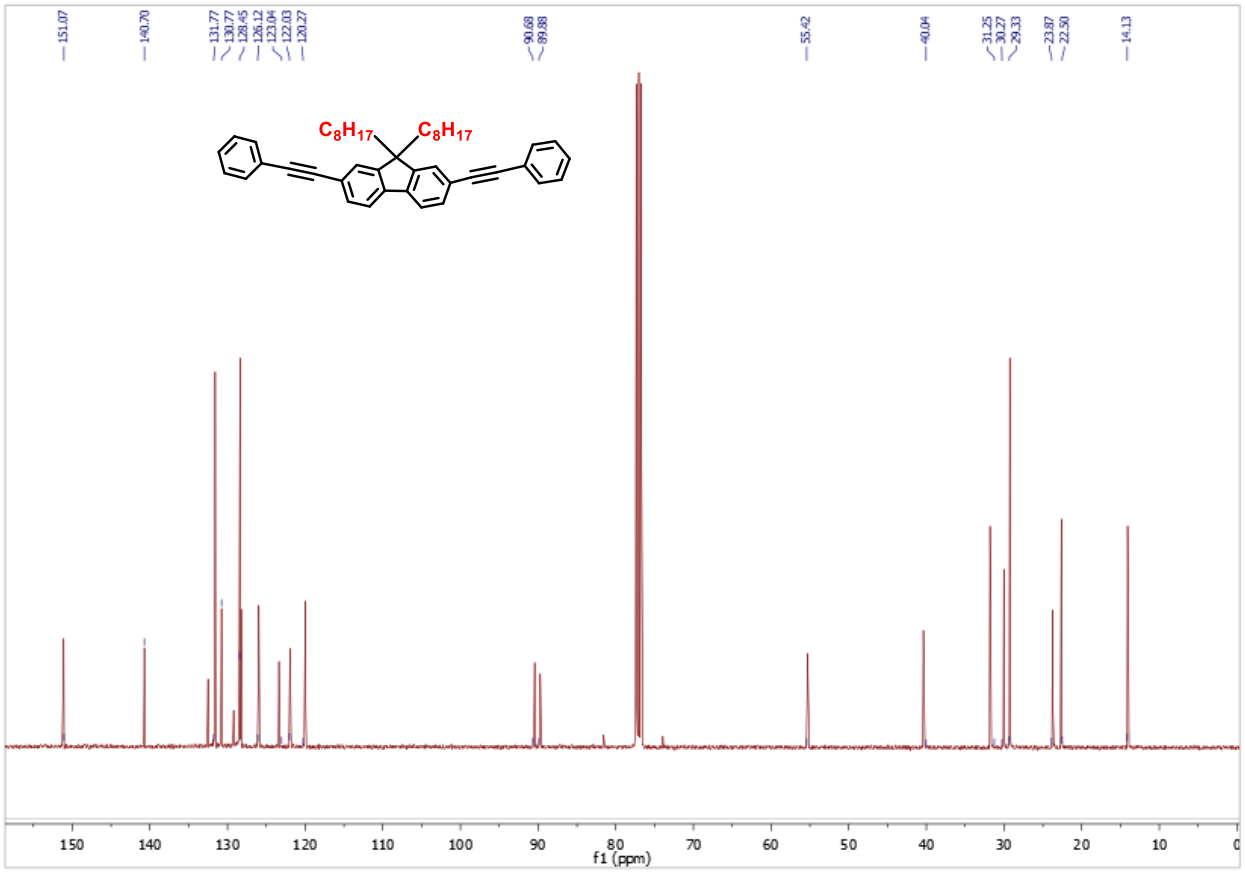


Figure S2. ^{13}C NMR (400 MHz, $CDCl_3$) of **1**



[9,9-dioctyl-2,7-bis(phenyl)-1-o-carboran-1-yl]-9H-fluorene (2)

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of **2**

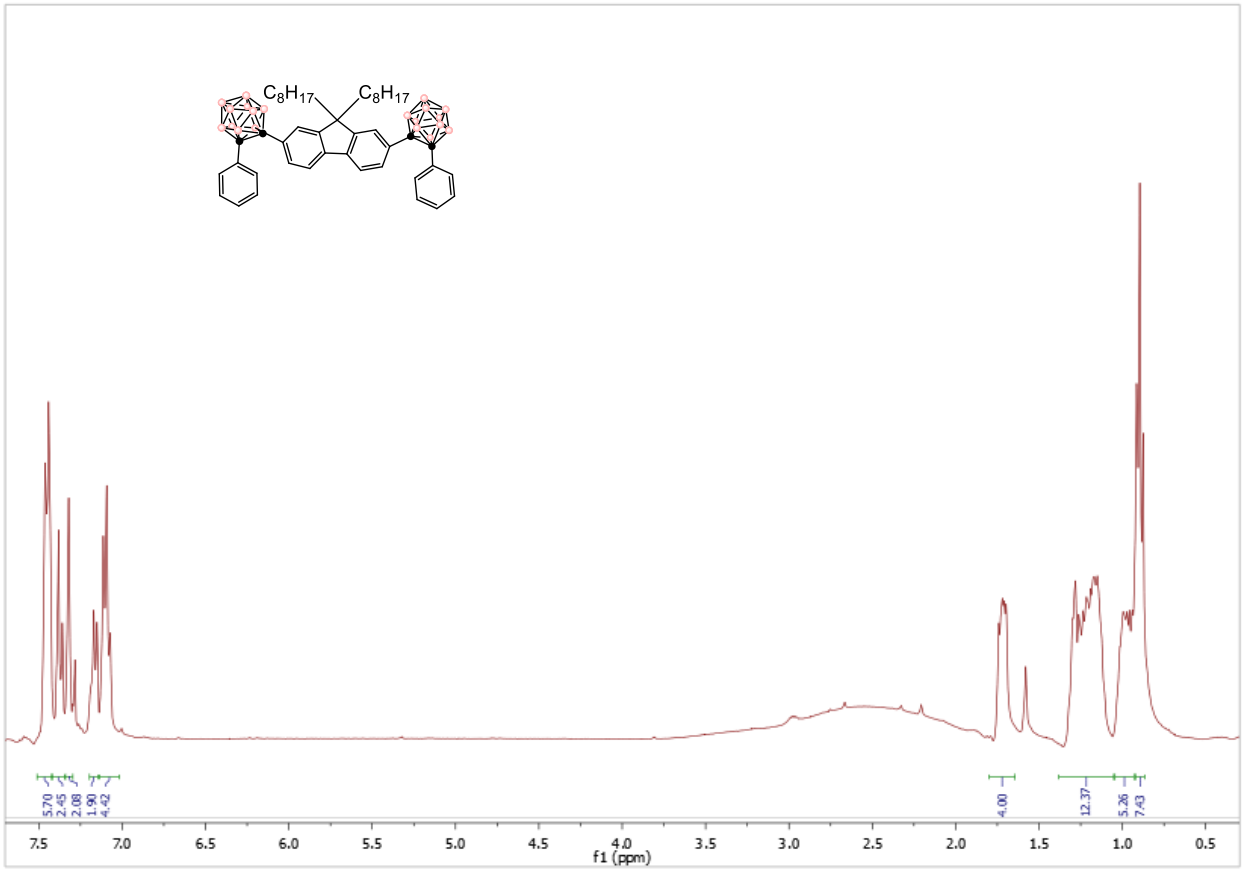


Figure S4. ^{13}**C NMR** (400 MHz, $CDCl_3$) of **2**

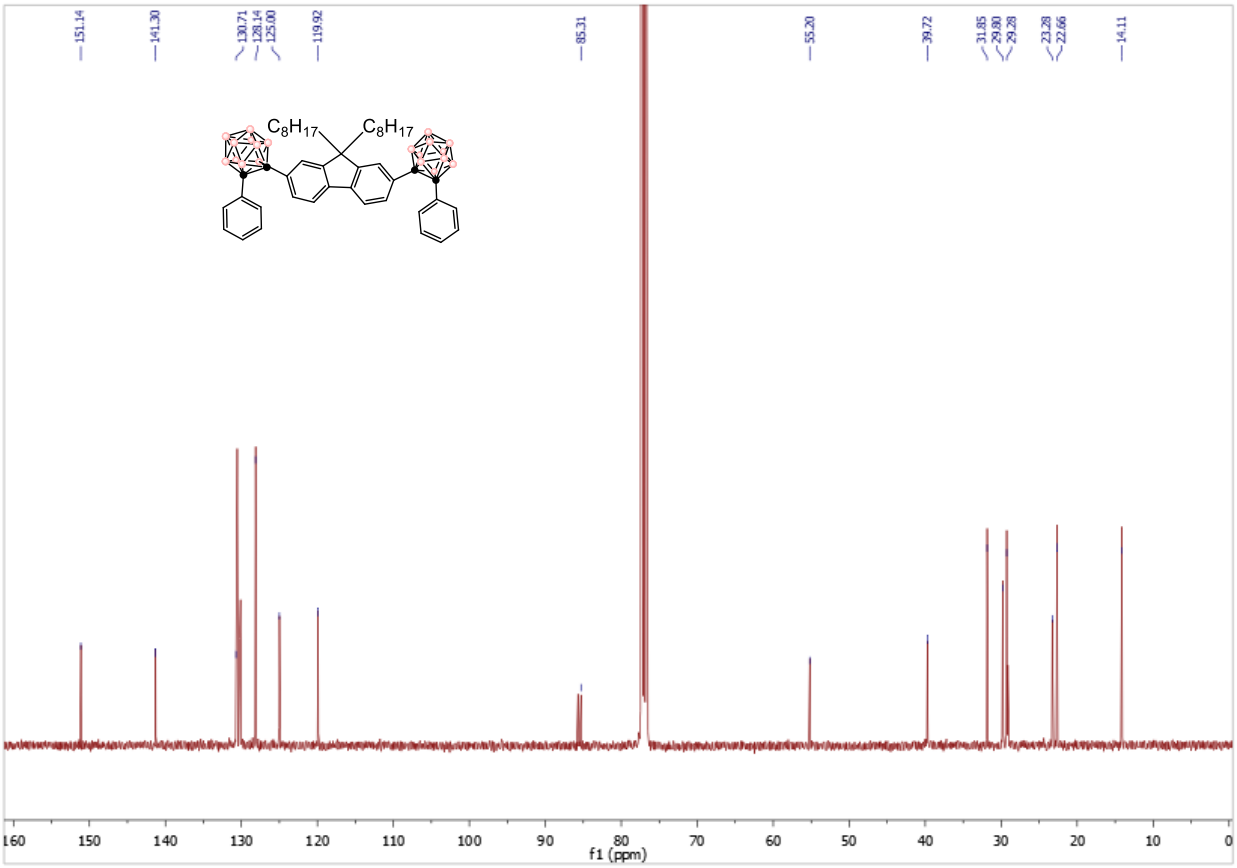
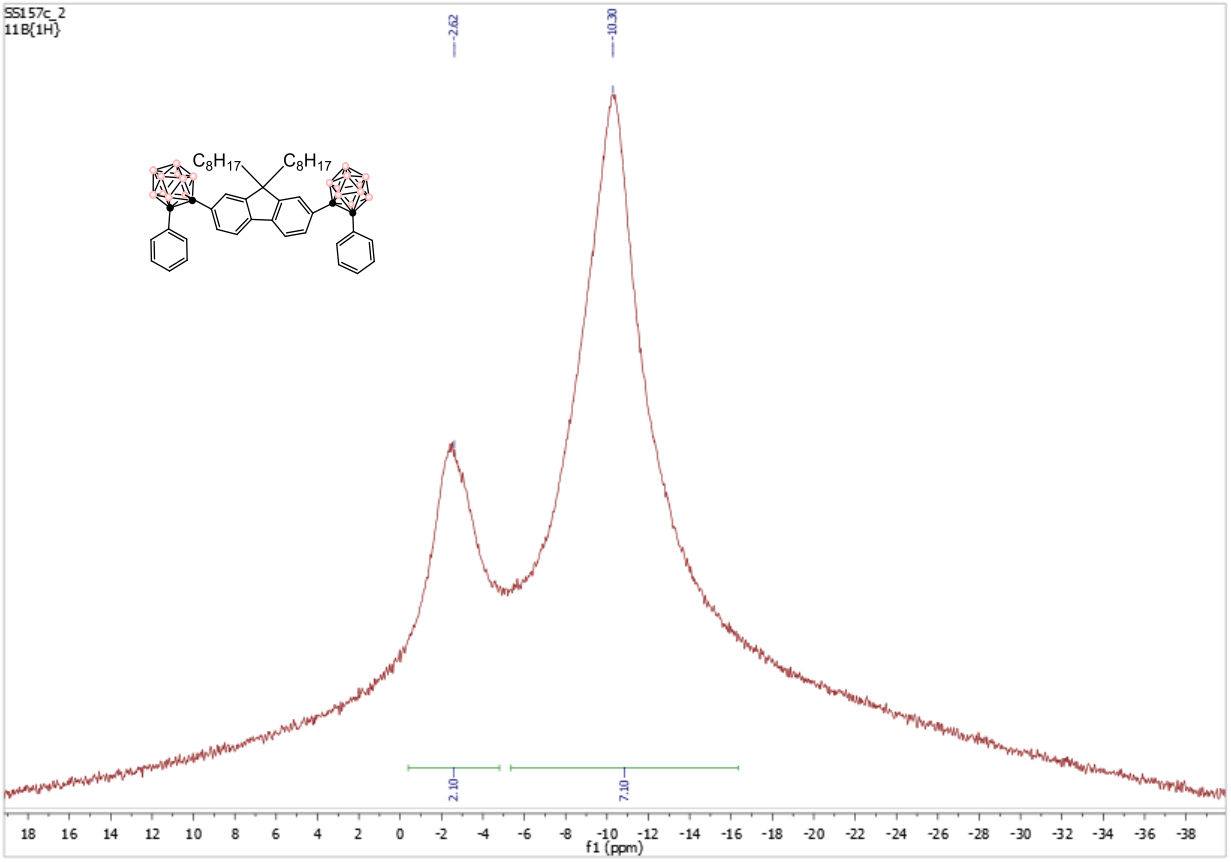


Figure S5. $^{11}B\{^{1}H\}$ NMR (400 MHz, $CDCl_3$) of **2**



2,7-bis(phenylethynyl)-9H-fluorene (3)

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of **3**

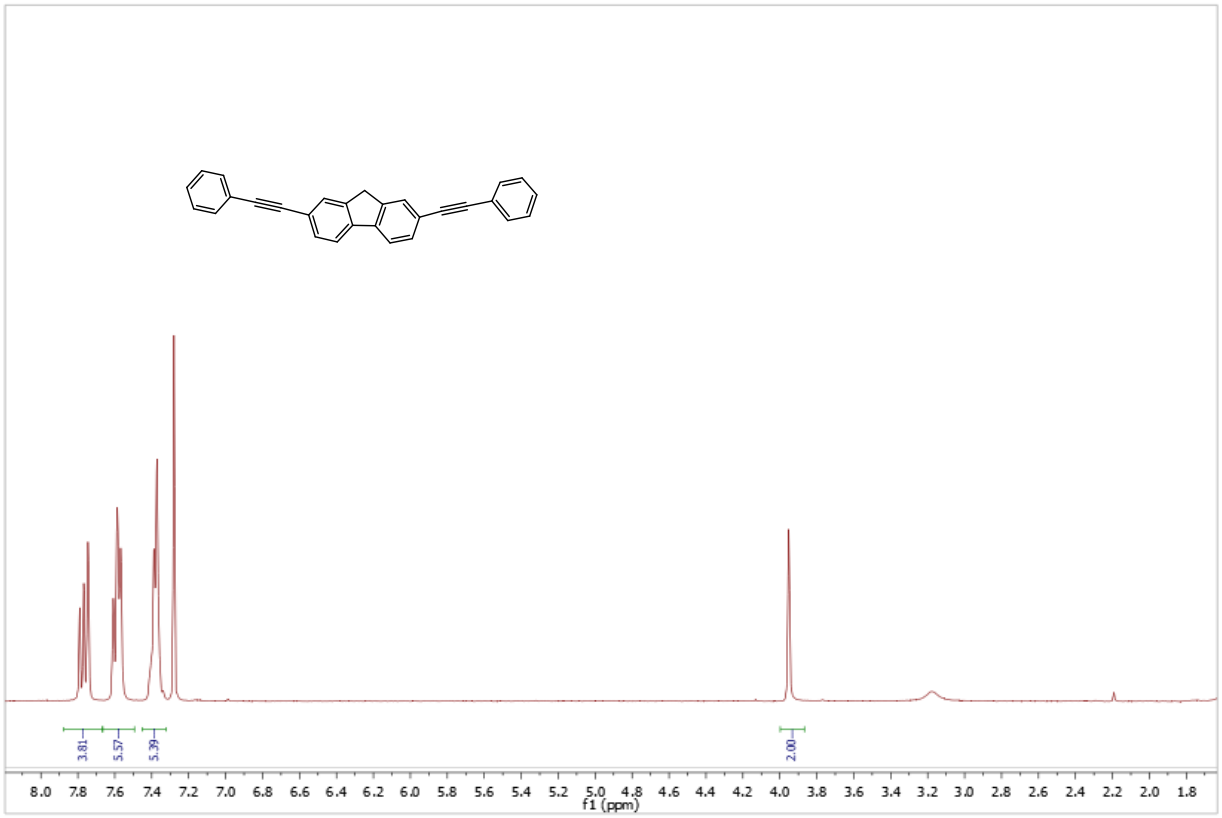
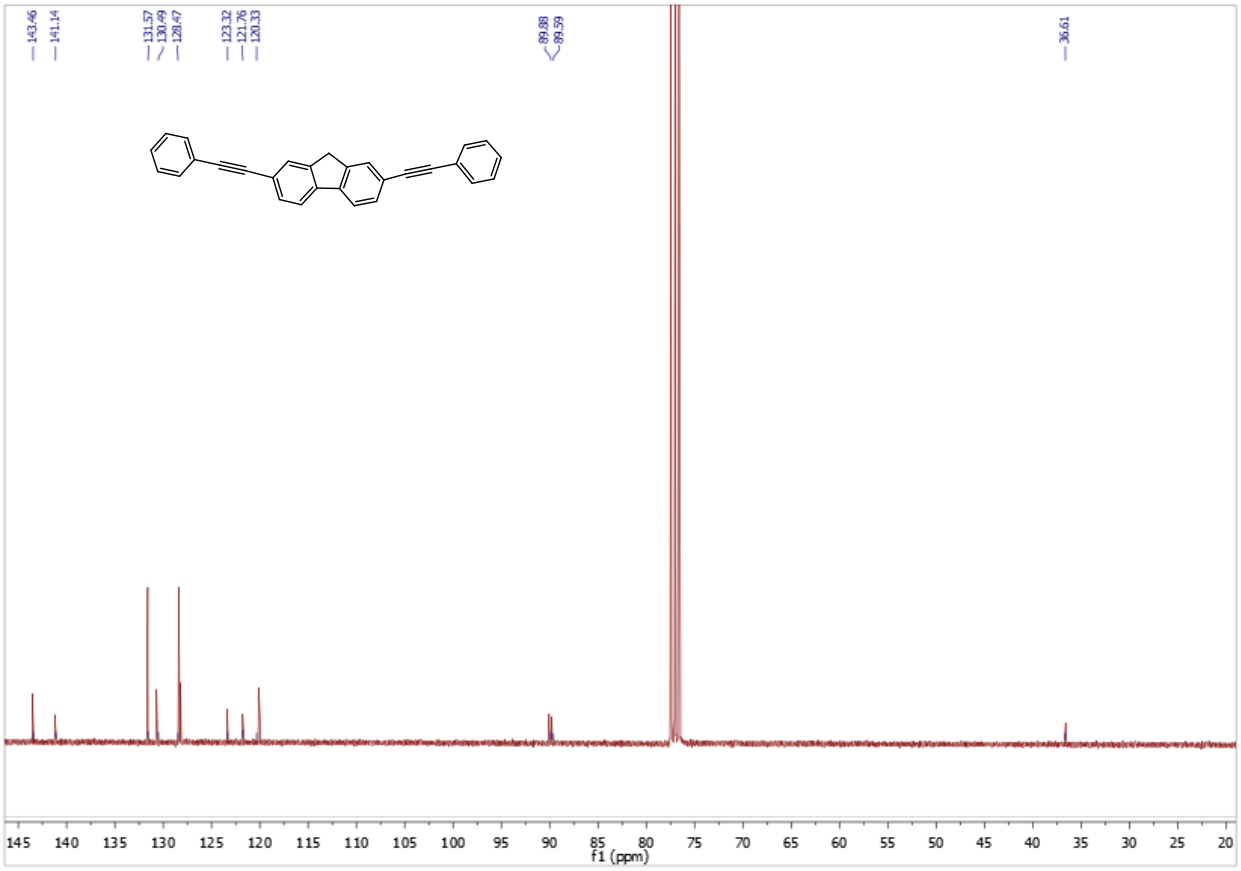


Figure S7 ^{13}C NMR (400 MHz, $CDCl_3$) of **3**



[2,7-bis(phenyl)-1-o-carboran-1-yl]-9H-fluorene (4)

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of **4**

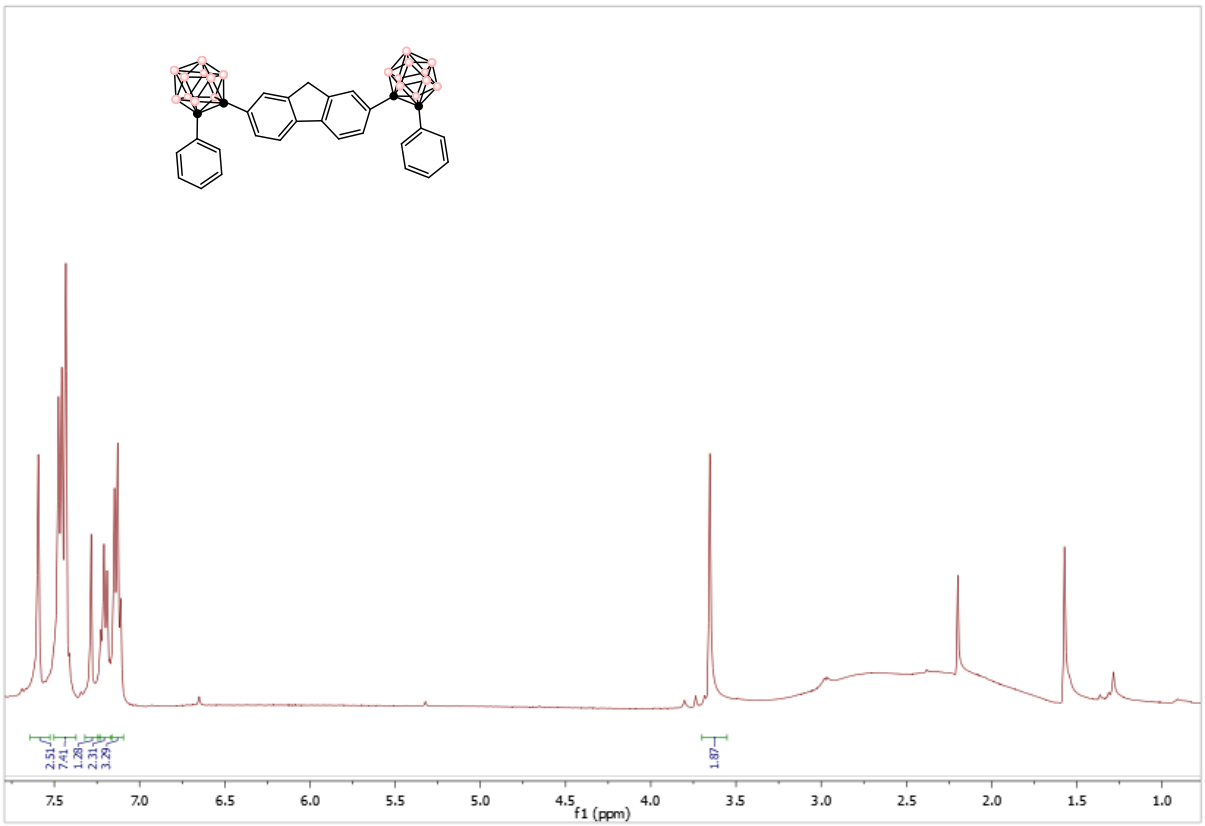


Figure S9. n^{13}C NMR (400 MHz, $CDCl_3$) of **4**

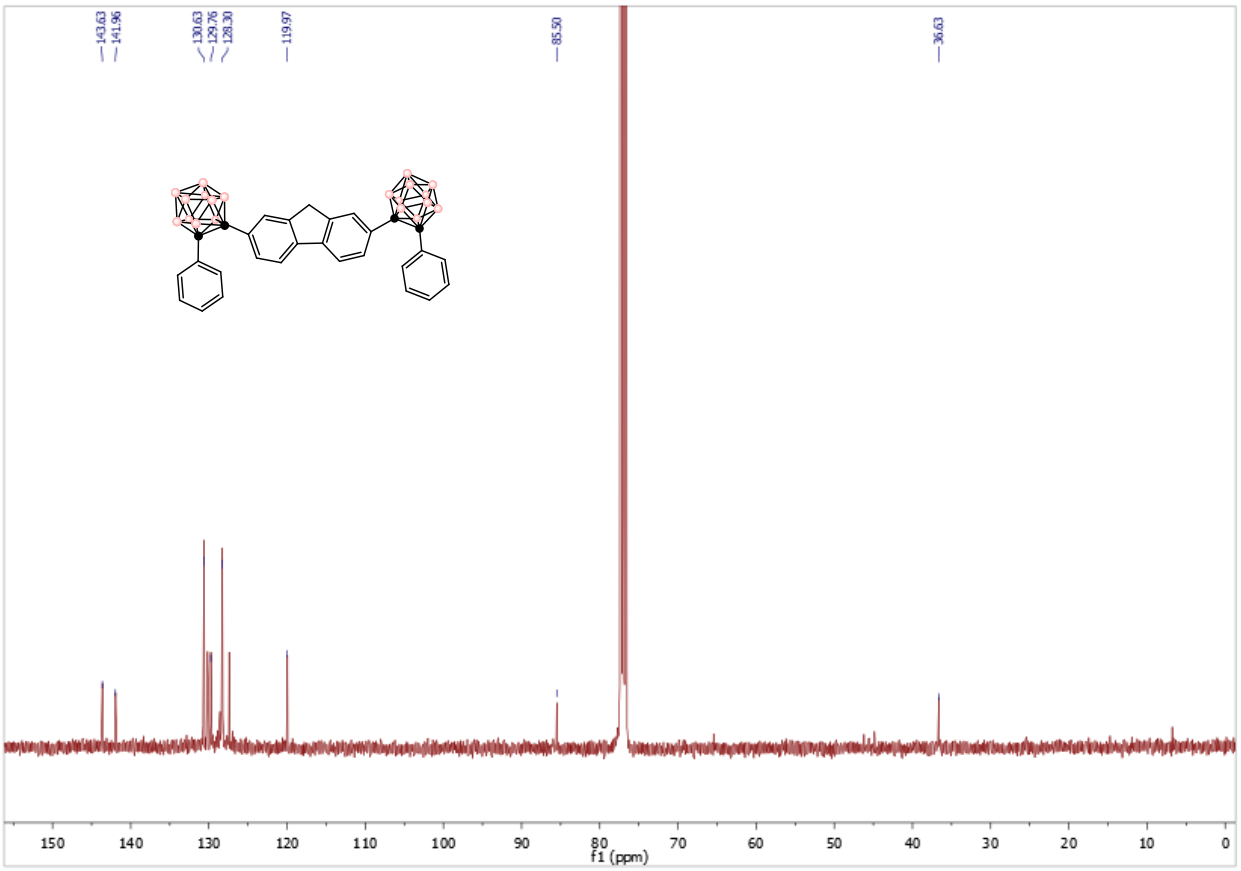
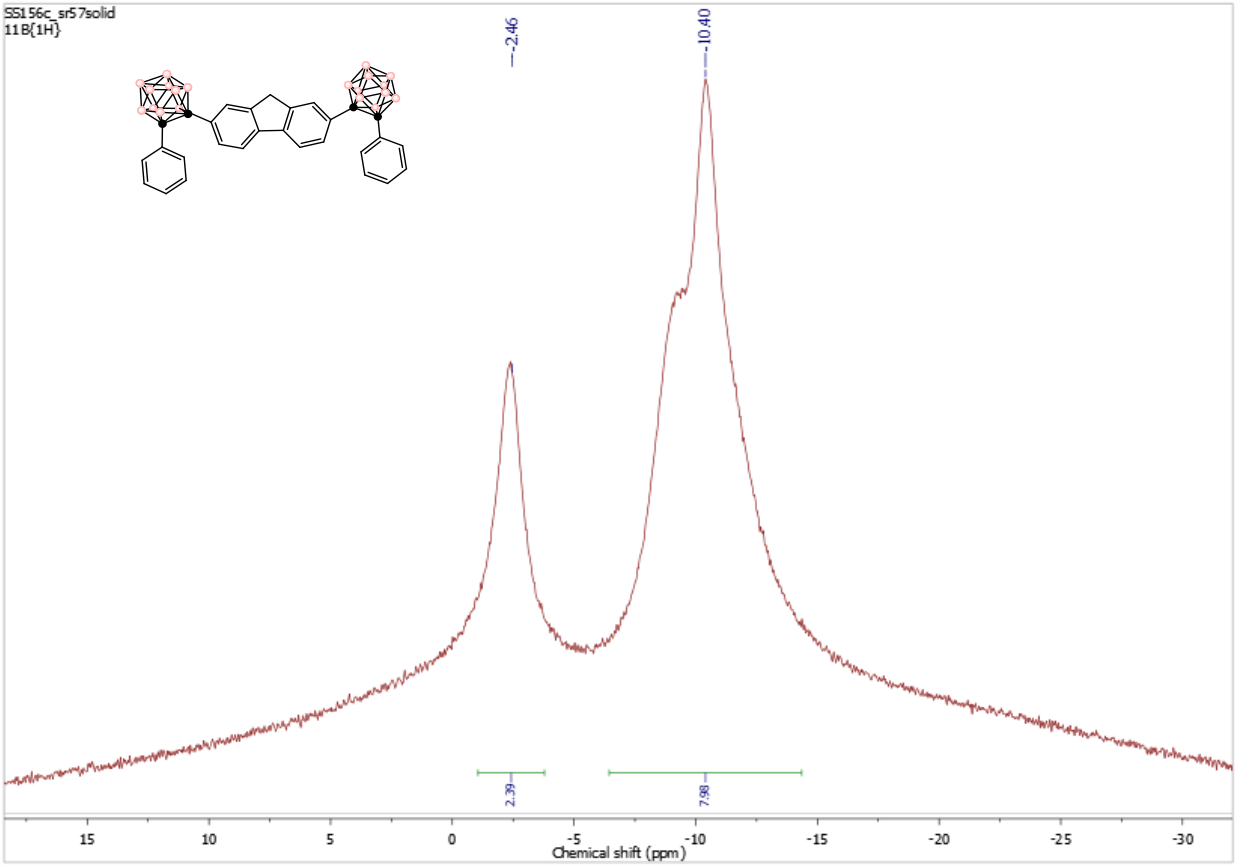


Figure S10. $^{11}B\{^{1}H\}$ NMR (400 MHz, $CDCl_3$) of **4**



2,5-bis((4-butylphenyl)ethynyl)thiophene (5)

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of **5**

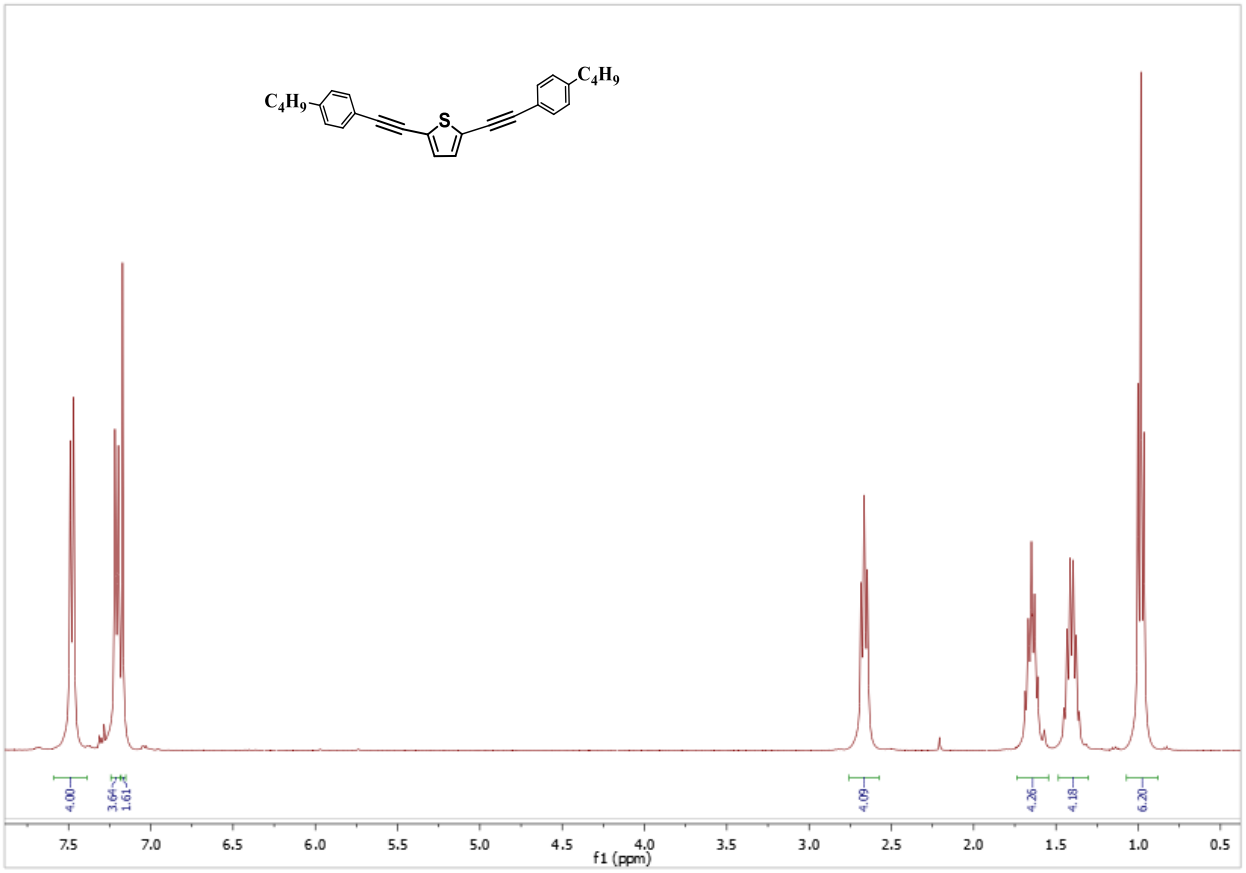
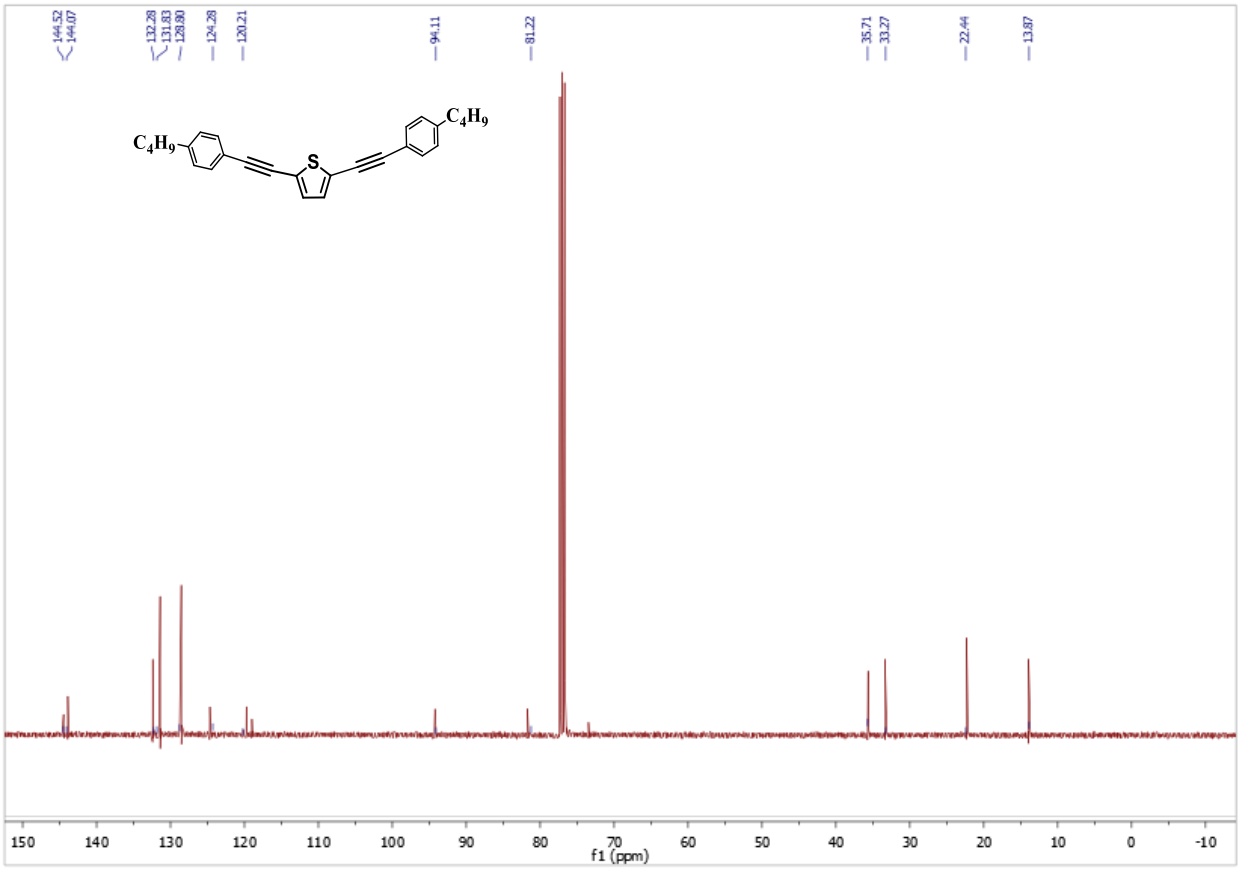


Figure S12. ^{13}C NMR (400 MHz, $CDCl_3$) of **5**



2,5-bis((4-butylphenyl)-*o*-carboran-1-yl)thiophene (6)

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of **6**

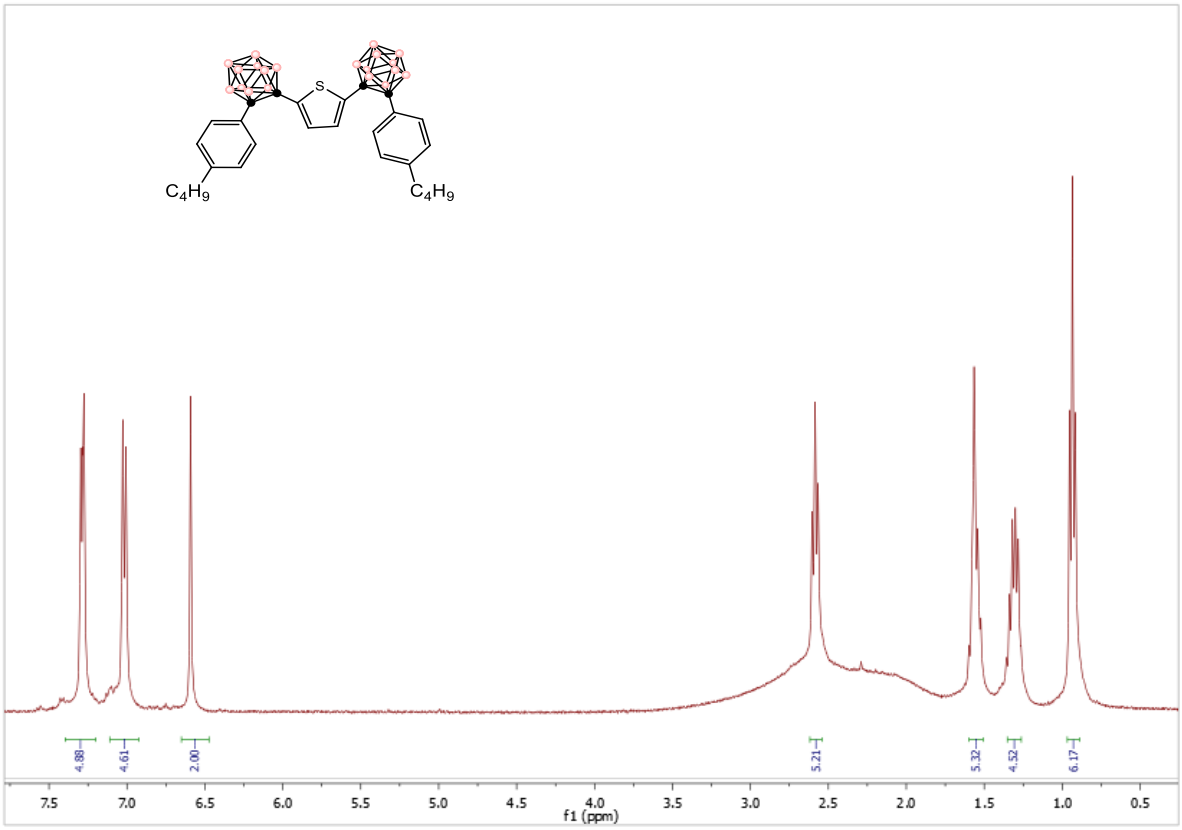


Figure S14. ^{13}**C NMR** (400 MHz, $CDCl_3$) of **6**

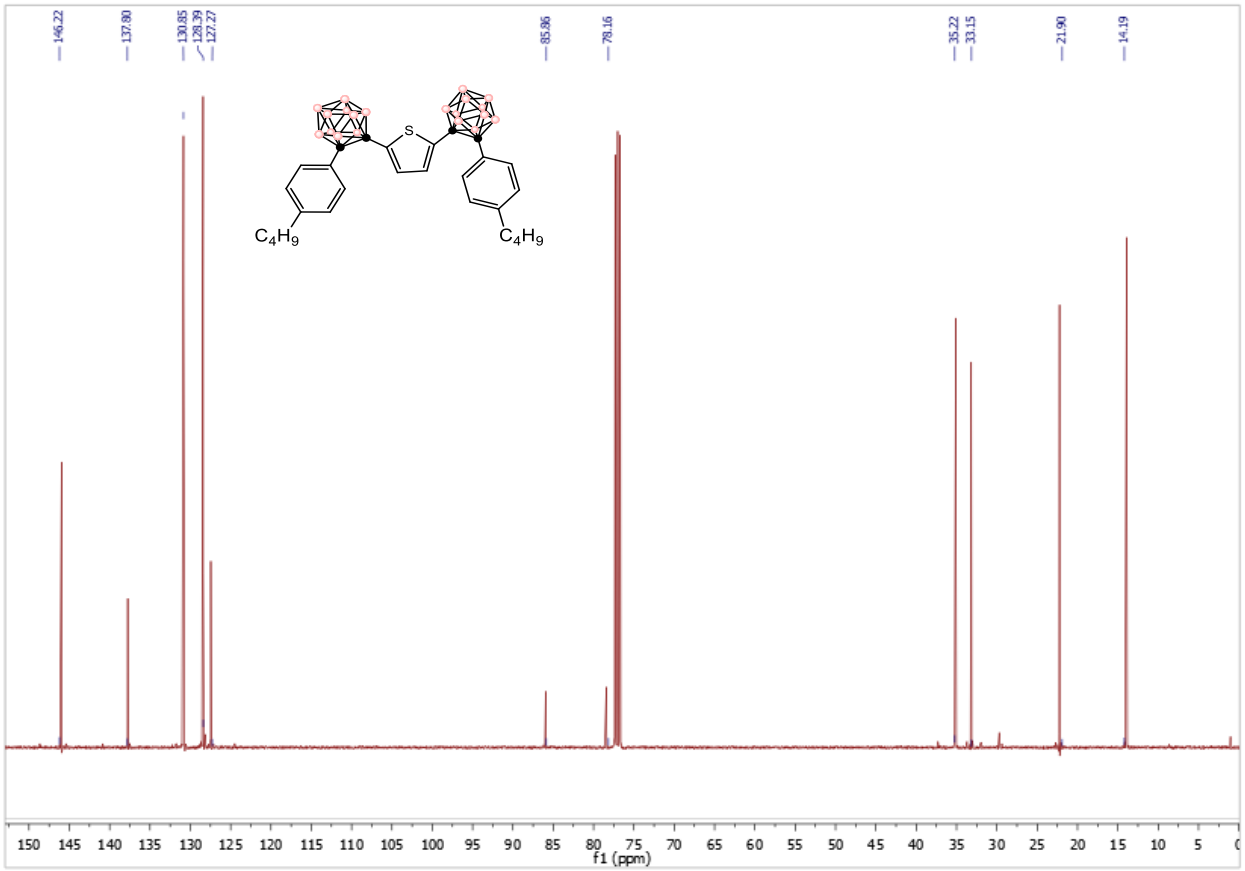
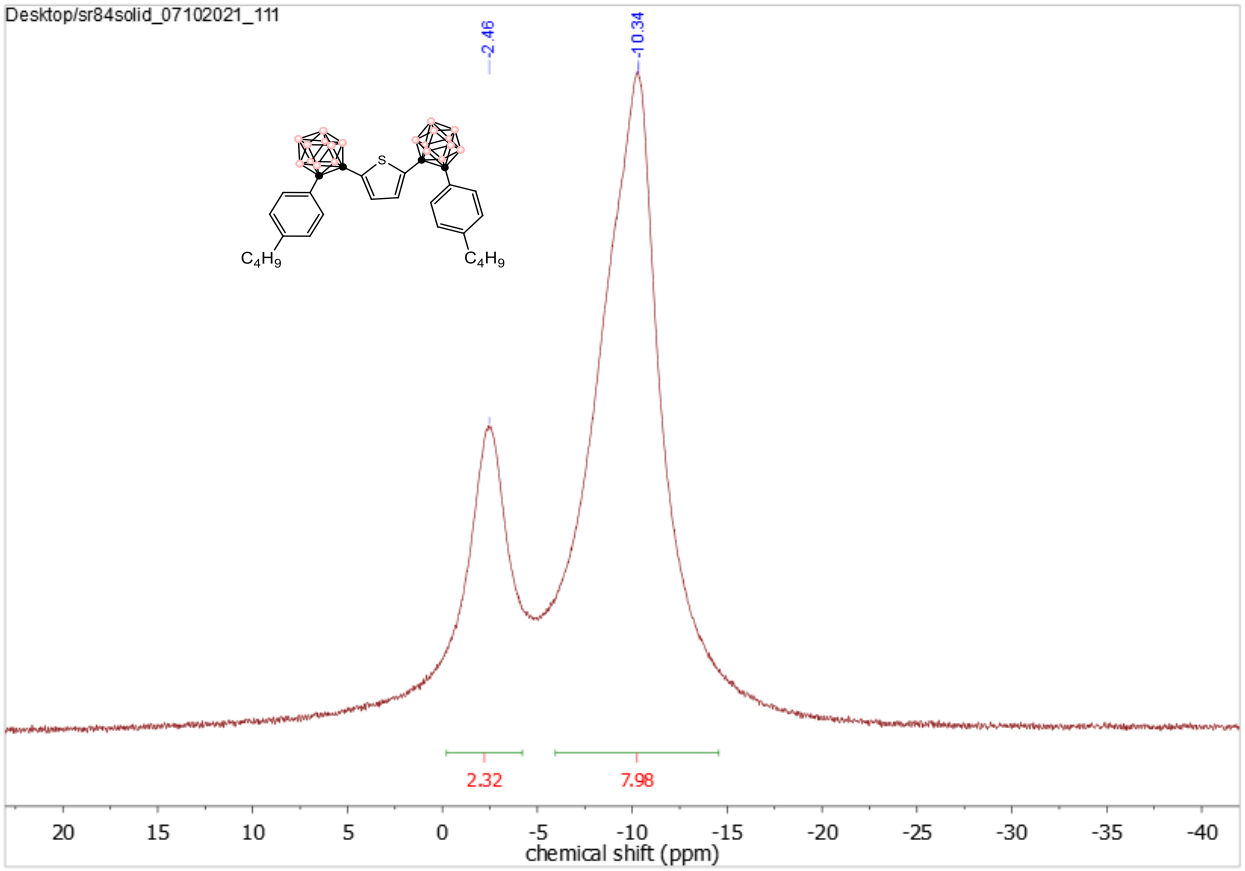


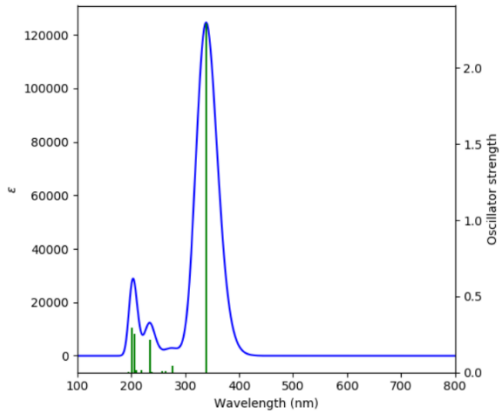
Figure S15. $^{11}B\{^{1}H\}$ **NMR** (400 MHz, $CDCl_3$) of **6**



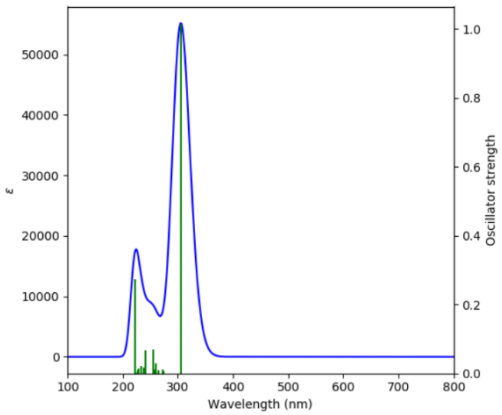
3. Photophysical properties: Comparison between experimental and simulated absorption spectra, and emission spectra of 1-6.

Simulated Absorption Spectra

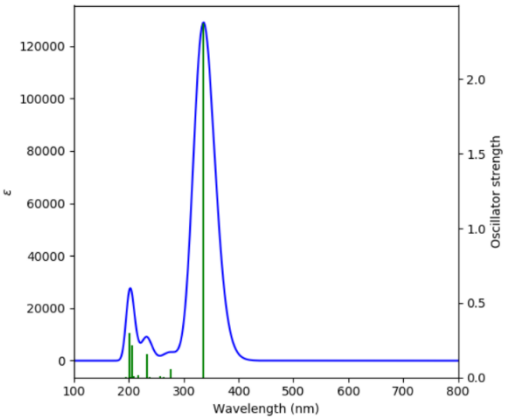
Compound 1' (CAM-B3LYP/6-31g*)



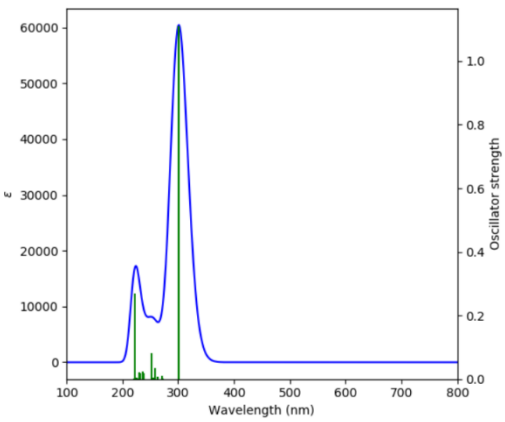
Compound 2' (B3LYP/6-31g*)



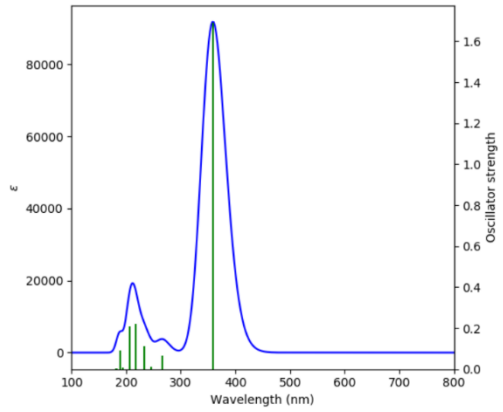
Compound 3 (CAM-B3LYP/6-31g*)



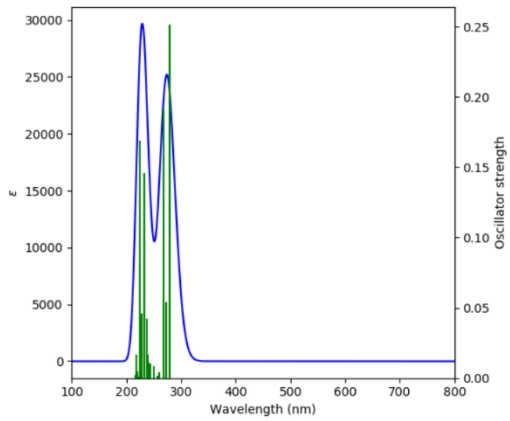
Compound 4 (B3LYP/6-31g*)



Compound 5' (CAM-B3LYP/6-31g*)



Compound 6' (B3LYP/6-31g*)



Experimental Absorption Spectra

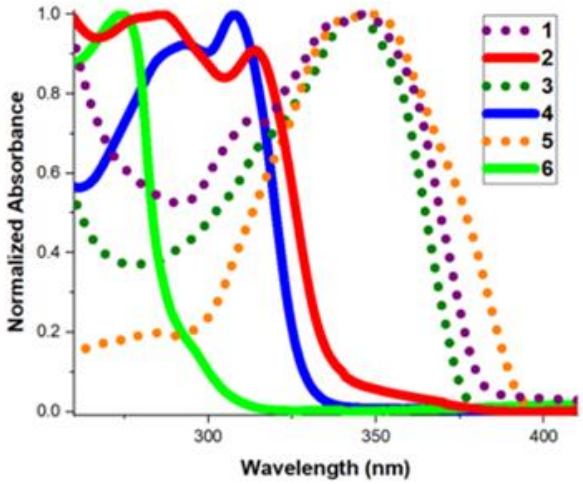


Figure S16: Comparison of absorption experimental and simulated spectra generated via GaussSum program[1]

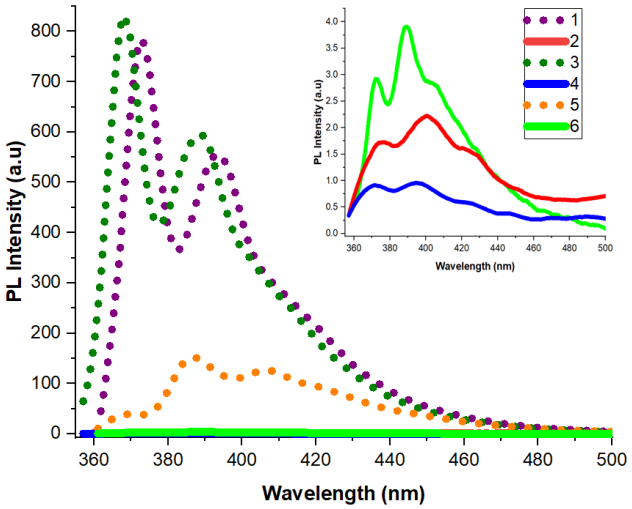
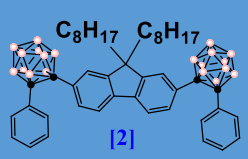
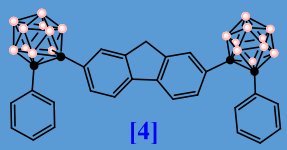
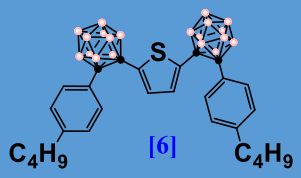


Figure S17. Fluorescence emission spectra of **1-6** in THF (3.10^{-5} to 1.10^{-6} M)

Photophysical data of **2**, **4** and **6** in different states.

States	2 	4 	6 
Solution (THF)	Abs – 286 nm, 314 nm Em – 404 nm Φ_F- 0.01	Abs – 293 nm, 308 nm Em – 372 nm Φ_F - < 0.01	Abs – 274 nm Em – 390 nm Φ_F - 0.19
Aggregation (THF:H_2O, 1:99 v/v)	Abs – 319 nm Em – 483 nm Φ_F - 0.06	Abs – 311 nm Em – 536 nm Φ_F – 0.01	--
Nanoparticles (H_2O suspension)	Abs – 318 nm Em – 478 nm Φ_F – 0.39	Abs – 310 nm Em – 528 nm Φ_F – 0.01	--
Solid	Abs – 319 nm Em – 477 nm Φ_F - 0.74	Abs – 319 nm Em – 500 nm Φ_F – 0.04	Abs – 280 nm Em – 591 nm Φ_F – 0.14

4. Theoretical Calculations (DFT)

To elucidate the origin of these photophysical properties, DFT calculations were performed. The Gaussian 09 program package[2] was used for all calculations, while Molden 4.0[3] and IQmol 2.15.0[4] were used for the visualization of the computed structures and orbitals. In order to reduce computational time, the long alkyl chains were replaced by methyl substituents for **1-6** (the notation ′ stands for using Me substituents instead of the alkyl branch). Geometry optimizations were carried out at the B3LYP/6-31G* level of theory. The results of these calculations were compared with the calculations at ω-B97XD/6-311+G**, however, the application of the higher level resulted in only marginal structural changes. During the investigation of the photophysical properties, the two levels of theory were compared for the *ortho*-carboranes (Table S1) and the largest deviation between the functionals and basis sets was only 14 nm. Due to the marginal differences in the structures and absorption maxima, B3LYP/6-31G* was chosen for optimization, in order to reduce computational demand. The B3LYP functional with 6-31G* basis set was utilized for **2'**, **4** and **6'**, as it has been successfully applied for the investigation of related carborane based fluorophores.[5] However, for the purely organic systems (**1'**, **3** and **5'**) the CAM-B3LYP functional was used, as the hybrid, long-range corrected CAM-B3LYP functional provided better results for extended conjugate organic systems, which was verified by test calculations as well (Table S2). Several rotamers have been investigated (Tables S3-S5), nonetheless, the differences proved to be small in all investigated cases, both in energy (ΔE_{max}=1.42 kcal/mol) and in the absorption maxima (ΔABS_{max}=7 nm) (Table S6). TD-DFT calculations have demonstrated that the HOMO-LUMO transitions have the highest contribution, and while **1'**, **3** and **5'** possess a conjugation that expands over the entire structure, in case of the **2'**, **4**, **6'** the carborane cages interrupt the conjugation (Tables S7-S9). Upon the investigation of the Kohm-Sham orbitals, all *ortho*-carboranes exhibit some CT characteristics, but for **6'** it is much more significant than **2'** and **4**, which exhibit stronger LE excitation character (Tables S10-S13). It should be highlighted that in case of **6'** the charge transfer occurs from the phenyl substituents towards the thiophene unit and the participation of the carborane units are marginal. Indeed, the lack of the AIE of **6'** in contrast of **2'** or **4** could be attributed to the lower participation of the carborane units in the charge transfer process. In order to further support this idea, the corresponding excited states (S_1) of **2'**, **4**, **6'** were optimized. Investigating the geometry of these structures (S_1 states) it could be established that in case of **2'** and **4** the $C_{cluster}$ - $C_{cluster}$ (C_c-C_c) distance elongated to 2.48 Å (similar values were reported recently),[6] which was in agreement with the postulated charge transfer towards the carborane units. These results indicate that the bond elongation proceeds when the compounds **2'** and **4** are depicted as single molecules and no strong fluorescence could be expected in diluted solution. On the other hand, in the S_1 state of **6'** the $C_{cluster}$ - $C_{cluster}$ distance is significantly shorter (2.26 Å), which was in agreement with the different nature of the CT process and the lack of the AIE.

Table S1: Comparison of the two functional and basis sets through the calculation of absorption maxima

	2’	2’-rot	4	4-rot	6’	6’-rot
Experimental values	**286, 314**		**293, 308**		**274**	
B3LYP/6-31G*	**305**	**306**	**301**	**302**	**286**	**279**
ωB97X-D/6-311+G**	**269**	**-**	**266**	**272**	**-**	**-**
B3LYP/6-31G*// ωB97X-D/6-311+G**	**294**	**297**	**289**	**291**	**276**	**265**

Table S2: The calculated absorption maxima at different levels of theory

	1’	2’	3	4	5’	6’
Experimental values	**349**	**286, 314**	**346**	**293, 308**	**348**	**274**
CAM-B3LYP/6-31G*	**339**	**-**	**336**	**276**	**359**	**-**
CAM-B3LYP/6-31G* PCM=THF	**346**	**284**	**343**	**280**	**370**	**259**
B3LYP/6-31+G*	**392**	**309**	**-**	**-**	**403**	**-**
B3LYP/6-31+G* PCM=THF	**401**	**315**	**398**	**311**	**418**	**292**
B3LYP/6-31G*	**385**	**305**	**382**	**301**	**397**	**285**
B3LYP/6-31G* PCM=THF	**-**	**-**	**392**	**308**	**413**	**291**
PBE1PBE/6-31G*	**373**	**298**	**371**	**294**	**387**	**-**

Table S3: Kohn-Sham canonical orbitals and their energies of the investigated rotamers of **2'** at B3LYP/6-31G* level of theory

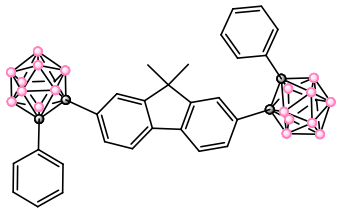
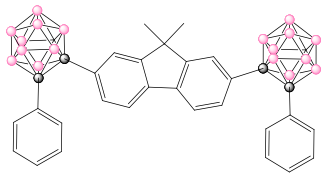
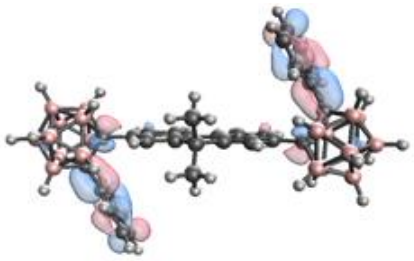
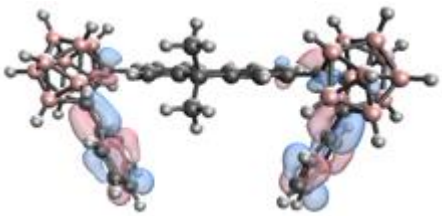
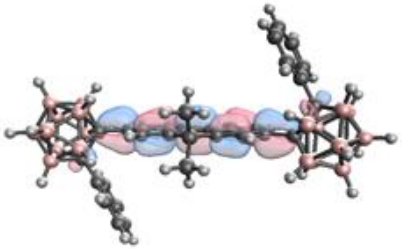
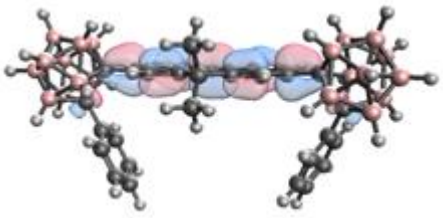
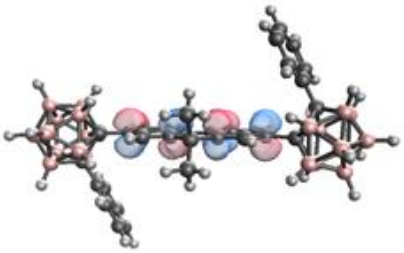
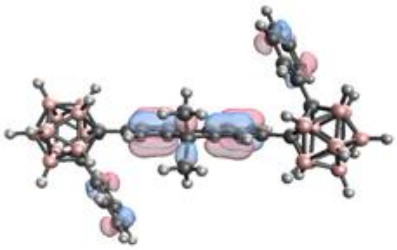
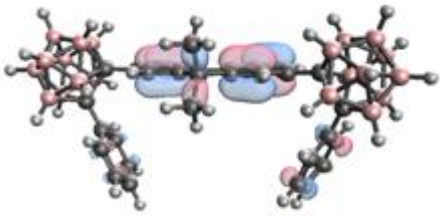
	2'	**2'-rot**
		
LUMO +1		
	-1.34 eV	**-1.36 eV**
LUMO		
	-2.02 eV	**-2.02 eV**
HOMO		
	-6.51 eV	**-6.51 eV**
HOMO -1		
	-7.24 eV	**-7.25 eV**

Table S4 Kohn-Sham canonical orbitals and their energies of the investigated rotamers of **4** at B3LYP/6-31G* level of theory

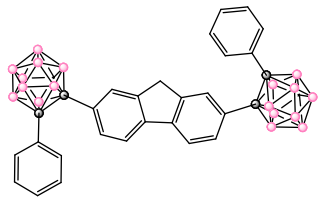
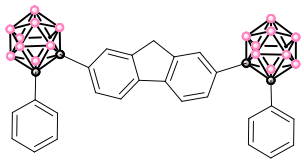
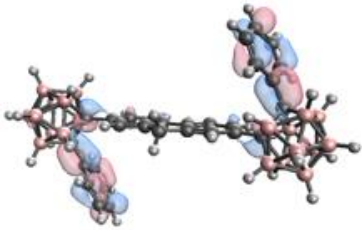
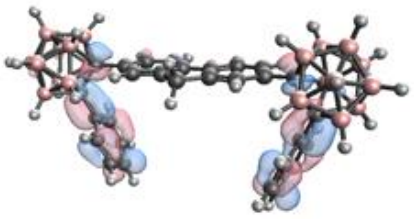
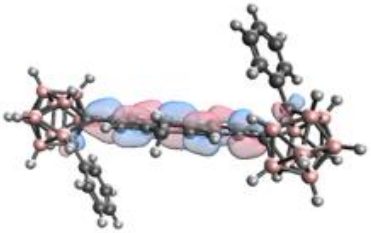
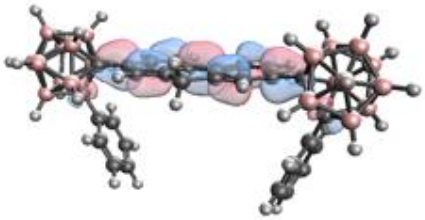
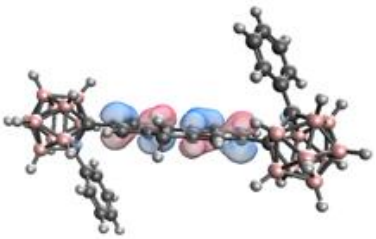
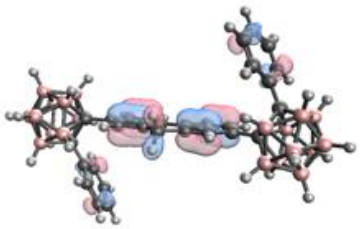
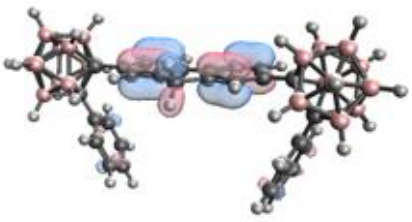
	4	**4-rot**
		
LUMO +1		
	-1.34 eV	**-1.37 eV**
LUMO		
	-2.01 eV	**-2.02 eV**
HOMO		
	-6.54 eV	**-6.54 eV**
HOMO -1		
	-7.23 eV	**-7.25 eV**

Table S5: Kohn-Sham canonical orbitals and their energies of the investigated rotamers of **6'** at B3LYP/6-31G* level of theory

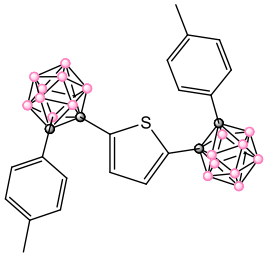
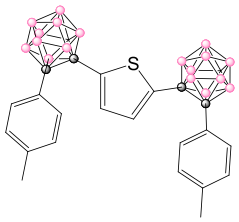
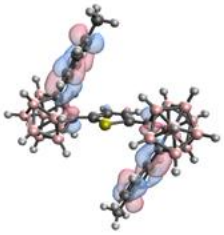
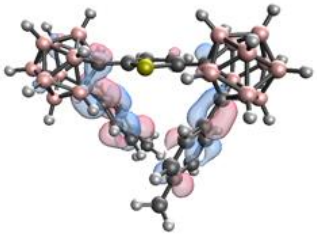
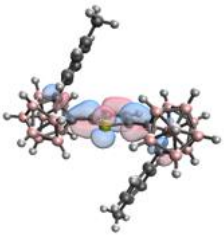
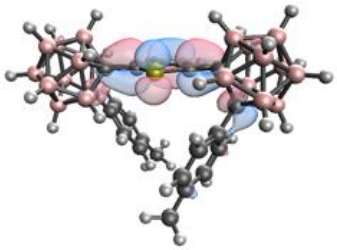
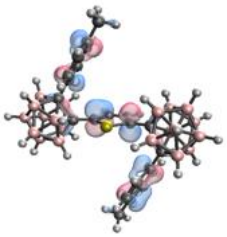
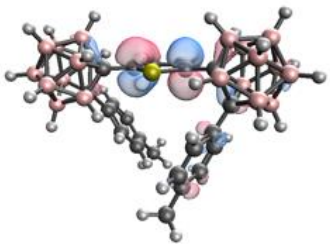
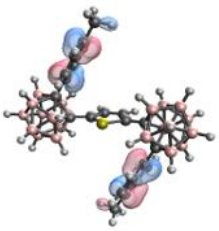
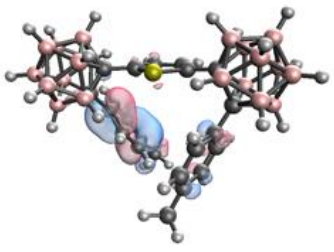
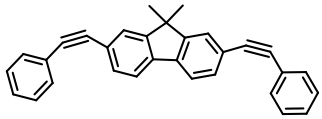
		
	6'	**6'-rot**
LUMO +1		
	-1.29 eV	**-1.39 eV**
LUMO		
	-2.08 eV	**-2.04 eV**
HOMO		
	-6.99 eV	**-7.01 eV**
HOMO -1		
	-7.05 eV	**-7.15 eV**

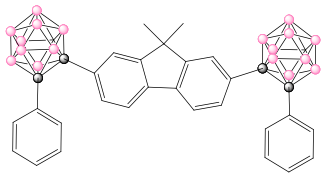
Table S6: Total energy and absorption maxima difference between different rotamers of the investigated systems

Compound	Energy (E) [Hartree]	ΔE [kcal/mol]	Absorption maxima (ABS) [nm]	ΔABS [nm]
2'	-1703.953120	0.39	305	1
2'-rot	-1703.952499		306	
4	-1625.324857	0.32	301	1
4-rot	-1625.324344		302	
6'	-1755.542797	1.42	286	7
6'-rot	-1755.540540		279	

Table S7: Kohn-Sham orbitals for compound **1' (**CAM-B3LYP/6-31G*) and the most stable rotamer of **2'** (B3LYP/6-31G*)

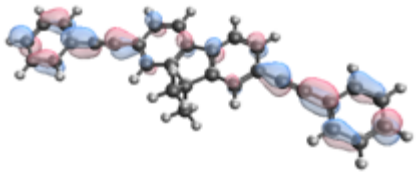


1'

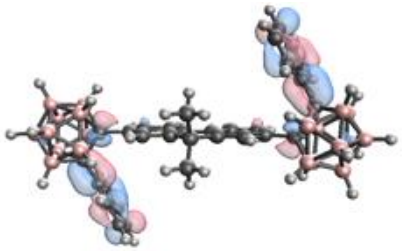


2'

LUMO +1

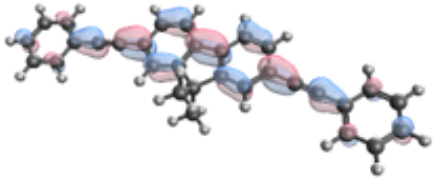


0.27 eV

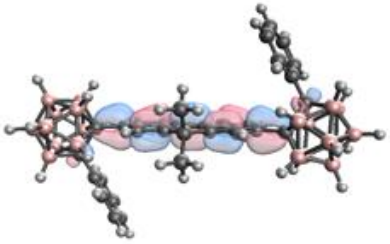


-1.34 eV

LUMO

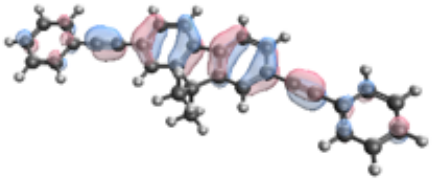


-0.66 eV

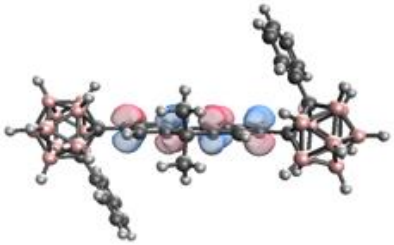


-2.02 eV

HOMO

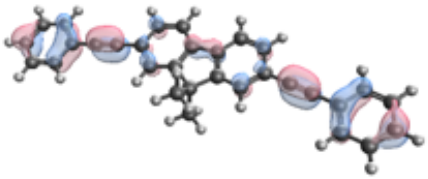


-6.45 eV

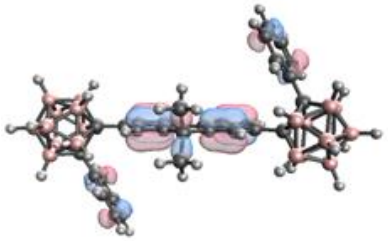


-6.51 eV

HOMO -1



-7.27



-7.24 eV

Table S8: Kohn-Sham orbitals for compound **3 (**CAM-B3LYP/6-31G*) and the most stable rotamer of **4** (B3LYP/6-31G*)

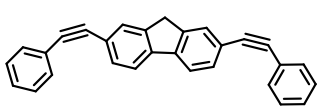
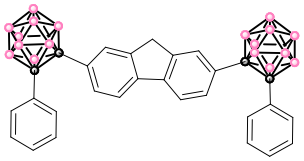
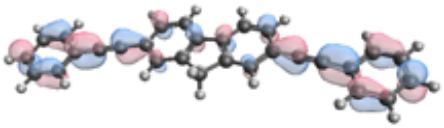
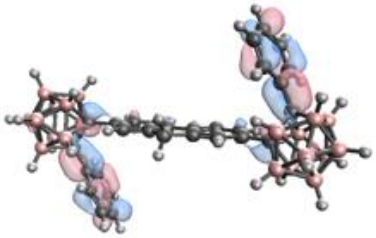
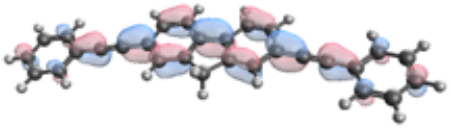
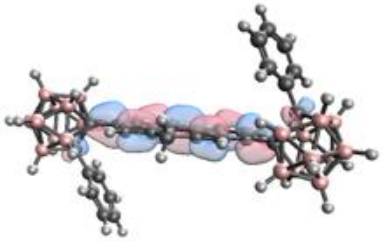
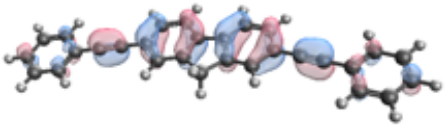
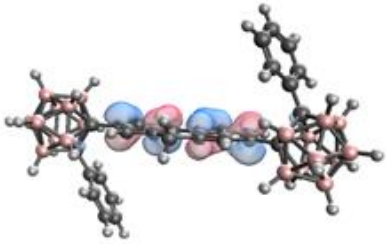
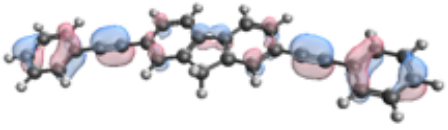
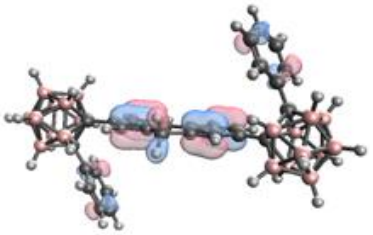
	 **3**	 **4**
LUMO +1	 **0.26 eV**	 **-1.34 eV**
LUMO	 **-0.65 eV**	 **-2.01 eV**
HOMO	 **-6.46 eV**	 **-6.54 eV**
HOMO -1	 **-7.27 eV**	 **-7.23 eV**

Table S9: Kohn-Sham orbitals for compound **5'** (CAM-B3LYP/6-31G*) and the most stable rotamer of **6'** (B3LYP/6-31G*)

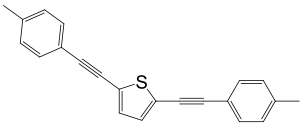
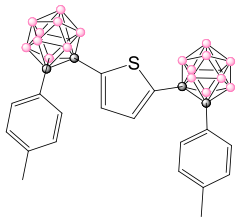
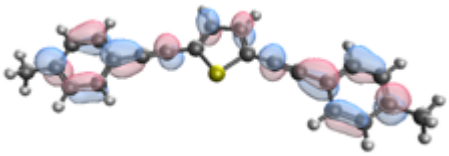
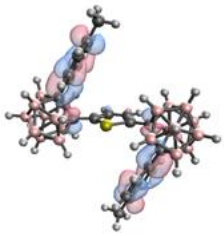
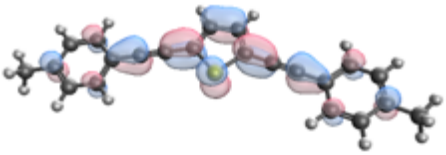
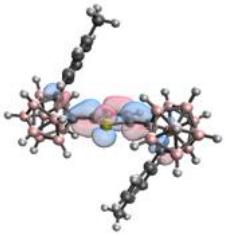
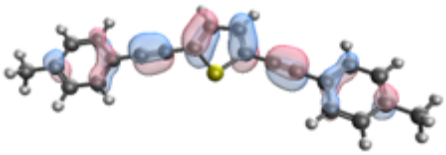
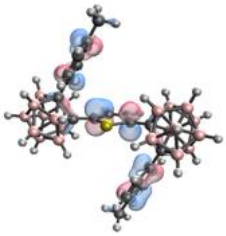
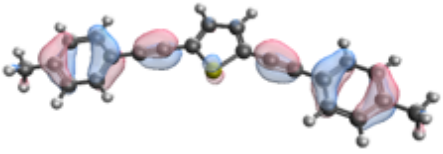
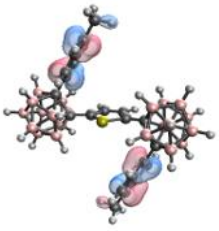
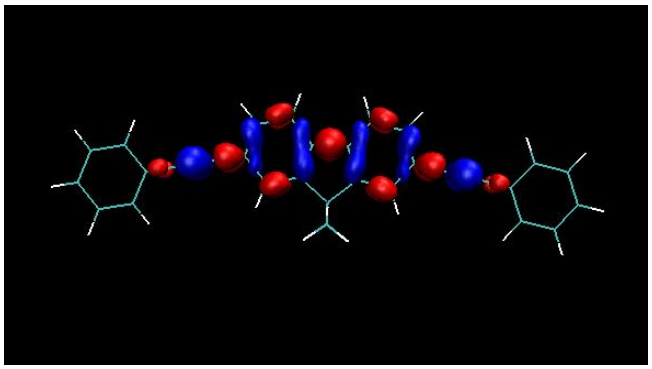
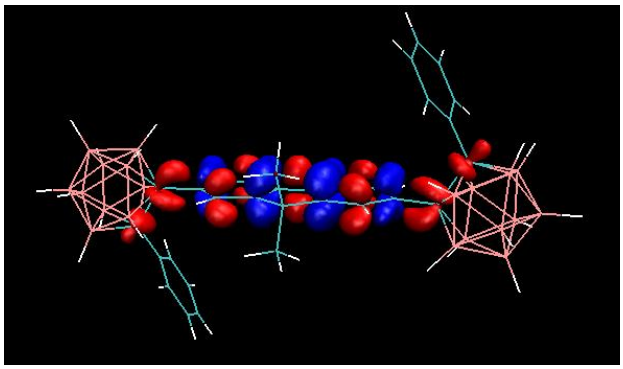
		
	5'	**6'**
LUMO +1		
	0.57 eV	**-1.29 eV**
LUMO		
	-0.72 eV	**-2.08 eV**
HOMO		
	-6.34 eV	**-6.99 eV**
HOMO -1		
	-7.56 eV	**-7.05 eV**

Table S10: Charge-density difference map. he blue and red parts correspond to the regions in which electron density is decreased and increased after electron excitation, respectively. Isosurface value: 0.0015 (**1'**, **3 , 5'** were calculated at CAM-B3LYP/6-31G* and **2'**, **4**, **6'** were calculated at B3LYP/6-31G*)

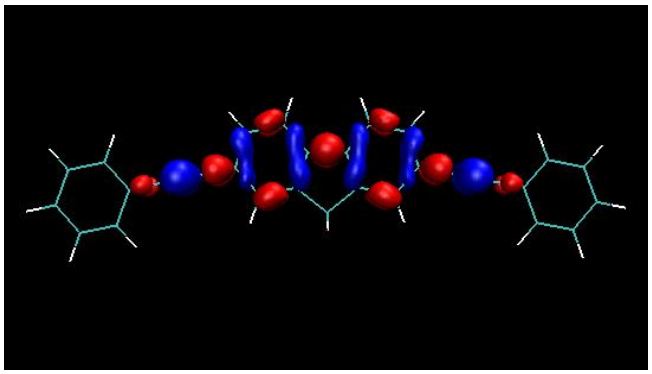
1'



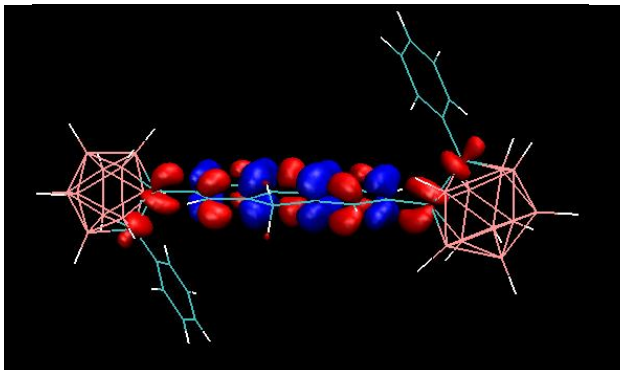
2'



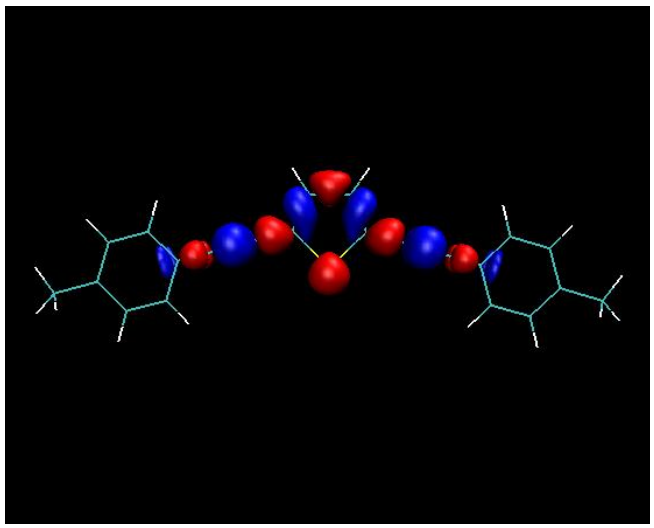
3



4



5'



6'

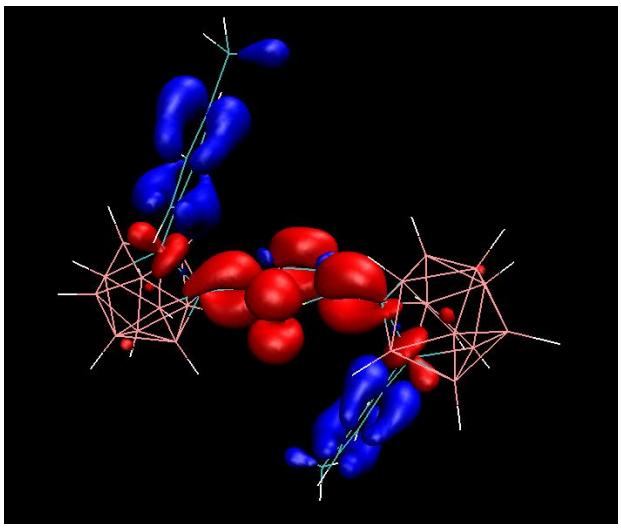


Table S11: HOMO-LUMO orbitals (at B3LYP/6-31G*) in S_0 and S_1 states for compound **2'**, S_1 shows a lengthening of one C_c-C_c bond.

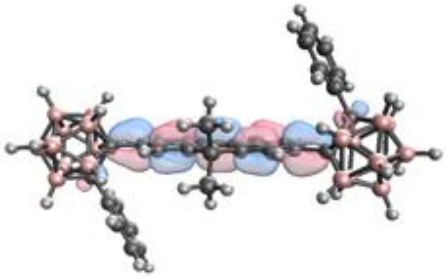
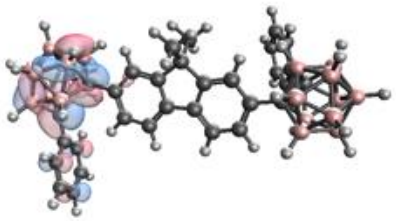
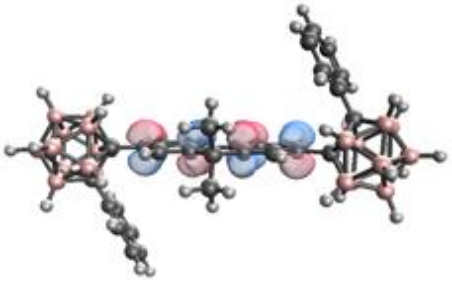
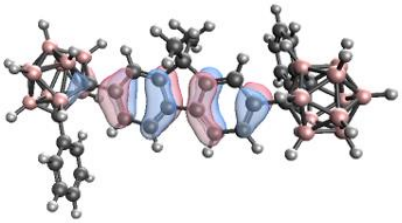
LUMO		
	-2.02 eV	**-3.83 eV**
HOMO		
	-6.51 eV	**-5.96 eV**
	S_0	**S_1**
C_c-C_c bond	**1.76 Å**	**2.48 Å**

Table S12: HOMO-LUMO orbitals (at B3LYP/6-31G*) in S_0 and S_1 states for compound **4**, S_1 shows a lengthening of one C_c-C_c bond.

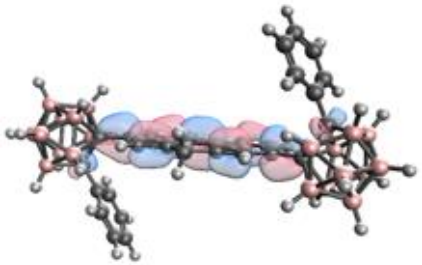
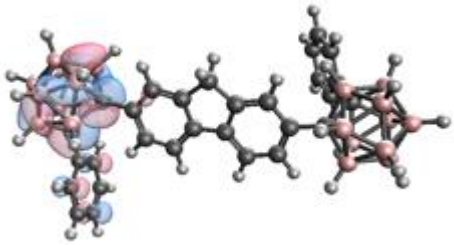
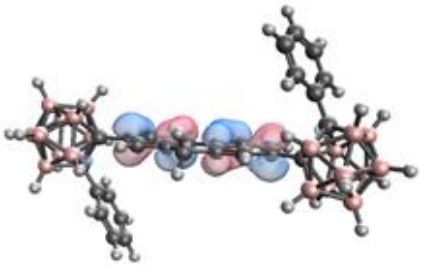
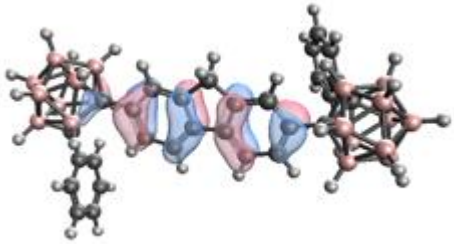
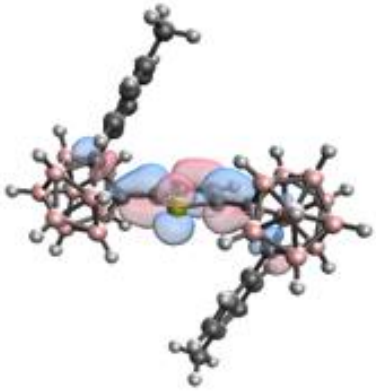
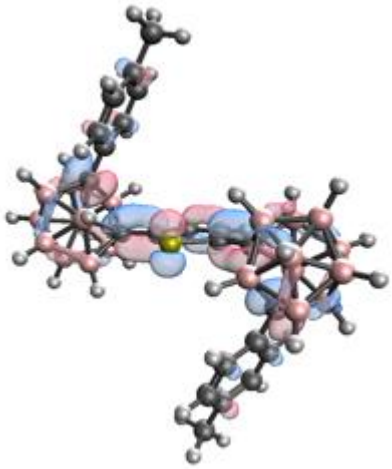
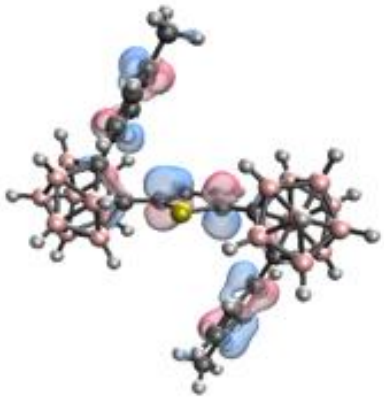
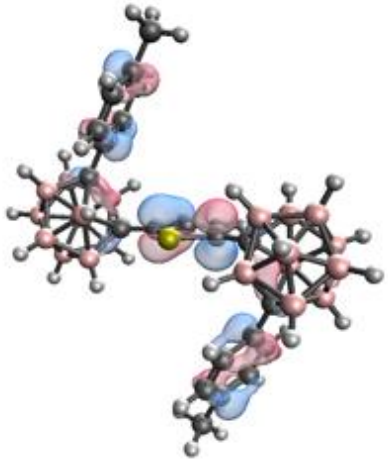
LUMO		
	-2.01 eV	**-3.86 eV**
HOMO		
	-6.54 eV	**-6.00 eV**
	S_0	**S_1**
C_c-C_c bond	**1.76 Å**	**2.48 Å**

Table S13: HOMO-LUMO orbitals (at B3LYP/6-31G*) in S_0 and S_1 states for compound **6'**, S_1 shows a lengthening of both C_c-C_c bonds.

LUMO		
	-2.08 eV	**-3.59 eV**
HOMO		
	-6.99 eV	**-6.66 eV**
	S_0	**S_1**
C_c-C_c bond	**1.77 Å**	**2.26 Å**

XYZ geometries and total energies of the investigated systems

Compound 1' (B3LYP/6-31G*)

E(RB3LYP) = -1194.47980212

Sum of electronic and zero-point Energies= -1194.053524

Sum of electronic and thermal Energies= -1194.027715

Sum of electronic and thermal Enthalpies= -1194.026771

Sum of electronic and thermal Free Energies= -1194.113333

C 7.45702100 0.16710100 -0.00009300

C 8.40599300 -0.87556400 -0.00006500

C 9.76803700 -0.58827000 -0.00008500

C 10.20972200 0.73731500 -0.00013900

C 9.27787800 1.77845900 -0.00017400

C 7.91391100 1.50088300 -0.00015300

H 8.05985900 -1.90459500 -0.00002700

H 10.48836400 -1.40196300 -0.00006100

H 11.27369200 0.95763500 -0.00015600

H 9.61570900 2.81135200 -0.00022000

H 7.18751400 2.30776300 -0.00018300

C 6.06202800 -0.12033900 -0.00008000

C 4.86974100 -0.36520400 -0.00006400

C 3.47439100 -0.64343800 0.00000600

C 2.53510100 0.41363200 0.00001900

C 1.18050900 0.12606700 0.00007700

C 0.73141700 -1.21184700 0.00011200

C 1.65091800 -2.26532100 0.00011400

C 3.01201300 -1.97854600 0.00006000

H 2.89616800 1.43830900 -0.00000500

C -0.00003100 1.09778100 0.00017100

C -0.73140800 -1.21188700 0.00006000

H 1.31457200 -3.29888700 0.00014500

H 3.73999300 -2.78375800 0.00004600

C -1.65080200 -2.26545700 0.00001400

C -3.01193100 -1.97879800 -0.00002800

C -3.47439900 -0.64374900 -0.00002800

C -2.53519200 0.41343400 0.00004600

C -1.18058200 0.12598800 0.00008200

H -1.31435500 -3.29898600 0.00002500
H -3.73982700 -2.78408900 -0.00005300
C -4.86974400 -0.36547700 -0.00005700
H -2.89642000 1.43805200 0.00005500
C -0.00016000 1.98363200 1.26615000
C -0.00016100 1.98410800 -1.26543300
C -6.06200800 -0.12050300 -0.00007400
C -7.45697500 0.16705000 -0.00011600
C -7.91375700 1.50086700 -0.00008900
C -9.27770200 1.77855200 -0.00008900
C -10.20963100 0.73748400 -0.00011800
C -9.76805400 -0.58813600 -0.00013600
C -8.40603200 -0.87553900 -0.00013000
H -7.18729500 2.30768800 -0.00005500
H -9.61545000 2.81147100 -0.00006300
H -11.27358300 0.95789000 -0.00011600
H -10.48844700 -1.40177100 -0.00014600
H -8.05998000 -1.90459800 -0.00013000
H -0.88621700 2.62848100 1.28627600
H -0.00025200 1.37351400 2.17493800
H 0.88588900 2.62850100 1.28646100
H -0.88615500 2.62905400 -1.28524500
H 0.88593400 2.62892000 -1.28556600
H -0.00037100 1.37436000 -2.17447100

Compound 2’ (B3LYP/6-31G*)

E(RB3LYP) = -1703.95311945
Sum of electronic and zero-point Energies= -1703.231874
Sum of electronic and thermal Energies= -1703.193447
Sum of electronic and thermal Enthalpies= -1703.192503
Sum of electronic and thermal Free Energies= -1703.300075
C -5.14338400 -2.51789900 0.60103000
C -5.67390100 -1.63396900 -0.35048700
C -5.89133800 -2.10672500 -1.65430300
C -5.57204100 -3.41859200 -1.99943900
C -5.03160400 -4.28457200 -1.04865600

C -4.82293700 -3.82946000 0.25303400
C -6.06494400 -0.22558900 0.01906100
B -7.22928000 0.10631800 1.22537300
B -7.55216300 0.43952600 -0.48708800
B -8.00519200 1.63500500 0.74808800
B -6.76988000 2.91249400 0.75931900
B -7.25954000 2.16495700 -0.78712200
B -6.02605900 0.97810700 -1.21877600
B -5.54853100 2.51634200 -0.47268600
B -5.22329500 2.18094800 1.23896700
B -6.72888800 1.62479400 1.99871000
B -5.50921500 0.44731200 1.50286800
C -4.83869400 1.04280700 0.02707800
C -3.40593700 0.69891300 -0.28839700
C -2.48463600 0.50595800 0.75847300
C -1.15552000 0.23417300 0.47036800
C -0.71747200 0.14980900 -0.86507300
C -1.61786400 0.34960700 -1.91132500
C -2.95173300 0.62543600 -1.61672100
C -0.00063100 -0.00376700 1.44329200
C 1.15492400 -0.23669800 0.46996500
C 0.71773200 -0.14580000 -0.86533400
C 1.61883000 -0.34029000 -1.91196600
C 2.95253500 -0.61745700 -1.61785700
C 3.40587400 -0.69747300 -0.28960000
C 2.48386600 -0.50969300 0.75759200
C 4.83847300 -1.04238200 0.02553800
B 5.50851800 -0.44901800 1.50246100
B 7.22876600 -0.10803400 1.22607500
B 7.55222000 -0.43906200 -0.48670300
B 8.00453700 -1.63626600 0.74703600
B 7.25934600 -2.16402500 -0.78917000
B 6.76893700 -2.91348800 0.75608800
B 6.72778400 -1.62740600 1.99718600
B 5.22238400 -2.18219900 1.23607800
B 5.54813600 -2.51541900 -0.47588400

B 6.02634900 -0.97632400 -1.21970700
C 6.06501200 0.22571600 0.01975900
C 5.67451300 1.63467400 -0.34817600
C 5.14248900 2.51714000 0.60385600
C 4.82258800 3.82921000 0.25734100
C 5.03332500 4.28632200 -1.04331300
C 5.57523500 3.42178900 -1.99457900
C 5.89395600 2.10939000 -1.65093600
C 0.25261500 1.23433200 2.33334200
C -0.25452400 -1.24671400 2.32645200
H -1.29473000 0.29978900 -2.94748700
H -3.64306800 0.79531600 -2.43224600
H -2.81443200 0.58354700 1.78839200
H -4.82592200 -0.20484700 2.20821300
H -8.26029900 -0.26430900 -1.12467900
H -7.70720600 -0.83106400 1.76980500
H -5.70165500 0.65935700 -2.30588200
H -4.85829200 3.24951100 -1.09713600
H -4.31220100 2.69057600 1.79924000
H -7.85171800 2.74124000 -1.64003300
H -7.00837000 4.04486600 1.02650000
H -6.93380700 1.81692800 3.15255600
H -9.14798800 1.83412200 1.00250700
H 1.29638500 -0.28529700 -2.94808200
H 3.64440200 -0.78311100 -2.43378900
H 7.00703500 -4.04626800 1.02188300
H 5.70260300 -0.65598700 -2.30654300
H 4.82478600 0.20220000 2.20827200
H 6.93218800 -1.82117000 3.15085000
H 4.31103900 -2.69247800 1.79533500
H 7.70668800 0.82854000 1.77189700
H 8.26076400 0.26544400 -1.12309300
H 7.85174300 -2.73925500 -1.64263700
H 4.85793000 -3.24754700 -1.10159000
H 9.14719500 -1.83599000 1.00159500
H 4.98572800 2.18699400 1.62320700

H 4.41200000 4.49489800 1.01126000
H 4.78465000 5.30938200 -1.31129000
H 5.75642500 3.76746100 -3.00836900
H 6.32884900 1.45670300 -2.39857900
H -6.32511900 -1.45296000 -2.40163900
H -5.75163800 -3.76273100 -3.01403300
H -4.78248500 -5.30721400 -1.31781400
H -4.41356900 -4.49630200 1.00659500
H -4.98827700 -2.18933200 1.62114900
H 2.81308000 -0.59212300 1.78733300
H 1.12554800 1.07372200 2.97619000
H 0.43254600 2.12766200 1.72696200
H -0.60970100 1.42826600 2.98110700
H 0.60728400 -1.44407300 2.97385800
H -1.12799700 -1.08970100 2.96945100
H -0.43390400 -2.13673700 1.71507300

Compound 2' (ω-B97XD/6-311+G)**

E(RwB97XD) = -1703.85051711
Sum of electronic and zero-point Energies= -1703.123545
Sum of electronic and thermal Energies= -1703.086267
Sum of electronic and thermal Enthalpies= -1703.085323
Sum of electronic and thermal Free Energies= -1703.191296
C 5.90535200 2.10090500 -1.68234600
C 5.47990200 1.63263600 -0.43885500
C 4.61468100 2.42257400 0.31597100
C 4.17814200 3.64941200 -0.16568500
C 4.60566700 4.10813700 -1.40431400
C 5.47431100 3.33049100 -2.15948000
C 5.94122100 0.28235400 0.04156600
B 5.95671500 -0.97123200 -1.14611100
B 5.49057200 -2.45755200 -0.31073700
B 5.16119800 -2.03724500 1.37784900
B 6.65806600 -1.42815400 2.11084900
B 6.71302500 -2.77031600 0.94100300
B 7.19982300 -2.10389300 -0.63422900

B 7.92659600 -1.47528400 0.86518900
B 7.45251800 -0.35946300 -0.42634400
B 7.12328400 0.06136600 1.26105000
B 5.42269300 -0.29772400 1.57573400
C 4.78274800 -0.95832400 0.11218000
C 3.35347100 -0.61340700 -0.20523700
C 2.93627300 -0.36891400 -1.51512400
C 1.61707300 -0.04188400 -1.79892900
C 0.70462200 0.03813700 -0.75724000
C 1.11204200 -0.20978900 0.55641200
C 2.42448200 -0.53362900 0.83558900
C -0.72985100 0.34249300 -0.74351100
C -1.17846700 0.28154100 0.57883100
C -0.04686900 -0.07217400 1.52929400
C -1.61389000 0.64795900 -1.76783000
C -2.95038600 0.86524300 -1.46082400
C -3.41250800 0.78144000 -0.14567200
C -2.50609900 0.50711400 0.88159100
C -4.86777300 0.97292900 0.17994800
B -5.47494500 0.12818500 1.56006000
B -6.81431100 1.09150400 2.16186200
B -5.36212600 1.89328400 1.52711400
B -5.69944600 2.43278800 -0.12682800
B -6.01709300 0.99156000 -1.10211700
B -7.36506400 1.96167300 -0.52518400
B -6.96793600 2.52387800 1.11562200
B -8.05936600 1.13941300 0.89366600
B -7.46532400 0.18973000 -0.47930500
B -7.12915400 -0.34965800 1.17152400
C -5.91192200 -0.35701200 -0.03000200
C -5.32720300 -1.62025900 -0.60269500
C -4.48103500 -2.43798800 0.14456900
C -3.93823900 -3.58819100 -0.41211200
C -4.23788200 -3.94150600 -1.72078800
C -5.08900800 -3.13816100 -2.46888000
C -5.62755400 -1.98525400 -1.91517000

C 0.20627100 1.05238600 2.54469000
C -0.32692700 -1.39904500 2.25195900
H -1.27913800 0.71309700 -2.79704900
H -3.64069200 1.10057100 -2.25830800
H -2.84505000 0.46429700 1.90940100
H -4.74241400 -0.54053100 2.19066300
H -8.08696400 -0.49249700 -1.21756200
H -7.50413100 -1.40396500 1.55319600
H -5.64830900 0.84447200 -2.20933100
H -5.07177400 3.30727800 -0.61649200
H -4.50738200 2.40635000 2.16356800
H -8.00650100 2.58659500 -1.30098400
H -7.32659600 3.57358500 1.53278400
H -7.04841400 1.09628600 3.32336200
H -9.21814200 1.17941300 1.13863700
H 1.31699800 0.14441200 -2.82396100
H 3.64710800 -0.43072700 -2.32663200
H 6.96476300 -3.88134100 1.26784700
H 5.63555900 -0.69805600 -2.24405100
H 4.72378000 0.37293100 2.24320200
H 6.86078700 -1.55902500 3.27093200
H 4.25499700 -2.53551000 1.95088400
H 7.58130200 1.04030500 1.74037000
H 8.15333000 0.32421800 -1.08813500
H 7.80449000 -2.71099000 -1.45253700
H 4.79925700 -3.22387700 -0.88777600
H 9.07124800 -1.63907900 1.12470800
H 4.26690600 2.08177300 1.28094700
H 3.50199700 4.24756700 0.43403000
H 4.26385200 5.06576900 -1.78007800
H 5.81921100 3.67923900 -3.12610600
H 6.57700200 1.50274000 -2.28461800
H -6.28909900 -1.36903600 -2.51024100
H -5.33490500 -3.40548300 -3.49004500
H -3.81325900 -4.83957600 -2.15453600
H -3.28095200 -4.20995200 0.18469500

H -4.23896400 -2.18371000 1.16667800
H 2.73147200 -0.72882900 1.85592000
H 1.06472800 0.81014800 3.17760600
H 0.40613200 1.99867400 2.03652500
H -0.66373100 1.18736300 3.19314600
H 0.52485600 -1.68567700 2.87489200
H -1.20234900 -1.30465700 2.90082300
H -0.51350200 -2.20015000 1.53284300

Compound 2'-rot (B3LYP/6-31G*)

E(RB3LYP) = -1703.95249869
Sum of electronic and zero-point Energies= -1703.231660
Sum of electronic and thermal Energies= -1703.193972
Sum of electronic and thermal Enthalpies= -1703.193028
Sum of electronic and thermal Free Energies= -1703.298969
C 5.42975800 2.47289500 1.24960200
C 5.27060500 1.75624300 0.05300500
C 4.57061700 2.36233900 -1.00090400
C 4.03090200 3.63952100 -0.85510600
C 4.18491300 4.33751100 0.34246200
C 4.89070900 3.75000800 1.39256900
C 5.89735000 0.39377000 -0.10286000
B 5.43331300 -0.60580600 -1.42534000
B 5.47164600 -2.29240000 -0.86710800
B 5.89603900 -2.27247800 0.85543800
B 7.52446000 -1.58242500 1.01280900
B 7.13624100 -2.65362500 -0.36293500
B 6.83141800 -1.62089000 -1.79012800
B 8.12116800 -1.19850300 -0.62790100
B 7.07158600 0.06913600 -1.30306600
B 7.49266500 0.09174400 0.42058100
B 6.10856800 -0.57102100 1.31419600
C 4.92092200 -1.04877100 0.16399400
C 3.45675600 -0.90981400 0.49363000
C 2.49370600 -1.13427900 -0.50850700
C 1.14350000 -1.06086200 -0.20094800

C 0.72486200 -0.75902600 1.10923400
C 1.66881600 -0.53937400 2.11217700
C 3.02465600 -0.62006300 1.79946700
C -0.05514500 -1.28337000 -1.12294700
C -1.21341800 -1.05473000 -0.15216900
C -0.74039500 -0.75402100 1.13910100
C -2.57546500 -1.11964100 -0.40577900
C -3.49558900 -0.87625200 0.63058100
C -3.00928800 -0.59163000 1.91924600
C -1.64186700 -0.52742000 2.17955900
C -4.97738300 -0.98448000 0.37943200
B -5.55549900 -0.86323600 -1.23978900
B -5.66383000 -2.38158200 -0.32398700
B -5.98421800 -1.94667500 1.36667700
B -6.06498100 -0.17416900 1.44587700
B -7.55491700 -1.12169900 1.44219500
B -7.31601100 -2.49575300 0.32372200
B -7.03344600 -1.82775100 -1.30866700
B -8.22301100 -1.06639100 -0.21464500
B -7.45980600 0.37535500 0.49280900
B -7.13735200 -0.05810600 -1.19759900
C -5.88049200 0.43713200 -0.15413500
C -5.15922300 1.74514200 -0.35757900
C -5.01812800 2.66158500 0.69543000
C -4.38838800 3.88850300 0.49278700
C -3.89295000 4.22628100 -0.76648500
C -4.04106100 3.32934900 -1.82452600
C -4.66990200 2.10174300 -1.62372100
C -0.07805100 -0.26027800 -2.28130800
C -0.07003400 -2.72198700 -1.68882200
H 1.36420200 -0.31503400 3.13069500
H 3.75192000 -0.46557400 2.58612100
H 2.81107400 -1.38073900 -1.51563600
H 5.76268200 -0.13316200 2.35196800
H 7.35891600 0.96969900 -2.01743600
H 8.07922800 1.00543000 0.89426300

H 4.62146400 -0.21269300 -2.18472600
H 4.65395900 -3.04012700 -1.28606000
H 5.36401600 -2.99599000 1.62808800
H 7.03722800 -1.96811500 -2.90703000
H 7.56715500 -3.75626800 -0.45710800
H 8.23335300 -1.89411900 1.91300800
H 9.27407600 -1.23682300 -0.91031300
H -1.29481900 -0.30864900 3.18566600
H -3.70616800 -0.43139900 2.73291200
H -7.82014300 -3.55645900 0.50036100
H -5.62298500 0.44324300 2.34712900
H -4.78095000 -0.69369800 -2.11201600
H -7.32891600 -2.39139500 -2.31134000
H -4.91381200 -3.25597500 -0.60096500
H -7.41159800 0.67938700 -2.08327900
H -7.95514600 1.41328200 0.77741500
H -8.22446600 -1.18020400 2.42118900
H -5.45811300 -2.52279900 2.25828900
H -9.39047100 -1.08267600 -0.43211000
H -4.79203300 1.42585800 -2.46158400
H -3.67285800 3.58478900 -2.81416200
H -3.40420000 5.18369900 -0.92418800
H -4.29212500 4.58218800 1.32322700
H -5.41226200 2.42562500 1.67613200
H 4.45336500 1.84380500 -1.94435600
H 3.49372600 4.08925400 -1.68538000
H 3.76575300 5.33363900 0.45391600
H 5.02901100 4.28649400 2.32701200
H 5.98835700 2.03877600 2.07040700
H -2.93137400 -1.37010700 -1.39814100
H -0.97668500 -0.39333900 -2.89423200
H -0.07025400 0.76708400 -1.90336900
H 0.79373200 -0.39458300 -2.93164000
H -0.96891700 -2.88955600 -2.29273700
H 0.80193000 -2.89343700 -2.32992700
H -0.05476100 -3.46410300 -0.88461200

Compound 2'-rot (ω-B97XD/6-311+G)**

E(RwB97XD) = -1703.85456532

Sum of electronic and zero-point Energies= -1703.127989

Sum of electronic and thermal Energies= -1703.090901

Sum of electronic and thermal Enthalpies= -1703.089957

Sum of electronic and thermal Free Energies= -1703.193084

C 3.41200400 1.59190700 1.44261800

C 4.23860000 1.59124000 0.32039500

C 4.00802200 2.53306800 -0.68279000

C 2.98196900 3.45970200 -0.56174400

C 2.16219400 3.45169200 0.55931400

C 2.37965100 2.51300400 1.55840100

C 5.34688000 0.58433200 0.15164800

B 5.47435300 -0.14916500 -1.40932300

B 5.98789100 -1.81785500 -1.13492900

B 6.11641500 -2.05479600 0.61456800

B 7.37200400 -0.96961400 1.24432000

B 7.57762800 -1.75964600 -0.33897600

B 7.16894700 -0.57488500 -1.59999300

B 8.03162300 -0.05544700 -0.13036900

B 6.72544100 0.94050100 -0.78990000

B 6.84926600 0.70329600 0.96028700

B 5.67645200 -0.53781800 1.41502900

C 4.91165400 -1.04668200 -0.05119600

C 3.44840900 -1.37523500 0.06690800

C 2.51602900 -0.83383500 -0.81907300

C 1.16979700 -1.05243900 -0.60802800

C 0.73331800 -1.83029700 0.46686400

C 1.65277900 -2.40331800 1.33481300

C 3.00472400 -2.16277200 1.13320900

C -0.00003800 -0.48453800 -1.39156800

C -1.16984900 -1.05250000 -0.60804000

C -0.73334100 -1.83031500 0.46687400

C -2.51608500 -0.83393700 -0.81907100

C -3.44843800 -1.37529300 0.06697500

C -3.00472100 -2.16276000 1.13331100
C -1.65276300 -2.40328500 1.33488800
C -4.91169100 -1.04670800 -0.05111200
B -5.47429700 -0.14919500 -1.40929800
B -5.98787200 -1.81786800 -1.13485500
B -6.11648600 -2.05473500 0.61464100
B -5.67653000 -0.53775600 1.41511800
B -7.37208500 -0.96951900 1.24430900
B -7.57764500 -1.75960900 -0.33898100
B -7.16890100 -0.57490100 -1.60002100
B -8.03158600 -0.05538800 -0.13044400
B -6.84927800 0.70335400 0.96023300
B -6.72538700 0.94050000 -0.78997200
C -5.34683800 0.58430400 0.15165900
C -4.23856400 1.59122700 0.32037700
C -3.41190700 1.59184000 1.44255300
C -2.37955100 2.51294200 1.55833700
C -2.16213700 3.45168600 0.55929800
C -2.98194200 3.45971700 -0.56173800
C -4.00798800 2.53307800 -0.68279300
C -0.00011800 1.05154400 -1.32882700
C -0.00000100 -0.96785900 -2.84869800
H 1.33099400 -3.01283100 2.17191200
H 3.72424100 -2.58057400 1.82516300
H 2.83791900 -0.20978900 -1.64163700
H 5.02815100 -0.51305100 2.39671900
H 6.80837800 2.02353200 -1.25472500
H 6.98874200 1.62613100 1.68616700
H 4.71146300 0.18020300 -2.24271700
H 5.53087700 -2.65999200 -1.82744300
H 5.77109400 -3.07133900 1.10747700
H 7.65180000 -0.56451600 -2.68183400
H 8.36732800 -2.62624900 -0.51112200
H 7.99496000 -1.25938900 2.20959700
H 9.15201900 0.32909600 -0.16229300
H -1.33093600 -3.01270900 2.17203600

H -3.72422000 -2.58049400 1.82532000
H -8.36742700 -2.62614200 -0.51109800
H -5.02824600 -0.51287700 2.39681900
H -4.71138200 0.18005900 -2.24271400
H -7.65171900 -0.56460900 -2.68187600
H -5.53082400 -2.66003000 -1.82731700
H -6.80827000 2.02354800 -1.25476000
H -6.98877000 1.62630000 1.68596700
H -7.99513900 -1.25928100 2.20952700
H -5.77119600 -3.07125100 1.10763100
H -9.15197100 0.32918900 -0.16243300
H -4.63443000 2.54680200 -1.56554700
H -2.82452600 4.18834400 -1.34868300
H -1.35966700 4.17456900 0.65238300
H -1.74506200 2.49285600 2.43702500
H -3.55855100 0.86377900 2.22786900
H 4.63448700 2.54679900 -1.56553300
H 2.82451700 4.18831300 -1.34869600
H 1.35971400 4.17456800 0.65237600
H 1.74521300 2.49296300 2.43712600
H 3.55874100 0.86388200 2.22794900
H -2.83799800 -0.20992500 -1.64164900
H -0.88739200 1.45768400 -1.82273400
H -0.00023000 1.39755300 -0.29303700
H 0.88718600 1.45779000 -1.82259500
H -0.88469800 -0.59717000 -3.37378000
H 0.88469200 -0.59711600 -3.37374800
H 0.00003300 -2.05895100 -2.90087700

Compound 2' – S_1 (B3LYP/6-31G*)

E(RB3LYP) = -1703.91307858
C 5.16398500 0.19181300 -2.70970000
C 5.56365200 0.77271900 -1.49660100
C 5.45154700 2.16504200 -1.35125400
C 4.93510200 2.94929900 -2.38132700
C 4.52407100 2.35871000 -3.57674600

C 4.64566200 0.97847300 -3.73756500
C 6.16164100 -0.05820000 -0.38903500
B 5.99995100 -1.77991300 -0.43445600
B 5.84092000 -2.34369200 1.24424100
B 5.82879900 -0.91169000 2.29349700
B 7.39615600 -0.09298500 2.11788900
B 7.31256700 -1.87817300 2.11452500
B 7.40634300 -2.42673000 0.41343200
B 8.38629000 -1.04185500 0.97070100
B 7.57887500 -0.98932600 -0.61626900
B 7.57188500 0.44522200 0.43370900
B 5.99125400 0.50847300 1.23845300
C 5.10978300 -0.88246500 0.73844000
C 3.61485800 -0.80165700 0.55205000
C 2.91506300 -1.95243500 0.11097200
C 1.53938200 -1.95011400 -0.02888900
C 0.82848800 -0.77037500 0.26661600
C 1.52165400 0.39475900 0.69658600
C 2.89784000 0.37428800 0.84338400
C -0.57397700 -0.48696300 0.22521300
C -0.77792000 0.87686300 0.61832700
C 0.55339700 1.54727600 0.94759400
C -1.67178300 -1.31322700 -0.11246000
C -2.93816700 -0.78257300 -0.05249000
C -3.16344900 0.58292300 0.33224200
C -2.04624300 1.40039800 0.66181700
C -4.52572200 1.10720100 0.38240100
B -5.71163100 0.33501900 1.31328100
B -6.74036400 1.76898600 1.89308500
B -5.05565800 2.14283500 1.54455100
B -4.94097300 2.59831600 -0.17003100
B -5.56643100 0.93622200 -0.94897600
B -6.55879800 2.50125000 -0.86442700
B -6.31176100 3.14150600 0.80481900
B -7.74656600 2.18688700 0.45733200
B -7.42214900 0.95385700 -0.78919000

B -7.53496800 0.48729300 0.95653900
C -6.55369800 -0.23461000 -0.11066400
C -6.58146200 -1.65461700 -0.48970300
C -6.67090700 -2.66815300 0.48754600
C -6.70564500 -4.01238100 0.12546000
C -6.64768400 -4.38522700 -1.22007100
C -6.55726000 -3.39367800 -2.20060200
C -6.52234400 -2.04812500 -1.84331400
C 0.83632700 2.73499100 -0.00199800
C 0.59891700 2.01679800 2.42001200
H -1.51844700 -2.34656200 -0.40815100
H -3.79759500 -1.39370400 -0.30049800
H -2.22794300 2.42853500 0.95354700
H -5.32636400 -0.48786700 2.08253800
H -8.16036200 0.64386600 -1.66840600
H -8.36326800 -0.19409400 1.46974800
H -5.05964200 0.59038200 -1.96933200
H -4.08160500 3.25681100 -0.66646800
H -4.28649300 2.44104400 2.40337400
H -6.79952100 3.20124900 -1.79695100
H -6.41853100 4.28964900 1.10285200
H -7.11892300 1.92087800 3.01162000
H -8.82758800 2.68233000 0.51958900
H 1.02239600 -2.84563300 -0.35883100
H 3.46822500 -2.85622000 -0.10967300
H 7.70837500 -2.53869900 3.01749400
H 5.39732000 -2.27299600 -1.32034300
H 5.41470400 1.51817000 1.42916100
H 7.85072900 0.54497200 3.00923500
H 5.09182100 -0.83356200 3.21779900
H 8.05768800 1.46377500 0.07603100
H 8.06301000 -0.95416800 -1.69625200
H 7.86433400 -3.47109500 0.08514300
H 5.12214100 -3.25901100 1.46225800
H 9.57008600 -1.08523000 1.04110500
H 5.78575400 2.64387600 -0.43816700

H 4.86311400 4.02501300 -2.24917100
H 4.12302400 2.97014700 -4.37993700
H 4.34392700 0.50776700 -4.66873600
H 5.26699000 -0.87534400 -2.86332100
H -6.46288500 -1.28526000 -2.61306700
H -6.52076400 -3.66938300 -3.25163500
H -6.67808900 -5.43443300 -1.50116200
H -6.78478800 -4.77288300 0.89829800
H -6.72650300 -2.38844800 1.53471700
H 3.42089900 1.25680300 1.18775700
H 1.82536000 3.16020200 0.20042200
H 0.80518600 2.42448900 -1.05092800
H 0.09202000 3.52414800 0.14476900
H 1.58245700 2.43594100 2.65852300
H -0.15014700 2.79568000 2.59415500
H 0.40053000 1.19083800 3.10991400

Compound 3 (B3LYP/6-31G*)

E(RB3LYP) = -1115.85165116
Sum of electronic and zero-point Energies= -1115.481503
Sum of electronic and thermal Energies= -1115.458743
Sum of electronic and thermal Enthalpies= -1115.457798
Sum of electronic and thermal Free Energies= -1115.538242
C -7.45950400 -0.34177500 0.00000700
C -8.40736500 0.70187500 0.00009300
C -9.76970600 0.41597600 0.00011200
C -10.21273100 -0.90915800 0.00004400
C -9.28196200 -1.95126400 -0.00004200
C -7.91771000 -1.67509500 -0.00006100
H -8.06018800 1.73055600 0.00014600
H -10.48920100 1.23040200 0.00017900
H -11.27692600 -1.12838600 0.00005900
H -9.62084800 -2.98380800 -0.00009500
H -7.19212500 -2.48270100 -0.00012900
C -6.06419100 -0.05580600 -0.00001200
C -4.87150200 0.18685600 -0.00002700

C -3.47599200 0.46431100 -0.00003100
C -2.53781400 -0.59307000 0.00000800
C -1.18409900 -0.30269200 0.00000400
C -0.73181900 1.03567400 -0.00003400
C -1.65272000 2.08829200 -0.00006900
C -3.01314200 1.79978100 -0.00006600
H -2.89509200 -1.61899300 0.00003900
C -0.00001800 -1.24954700 0.00004300
C 0.73181800 1.03565100 -0.00002700
H -1.31762500 3.12219700 -0.00009600
H -3.74166200 2.60449800 -0.00009000
C 1.65274300 2.08826000 -0.00005800
C 3.01315100 1.79971800 -0.00005200
C 3.47598000 0.46422600 -0.00001200
C 2.53779100 -0.59312900 0.00002000
C 1.18407300 -0.30271100 0.00001100
H 1.31766500 3.12217000 -0.00009100
H 3.74169500 2.60441200 -0.00007600
C 4.87149200 0.18678400 -0.00000300
H 2.89503500 -1.61906300 0.00005500
H -0.00003200 -1.90768200 0.87977500
H -0.00001800 -1.90774900 -0.87963900
C 6.06418800 -0.05584800 0.00000400
C 7.45950800 -0.34178200 0.00001200
C 7.91774100 -1.67509400 -0.00006000
C 9.28199900 -1.95123500 -0.00005100
C 10.21274700 -0.90911000 0.00002900
C 9.76969400 0.41601500 0.00010000
C 8.40734700 0.70188600 0.00009200
H 7.19217200 -2.48271400 -0.00012200
H 9.62090700 -2.98377200 -0.00010600
H 11.27694600 -1.12831500 0.00003600
H 10.48917200 1.23045700 0.00016200
H 8.06015000 1.73056100 0.00014700

Compound 4 (B3LYP/6-31G*)

E(RB3LYP) = -1625.32485737

Sum of electronic and zero-point Energies= -1624.659806

Sum of electronic and thermal Energies= -1624.624426

Sum of electronic and thermal Enthalpies= -1624.623482

Sum of electronic and thermal Free Energies= -1624.724930

C -5.89333200 -2.11344600 -1.52535800

C -5.67570100 -1.63902800 -0.22217300

C -6.06723100 -0.23038200 0.14573900

C -4.84123500 1.03842200 0.15224000

C -3.40842800 0.69430700 -0.16257100

C -2.95393700 0.61797000 -1.49121000

C -1.62055600 0.34313800 -1.78724000

C -0.71819300 0.14651700 -0.74163100

C -1.15931100 0.23340200 0.59415700

C -2.48780400 0.50458000 0.88480100

C 0.71826000 -0.14640500 -0.74163900

C 1.15932000 -0.23360800 0.59415000

C -0.00001900 -0.00023000 1.54247600

C 1.62067100 -0.34270500 -1.78726000

C 2.95406500 -0.61753100 -1.49125800

C 3.40849500 -0.69418900 -0.16262700

C 2.48782400 -0.50477100 0.88476400

C -5.57309800 -3.42544900 -1.86909300

C -5.03138000 -4.28981100 -0.91755400

C -4.82259400 -3.83304200 0.38353400

C -5.14416700 -2.52143300 0.73019800

B -6.02839300 0.97188400 -1.09354800

B -5.55116600 2.51125400 -0.34947500

B -5.22588300 2.17793700 1.36260300

B -5.51160800 0.44459600 1.62877600

B -6.73146000 1.62252500 2.12300100

B -6.77261200 2.90868100 0.88200600

B -7.26203100 2.15909600 -0.66351800

B -8.00772600 1.63096900 0.87230700

B -7.23159200 0.10297600 1.35160800

B -7.55436200 0.43392800 -0.36133300

C 4.84134700 -1.03819800 0.15224900
C 6.06714200 0.23027400 0.14579900
C 5.67562800 1.63897600 -0.22203200
C 5.14391200 2.52132400 0.73027700
C 4.82236400 3.83295100 0.38361900
C 5.03139300 4.28980300 -0.91739100
C 5.57331600 3.42549700 -1.86887000
C 5.89351000 2.11348700 -1.52514200
B 5.51154300 -0.44472800 1.62895900
B 6.73143800 -1.62270200 2.12298900
B 5.22587400 -2.17800300 1.36251100
B 5.55108000 -2.51106400 -0.34960800
B 6.02848200 -0.97175600 -1.09361100
B 7.26202400 -2.15910900 -0.66364200
B 6.77251200 -2.90877000 0.88181800
B 8.00766700 -1.63108700 0.87224800
B 7.55443900 -0.43399900 -0.36128900
B 7.23148800 -0.10309700 1.35160300
H 1.29888100 -0.29116300 -2.82368000
H 3.64633400 -0.78470800 -2.30653300
H 2.81404600 -0.58412000 1.91567400
H 4.82790500 0.20621700 2.33506000
H 8.26242800 0.27084200 -0.99791900
H 7.70937300 0.83358800 1.89725400
H 5.70392400 -0.65163700 -2.18027900
H 4.86075900 -3.24335400 -0.97500500
H 4.31484300 -2.68855100 1.92199300
H 7.85423600 -2.73408300 -1.51740200
H 7.01112600 -4.04146300 1.14746700
H 6.93643400 -1.81640700 3.27653300
H 9.15050600 -1.83031300 1.12634500
H -1.29873100 0.29184400 -2.82366200
H -3.64616400 0.78541300 -2.30646300
H -7.01124800 4.04134000 1.14778300
H -5.70391700 0.65181000 -2.18025700
H -4.82796600 -0.20633400 2.33489500

H -6.93640200 1.81615400 3.27657000
H -4.31491700 2.68833300 1.92233300
H -7.70940100 -0.83377800 1.89720200
H -8.26247300 -0.27062300 -0.99814900
H -7.85421300 2.73408300 -1.51729200
H -4.86079100 3.24350600 -0.97485800
H -9.15056700 1.83024200 1.12635400
H -4.98907600 -2.19157300 1.74991200
H -4.41211200 -4.49860800 1.13760700
H -4.78131400 -5.31248900 -1.18566700
H -5.75285900 -3.77093500 -2.88320000
H -6.32796800 -1.46085600 -2.27323600
H -0.17262300 -0.86295400 2.20034500
H 0.17254200 0.86233600 2.20056600
H 6.32828100 1.46093800 -2.27298000
H 5.75327400 3.77104900 -2.88291900
H 4.78136500 5.31249000 -1.18550800
H 4.41171800 4.49844800 1.13766400
H 4.98865700 2.19146200 1.74996000
H -2.81404400 0.58368500 1.91572400

Compound 4 (ω-B97XD/6-311+G)**

E(RwB97XD) = -1625.21757979
Sum of electronic and zero-point Energies= -1624.547073
Sum of electronic and thermal Energies= -1624.513610
Sum of electronic and thermal Enthalpies= -1624.512666
Sum of electronic and thermal Free Energies= -1624.610371
C -4.64339500 -2.42867000 0.48913700
C -5.48886100 -1.64778300 -0.29696800
C -5.88774200 -2.13415700 -1.54241200
C -5.45016400 -3.37210400 -1.99091300
C -4.60124600 -4.14062900 -1.20460200
C -4.20011500 -3.66416100 0.03606300
C -5.96910800 -0.29568000 0.15822600
B -5.99957800 0.93825500 -1.04683500
B -5.56252500 2.44590400 -0.23259500

B -5.23189000 2.05778700 1.46433400
B -6.72292900 1.43513600 2.19828600
B -6.79496600 2.75823300 1.00836900
B -7.26321600 2.05902900 -0.55876800
B -7.98679900 1.44239100 0.94696800
B -7.48926500 0.31437900 -0.32548700
B -7.16006600 -0.07451000 1.36873400
B -5.46697800 0.31711600 1.68389100
C -4.83026200 0.96778100 0.21644400
C -3.39212500 0.66363500 -0.10114600
C -2.47731100 0.49392100 0.94144700
C -1.15348900 0.22748900 0.65013100
C -0.71940400 0.13871300 -0.67753500
C -1.61859700 0.31571000 -1.71923200
C -2.94884400 0.57708900 -1.42295900
C 0.72011200 -0.14012700 -0.67757000
C 1.15367900 -0.23200900 0.65005000
C -0.00014900 -0.00366100 1.59543900
C 2.47751300 -0.49848500 0.94129500
C 3.39288400 -0.66513700 -0.10131600
C 2.95003900 -0.57582600 -1.42309000
C 1.61979500 -0.31437100 -1.71930100
C 4.83130900 -0.96820400 0.21609600
B 5.46751700 -0.31717900 1.68365100
B 6.72468100 -1.43395000 2.19766600
B 5.23420000 -2.05804700 1.46373800
B 5.56505200 -2.44545700 -0.23332300
B 6.00051000 -0.93716700 -1.04730600
B 7.26532900 -2.05674200 -0.55955600
B 6.79797300 -2.75673800 1.00748400
B 7.98842200 -1.43964300 0.94623700
B 7.48959400 -0.31190900 -0.32592300
B 7.16013900 0.07631900 1.36835700
C 5.96881200 0.29644500 0.15805100
C 5.48709000 1.64817900 -0.29668800
C 5.88619600 2.13574900 -1.54157700

C 5.44749500 3.37348400 -1.98958200
C 4.59718400 4.14055000 -1.20334000
C 4.19568800 3.66280600 0.03672100
C 4.64009400 2.42754500 0.48929600
H 1.29950300 -0.25031900 -2.75309900
H 3.65038900 -0.71685000 -2.23395600
H 2.80103100 -0.58635100 1.97107300
H 4.76881500 0.33503900 2.36854300
H 8.17444900 0.39391200 -0.98118600
H 7.60205600 1.05534300 1.86241300
H 5.66705600 -0.64938800 -2.13800400
H 4.88513900 -3.21443700 -0.82047800
H 4.33422500 -2.57436100 2.03114200
H 7.87564800 -2.64089900 -1.39034300
H 7.07133400 -3.86836300 1.31437400
H 6.93527200 -1.57728700 3.35486200
H 9.13681900 -1.58739500 1.19874600
H -1.29786200 0.25410000 -2.75304200
H -3.64877200 0.72057200 -2.23376200
H -7.06711600 3.87009100 1.31549200
H -5.66637600 0.65052500 -2.13760800
H -4.76884600 -0.33596300 2.36855100
H -6.93326600 1.57847900 3.35552900
H -4.33129100 2.57302200 2.03173200
H -7.60296700 -1.05316400 1.86264100
H -8.17485600 -0.39065200 -0.98084300
H -7.87300500 2.64399100 -1.38937700
H -4.88186100 3.21428500 -0.81966500
H -9.13502300 1.59125100 1.19961800
H -4.32102600 -2.07598400 1.45867100
H -3.54017600 -4.25571100 0.65990900
H -4.25477800 -5.10538700 -1.55719200
H -5.77475000 -3.73513700 -2.95927900
H -6.54639200 -1.54468700 -2.16708400
H -0.17298200 -0.86882400 2.24361900
H 0.17231100 0.85939300 2.24651200

H 6.54590700 1.54737200 -2.16617100

H 5.77230800 3.73750400 -2.95750000

H 4.24990500 5.10517200 -1.55550500

H 3.53462200 4.25318700 0.66048100

H 4.31737800 2.07380500 1.45831700

H -2.80133200 0.57952200 1.97126700

Compound 4-rot (B3LYP/6-31G*)

E(RB3LYP) = -1625.32434441

Sum of electronic and zero-point Energies= -1624.659579

Sum of electronic and thermal Energies= -1624.624049

Sum of electronic and thermal Enthalpies= -1624.623104

Sum of electronic and thermal Free Energies= -1624.726386

C -5.13453000 2.43998800 0.99915800

C -5.25206900 1.70105100 -0.18793400

C -4.79038000 2.27672200 -1.38187600

C -4.20963100 3.54364300 -1.38429900

C -4.08259400 4.26200500 -0.19531700

C -4.55233800 3.70663200 0.99472400

C -5.91945800 0.34934600 -0.19949500

B -7.15262200 -0.02401100 -1.32039900

B -7.49565600 0.12050700 0.41464500

B -8.19653200 -1.22045300 -0.52183700

B -6.97058100 -1.74628600 -1.71154600

B -7.23096200 -2.67837200 -0.20887000

B -7.53213300 -1.51323800 1.11139300

B -6.08336900 -0.51770200 1.28169900

B -5.92786300 -2.25049100 0.92212600

B -5.58329100 -2.39301900 -0.81278200

B -5.53551100 -0.74507800 -1.47423400

C -4.95934700 -1.10038800 0.11236700

C -3.48369000 -0.98157300 0.39237400

C -3.01459400 -0.83804000 1.71082800

C -1.65198300 -0.78810800 1.99544500

C -0.73511800 -0.88879800 0.94862800

C -1.19273200 -1.04225200 -0.37537500

C -2.55041100 -1.09016500 -0.65488600
C 0.73072700 -0.89088600 0.94014200
C 1.17266400 -1.04548900 -0.38914300
C -0.01566700 -1.15035200 -1.32454900
C 2.52690200 -1.09681500 -0.68398900
C 3.47259600 -0.99196900 0.35280900
C 3.01906600 -0.84684500 1.67630500
C 1.65981800 -0.79252500 1.97621000
C 4.94360000 -1.11529600 0.05040900
B 5.49868800 -0.68422700 -1.52563500
B 5.53469600 -2.36494700 -0.95007800
B 5.90978900 -2.31931600 0.78369900
B 7.18794200 -2.70414500 -0.39211600
B 8.16769600 -1.24379400 -0.64547000
B 6.91550600 -1.69102600 -1.83944000
B 7.12729200 0.00658400 -1.36442200
B 7.49925100 0.05396900 0.36995700
B 7.52652400 -1.61294300 0.98193000
B 6.09366200 -0.61001800 1.22849300
C 5.91752700 0.33641500 -0.20358100
C 5.27443500 1.69525500 -0.09026200
C 4.66211600 2.30139100 -1.19766600
C 4.10727000 3.57615600 -1.09518800
C 4.15807200 4.27200200 0.11250500
C 4.77712600 3.68504100 1.21618600
C 5.33158300 2.41028500 1.11611500
H -7.68999500 -3.77371700 -0.20952500
H -5.67710500 -0.03328900 2.27608500
H -4.76000700 -0.40676400 -2.29522300
H -7.23725400 -2.15548700 -2.79400700
H -4.79703500 -3.18084300 -1.21885200
H -7.45547300 0.83386800 -2.07929700
H -8.03574200 1.07807200 0.85637000
H -8.20268900 -1.75293300 2.06165200
H -5.37919900 -2.93804900 1.71585000
H -9.36146600 -1.24971500 -0.75096800

H -3.72155100 -0.78183200 2.52903100
H -1.31991200 -0.68250400 3.02451200
H -2.89060500 -1.22794300 -1.67475700
H 9.32842900 -1.27542600 -0.89470700
H 5.71072500 -0.16589700 2.25055300
H 4.71312800 -0.30205300 -2.31715500
H 7.15732800 -2.04750200 -2.94609800
H 7.42744200 0.90001100 -2.08242300
H 4.73241800 -3.12141400 -1.38324000
H 5.36359300 -3.03969000 1.54944800
H 8.21043700 -1.90897700 1.90641300
H 8.06265200 0.97865500 0.85060400
H 7.63130200 -3.80383900 -0.45908800
H 2.85530500 -1.23519300 -1.70781600
H 1.33995800 -0.68517900 3.00894800
H 3.73485300 -0.79107400 2.48657600
H -0.02016700 -2.09907400 -1.87828700
H -0.01913800 -0.35061200 -2.07781700
H -4.89621500 1.74132000 -2.31764600
H -3.86182100 3.96962400 -2.32118200
H -3.63063800 5.24999000 -0.19773900
H -4.47274100 4.26035600 1.92593300
H -5.50908900 2.03354300 1.93065200
H 5.82329100 1.97775700 1.97917400
H 4.83576500 4.22007300 2.15978900
H 3.72699200 5.26620500 0.19055100
H 3.64003900 4.02599100 -1.96671100
H 4.62778800 1.78498900 -2.14904700

Compound 4-rot (ω-B97XD/6-311+G)**

E(RwB97XD) = -1625.21833720
Sum of electronic and zero-point Energies= -1624.547565
Sum of electronic and thermal Energies= -1624.513326
Sum of electronic and thermal Enthalpies= -1624.512382
Sum of electronic and thermal Free Energies= -1624.612030
C -4.51433800 1.58181100 -2.28552400

C -4.67357300 1.46024900 -0.90486300
C -3.88975000 2.25148800 -0.06728700
C -2.96271000 3.13850300 -0.59726700
C -2.80967000 3.25356800 -1.97243400
C -3.59267900 2.47427700 -2.81478700
C -5.65812900 0.46182600 -0.35537100
B -7.06430300 0.03454000 -1.22243000
B -7.16871700 0.90041400 0.31750200
B -8.24546300 -0.47756900 -0.00650600
B -7.31907500 -1.69597000 -0.91765200
B -7.58797300 -1.90198400 0.82776700
B -7.48723300 -0.29581100 1.59189500
B -5.85761500 0.31580300 1.34863900
B -6.10581100 -1.40845900 1.66193800
B -5.99846000 -2.27399200 0.12119100
B -5.69008200 -1.07704100 -1.14118800
C -5.02943200 -0.90067100 0.44010500
C -3.53807800 -0.95997400 0.63182500
C -2.67523700 -1.11454100 -0.45416600
C -1.30970400 -1.10524900 -0.24385500
C -0.78454500 -0.95227400 1.04336000
C -1.63502200 -0.81425300 2.13216500
C -3.00530600 -0.81465500 1.91666100
C 0.67885200 -0.97045800 0.95281900
C 1.03750900 -1.13349100 -0.39042300
C -0.19621300 -1.23547200 -1.25327400
C 1.65810200 -0.85785000 1.92905200
C 2.99287400 -0.90665900 1.55222400
C 3.36032500 -1.06181100 0.21371900
C 2.36719900 -1.17681100 -0.76266500
C 4.80547000 -1.09042900 -0.20540700
B 5.19223700 -0.22866900 -1.65362900
B 5.30671300 -1.99367100 -1.56485500
B 5.83036800 -2.43292000 0.06846900
B 7.00097400 -2.41220100 -1.27002800
B 7.92722500 -0.90035500 -1.17170900

B 6.59190300 -1.04473500 -2.33654100
B 6.80318500 0.45676200 -1.41113800
B 7.32962000 0.01471300 0.21999700
B 7.45077600 -1.75248400 0.31860100
B 6.04301700 -0.93383900 0.98119400
C 5.69006900 0.35580300 -0.11411700
C 5.00606900 1.55518000 0.48662100
C 5.44433500 2.04894000 1.71555300
C 4.82286300 3.14262900 2.30110900
C 3.74584500 3.75377100 1.67192300
C 3.30093800 3.26570200 0.45068800
C 3.92792800 2.17719200 -0.14057600
H -8.26592800 -2.76756700 1.26971400
H -5.22371300 0.99863800 2.06678200
H -4.97031700 -1.24865700 -2.05581100
H -7.79142800 -2.39557200 -1.74906300
H -5.43966900 -3.31348700 0.04888100
H -7.26927400 0.59714300 -2.24117000
H -7.42051200 2.05531700 0.34524000
H -8.07583600 0.00147400 2.57624100
H -5.63640700 -1.87398500 2.64149700
H -9.40407200 -0.30440200 -0.18560900
H -3.67280900 -0.69818000 2.76059800
H -1.24454900 -0.70097600 3.13729000
H -3.06702200 -1.22402700 -1.45606200
H 9.05963900 -0.80604400 -1.50788300
H 5.75210100 -0.79336300 2.11237400
H 4.32070500 0.31699800 -2.22542300
H 6.73670300 -1.06285100 -3.51240700
H 7.01675000 1.53587000 -1.84469400
H 4.48700900 -2.63730900 -2.12213200
H 5.35137500 -3.35976600 0.62480500
H 8.22262900 -2.26638700 1.05609600
H 7.92590200 0.78746500 0.88556800
H 7.45123200 -3.42437100 -1.69099500
H 2.63757600 -1.30132200 -1.80405000

H 1.39759900 -0.73126900 2.97375300
H 3.75451100 -0.81400700 2.31306500
H -0.24073500 -2.19140300 -1.78492700
H -0.23662700 -0.44203500 -2.00638500
H -5.11434800 0.97735200 -2.95355600
H -3.48722200 2.55921400 -3.89020900
H -2.08800600 3.94913800 -2.38551500
H -2.35928100 3.74127600 0.07145300
H -3.98982800 2.17236400 1.00577000
H 6.27909100 1.57970600 2.22001600
H 5.18338000 3.51589000 3.25270900
H 3.25780000 4.60621800 2.13044000
H 2.46004000 3.73225400 -0.04932400
H 3.56314300 1.80994700 -1.08951300

Compound 4 – S_1 (B3LYP/6-31G*)

E(RB3LYP) = -1625.28436527
C 5.45096700 -2.33070100 1.28529500
C 5.57814100 -0.94098100 1.44175500
C 5.17241000 -0.36367800 2.65468000
C 4.63331500 -1.15108300 3.67113300
C 4.49673100 -2.52856900 3.49899800
C 4.91373300 -3.11569000 2.30406100
C 6.19772000 -0.10949300 0.34678500
B 7.61147200 -0.62104000 -0.46512500
B 7.62140100 0.80647300 0.59406400
B 8.44549100 0.86192200 -0.98411300
B 7.39171300 1.71648500 -2.13313500
B 7.47305800 2.25255200 -0.42761200
B 6.05248800 1.61277400 0.40132100
B 5.91477200 2.19072200 -1.27452700
B 5.90127000 0.76508000 -2.33366500
B 7.45837100 -0.07003300 -2.14746400
B 6.03856100 -0.66340200 -1.28580800
C 5.16581200 0.73341500 -0.78765600
C 3.66770000 0.66615300 -0.62415700

C 2.93854700 -0.47908300 -0.99769900
C 1.56128900 -0.48456300 -0.86809300
C 0.87564000 0.66007000 -0.37245000
C 1.60025200 1.80977700 -0.00182000
C 2.97751300 1.79964200 -0.12774500
C 0.57179100 -1.58189000 -1.19324000
C -0.75243000 -0.94380900 -0.83138100
C -0.53143900 0.39029100 -0.35282200
C -1.62236600 1.20179100 0.04074400
C -2.89237200 0.68277700 -0.03986100
C -3.13109600 -0.65503500 -0.50509600
C -2.02284500 -1.45631400 -0.90288800
C -4.49398400 -1.17390500 -0.55836400
B -5.71242800 -0.33912700 -1.39196100
B -7.52513600 -0.52967200 -0.99478600
B -7.35691800 -1.12003200 0.70689100
B -7.71438500 -2.26224500 -0.61552600
B -6.48536700 -2.66442500 0.64302400
B -6.28694200 -3.18071800 -1.07459700
B -6.75205800 -1.73352700 -2.04556900
B -5.05599100 -2.12401500 -1.77694100
B -4.89012600 -2.70302900 -0.10346400
B -5.49601100 -1.10154800 0.81053900
C -6.51409200 0.11931000 0.09094800
C -6.53609900 1.50870000 0.57230100
C -6.65966600 2.58851500 -0.32722200
C -6.68797200 3.90336600 0.13045400
C -6.58999900 4.18031200 1.49666800
C -6.46657800 3.12223800 2.40103800
C -6.43779700 1.80563900 1.94793400
H 1.09272200 2.69222700 0.37457500
H 3.54009400 2.68204200 0.14851900
H 3.45093500 -1.34751700 -1.39093600
H 5.45333700 -1.66619500 -1.48618300
H 8.09379900 0.76066100 1.67883500
H 8.08348600 -1.64683600 -0.10969100

H 5.44948600 2.10591300 1.28664900
H 5.20368500 3.11270900 -1.49102300
H 5.17310500 0.70015600 -3.26597100
H 7.93771600 3.29006300 -0.08718400
H 7.80344600 2.37878400 -3.02763100
H 7.91591400 -0.70632100 -3.03844700
H 9.63031300 0.89452200 -1.04188800
H -1.46007800 2.21376400 0.39874200
H -3.74571900 1.28191100 0.25425300
H -6.39902400 -4.30443700 -1.45270900
H -4.96106500 -0.82645000 1.83790100
H -5.35056100 0.53981500 -2.10823900
H -7.16183300 -1.80535200 -3.16106100
H -4.31242100 -2.35459300 -2.67794900
H -8.37090100 0.18140400 -1.43380200
H -8.06798400 -0.87890400 1.62889300
H -6.69530600 -3.42997700 1.53033100
H -4.01521800 -3.39113300 0.31971700
H -8.79498200 -2.75800000 -0.68110900
H -6.74752500 2.38422100 -1.38952400
H -6.79380000 4.71627300 -0.58361400
H -6.61547800 5.20680000 1.85223200
H -6.39941200 3.32261600 3.46747900
H -6.35324000 0.99062600 2.65969800
H 0.61096700 -1.87229900 -2.25119400
H 0.76184000 -2.49298700 -0.61114400
H 5.28717200 0.70095200 2.81721800
H 4.32693700 -0.68331800 4.60227000
H 4.07881600 -3.14058900 4.29308600
H 4.82907300 -4.18931000 2.16287300
H 5.78849100 -2.80713800 0.37223200
H -2.20991300 -2.46329400 -1.25773300

Compound 5’ (B3LYP/6-31G*)

E(RB3LYP) = -1246.07059630

Sum of electronic and zero-point Energies= -1245.766642

Sum of electronic and thermal Energies= -1245.746914

Sum of electronic and thermal Enthalpies= -1245.745970

Sum of electronic and thermal Free Energies= -1245.819496

C -5.16282400 0.03486500 -0.00000000

C -3.79135000 -0.33924100 0.00000000

C -2.61814900 -0.66960600 0.00000000

C -1.26178800 -1.02901800 0.00000000

S 0.00000000 0.19589900 -0.00000000

C 1.26228400 -1.02754700 0.00000000

C 0.70653300 -2.29732700 0.00000000

C -0.70442600 -2.29809800 0.00000000

C -5.53933500 1.39457600 -0.00000000

C -6.88104900 1.75368500 -0.00000000

C -7.89689200 0.78463000 -0.00000000

C -7.51828300 -0.56401100 0.00000000

C -6.17844700 -0.94060100 0.00000000

C -9.35079000 1.19255400 -0.00000000

H -4.76744500 2.15807700 -0.00000000

H -7.14888100 2.80811600 -0.00000000

H -8.28661900 -1.33362100 0.00000000

H -5.90522000 -1.99136100 0.00000000

H -1.31259000 -3.19527500 0.00000000

H 1.31550300 -3.19392900 0.00000000

C 2.61838100 -0.66675000 0.00000000

H -10.01162800 0.32021300 -0.00000000

H -9.59633600 1.79784900 0.88169700

H -9.59633600 1.79784900 -0.88169700

C 3.79127300 -0.33533400 0.00000000

C 5.16259100 0.03938900 -0.00000000

C 5.53868600 1.39920800 -0.00000000

C 6.88029300 1.75870400 -0.00000000

C 7.89643900 0.78995300 -0.00000000

C 7.51823700 -0.55880400 0.00000000

C 6.17850800 -0.93577600 0.00000000

H 4.76655700 2.16246900 -0.00000000

H 7.14780100 2.81321800 -0.00000000

C 9.35019000 1.19838000 -0.00000000

H 8.28678900 -1.32819800 0.00000000

H 5.90558300 -1.98661100 0.00000000

H 10.01134000 0.32628300 -0.00000000

H 9.59549100 1.80377900 -0.88169300

H 9.59549100 1.80377900 0.88169300

Compound 6' (B3LYP/6-31G*)

E(RB3LYP) = -1755.54279781

Sum of electronic and zero-point Energies= -1754.944980

Sum of electronic and thermal Energies= -1754.910514

Sum of electronic and thermal Enthalpies= -1754.909569

Sum of electronic and thermal Free Energies= -1755.013133

C -2.32133300 -1.36515700 -0.22277700

C -1.09374500 -0.61226700 -0.57531000

S -0.00136300 -0.00096100 0.63919600

C 1.09228000 0.60788800 -0.57542900

C 2.31854300 1.36296500 -0.22298900

C 3.80621700 0.45571100 0.11375700

B 2.93488600 1.26063500 1.37547500

B 2.28649200 2.78476600 0.72160900

B 2.70906500 2.82980900 -1.00217100

B 3.66750300 3.75863900 0.17140500

B 5.15663600 2.85430800 0.51205800

B 4.71035400 1.30978000 1.27378200

B 5.13561600 1.35845800 -0.45129400

B 4.47806500 2.85727900 -1.14291800

B 3.60880900 1.33471000 -1.36287900

C -3.80729000 -0.45487400 0.11296300

B -4.71357800 -1.30656600 1.27299300

B -5.13836200 -1.35509700 -0.45221700

B -3.61119100 -1.33483800 -1.36319600

B -2.71449200 -2.83152400 -1.00148900

B -2.29245600 -2.78668300 0.72242100

B -3.67524800 -3.75797700 0.17207200

B -4.48353200 -2.85555500 -1.14294300

B -5.16270900 -2.85050000 0.51178700
B -3.79653200 -2.77822800 1.66341500
B -2.93803700 -1.26102000 1.37541300
B 3.79018500 2.77973000 1.66321400
C -3.77836100 1.04782100 0.07406800
H -3.61959700 -4.94416100 0.19062600
H -2.33764600 -0.60951300 2.15558300
H -3.45107000 -0.73543800 -2.36629400
H -5.01114100 -3.37868200 -2.06915500
H -1.94451500 -3.22650200 -1.81037700
H -6.05268800 -0.73394200 -0.87831700
H -5.33740500 -0.65568300 2.04105300
H -3.83271600 -3.24495500 2.75456400
H -1.22985800 -3.14536100 1.10379900
H -6.19329600 -3.37603700 0.77975700
C 3.78047800 -1.04703400 0.07505900
H 6.18608600 3.38200700 0.78014800
H 3.45032300 0.73450600 -2.36576600
H 2.33539500 0.60838700 2.15570600
H 3.82498100 3.24699500 2.75417800
H 5.33522700 0.66049500 2.04234300
H 1.22303300 3.14145900 1.10244700
H 1.93857100 3.22283800 -1.81150700
H 5.00501600 3.38105900 -2.06913900
H 6.05141600 0.73904400 -0.87677400
H 3.60941500 4.94471400 0.18946700
C 0.61758400 0.34285800 -1.83919400
C -0.61755700 -0.35014400 -1.83912000
H 1.13513600 0.64555000 -2.74089100
H -1.13428400 -0.65454100 -2.74072100
C -4.02365700 1.74872100 -1.11588400
C -4.03355400 3.14104800 -1.13450400
C -3.80242500 3.88728800 0.02721300
C -3.58004100 3.18381600 1.21782700
C -3.56819000 1.79242200 1.24542200
H -4.22375800 1.20892600 -2.03362700

H -4.22916500 3.65563500 -2.07207500
C -3.77665300 5.39594600 -0.00315600
H -3.41592900 3.73190700 2.14234800
H -3.40854300 1.28658800 2.19035500
H -4.16048600 5.82241900 0.92953900
H -2.75158800 5.76770900 -0.13253600
H -4.37429600 5.79121600 -0.83075000
C 4.03040500 -1.74740000 -1.11436900
C 4.04381700 -3.13958300 -1.13296900
C 3.81158900 -3.88643900 0.02827300
C 3.58441900 -3.18356400 1.21819600
C 3.56914500 -1.79208900 1.24579100
H 4.23155400 -1.20706600 -2.03156500
H 4.24318800 -3.65367900 -2.07003300
C 3.78978800 -5.39514300 -0.00286400
H 3.41933200 -3.73207200 2.14227800
H 3.40602600 -1.28672000 2.19037600
H 4.14889500 -5.82099800 0.93980900
H 2.76949000 -5.76910000 -0.16067500
H 4.41058200 -5.78899900 -0.81401900

Compound 6' (ω-B97XD/6-311+G)**

E(RwB97XD) = -1755.48250393
Sum of electronic and zero-point Energies= -1754.879118
Sum of electronic and thermal Energies= -1754.846266
Sum of electronic and thermal Enthalpies= -1754.845322
Sum of electronic and thermal Free Energies= -1754.942802
C 2.85180100 2.29263300 -1.56417500
C 3.02425900 1.81968100 -0.26345000
C 2.65338200 2.64564100 0.79491100
C 2.10478500 3.89718300 0.55656300
C 1.91469100 4.36844300 -0.74008500
C 2.31139800 3.54748500 -1.79489200
C 3.55133600 0.43018500 -0.03903300
B 4.61485500 -0.31735500 -1.14031100
B 5.12630300 0.07099600 0.51253500

B 3.72839500 -0.16091700 1.57187200
B 3.25646700 -1.87115700 1.52646500
B 2.75153400 -2.26236100 -0.12714000
B 4.37427000 -2.70845400 0.43338600
B 4.96875900 -1.40408200 1.49087000
B 5.52493700 -1.51064300 -0.19668500
B 4.14539500 -2.03108800 -1.19815200
B 2.90672400 -0.78696300 -1.09383300
C 2.45402100 -0.72385600 0.55655400
C 1.08915600 -0.26430700 0.90157500
S -0.08145700 0.09776900 -0.31052400
C -1.27485000 0.45573400 0.88287200
C -0.77474700 0.31527700 2.14557100
C 0.57985400 -0.09183500 2.15655300
C -2.67757600 0.76445400 0.51848600
B -3.11204800 0.76981400 -1.13695500
B -3.17410600 2.24897800 -0.16421400
B -3.64407800 1.78139200 1.47971700
B -4.85148700 2.46528900 0.37267700
B -5.81857700 1.12471600 -0.27870700
B -4.50779100 1.83290600 -1.25691500
B -4.73946100 0.07086200 -1.21097700
B -5.22021700 -0.39099800 0.43162200
B -5.27791500 1.08654600 1.41766600
B -3.88223700 0.02283700 1.51153900
C -3.60408800 -0.53139600 -0.09592400
C -2.88051000 -1.83039500 -0.31690100
C -2.62594600 -2.26813400 -1.61583600
C -1.86275900 -3.40253200 -1.84477500
C -1.31609000 -4.13003200 -0.78913000
C -1.59913000 -3.70495500 0.50734600
C -2.37261200 -2.57854400 0.74365000
C -0.42353900 -5.31448800 -1.03895100
C 1.27415400 5.70520500 -0.99674500
H 4.65196400 -3.84597600 0.61684100
H 2.11139700 -0.44672600 -1.89452700

H 3.45079800 0.53563100 2.47809300
H 5.66684800 -1.58980100 2.42977500
H 2.66185100 -2.30390100 2.45210900
H 5.83746100 0.99100400 0.72452400
H 4.99675100 0.32935200 -2.05233400
H 4.25912500 -2.65691300 -2.19773800
H 1.80245100 -2.94252100 -0.31842600
H 6.64528000 -1.77375900 -0.47909700
H -6.95943000 1.23831500 -0.57785100
H -3.52729600 -0.63365500 2.42066200
H -2.26841100 0.54312300 -1.92828100
H -4.69166000 2.44147000 -2.25661100
H -5.01678100 -0.61573800 -2.13163500
H -2.32930100 3.05770300 -0.34052000
H -3.12945700 2.28489600 2.41769700
H -6.00857900 1.17106300 2.34636100
H -5.80068700 -1.40156500 0.62946400
H -5.28876900 3.55164100 0.55467700
H -1.36669200 0.48252900 3.03500400
H 1.15390100 -0.26917100 3.05564800
H 2.77865900 2.31456800 1.81618500
H 1.81627100 4.51631300 1.39967700
H 2.18736000 3.89070100 -2.81687300
H 3.13649200 1.67584000 -2.40724700
H 1.67502800 6.16992600 -1.89997600
H 0.19468500 5.58921200 -1.13497000
H 1.43022600 6.38957900 -0.16061100
H -2.55757400 -2.27631900 1.76473400
H -1.20000300 -4.25750500 1.35162800
H -1.67615700 -3.71664900 -2.86646000
H -3.01347600 -1.71347600 -2.46097300
H -0.63693000 -5.77879500 -2.00368400
H 0.62628500 -5.00398100 -1.04438600
H -0.53886300 -6.07100100 -0.25989500

Compound 6’-rot (B3LYP/6-31G*)

E(RB3LYP) = -1755.54053998

Sum of electronic and zero-point Energies= -1754.942647

Sum of electronic and thermal Energies= -1754.908314

Sum of electronic and thermal Enthalpies= -1754.907370

Sum of electronic and thermal Free Energies= -1755.008657

C 2.84961800 -1.21876800 -0.66263400

C 1.37313500 -1.17854500 -0.79519600

S 0.30764000 -1.62156800 0.51192100

C -1.10270500 -1.40598300 -0.49449500

C -2.46254300 -1.63820600 0.05641400

B 3.83441500 -1.72926200 -1.96037700

H 3.27981500 -2.07342000 -2.94869100

H 3.07108000 -3.67221100 -0.41743200

B 3.71627000 -2.68035600 -0.46549100

B 5.30115100 -2.40290100 -1.21832600

H 5.88060700 -3.29831800 -1.74023400

H 5.88510500 -0.43484500 -2.87206100

B 5.30671800 -0.74194700 -1.88160300

B 6.11987300 -1.10247700 -0.32940600

H 7.29917200 -1.05011900 -0.20066600

B 5.17028000 0.38913000 -0.52066000

H 5.54568200 1.51260000 -0.50535700

H 5.33712600 -0.08971200 2.02591200

B 5.04481600 -0.55905400 0.97849800

B 5.11131900 -2.28372000 0.55551600

H 5.55067700 -3.07875100 1.31979600

C 3.66468400 0.08243800 0.21686600

C 2.86188100 1.18204700 0.85710800

B 3.54994700 -1.51837700 0.87238000

H 2.82268800 -1.70779200 1.78307000

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C -3.61016100 -0.30237400 0.04555500

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B -3.79079400 -1.66282200 -1.02433100

B -3.29216200 -3.12512200 -0.14180200
B -2.71633700 -2.58404200 1.44856700
B -4.34330200 -3.27539200 1.28237400
B -5.00843400 -2.70354800 -0.27499900
B -5.50892000 -1.93533700 1.26081800
B -4.07319600 -1.84337500 2.32126500
B -2.88492000 -0.81141200 1.52235100
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H -4.59211800 -4.34545700 1.73265700
H -2.05902300 -0.13666400 2.02592600
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H -4.97191200 0.61925200 1.89575800
H -4.12317700 -1.88011200 3.50690800
H -1.75975500 -3.07054600 1.94981700
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C -3.74670400 1.37801000 -1.82632800
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C -2.54553400 3.49415200 -1.78091300
C -2.01670800 3.12163300 -0.54130800
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H -3.85430700 2.85569200 -3.37324400
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H -1.48144400 5.37914100 -1.81775300
H -1.75514300 4.67011100 -3.41734700
H -3.08836700 5.43949000 -2.55715500
C -0.74380000 -1.01762600 -1.76399100
C 0.65752100 -0.88415800 -1.93214800
H 1.12483600 -0.59863500 -2.86678200
H -1.45921900 -0.82642200 -2.55314000
C 2.47079000 1.09507400 2.20335000

C 1.78810600 2.13977900 2.81777900
C 1.47693800 3.31594500 2.12165200
C 1.87308100 3.40098000 0.78230700
C 2.55378800 2.35698300 0.15797200
H 2.71201000 0.21181300 2.78274100
H 1.50090800 2.04140300 3.86193400
C 0.76795700 4.45823000 2.80919900
H 1.65828000 4.30379700 0.21562200
H 2.85717300 2.47133000 -0.87578300
H 0.43372400 5.21462200 2.09219700
H -0.10738900 4.10872000 3.36852100
H 1.43034500 4.95642600 3.52859300

Compound 6'-rot (ω-B97XD/6-311+G)**

E(RwB97XD) = -1755.48395949
Sum of electronic and zero-point Energies= -1754.879813
Sum of electronic and thermal Energies= -1754.847381
Sum of electronic and thermal Enthalpies= -1754.846436
Sum of electronic and thermal Free Energies= -1754.939794
C -1.90486000 1.75063300 0.00173900
C -2.95721000 1.05330700 -0.58537500
C -3.54175100 1.58219900 -1.73756800
C -3.08993100 2.77386000 -2.28032200
C -2.03566200 3.47644100 -1.69707600
C -1.45588100 2.94151000 -0.55148700
C -3.44959800 -0.25799900 -0.03991800
B -4.45637700 -0.37779000 1.33479500
B -5.05687900 -0.76248700 -0.28773900
B -3.73822700 -1.50845300 -1.21139600
B -3.30600100 -3.03890200 -0.42874700
B -2.69750600 -2.64687800 1.18927700
B -4.35645700 -3.23439900 0.98843400
B -5.00040900 -2.52267500 -0.51236700
B -5.44262500 -1.83313700 1.07028300
B -4.00968200 -1.90370300 2.12339100
B -2.76475300 -0.88697400 1.40911100

C -2.41671200 -1.61039900 -0.12900500
C -1.05043900 -1.38701800 -0.66303700
S 0.32671900 -1.79123300 0.29549000
C 1.40132800 -1.10942200 -0.87054500
C 0.71916400 -0.62245500 -1.94750600
C -0.68244300 -0.78401600 -1.83110700
C 2.86888100 -1.10296500 -0.66993000
B 3.93791500 -1.38440700 -1.96834600
B 3.79634400 -2.53329000 -0.62631100
B 5.39913700 -2.07059100 -1.23075200
B 5.34024700 -0.34213500 -1.66224200
B 6.07754900 -0.86033300 -0.12320400
B 5.10954400 -2.20830800 0.52200600
B 3.49070900 -1.59809800 0.84923200
B 4.89510100 -0.56848100 1.17222800
B 5.04057300 0.57698000 -0.17435300
B 3.71906600 0.24744300 -1.30971000
C 3.51983400 0.06794600 0.39719500
C 2.58633000 1.03059200 1.07556800
C 2.45765600 2.33210400 0.59256000
C 1.60769800 3.23553500 1.21043100
C 0.83859400 2.86847700 2.31375400
C 0.99208200 1.57532000 2.80926000
C 1.86099800 0.67421100 2.21101400
C -0.14701600 3.82574000 2.92579300
C -1.55270100 4.77361600 -2.28729200
H 3.44816500 -1.62242700 -3.01767300
H 3.20827800 -3.54974900 -0.76005000
H 6.06284500 -2.84959300 -1.82773000
H 5.95155300 0.13352100 -2.55875000
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H 5.55231800 -3.07466700 1.19735700
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H -1.89898000 -0.29562600 1.94476100
H -3.51381200 -1.26440700 -2.34231800
H -5.77071500 -3.06842900 -1.22785700
H -2.77191200 -3.86128400 -1.08852600
H -5.78445100 -0.01841700 -0.84658900
H -4.75249600 0.63832300 1.86165200
H -4.05775600 -2.02269400 3.30110800
H -1.76470300 -3.22006500 1.63595100
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H -4.35697800 1.05848000 -2.22021500
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H -0.62610200 5.10462900 -1.81494300
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H -2.29953700 5.56156400 -2.15231500
H 1.20630200 -0.16091400 -2.79503900
H -1.39071700 -0.43076000 -2.56667100
H 1.97069000 -0.31131500 2.64205000
H 0.43004200 1.26534500 3.68432800
H 1.53883400 4.24663500 0.82086500
H 3.03371500 2.65109000 -0.26637000
H 0.16644600 4.86264700 2.78815300
H -1.12942700 3.71179300 2.45449000
H -0.27160100 3.64237900 3.99473000

Compound 6' – S_1 (B3LYP/6-31G*)

E(RB3LYP) = -1755.52225761
C 4.79590300 1.33981600 1.06723600
C 4.36125300 0.69936600 -0.11593500
C 4.18771400 1.49555000 -1.27118700
C 4.42875000 2.85995700 -1.23804100
C 4.84876900 3.49925300 -0.05588800
C 5.03502800 2.70526200 1.09098300
C 4.13113000 -0.75541800 -0.15069700

B 3.53637200 -1.56684700 1.27081500
B 4.22501400 -3.23444600 1.15982700
B 5.14256100 -1.88440300 0.47520500
B 4.73255300 -1.77992900 -1.28031200
B 3.57442300 -3.07095500 -1.63640700
B 4.91800800 -3.37558700 -0.48931300
B 3.32938500 -4.05715700 -0.15655100
B 2.47412100 -3.03076000 1.03213200
B 2.06649200 -2.93444600 -0.73333500
B 2.94780900 -1.42068800 -1.24112600
C 2.09331500 -1.62926700 0.26625400
C 0.99619500 -0.77306400 0.59896700
S 0.00021500 0.00008200 -0.62943600
C -0.99587100 0.77319800 0.59896100
C -0.54988300 0.42017200 1.89309600
C 0.55014100 -0.42006600 1.89310300
C -2.09291300 1.62939700 0.26624900
B -2.94776400 1.42050500 -1.24112100
B -3.57446200 3.07075600 -1.63650100
B -4.91801800 3.37542300 -0.48937100
B -4.22491900 3.23442000 1.15973600
B -3.32939300 4.05704700 -0.15673100
B -2.06645400 2.93432600 -0.73355100
B -2.47400800 3.03077100 1.03201900
B -3.53624200 1.56685700 1.27079100
B -5.14246900 1.88433600 0.47523000
B -4.73253700 1.77974300 -1.28028300
C -4.13087800 0.75541100 -0.15059600
C -4.36119500 -0.69936000 -0.11575900
C -4.18771700 -1.49564600 -1.27102700
C -4.42895200 -2.85993500 -1.23784800
C -4.84918000 -3.49917600 -0.05560000
C -5.03526500 -2.70518700 1.09122800
C -4.79594600 -1.33972900 1.06743600
C -5.06826500 -4.98685800 -0.01637400
C 5.06734800 4.98701500 -0.01607000

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H -2.45189700 0.70478700 -2.04547100
H -3.46431500 0.95215400 2.28201500
H -4.66638300 3.81601000 2.09725800
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H 5.43060100 5.36605000 -0.97716200
H 4.12666800 5.51297700 0.20188500
H 5.78373100 5.26902700 0.76211100

5. Two-photon absorption (TPA)

The structures for all the *o*-carborane precursors **1**, **3** and **5** retain C_{2v} symmetries and imply a long range π-electronic delocalisation. These quadrupolar architectures constitute a relevant building platform for the construction of two-photon activable chromophores. As an illustrating example, **Figure S18** shows the one- (1PA) and two-photon absorption (2PA) spectra for precursors **1**, **3** and **5** in dichloromethane.

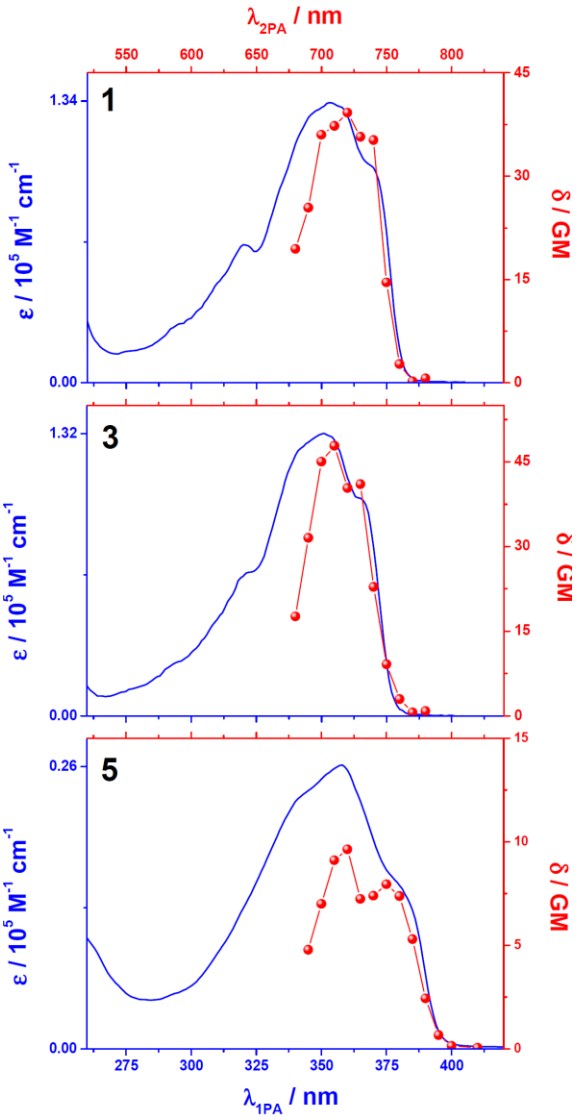


Figure S18. One- and two-photon absorption spectra of **1**, **3** and **5** in dichloromethane.

The 2PA bands match relatively well their respective 1PA bands. Note that the maxima 2PA cross sections (δ_{MAX}) of this series are in the 10-50 GM range. Such weak values should be mainly attributed to the theoretically 2PA forbidden character of the S_0-S_1 transition for chromophores with quadrupolar electronic symmetry.[7] It is worth noting that despite the absence of any electron donor or acceptor groups at their rims, these precursors can be two-photon activated in the NIR range. However, the introduction of *o*-carborane subunits into the π-conjugated backbone reduces significantly the conjugation length within the *o*-carborane dyes as clearly indicated by the strong band hypsochromy observed when comparing the absorption spectra of **2**, **4** and **6** with respect to those of their precursors. As a consequence, each *o*-carborane derivative

should be viewed as a A-π-A quadrupole whose π-electron relay presents a reduced size only involving a fluorenyl linker for the **2** and **4** derivatives and a thienyl one for **6**. In this context, the 2PA spectra of this *o*-carborane series should be significantly blue shifted out of our measurements spectral range.

The two-photon absorption (2PA) measurements were performed with femtosecond mode-locked laser pulse using a Ti: Sapphire laser (Coherent, Chameleon Ultra II: pulse duration: ~140 fs; repetition rate: 80 MHz; wavelength range: 680-1040 nm). A relative two-photon excited fluorescence (2PEF) method[8,9] was employed to measure the two-photon absorption cross-sections, δ. This well-established method consists in recording the luminescence signal of the excited dyes upon two-photon absorption by tightly focusing a *fs*-pulse excitation laser into an optical cell containing a solution with the chromophore. The luminescence signal whose intensity displays a quadratic dependence with the laser excitation power was typically collected at a perpendicular direction from the laser excitation beam. The measurements of 2PA cross-sections were performed relative to a set of two reference molecules (*r*): prodan in toluene[10] and *p*-bis(o-methyl-styryl) benzene in cyclohexane.[7] The value of δ for a sample (*s*) is given by:

$$\delta_S = \frac{S_S \Phi_r \eta_r c_r}{S_r \Phi_S \eta_S c_S} . \delta_r$$

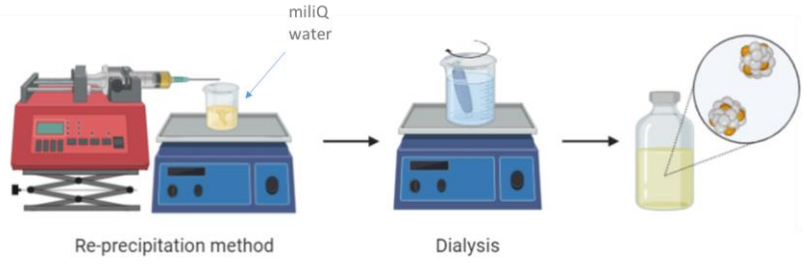
Where *S* is the detected two-photon excited fluorescence integral area, *c* the concentration of the chromophores, and Φ is the fluorescence quantum yield of the chromophores. η is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved. The measurements were conducted in a regime where the luminescence signal showed a quadratic dependence on the intensity of the excitation beam. For the calibration of the two-photon absorption spectra, the two-photon excited luminescence signal of each compound was recorded at the same excitation wavelength as that used for standards. The concentration of the solutions was about 10^{-4} M for all compounds. The laser intensity was in the range of 0.2-2 x 10^9 W/cm^2. The experimental error on the reported cross section is 15 – 20%.

6. Preparation of nanoparticles.

The reprecipitation method is a single-step self-assembly method for obtaining organic nanoparticles. It is the most popular solvent-exchange process that has been developed over a decade by several groups such as Nakanishi´s, Majima´s, Yao´s, Park´s, Barbara´s, Horn and coworkers. These groups have successfully studied the preparation, size dependency of the luminescence and emission enhancement of various nanoparticles.[11,12] The precipitation method generally consists of dropping a concentrated solution of a water miscible organic solvent solution of an hydrophobic compound in a large amount of an anti-solvent, usually water, under vigorous stirring. The fast mixing of the two solvents induces the precipitation of the organic compound in micro/nano aggregates since the organic molecule is no more soluble in the new solvent mixture. The experimental parameters involved in the preparation technique to control the particle size are temperature, concentrations, volume and velocity of the injection, nature and volume of the miscible solvent, and composition and time and agitation speed (rpm) of the non-solvent. Therefore, both kinetics and thermodynamics processes are considered for the growth of organic nanoparticles.[13]

In our experiment, carborane-containing compounds **2**, **4** and **6** were dissolved in THF in a 10^{-3} M concentration. Then, 1 ml of this solution was taken in a Hamilton microsyringe and added with a rate of 1 ml/ hour using a 4.61 mm diameter of the syringe to a volume of 9 ml milliQ water under vigorous stirring (400 rpm) at room temperature (Figure S19) for 1 hour. The mixture was kept stirring for an hour after the addition of THF and over a duration of time, the precipitation in the mixture appeared and the solubility of the organic material decreases homogeneously thus these molecules aggregate and form nanoparticles.[14] Therefore, the final concentration was 10^{-4} M. In order to obtain a NP suspension in pure water for biological applications, the THF is remove with a dialysis procedure using a D9652-100FT dialysis tubing cellulose membrane purchased from Sigma Aldrich. Samples were dialyzed in 500 mL of milliQ water, and water was changed every 6 hours during 72 hours. Later, the NPs in water suspension were diluted from 10^{-4} M to 10^{-6} M concentration and further characterized with DLS, TEM, UV-Vis and fluorescence spectroscopy techniques. To our knowledge, this is the first time that NPs of carborane-based fluorophores have been prepared following this methodology

(a)



(b)

Figure S19. (a) Preparation of NPs and aqueous solution turns turbid as **2** dissolved in THF is added dropwise. (b) Schematic representation of reprecipitation method followed by dialysis.

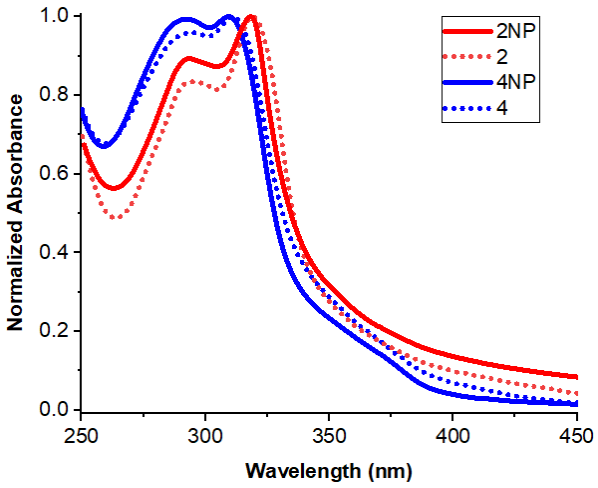


Figure S20. Normalised absorption of **2** in aggregation state (dotted line) and as NPs in water (solid line)

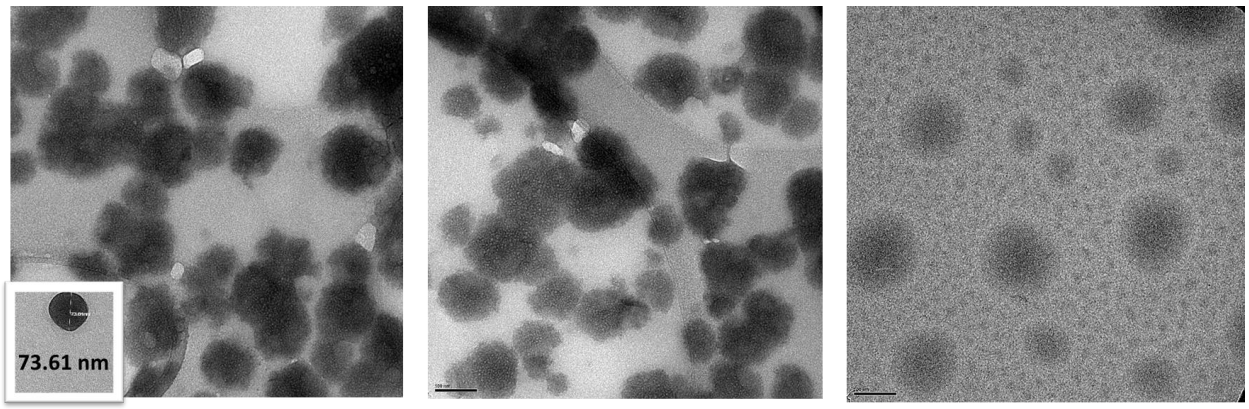


Figure S21. TEM image of **2**, **4** and **6** NPs using ultrathin carbon film on lacey carbon support film, 400 mesh, Copper

Compound	Concentration	Average size (nm)	PDI
2	**1.0 x 10 $^{-5}$ M**	**84.30 ± 10**	**0.09**
4	**1.0 x 10 $^{-5}$ M**	**72.37 ± 10**	**0.10**
6	**1.0 x 10 $^{-5}$ M**	**122.10 ± 10**	**0.12**

Table S14: Size and PDI data of **2**, **4** and **6** nanoparticles

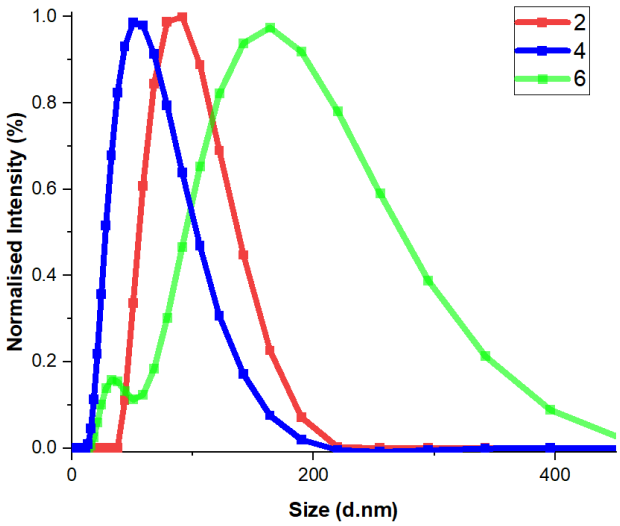


Figure S22. Size distribution by intensity plot of **2**, **4** and **6** NPs.

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