

Structure-Property Relationship on Aggregation-Induced Enhanced Emission (AIEE) of the Spirobifluorene Derivatives including Herringbone and T-type aggregation mode in solid phase: Synthesis, Crystallography, DFT, Optical and Thermal Properties

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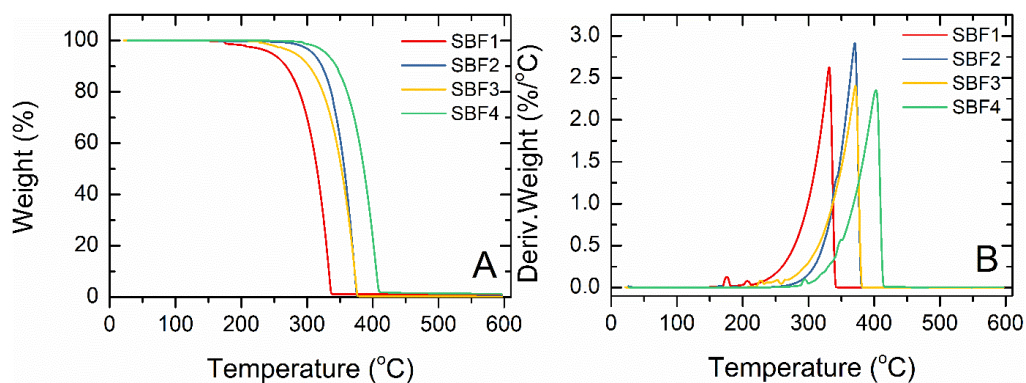


Figure S1: A) %Weight change thermogram of SBF1, SBF2, SBF3 and SBF4, B) Derivative weight change thermogram of SBF1, SBF2, SBF3 and SBF4.

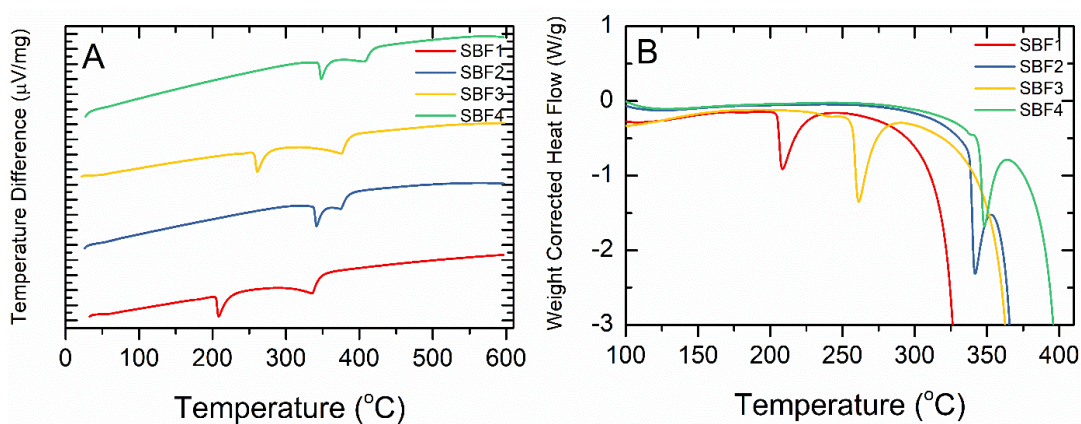


Figure S2: A) Temperature difference to temperature thermogram of SBF1, SBF2, SBF3 and SBF4, B) Weight corrected heat flow to temperature thermogram of BF1, SBF2, SBF3 and SBF4.

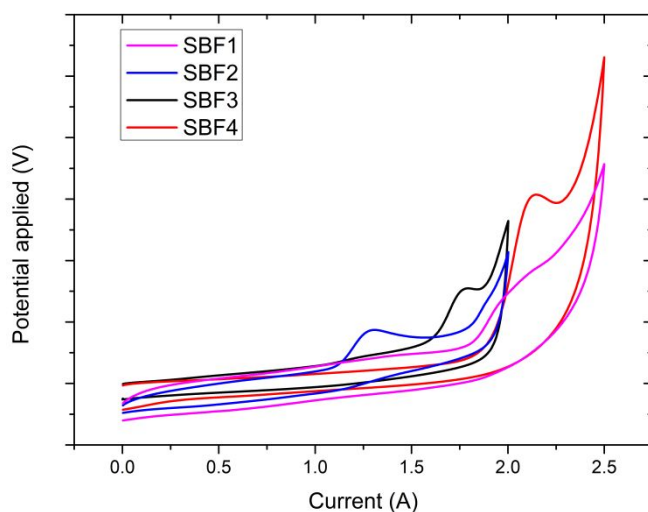


Figure S3. Cyclic voltammograms of SBF compounds: working electrode, glassy carbon; auxiliary electrode, Pt wire; reference electrode, Ag wire.

$$I_p = -e(E_{1/2(\text{ox,dye})} + 4.4) \text{ eV} \quad (1)$$

$$E_a = -e(E_{1/2(\text{red,dye})} + 4.4) \text{ eV} \quad (2)$$

$$E_g = I_p - E_a \quad (3)$$

$$E_g^{\text{opt}} = \frac{1241}{\lambda(\text{nm})} \quad (4)$$

Table S1. The crystallographic details of the SBF molecules.

Name	SBF1	SBF2	SBF3	SBF4
Empirical formula	C ₂₅ H ₁₆	C ₂₅ H ₁₄ Br ₂	C ₂₃ H ₁₄ N ₂	C ₂₃ H ₁₂ Br ₂ N ₂
Formula weight	316.41	474.20	318.38	476.17
Temperature (K)	150.00(10)	150.00(10)	150.00(10)	150.00(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	C2/c	P2 ₁ /c	C2/c
<i>Unitcell dimensions</i>				
<i>a</i> (Å)	10.1741(5)	14.4370(11)	10.1216(5)	18.6035(11)
<i>b</i> (Å)	10.2499(7)	16.6336(9)	11.5624(7)	10.0249(4)
<i>c</i> (Å)	16.7098(13)	8.0112(6)	13.8344(27)	30.4375(15)
<i>β</i> (°)	96.564(6)	96.232(8)	93.052(5)	97.044(5)
Volume (Å ³)	1731.1(2)	1912.4(2)	1616.75(14)	5633.75(5)
<i>Z</i>	4	4	4	12
<i>D</i> _{calc} (g/cm ⁻³)	1.2139	1.6468	1.3079	1.6841
Absorption coefficient (mm ⁻¹)	0.069	4.245	0.077	4.326
<i>F</i> (000)	664.3	934.2	664.3	2802.5
Crystal size (mm)	0.312×0.241×0.168	0.563×0.358×0.195	0.538×0.402×0.323	0.427×0.328×0.287
2θ range (°)	5.95-51.36	6.08-51.36	5.9-52.74	6.54-51.36
h ranges	-9→12	-17→14	-12→11	-22→22
k range	-12→8	-8→20	-12→14	-12→7
l range	-20→14	-9→7	-17→14	-37→19
Reflections collected/unique	6092/3261	3147/1804	5393/3268	9057/5296
Data / restraints / parameters	3261/0/291	1804/0/124	3268/0/282	5296/0/366
Goodness of fit on <i>F</i> ²	1.038	1.054	1.072	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0615 wR ₂ = 0.0807	R ₁ = 0.0364 wR ₂ = 0.0679	R ₁ = 0.0451 wR ₂ = 0.0906	R ₁ = 0.0450 wR ₂ = 0.0812
<i>R</i> indices (alldata)	R ₁ = 0.1611 wR ₂ = 0.1202	R ₁ = 0.0611 wR ₂ = 0.0783	R ₁ = 0.0701 wR ₂ = 0.1057	R ₁ = 0.0908 wR ₂ = 0.1010
Largest difference peak and hole (e Å ⁻³)	0.40/-0.39	0.60/-0.65	0.24/-0.27	0.59/-0.64

Table S2. Theselectedgeometricparametersobtainedfrom SCXRD fortheSBF molecules.

Parameter	Experimental SBF1	Optimized SBF1	Experimental SBF2	Optimized SBF2	Experimental SBF3	Optimized SBF3	Experimental SBF4	Optimized SBF4
<i>Bond length (Å)</i>								
C13–C14	-	-	-	-	1.519(4)	1.523(2)	-	-
C13–C25	-	-	-	-	1.517(4)	1.525(2)	-	-
C5–C13	-	-	-	-	1.525(4)	1.519(2)	-	-
C8–C13	-	-	-	-	1.525(3)	1.516(2)	-	-
C12–Br1	-	-	1.895(4)	1.918(4)	-	-	-	-
C7–C8	-	-	1.533(4)	1.531(4)	-	-	-	-
N1–C1	1.337(5)	1.338(5)	-	-	-	-	1.341(3)	1.337(2)
N1–C5	1.329(5)	1.333(4)	-	-	-	-	1.339(2)	1.332(2)
N2–C6	1.334(5)	1.330(4)	-	-	-	-	1.343(19)	1.337(2)
N2–C10	1.334(5)	1.339(4)	-	-	-	-	1.338(2)	1.332(2)
<i>Bond Angle (°)</i>								
C8–C13–C5	-	-	-	-	100.7(2)	101.40(2)	-	-
C14–C13–C25	-	-	-	-	101.4(2)	100.67(2)	-	-
C8–C13–C14	-	-	-	-	115.1(2)	114.03(2)	-	-
C5–C13–C25	-	-	-	-	114.02(16)	115.04(2)	-	-
C12–C13–Br1	-	-	118.97(4)	119.04(4)	-	-	-	-
C5–C7–C8	-	-	113.76(4)	113.71(4)	-	-	-	-
C5–N1–C1	114.6(4)	115.09(2)	-	-	-	-	114.55(17)	115.75(2)
C10–N2–C6	114.4(4)	115.14(2)	-	-	-	-	114.62(15)	115.74(2)
C2–C1–N1	124.6(4)	124.84(2)	-	-	-	-	124.9(2)	124.14(2)
N1–C5–C6	126.8(4)	126.68(4)	-	-	-	-	126.65(16)	126.91(2)
N2–C6–C5	126.6(4)	126.42(2)	-	-	-	-	126.54(15)	126.90(2)
C23–C11–C4	113.4(3)	112.82(2)	-	-	-	-	111.97(12)	113.75(2)
C23–C11–C7	113.4(3)	115.11(2)	-	-	-	-	113.45(11)	113.73(7)

Table S4. Detailed interactions geometry of the SBF molecules.

Molecule	Nonclassical Hydrogen Bond Geometry					Symmetry			
SBF1	D—H...A	D—H	H...A	D...A	D—H...A				
	<i>The nonclassical hydrogen bonds were not observed in the crystal structure of the molecule.</i>								
SBF2	<i>The nonclassical hydrogen bonds were not observed in the crystal structure of the molecule.</i>								
SBF3	C8-H8...N2	0.985(5)	2.478(5)	3.432(5)	163.1(4)	1-x,1/2+y,3/2-z			
SBF4	C22-H22...N2	0.929(5)	2.392(5)	3.317(5)	173.7(4)	1-x,1-y,1-z			
	C25-H25...Br3	0.930(6)	2.901(4)	3.648(4)	138.3(4)	x,1+y,z			
Intramolecular and intermolecular π-π stacking interactions									
Rings i-j		R_c^a	$R1^b$	$R2^c$	α^d	β^e	γ^f	d	Symmetry
SBF1	Cg3...Cg4	4.6681 (10)	-2.1172(7)	-4.2593(7)	40.75(9)	24.2	63		1-x,-1/2-y,3/2-z
	Cg2...Cg4	4.947(10)	-3.4122(7)	-4.5577(7)	62.76(9)	22.9	46.4	-	1-x,1/2-y,3/2-z
	Cg6...Cg4	4.919(11)	1.5220(7)	-4.6032(7)	64.62(9)	20.6	72.00	-	-1+x,y,z
	Cg4...Cg5	5.345 (10)	4.5887(7)	-4.5308(7)	86.33(8)	59.6	89.1	-	1-x,2-y,1-z
	Cg5...Cg5	4.669(10)	-3.2230(7)	-3.2230(7)	00.0(8)	46.3	46.3	-	-x,2-y,1-z
	Cg3...Cg3	4.704(10)	-3.1398(7)	-3.1398(7)	00.0(8)	48.1	48.1		1-x,1-y,1-z
	Cg2...Cg3	3.882(10)	-0.0317(7)	-2.2235(7)	88.94(8)	55.1	89.5		x,y,z
	Cg1...Cg6	3.919(10)	-0.1075(7)	-2.0472(7)	85.80(8)	58.5	88.4	-	x,y,z
SBF2	Cg4...Cg4	4.4939(4)	-3.2909(5)	-3.2908(6)	0.00(4)	42.0	42.9	3.0 60	1-x,1-y,1-z
	Cg2...Cg4	4.6356(4)	-3.2946(5)	-3.2946(6)	1.66(4)	46.3	44.7		1-x,1-y,1-z
	Cg3...Cg3	5.255(4)	-3.8092(5)	-3.8090(6)	0.00(4)	43.5	43.5		1-x,y,1/2-z
	Cg1...Cg4	3.9177(4)	-0.0774(5)	-2.0775(6)	89.65(4)	58	88.92		X,y,z
SBF3	Cg1...Cg3	4.3841(4)	-3.4685(4)	-3.3390(5)	2.69	40.4	37.7		1-x,1-y,1-z
	Cg3...Cg4	3.9063(4)	-3.3075(4)	-3.3602(5)	4.22	30.7	32.1		1-x,1-y,1-z
	Cg1...Cg6	3.8792(4)	-0.0512(4)	-2.2569(5)	89.38	54.5	89.2		x,y,z
	Cg2...Cg4	3.9231(4)	-000626(4)	-1.866(5)	89.33	59.6	89.1		x,y,x
SBF4	Cg1...Cg3	3.908(3)	-0.064(19)	2.022(2)	89.9(2)	58.8(2)	89.1		1-x,y,1/2-z
	Cg2...Cg4	3.907(3)	-0.901(3)	-3447(4)	82.8(4)	29.2	76.8		1-x,y,1/2-z
	Cg13...Cg14	3.959(2)	3.4366(16)	3.4366(16)	0.14(19)	29.8	29.8		1-x,1-y,1-z
	Cg16...Cg16	4.154(2)	-3.458(3)	-3.431(13)	1.3(3)	22.8	21.7		3/2-x,3/2-y,1-z
	Cg11...Cg16	3.89(2)	0.122(17)	2.0803(17)	86.0(2)	57.7	88.21		x,y,z
	Cg11...Cg15	3.892(2)	0.0952(17)	-2.0821(17)	89.4(2)	57.7	88.6		x,y,z

	Cg2...Cg4	3.907(3)	0.0549(19)	2.084(2)	89.5(2)	57.8	89.2		x,y,z
	Cg1...Cg3	3.908(3)	-0.0637(19)	2.022(2)	89.9(2)	58.8	89.1		x,y,z
C—H...π interactions									
	X—H...Cg	H...Cg	X—H...Cg	X...Cg	d	γ^f	X—H,pi		Symmetry
SBF1	C4—H4...Cg2	2.94(2)	93.1(4)	3.166(4)	2.82	16.33	13		x,y,z
	C10—H10...Cg3	2.92(3)	123.8(7)	3.564(2)	2.91	2.02	35		1-x,1/2+y,3/2-z
	C12—H12...Cg6	2.81(2)	141.1(2)	3.650(2)	2.76	10.86	50		1-x,-1/2+y,3/2-z
	C18—H18...Cg4	2.84(3)	148.1(2)	3.757(3)	-2.64	21.7	75		1-x,2-y,1-z
	C24—H24...Cg1	2.99(3)	93.2(4)	3.22(3)	2.8	20.36	16		x,y,z
SBF2	C12—Br1...Cg1	3.8186(3)	160.05(5)	5.635	3.34	29.01	79.25		3/2-x,1/2-y,1-z
	C12—Br1...Cg3	3.8355(3)	157.35(5)	5.631	-3.65	28.69	80.38		1/2+x,1/2-y,-1/2+z
SBF3	C14—H14...Cg4	2.652(17)	144.2(13)	3.4977(19)	2.61	10.31	61		x,3/2-y,-1/2+z
	C22—H22...Cg1	2.968(16)	92.1(10)	3.1608(19)	2.85	16.51	14		x,-y,z
SBF4	C9—H9...Cg15	2.662(5)	171.3(5)	3.6172(17)	2.63	8.9	79		3/2-x,1/2-y,1-z
	C33-H33...Cg13	2.712(6)	166.3(6)	3.622(6)	-2.70	4.5	80		x,1+y,z
	C21-Br2...Cg14	3.6172(17)	162.9(15)	5.463(5)	-3.461	16.9	74.9		x,1+y,z

Ring's names:

For SBF1: Cg1: C5/C6/C7/C8/C13; Cg2: C13/C14/C15/C20/C25; Cg3: C1/C6; Cg4: C7/C12; Cg5: C14/C19; Cg6: C20/C25.

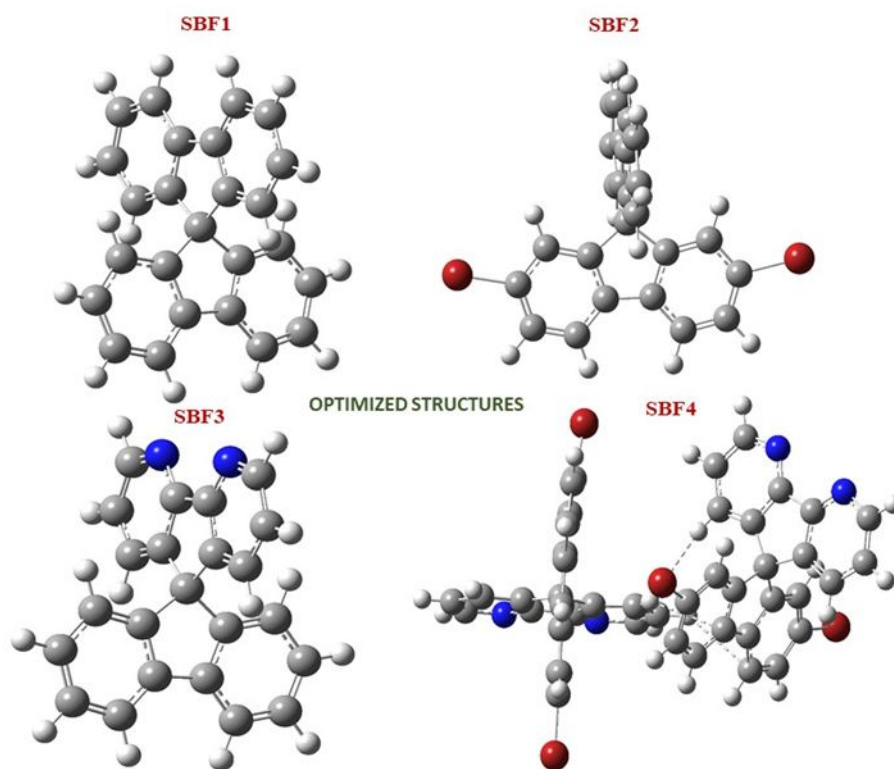
For SBF2: Cg1: C5/C6/C5a/C6a/C7; Cg2: C7/C8/C9/C8a/C9a; Cg3: C1/C6; Cg4: C8/C13

For SBF3: Cg1: C4/C5/C6/C7/C11; Cg2: C11/c12/C17/C18/C23; Cg3: N1-C1/C5; Cg4: N2-C6/C10; Cg6: C18/C23.

For SBF4: Cg1: C26/C27/C26a/C27a/C30; Cg2: C30/C31/C32/C31a/C32a; Cg3: N3-C31/C35; Cg4: C24/C29; Cg11: C4/C5/C6/C7/C11; Cg13: N1-C1/C5; Cg14: N2-C6/C10; Cg15: C12/C17; Cg16: C18/C23.

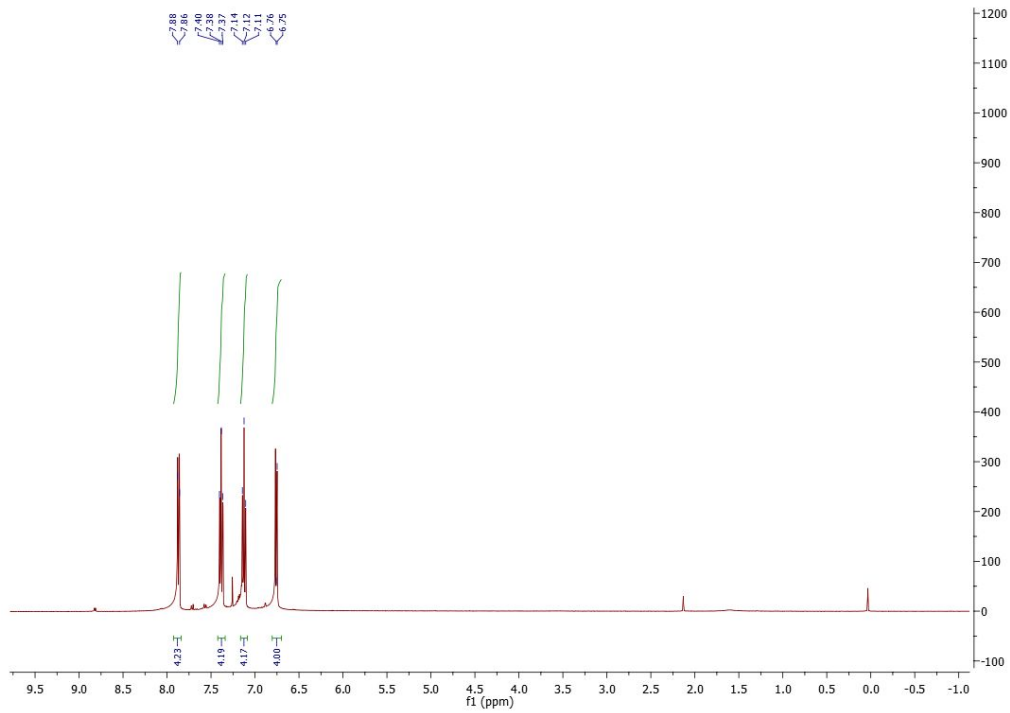
^aCentroid distance between ring i and ring j; ^bVertical distance from ring centroid i to ring j; ^cVertical distance from ring centroid j to ring i; ^dDihedral angle between the first ring mean plane and the second ring mean plane of the partner molecule;

^eAngle between centroids of first ring and second ring mean planes; ^fAngle between the centroid of the first ring

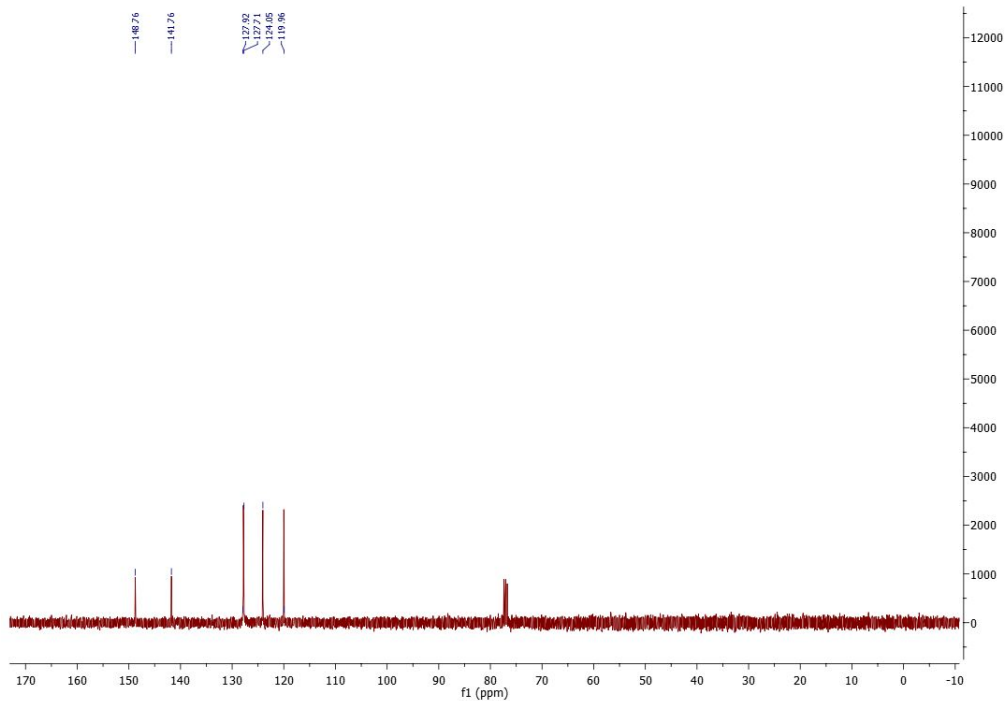


FigureS5. The most favourable optimized structure of the SBF molecules.

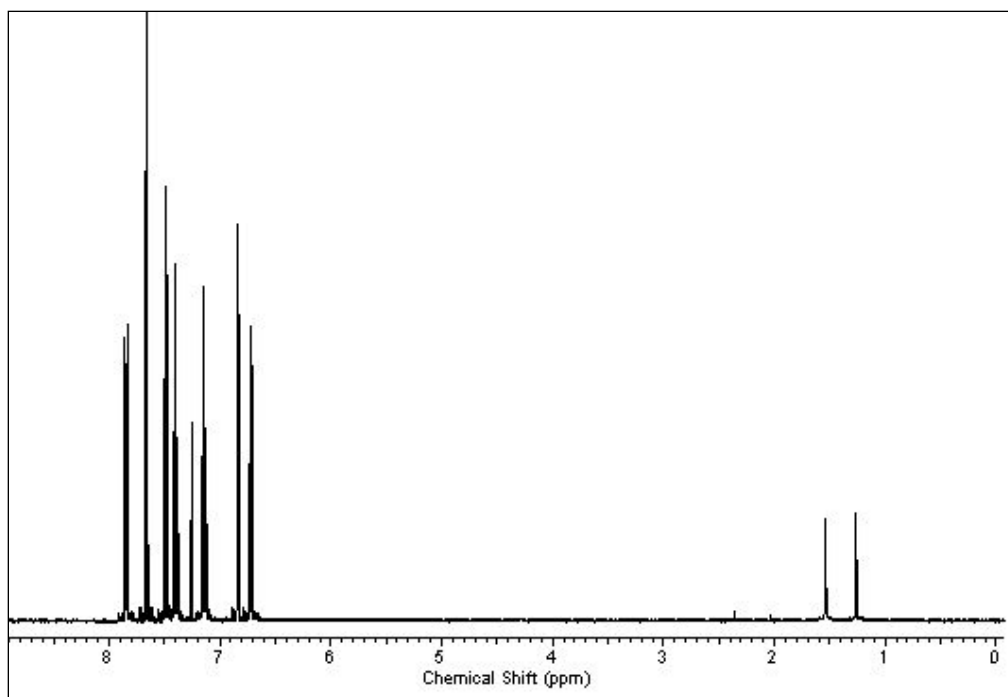
^1H and ^{13}C NMR Spectrum of SBF molecules



FigureS6: ^1H NMR spectrum of SBF-1

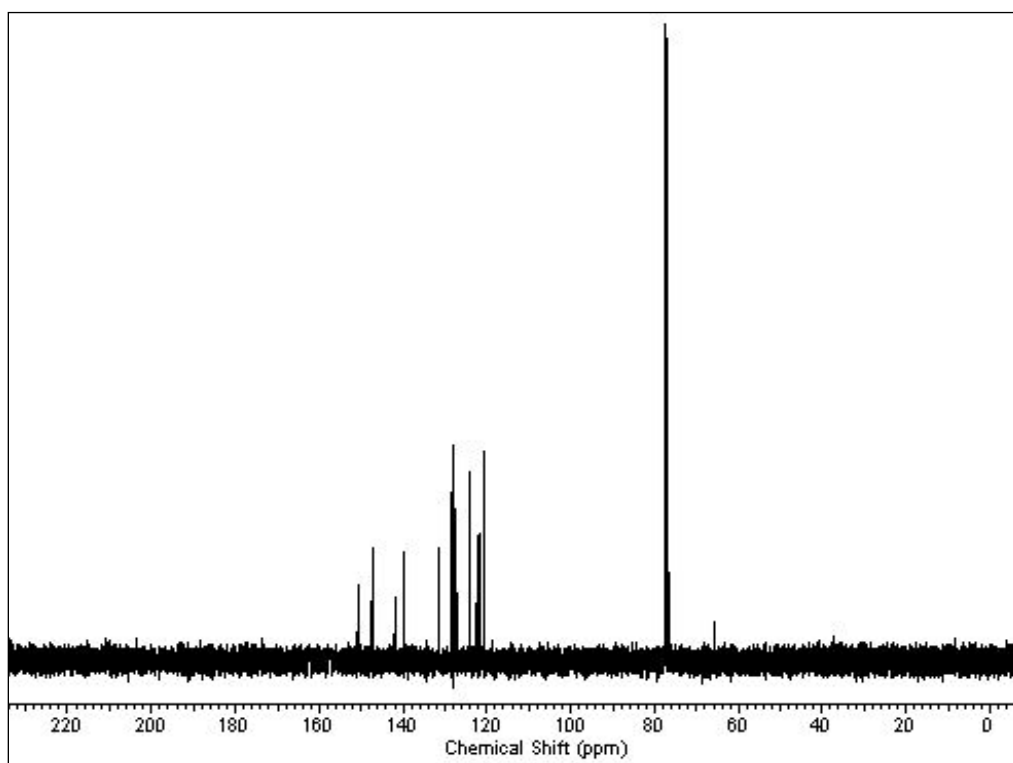


FigureS7: ^{13}C NMR spectrum of SBF-1



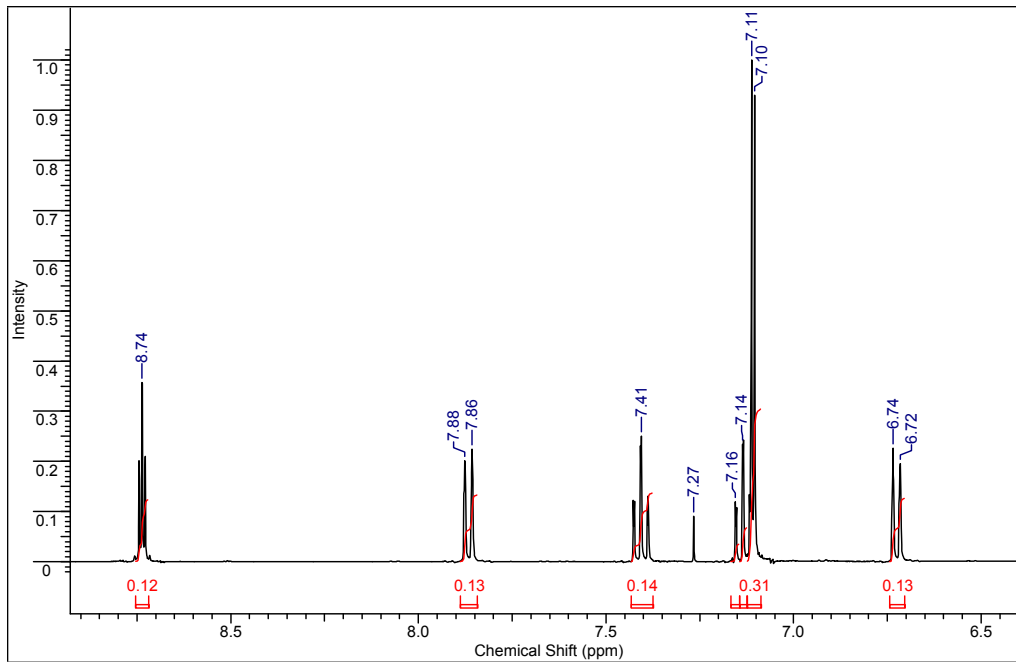
FigureS8: ¹H NMR spectrum of SBF-2

¹H NMR (400 MHz, CDCl₃): δ (TMS, ppm): 7.86-7.84 (dd), 7.66-7.65 (d), 7.50-7.47 (dd), 7.42-7.38 (dt), 7.16-7.12 (dt), 6.84-6.83 (d), 6.73-6.71 (dd).



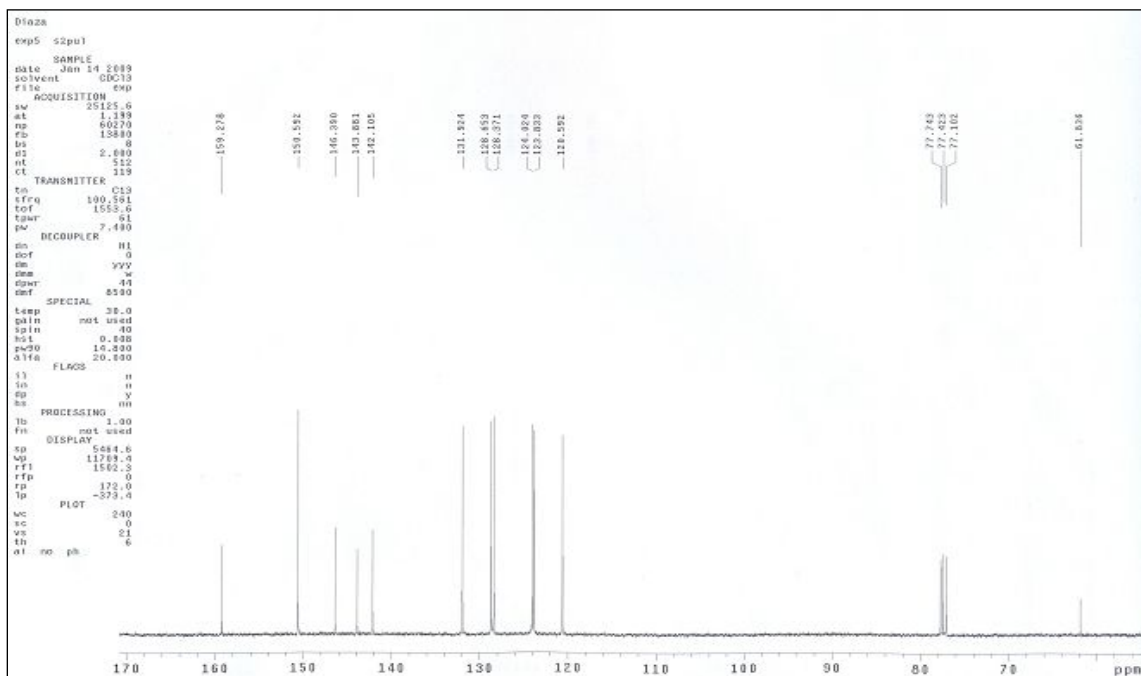
FigureS9: ¹³C NMR spectrum of SBF-2

¹³C NMR (100 MHz, CDCl₃): δ (TMS, ppm): 150.80, 147.30, 141.93, 139.87, 131.36, 128.51, 127.56, 124.27, 121.58, 120.40, 65.86 (spiro-C).

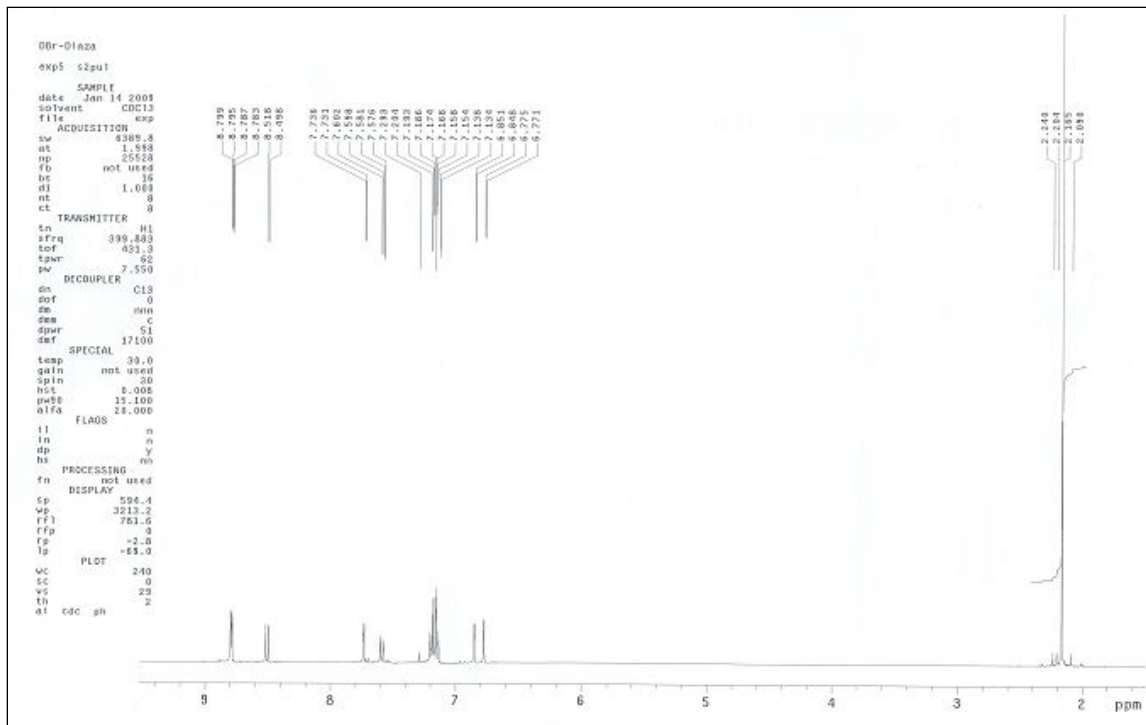
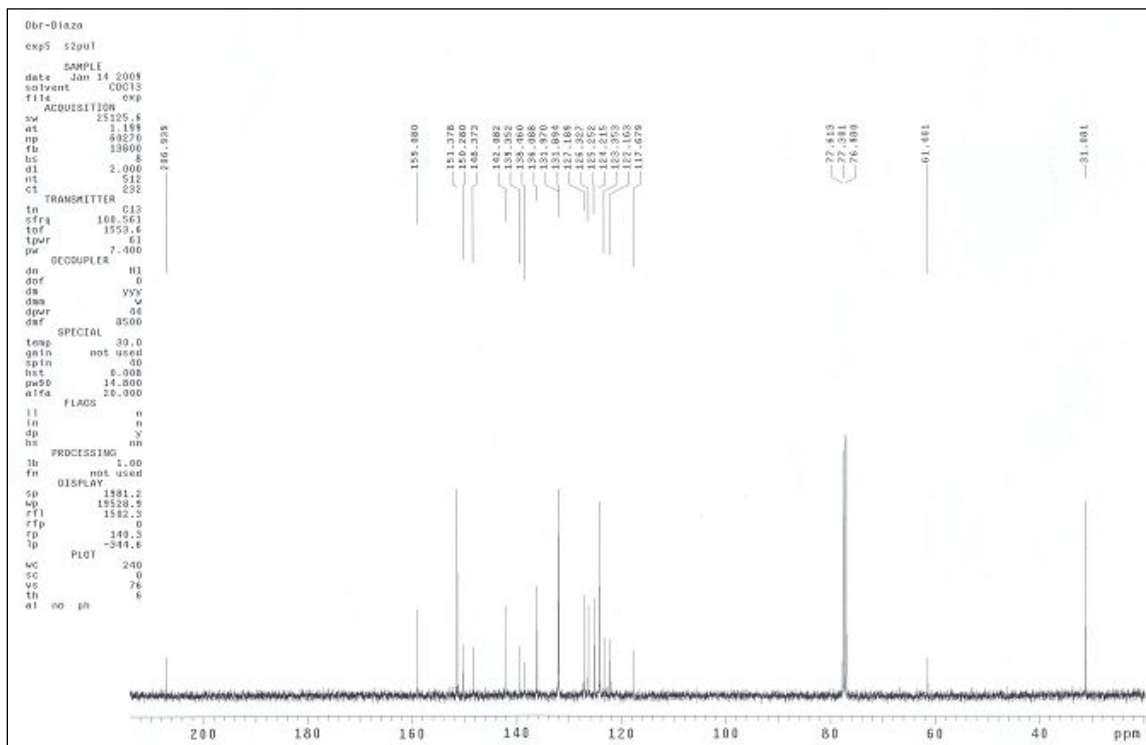


FigureS10: ^1H NMR spectrum of SBF-3

^1H NMR (400 MHz, CDCl_3): δ (TMS, ppm) 8,74 (d, aromatik), 7,88-7,86 (dt, aromatik), 7,41 (dt, aromatik), 7,16-7,14 (dt, aromatik), 7,11(dt, alifatik), 7,10 (d). 6,74, 6,72(dd, aromatik)



FigureS11: ^{13}C NMR spectrum of SBF-3

FigureS12: ^1H NMR spectrum of SBF-4FigureS13: ^{13}C NMR spectrum of SBF-4