Supporting Information

A "Strongly" Self-Catenated Metal-Organic Framework With the Highest Topological Density among (3,4)-Coordinated Nets

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Materials and Methods

All of the reagents and solvents employed were commercially available and used as received without further purification. ^{1}H NMR spectra were recorded on a Bruker AVANCE-400 NMR Spectrometer. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer. X-ray powder diffractions were measured on a Bruker AXS D8 Advance with Cu K_α (λ = 1.5418 Å, 40.0 kV, 30.0 mA) radiation. Photoluminescence spectra were measured on a Hitachi F-4500 Fluorescence Spectrophotometer (slit width: 5 nm; sensitivity: high). Thermogravimetric analysis (TGA) was carried out in a static N_2 with a heating rate of 10 °C/min.

Synthesis of ligand H₃L, compounds SDU-9
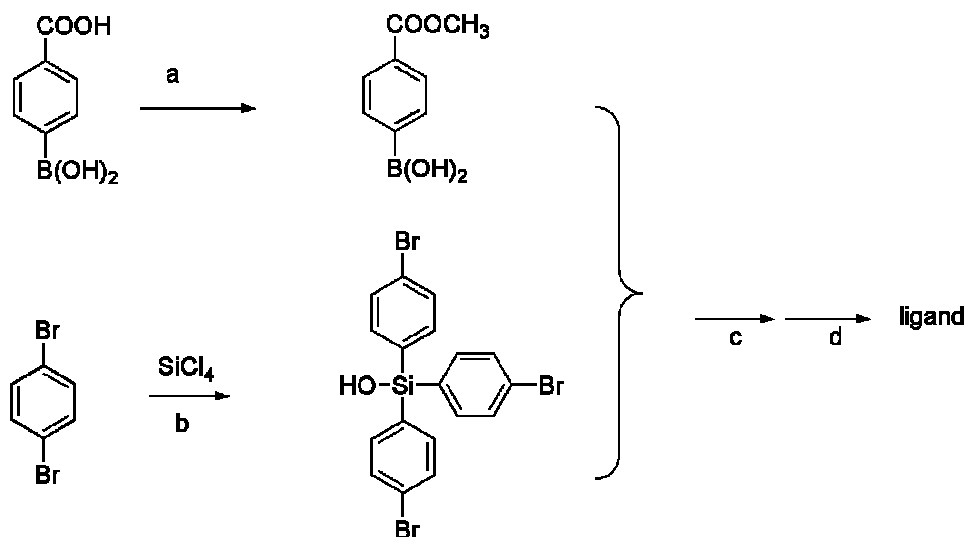
Preparation of 4-Methoxycarbonylphenylboronic

4.6 g 4-Boronobenzoic acid was dissolved in 100 mL anhydrous MeOH. 12.5 mL $SOCl_2$ was added very slowly through the flask wall under magnetic stirring. The solution was disturbed at 45-50 °C for 2 hours and then concentrated on rotary evaporator. 50 mL brine was added. The mixture was extracted with ether acetate (50 * 3). The organic phase was dried over anhydrous magnesium sulfate and dried on rotary evaporator to give white powder (4 g). ^{1}H NMR ($CDCl_3$): 3.95, 3H; 8.14, 2H; 8.27, 2H.

Preparation of hydroxytris(4-bromophenyl)silane:

A solution of n-BuLi (20 mL, 50 mmol, 2.5M in hexanes) in 100 mL Et_2O was added to a solution of 1,4-dibromobenzene (11.8 g, 50 mmol) in 100 mL Et_2O at -78 °C and stirred for 3 hours under N_2. Perchlorosilane (2.84 g, 16.7 mmol) was then added dropwise and the reaction mixture was heated at reflux for 2 h. After being quenched with 50 mL H_2O, the organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$. Removal of the solvents under a vacuum yielded a yellow oil, which was recrystallized from hot $CHCl_3$:EtOH (v:v = 1:3) to obtain white solids $HOSi(4-C_6H_4Br)_3$ (4.1 g). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.34 (t, 4H), 7.49 (dd, 4H).

Preparation of 4,4`,4``-(hydroxysilanetriyl)tris(triphenyl-4-carboxylic acid):

4-Methoxycarbonylphenylboronic (3.2 g, 18 mmol), hydroxytris(4-bromophenyl)silane (2 g, 4.13 mmol), and CsF (6 g, 39.5 mmol) were mixed in DME (50 mL), and the mixture was deaerated using N_2 for 10 min. $Pd(PPh_3)_4$ (0.3 g, 0.26 mmol) was added to the stirred reaction mixture and the mixture was heated at 90 ^{o}C for 48 h under N_2, after which DME was removed under a vacuum. The resultant solid was washed with water (30 mL) and methylene dichloride (60 mL), respectively, and then dried under a vacuum. The pale solid was filtered and dried after refluxing in MeOH for 24 h. Yield: 59%. ^{1}H-NMR (300 MHz, CDCl$_3$): δ/ppm = 0.98 (s, 1H), 3.943 (s, 3H), 7.6 (h, 6H), 8.0 (d, 2H), 8.7 (t, 1H). The ester (1.1 g, 1.7 mmol) was then suspended in a mixture of THF (20 mL) and MeOH (20 mL), to which 5 mL of 2 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and THF and MeOH were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 2. The solid was collected by filtration, washed with water and MeOH, and dried to give H$_3$**L** (0.95 g, 95.9% yield). ^{1}H-NMR (300 MHz, DMSO): δ/ppm: 7.7 (d, 2H), 7.8 (t, 1H), 7.8 (t, 2H), 8.0 (t, 1H), 13.4 (s, 1H).

Compound SDU-9

The H$_3$**L** (2.5 mg, 0.005 mmol), Cu(NO$_3$)$_2$·6H$_2$O (5 mg, 0.018 mmol) were dissolved in DMF/EtOH/H$_2$O (1/1/1, v/v/v, 1 mL). Then it was heated in a sealed tube, slowly heated to 75 °C from room temperature in 500 min, kept at 75 °C for 2000 min, and then slowly cooled to 30 °C in 600 min. The green crystalline block that formed was collected, washed with DMF, and dried in the air. Yield: *Ca*. 40 % based on Cu. Elemental analysis: Anal. Calc. for C$_{78}$H$_{80}$Cu$_3$Si$_2$O$_{29}$: C 54.21, H 4.67 %. Found: C 54.39, H 4.31 %.

X-ray Crystallography

Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source (MoKα radiation, graphite monochromated). All absorption corrections were performed with the SADABS program [S1]. All the structures were solved by direct methods using SHELXS-97 [S2] and refined by full-matrix least-squares techniques using SHELXL-97 [S3]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The crystallographic details of the crystal are summarized in Table **S1**, **S2** and **S3**. The treatment for the guest molecules in the **SDU-9** involves the use of the SQUEEZE program of PLATON [S4].

References

[S1] R.H. Blessing, Acta. Crystallogr. 1995, A51, 33.

[S2] G.M. Sheldrick, *SHELXS 97: Program for Crystal Structure Solution,* University of Göttingen: Göttingen, Germany, 1997.

[S3] G.M. Sheldrick, *SHELXL 97: Program for Crystal Structure refinement,* University of Göttingen: Göttingen, Germany, 1997.

[S4] Spek, A. *J. Appl. Crystallogr.* 2003, 36, 7-13.

Table S1. The table of self-catenation produced in the output of TOPOS

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Ring links
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Cycle 1	Cycle 2	Chain	Cross	Link	Hopf	Loop	Mult
12a	12a	5	1	1	*		4
12a	12a	4	1	1	*		19
12a	12a	4	2	0			5
12a	12a	4	3	1	*		1
12a	12a	3	1	1	*		27
12a	12a	3	2	0			8
12a	12a	3	2	2	M		2
12a	12a	3	3	1	*		3
12a	12a	2	1	1	*		21
12a	12a	2	2	0			6
12a	12a	2	3	1	*		1
12a	12a	2	4	0			3
12a	12a	1	1	1	*		16
12a	12a	1	2	0			2
12a	12a	1	3	1	*		2
12a	12b	4	1	1	*		8
12a	12b	4	2	0			1
12a	12b	3	1	1	*		14
12a	12b	3	2	0			2
12a	12b	3	3	1	*		1
12a	12b	3	4	0			1
12a	12b	2	1	1	*		6
12a	12b	2	2	0			5
12a	12b	2	4	0			1
12a	12b	1	1	1	*		3
12a	12b	1	2	0			5
12a	12b	1	3	1	*		3
12a	12c	4	1	1	*		4
12a	12c	4	2	0			3
12a	12c	3	1	1	*		10
12a	12c	3	2	2	M		1
12a	12c	3	2	0			2
12a	12c	3	3	1	*		2
12a	12c	2	1	1	*		14
12a	12c	2	2	0			4
12a	12c	2	3	1	*		1
12a	12c	2	4	0			1
12a	12c	1	1	1	*		5
12a	12c	1	2	0			3
12a	12c	1	3	1	*		1
12a	12c	1	4	0			1
12a	12d	4	1	1	*		12
12a	12d	4	2	0			2
12a	12d	4	3	1	*		1
12a	12d	3	1	1	*		11
12a	12d	3	2	0			4

12a	12d	3	3	1	*		2
12a	12d	2	1	1	*		10
12a	12d	2	2	0			5
12a	12d	2	3	1	*		2
12a	12d	1	1	1	*		6
12a	12d	1	2	0			2
12a	12d	1	4	0			1
12b	12a	4	1	1	*		12
12b	12a	4	3	1	*		2
12b	12a	4	5	1	*		2
12b	12a	4	6	0			8
12b	12a	3	1	1	*		24
12b	12a	3	2	0			4
12b	12a	3	4	0			2
12b	12a	3	5	1	*		6
12b	12a	3	6	0			2
12b	12a	2	1	1	*		12
12b	12a	2	2	0			8
12b	12a	2	4	0			2
12b	12a	2	6	0			2
12b	12a	1	1	1	*		10
12b	12a	1	2	0			6
12b	12a	1	3	1	*		2
12b	12b	5	1	1	*		2
12b	12b	5	2	2	M		1
12b	12b	4	2	2	M		1
12b	12b	3	1	1	*		14
12b	12b	3	3	1	*		2
12b	12b	3	5	1	*		4
12b	12b	3	6	0			2
12b	12b	2	1	1	*		10
12b	12b	2	2	0			2
12b	12b	2	6	0			2
12b	12b	1	2	0			2
12b	12b	1	6	0			2
12b	12c	4	1	1	*		4
12b	12c	4	6	0			2
12b	12c	3	1	1	*		6
12b	12c	3	5	1	*		2
12b	12c	3	6	0			2
12b	12c	3	7	1	*		2
12b	12c	2	1	1	*		10
12b	12c	2	2	0			6
12b	12c	1	1	1	*		4
12b	12c	1	2	0			2
12b	12c	1	6	0			2
12b	12d	5	1	1	*		2
12b	12d	4	1	1	*		8
12b	12d	4	5	1	*		2
12b	12d	3	1	1	*		10
12b	12d	3	2	0			2
12b	12d	3	3	1	*		2
12b	12d	3	4	0			2
12b	12d	3	5	1	*		2

12b	12d	3	7	1	*		2
12b	12d	2	1	1	*		8
12b	12d	2	2	0			2
12b	12d	2	5	1	*		2
12b	12d	2	6	0			2
12b	12d	1	1	1	*		6
12b	12d	1	2	0			2
12c	12a	4	1	1	*		8
12c	12a	3	1	1	*		24
12c	12a	3	2	2	M		2
12c	12a	2	1	1	*		30
12c	12a	2	2	0			4
12c	12a	1	1	1	*		12
12c	12a	1	2	0			2
12c	12b	4	1	1	*		4
12c	12b	3	1	1	*		10
12c	12b	2	1	1	*		10
12c	12b	2	2	0			6
12c	12b	1	1	1	*		4
12c	12c	5	1	1	*		2
12c	12c	5	2	2	M		1
12c	12c	3	1	1	*		10
12c	12c	3	2	0			2
12c	12c	2	1	1	*		18
12c	12c	1	1	1	*		4
12c	12d	5	1	1	*		2
12c	12d	4	1	1	*		4
12c	12d	3	1	1	*		14
12c	12d	2	1	1	*		18
12c	12d	1	1	1	*		2
12c	12d	1	2	0			2
12d	12a	4	1	1	*		24
12d	12a	4	2	0			6
12d	12a	4	3	1	*		2
12d	12a	4	4	0			2
12d	12a	3	1	1	*		24
12d	12a	3	2	0			6
12d	12a	3	3	1	*		2
12d	12a	2	1	1	*		22
12d	12a	2	2	0			8
12d	12a	2	3	1	*		2
12d	12a	1	1	1	*		12
12d	12a	1	2	0			12
12d	12b	5	1	1	*		2
12d	12b	4	1	1	*		8
12d	12b	4	3	1	*		2
12d	12b	3	1	1	*		12
12d	12b	3	2	0			6
12d	12b	3	3	1	*		4
12d	12b	2	1	1	*		10
12d	12b	2	2	0			2
12d	12b	1	1	1	*		2
12d	12b	1	2	0			2
12d	12b	1	3	1	*		4

12d	12c	5	1	1	*		2
12d	12c	4	1	1	*		2
12d	12c	4	3	1	*		2
12d	12c	3	1	1	*		10
12d	12c	3	2	0			4
12d	12c	3	3	1	*		4
12d	12c	2	1	1	*		18
12d	12c	2	2	0			2
12d	12c	1	1	1	*		2
12d	12c	1	2	0			8
12d	12d	5	1	1	*		6
12d	12d	4	1	1	*		6
12d	12d	4	2	0			4
12d	12d	4	4	0			1
12d	12d	3	1	1	*		16
12d	12d	3	2	0			2
12d	12d	3	3	1	*		2
12d	12d	2	1	1	*		10
12d	12d	2	2	0			4
12d	12d	2	3	1	*		2
12d	12d	1	1	1	*		4
12d	12d	1	2	0			4

Table S2. Crystallographic Data for SDU-9

Complexes	SDU-9
Formula	$C_{78}Cu_3O_{17}Si_2H_{50}$
M_r	1505.98
Crystal system	cubic
Space group	F432
a (Å)	33.4952 (7)
b (Å)	33.4952 (7)
c (Å)	33.4952 (7)
α (deg)	90
β (deg)	90
γ (deg)	90
Z	16
V (Å^3)	37579.2 (14)
D_c(g cm^{-3})	1.065
μ(mm^{-1})	1.47
F(000)	12304.0
no. of unique reflns	2546
no. of obsd reflns[I > 2σ(I)]	5827
Parameters	143
GOF	0.914
Final R indices [I > 2σ(I)][a,b]	$R_1 = 0.0939$, $wR_2 = 0.2770$
R indices (all data)	$R_1 = 0.1400$, $wR_2 = 0.3138$
⊗ρ (e Å^{-3})	0.56 and -0.29

Table S3. Bond Distances (Å) and Angles (°) for SDU-9.

C1—O1	1.225 (13)	C9—C8	1.3900
C1—O2	1.284 (12)	C9—H9	0.9300
C1—C2	1.508 (16)	C8—C13	1.3900
C2—C3	1.379 (17)	C8—H8	0.9300
C2—C7	1.401 (15)	C13—Si	1.914 (7)
C3—C4	1.454 (16)	Cu1—O2[i]	1.951 (6)
C3—H3	0.9300	Cu1—O2[ii]	1.951 (6)
C4—C5	1.335 (14)	Cu1—O2[iii]	1.951 (6)
C4—H4	0.9300	Cu1—O2	1.951 (6)
C5—C6	1.410 (15)	Cu1—O1W	2.289 (13)
C5—C10	1.471 (12)	Cu1—Cu2	2.615 (3)
C6—C7	1.401 (17)	Cu2—O1[iii]	1.943 (8)
C6—H6	0.9300	Cu2—O1[ii]	1.943 (8)
C7—H7	0.9300	Cu2—O1[i]	1.943 (8)
C12—C11—H11	120.0	O1[ii]—Cu2—Cu1	84.0 (2)
C11—C10—C9	120.0	O1[i]—Cu2—Cu1	84.0 (2)
C11—C10—C5	119.7 (8)	O1—Cu2—Cu1	84.0 (2)
C9—C10—C5	120.1 (8)	O2W—Cu2—Cu1	180.0
C10—C9—C8	120.0	C1—O1—Cu2	122.9 (7)
C10—C9—H9	120.0	C1—O2—Cu1	120.0 (8)
C8—C9—H9	120.0	Si—O3—H3A	109.5
C13—C8—C9	120.0	O3—Si—C13[iv]	106.4 (8)
C13—C8—H8	120.0	O3—Si—C13	106.4 (5)
C9—C8—H8	120.0	C13[iv]—Si—C13	112.4 (7)
C8—C13—C12	120.0	O3—Si—C13[v]	106.4 (9)
C8—C13—Si	120.3 (7)	C13[iv]—Si—C13[v]	112.4 (7)
C12—C13—Si	118.4 (7)	C13—Si—C13[v]	112.4 (7)

Symmetry codes: (i) −x+2, y, −z; (ii) −z+1, y, x−1; (iii) z+1, y, −x+1; (iv) −y+1, −z+1/2, x−1/2; (v) z+1/2, −x+1, −y+1/2

Table S4. Bond Distances (Å) and Angles (°) for SDU-9.

C12—C11	1.3900	Cu2—O1	1.943 (8)
C12—C13	1.3900	Cu2—O2W	2.123 (13)
C12—H12	0.9300	O3—Si	1.65 (3)
C11—C10	1.3900	O3—H3A	0.8200
C11—H11	0.9300	Si—C13^{iv}	1.914 (10)
C10—C9	1.3900	Si—C13^{v}	1.914 (14)
O1—C1—O2	127.0 (11)	O2^{i}—Cu1—O2^{ii}	89.50 (4)
O1—C1—C2	120.7 (10)	O2^{i}—Cu1—O2^{iii}	89.50 (4)
O2—C1—C2	112.0 (11)	O2^{ii}—Cu1—O2^{iii}	169.3 (4)
C3—C2—C7	117.6 (11)	O2^{i}—Cu1—O2	169.3 (4)
C3—C2—C1	120.5 (11)	O2^{ii}—Cu1—O2	89.50 (4)
C7—C2—C1	121.7 (11)	O2^{iii}—Cu1—O2	89.50 (4)
C2—C3—C4	121.9 (11)	O2^{i}—Cu1—O1W	95.4 (2)
C2—C3—H3	119.1	O2^{ii}—Cu1—O1W	95.4 (2)
C4—C3—H3	119.1	O2^{iii}—Cu1—O1W	95.4 (2)
C5—C4—C3	119.2 (12)	O2—Cu1—O1W	95.4 (2)
C5—C4—H4	120.4	O2^{i}—Cu1—Cu2	84.6 (2)
C3—C4—H4	120.4	O2^{ii}—Cu1—Cu2	84.6 (2)
C4—C5—C6	118.6 (11)	O2^{iii}—Cu1—Cu2	84.6 (2)
C4—C5—C10	119.3 (11)	O2—Cu1—Cu2	84.6 (2)
C6—C5—C10	122.0 (10)	O1W—Cu1—Cu2	180.0
C7—C6—C5	122.6 (9)	O1^{iii}—Cu2—O1^{ii}	168.0 (5)
C7—C6—H6	118.7	O1^{iii}—Cu2—O1^{i}	89.37 (5)
C5—C6—H6	118.7	O1^{ii}—Cu2—O1^{i}	89.37 (5)
C6—C7—C2	119.1 (11)	O1^{iii}—Cu2—O1	89.37 (5)
C6—C7—H7	120.5	O1^{ii}—Cu2—O1	89.37 (5)
C2—C7—H7	120.5	O1^{i}—Cu2—O1	168.0 (5)
C11—C12—C13	120.0	O1^{iii}—Cu2—O2W	96.0 (2)
C11—C12—H12	120.0	O1^{ii}—Cu2—O2W	96.0 (2)
C13—C12—H12	120.0	O1^{i}—Cu2—O2W	96.0 (2)
C10—C11—C12	120.0	O1—Cu2—O2W	96.0 (2)
C10—C11—H11	120.0	O1^{iii}—Cu2—Cu1	84.0 (2)

Symmetry codes: (i) −x+2, y, −z; (ii) −z+1, y, x−1; (iii) z+1, y, −x+1; (iv) −y+1, −z+1/2, x−1/2; (v)

z+1/2, −x+1, −y+1/2.

Fig. S1: PXRD spectrum of SDU-9

Fig. S2: IR spectrum of SDU-9

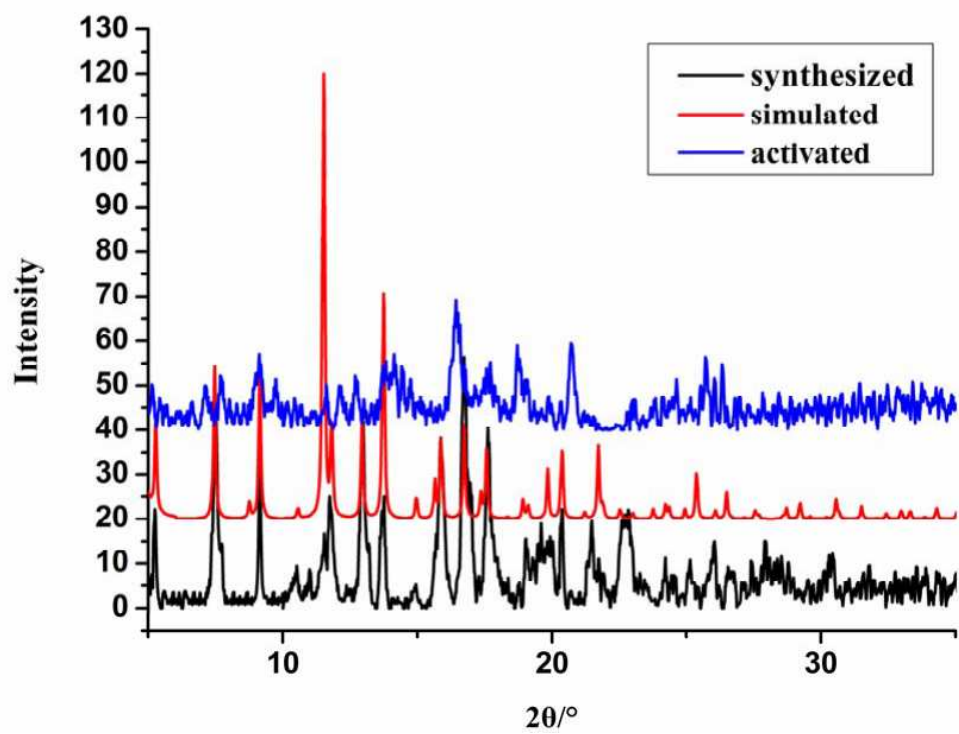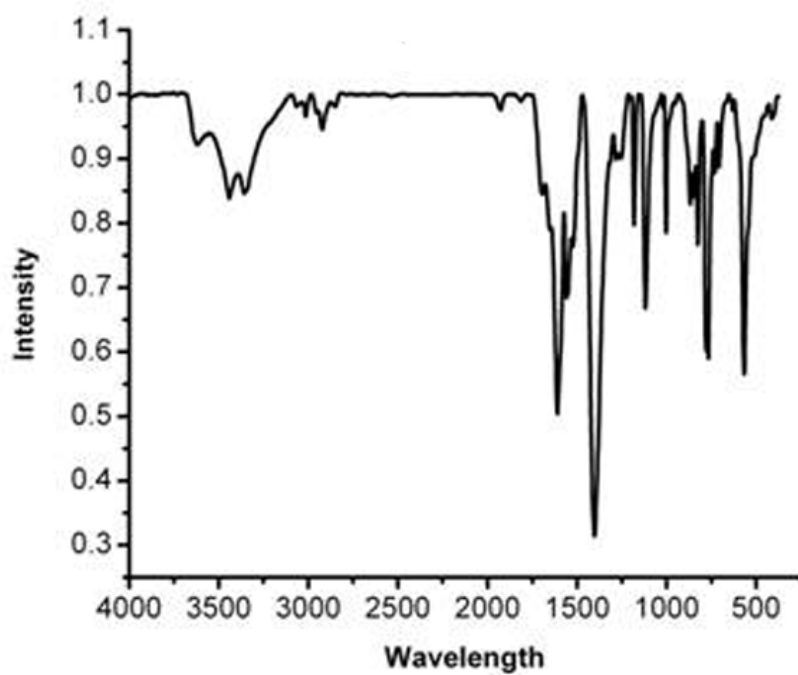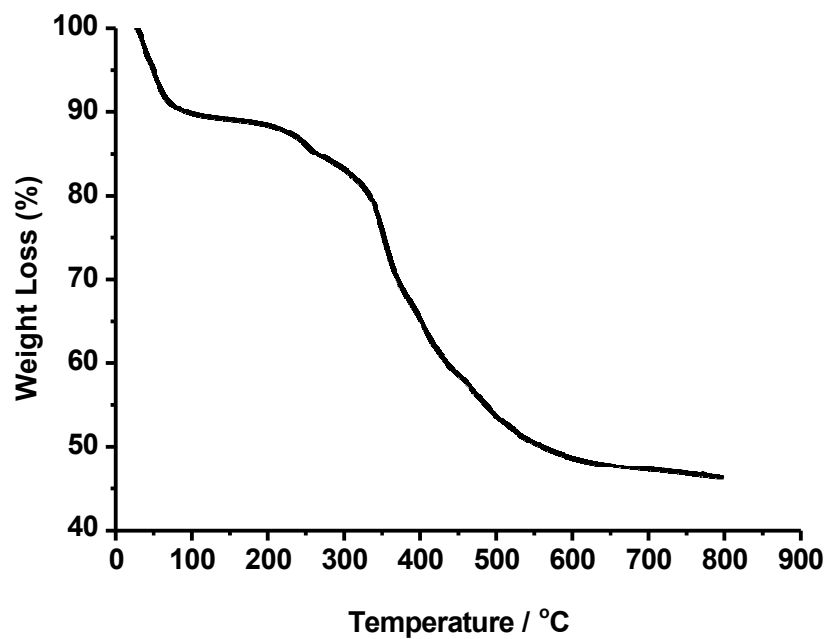**Fig. S3: TGA curve of SDU-9**

Fig. S4: Conformations of four non-equivalent 12-rings in SDU-9.