Stabilization of bicontinuous cubic phase in siloxane-terminated mesogens, 1,2-bis[4'-(*n*-(oligodimethylsiloxyl)alkoxy)benzoyl]hydrazine

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Supplementary Materials (16 pages)

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1. Materials

1.1 Preparation of 10-bromo-1-n-decene

Carbon tetrabromide (16.6 g, 50.1 mmol) and 9-*n*-decen-1-ol (9.19 mL, 50.0 mmol) were dissolved in dichloromethane (50 mL) and the solution was stirred at 0 °C, to which a dichloromethane (50 mL) solution of triphenylphosphine (13.2 g, 50.3 mmol) was added dropwise while stirring. After stirring at 0 °C for 1h, the solution was further stirred at room temperature for 1 d. After that, *N*,*N*-diisopropylethylamine (DIPEA) (2 mL) was added to neutralize the solution. After the evaporation of the solvent, *n*-hexane was added and the precipitate was removed by filtration. The filtrate was purified by column chromatography (eluent: *n*-hexane) to give a colorless liquid (10.4 g, 47.5 mmol, 95 %). ¹H NMR (392 MHz, CDCl₃) δ = 1.22 – 1.33 (m, 8H, (CH₂)₄), 1.42 (tt, *J*₁ = 14.8 Hz, *J*₂ = 9.01 Hz, 2H, CH₂CH₂CH₂Br), 1.84 (tt, *J*₁ = 13.9 Hz, *J*₂ = 7.18 Hz, 2H, CH₂CH₂Br), 2.04 (dt, *J*₁ = 14.8 Hz, *J*₂ = 7.17 Hz, 2H, H₂C=CHCH₂), 3.39 (t, *J* = 6.74 Hz, 2H, CH₂Br), 4.91 – 5.00 (m, 2H, H₂C=CHCH₂), 5.75 – 5.85 (m, 1H, H₂C=CHCH₂).

1.2 Preparation of Ethyl 4-(9'-n-decenyloxy)benzoate

Ethyl 4-hydroxybenzoate (9.49g, 57.1 mmol) and 10-Bromo-1-*n*-decene (10.4 g, 47.5 mmol) were dissolved in DMF (50 mL) at 60 °C while stirring, to which KI (9.50g, 57.2 mmol) and K₂CO₃ (12.5g, 90.4 mmol) were added and stirred for 20 h. After that, water and ethyl acetate were added and the organic layer was separated. The oily solution was washed with brine and after drying with Na₂SO₄, the solvent was removed by evaporation. The product was purified by chromatography (eluent: *n*-hexane : ethyl acetate = 4 : 1) to give a colorless liquid (9.88g, 32.5 mmol, 68 %).

¹H NMR (392 MHz, CDCl₃) δ = 1.29 – 1.38 (m, 11H, (CH₂)₄ and CH₃), 1.44 (tt, *J*₁ = 13.9 Hz, *J*₂ = 6.70 Hz, 2H, C*H*₂CH₂CH₂O), 1.77 (tt, *J*₁ = 13.5 Hz, *J*₂ = 7.07 Hz, 2H, C*H*₂CH₂O), 2.03 (dt, *J*₁ = 13.0 Hz, *J*₂ = 5.28 Hz, 2H, H₂C=CHC*H*₂), 3.97 (t, *J* = 6.50 Hz, 2H, CH₂O), 4.32 (q, *J* = 7.18 Hz, 2H, C*H*₂CH₃), 4.90 – 5.00 (m, 2H, *H*₂C=CHCH₂), 5.74 – 5.83 (m, 1H, H₂C=CHCH₂), 6.87 (d, *J* = 8.97 Hz, 2H, Ar-H), 7.97 (d, *J* = 8.97 Hz, 2H, Ar-H).

1.3 Preparation of 4-(9'-n-Decenyloxy)benzoic acid

To ethyl 4-(9'-*n*-decenyloxy)benzoate (9.88 g, 32.5 mmol) in methanol (60 mL) was added an aqueous solution (50 mL) of NaOH (1.66 g, 41.6 mmol) and refluxed at 100 °C for 9 h. Afterward, the solution was acidified with HCl (6 mL) in an ice bath. The organic layer was separated to ethyl acetate, washed with brine, dried with Na₂SO₄. After evaporating the solvent, the product was obtained as a while solid (7.72 g, 27.9 mmol, 86 %). ¹H NMR (392 MHz, CDCl₃) δ = 1.31 – 1.39 (m, 8H, (CH₂)4), 1.45 (tt, *J*₁ = 13.5

Hz, $J_2 = 7.18$ Hz, 2H, $CH_2CH_2CH_2O$), 1.79 (tt, $J_1 = 13.9$ Hz, $J_2 = 7.06$ Hz, 2H, CH_2CH_2O), 2.04 (dt, $J_1 = 14.4$ Hz, $J_2 = 7.04$ Hz, 2H, $H_2C=CHCH_2$), 4.01 (t, J = 6.50 Hz, 2H, CH_2O), 4.91 – 5.01 (m, 2H, $H_2C=CHCH_2$), 5.75 – 5.84 (m, 1H, $H_2C=CHCH_2$), 6.92 (d, J = 8.97Hz, 2H, Ar-H), 8.04 (d, J = 8.97 Hz, 2H, Ar-H).

1.4 Synthesis of bis-C8C=C

Under a nitrogen atmosphere, 4-(9'-n-decenyloxy)benzoic acid (7.7 g, 28 mmol) was dissolved in 40 mL of distilled chloroform containing a catalytic amount of distilled DMF and thionyl chloride (4.1 mL, 56 mmol). The mixture was stirred at 60 °C for 1 h. After that, the remaining thionyl chloride was removed under a reduced pressure to give the acid chloride. Under a nitrogen atmosphere, hydrazine monohydrate (0.68 mL, 14 mmol) and DIPEA (7.2 mL, 42 mmol) were dissolved in a distilled THF (30 mL) while stirring in an ice bath, to which the above acid chloride was added dropwise. After stirring for 1 h, water and chloroform were added and the aqueous layer was separated. The organic layer was washed with brine and after drying with Na₂SO₄, the solvent was removed by evaporation. The product (**bis-C8C=C**) was recrystallized from methanol, purified by chromatography (eluent: chloroform) to give a white solid (4.45g, 9.22 mmol, 66 %). ¹H NMR (392 MHz, CDCl₃) $\delta = 1.32 - 1.40$ (m, 16H, (CH₂)₄), 1.45 (tt, $J_1 = 13.5$ Hz, $J_2 = 13.5$ Hz, 6.74 Hz, 4H, CH₂CH₂CH₂O), 1.79 (tt, J₁ = 13.5 Hz, J₂ = 6.96 Hz, 4H, CH₂CH₂O), 2.04 $(dt, J_1 = 13.9 \text{ Hz}, J_2 = 7.04 \text{ Hz}, 4\text{H}, \text{H}_2\text{C}=\text{CHC}H_2), 3.99 (t, J = 6.52 \text{ Hz}, 4\text{H}, \text{CH}_2\text{O}), 4.91$ -5.01 (m, 4H, H₂C=CHCH₂), 5.77 - 5.84 (m, 2H, H₂C=CHCH₂), 6.92 (d, J = 8.54 Hz, 4H, Ar-H), 7.81 (d, *J* = 8.54 Hz, 4H, Ar-H), 9.19 (s, 2H, NH).

1.5 Synthesis of bis-C10Si2

Under a nitrogen atmosphere, 1,2-bis(4'-(*n*-dec-9''-en-1''-yloxy)benzoyl)hydrazine (**bis-C8C=C**) (0.55 g, 1.0 mmol) was dissolved in 10 mL of dry toluene while heating at 60 °C. Pentamethyldisiloxane (0.45 mL, 2.3 mmol) and then one drop of Karstedt's-catalyst (dry toluene solution) was added. The mixture was stirred at 60 °C for 6 h. After evaporating the solvent the crude product was purified by chromatography (eluent: hexane : ethylacetate = 5 : 1) to give a white solid (0.56 g, 0.66 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ = 0.022 (s, 12H, Si(CH₃)₂), 0.048 (s, 18H, Si(CH₃)₃), 0.490 (t, *J* = 7.41 Hz, 4H, SiCH₂), 1.28 – 1.34 (m, 24H, (CH₂)₆), 1.45 (tt, *J*₁ = 13.9 Hz, *J*₂ = 7.19 Hz, 4H, CH₂CH₂CD), 1.78 (tt, *J*₁ = 13.4 Hz, *J*₂ = 6.94 Hz, 4H, CH₂CH₂O), 3.97 (t, *J* = 6.47 Hz, 4H, CH₂O), 6.89 (d, *J* = 9.02 Hz, 2H, Ar-H), 7.80 (d, *J* = 9.02 Hz, 2H, Ar-H), 9.38 (s, 2H, NH); Elemental calcd for C₄₄H₈₀N₂O₆Si₄ (%): C, 62.51; H, 9.54; N, 3.31. Found; C, 62.42; H, 9.64; N, 3.31.

1.6 Synthesis of C10Si2-C8C=C

Under a nitrogen atmosphere, 1,2-bis(4'-(*n*-dec-9"-en-1"-yloxy)benzoyl)hydrazine (**bis-C8C=C**) (0.55 g, 1.0 mmol) was dissolved in 15 mL of dry toluene while heating at 60 °C. Pentamethyldisiloxane (0.18 mL, 0.9 mmol) and then one drop of Karstedt's-catalyst (dry toluene solution) was added. The mixture was stirred at 60 °C for 5.5 h. After evaporating the solvent the crude product was purified by chromatography (eluent: chloroform : ethyl acetate = 40 : 1) to give a white solid (0.18 g, 0.25 mmol, 28%). ¹H NMR (392 MHz, CDCl₃) δ = 0.021 (s, 6H, Si(CH₃)₂), 0.046 (s, 9H, Si(CH₃)₃), 0.489 (t, *J* = 7.39 Hz, 2H, SiCH₂), 1.27 – 1.39 (m, 24H, (CH₂)₆), 1.45 (tt, *J*₁ = 14.8 Hz, *J*₂ = 6.74 Hz, 4H, CH₂CH₂CH₂O), 1.79 (tt, *J*₁ = 13.9 Hz, *J*₂ = 6.74 Hz, 4H, CH₂CH₂O), 2.03 (dt, *J*₁ = 14.3 Hz, *J*₂ = 7.03 Hz, 2H, H₂C=CHCH₂), 3.99 (t, *J* = 6.72 Hz, 4H, CH₂O), 4.91 – 5.01 (m, 2H, *H*₂C=CHCH₂), 5.77 – 5.84 (m, 1H, H₂C=CHCH₂), 6.92 (d, *J* = 8.95 Hz, 4H, Ar-H), 7.81 (d, *J* = 8.52 Hz, 4H, Ar-H), 9.24 (s, 2H, NH); Elemental calcd for C₃₉H₆₄N₂O₅Si₂ (%): C, 67.19; H, 9.25; N, 4.02. Found; C, 67.20; H, 8.95; N, 4.11.

1.7 Synthesis of bis-C10Si3

Under a nitrogen atmosphere, 1,9-decadiene (1.1 mL, 6.0 mmol) was added to hexachloroplatinic(IV) acid hexahydrate (0.51 g, 0.98 mmol) dissolved in ethanol (4 mL) and stirred at room temperature, to which NaHCO₃ (0.68 g, 8.1 mmol) was added slowly while stirring. After the bubbling ceased, the solution temperature was raised to 60 °C and further stirred for 4 h. From the obtained dark red solution the precipitate was removed by filtration. After that, the solution was concentrated by evaporation, to which distilled toluene was added and the precipitate was removed again. This procedure was repeated 6 times to completely remove remaining unreacted NaHCO₃ and by-produced NaCl. The obtained product (0.34 g, 1.0 mmol) was further diluted with distilled toluene to make a 0.1 M catalyst solution of platinum-1,9-decadiene complex used in the next step [S1].

Under a nitrogen atmosphere, 1,2-bis(4'-(*n*-dec-9''-en-1''-yloxy)benzoyl)hydrazine (**bis-C8C=C**) (0.55 g, 1.0 mmol) was dissolved in 10 mL of dry toluene while the temperature was maintained at 65 °C. 1,1,1,3,3,5,5-heptamethyltrisiloxane (0.60 mL, 2.2 mmol) and the platinum-1,9-decadiene catalyst (0.01 mmol) in dry toluene solution (0.1 M, 0.1 mL) was added. The mixture was stirred at 65 °C for 1.5 h. After evaporating the solvent the crude product was purified by chromatography (eluent: hexane : ethyl acetate = 3 : 1) to give a white solid (0.57 g, 0.57 mmol, 57%). The product was further purified using acetonitrile and activated carbon. ¹H NMR (392 MHz, CDCl₃) δ = 0.007 (s, 12H,

Si(CH₃)₂-CH₂), 0.047 (s, 12H, (CH₃)₃Si O Si(CH₃)₂), 0.080 (s, 18H, (CH₃)₃Si), 0.517 (t, J = 7.62 Hz, 4H, SiCH₂), 1.29 – 1.40 (m, 24H, (CH₂)₆), 1.45 (tt, $J_1 = 13.9$ Hz, $J_2 = 7.18$ Hz, 4H, CH₂CH₂CH₂O), 1.79 (tt, $J_1 = 13.5$ Hz, $J_2 = 7.07$ Hz, 4H, CH₂CH₂O), 3.98 (t, J = 6.50 Hz, 4H, CH₂O), 6.91 (d, J = 9.01 Hz, 4H, Ar-H), 7.80 (d, J = 8.54 Hz, 4H, Ar-H), 9.28 (s, 2H, NH); Elemental calcd for C₄₈H₉₂N₂O₈Si₆ (%): C, 58.01; H, 9.33; N, 2.82. Found; C, 57.90; H, 9.41; N, 2.84.

2. Solubility Data

		Solvents				
Compounds	Temperature/°C	hexane	chloroform	tetrahydrofuran	ethyl acetate	acetone
		(0)	(1.04)	(1.75)	(1.78)	(2.88)
Bis-C18	25	0	0	0	0	0
	~45		1 mg/mL	3 mg/mL		
Bis-C10Si2	25	7 mg/mL	>>15 mg/mL	>>15 mg/mL	14 mg/mL	7 mg/mL

Table S1. Solubility data of the compounds

The values in parentheses below the solvent name show the dipole moment value (in Debye), cited from [S2].

3. Textures by Optical Microscopy

Polarized optical microscopy experiments were carried out on a Olympus BX53P equipped with a heating stage (Mettler FP82HT) and controller (Mettler FP90).

3.1 bis-C10Si2



Fig. S1. Textures of **bis-C10Si2** on heating after being annealed at 296 K for 2 weeks: (a) 299 K (Cr), (b) 373 K (Cub_{bi}), (c) 428 K (Col_{hd}), and (d) 453 K (Iso).



Fig. S2. Textures of **bis-C10Si2** on cooling from the isotropic melt: (a) 427 K (Col_{hd}), (b) 373 K (Cub_{bi}), and (c) 310 K (Cub_{bi}).



Fig. S3. Textures of **bis-C10Si2** on the subsequent heating immediately after cooling to room temperature: (a) 334 K (Cub_{bi}), (b) 373 K (Cub_{bi}), and (c) 427 K (Col_{hd}).

3.2 C10Si2-C8C=C



Fig. S4. Textures of **C10Si2-C8C=C** at (a) 397 K (Cub_{bi}) and (b) 417 K (Cub_{bi}) on heating; at (c) 377 K (Cub_{bi}) and (d) at 336 K (Cr) on cooling from the isotropic melt; (e) at 336 K on the subsequent heating after cooling to room temperature

3.3 bis-C10Si3



Fig. S5. Textures of **bis-C10Si3** (a) immediately after taking out from refrigerator (253 K) (Cub_{bi}) ; (b) at 295 K (Colob d), (c) at 354 K (Colhd), and (d) at 444 K (Iso) on heating; (e) at 394 K (Colhd) and (f) at 323 K (Colob d) on cooling.

4. DSC Traces and Transition Enthalpies

Differential scanning calorimetry (DSC) measurement was carried out using DSC7020 manufactured by SII Nanotechnologies Inc. and calibrated with indium, zinc, tin, and lead standards. The DSC sample room was purged with dry nitrogen gas during the measurement at the flow rate of 40 mL min⁻¹. The scanning rate was in most cases 5 K min⁻¹, and the temperature was kept for 5 min at their lowest and highest temperatures. For the cooling of samples a quench cooler accessory was used. In case of **bis-C10Si2** and **bis-C10Si3**, the samples were first cooled from room temperature to 150 K and 170 K, respectively, before the first heating (1H) scans. In those cases, the cooling scan separately made showed no thermal anomaly except the glass transition. Transition temperatures were determined from the DSC peak temperatures, and glass transition temperatures (T_g) were determined as a midpoint temperature of the DSC baseline shift.

4.1. bis-C10Si2

Table S2. DSC parameters for **bis-C10Si2**; transition temperatures (in K) and enthalpy changes (in kJ mol⁻¹ in parentheses)

run	g	Cr	la3d	Cul	b _{bi} (a)	Col _{hd}	lso
1H		\bullet	324.2 (49.1)	422.6 (2.0)			432.2 (9.8) 🌑
1C		173.5			415.7 (-1.	7) 🔴	430.9 (-9.2)
2H		187.9			423.2 (2.	2) 🌑	432.1 (10.4) 🔴
2C		173.5			415.2 (-1.	5) 🌑	430.9 (-8.8)
ЗH		188.6		•	423.3 (2.	2) 🌑	432.0 (10.0)

(a) Coexistence of Im3m and Ia3d phases.



Fig. S6. DSC thermograms of C10Si2-C8C=C (5 K min⁻¹).

Table S3. DSC parameters for **C10Si2-C8C=C**; transition temperatures (in K) and enthalpy changes (in kJ mol⁻¹ in parentheses)

run	Cr	lm3m	Cub _{bi} ^(a)	Liq
1H	\bullet	377.3 (37.4) 🌑 411	.6 (0.5) • 428.9 (9.6)	
1C	\bullet	362.7 (-36.4) • ~40	0 ^(b) 425.4(-8.7)	\bullet
2H	\bullet	377.7 (37.4) 🌑 415	.9 (0.5) • 429.2 (9.1)	
2C	\bullet	361.9 (-36.2) • ~40	0 ^(b) 425.6 (-9.4) 🌑
3H	\bullet	377.6 (37.4) 🌑 416	.2 (0.6) • 429.0 (8.7)	

(a) Coexistence of *Im3m* and *Ia3d* phases. (b) determined by XRD.



Fig. S7. DSC thermograms of bis-C10Si3 (5 K min⁻¹).

Table S4. DSC parameters for **bis-C10Si3**; transition temperatures (in K) and enthalpy changes (in kJ mol⁻¹ in parentheses)

run g	lm3m	Col _{obd}	Col _{hd}	lso
1C 🌑				
1H 🌑 176	294.6 (0.95) • ~340 ^(a)	431.0 (10.3)	\bullet
2C 🌑	279.5 (-1.58)	B) ● ~390 ^(a)	430.6 (-11.5) 🌒
2H 🌑 176	289.4 (1.43) • ~340 ^(a)	431.7 (11.3)	\bullet
3C 🔴	279.5 (-1.94	4) • ~390 ^(a)	430.5 (-11.1) 🌒
3H 🌑 176	289.8 (1.35) • ~340 ^(a)	431.5 (11.1)	\bullet

(a) determined by XRD.

5. XRD Data

Table S5. Experimental and calculated 2θ for the Col_{obd} phase of the **bis-C10Si3** 315.9 K.

(<i>hk</i>)	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °			
(01)	1.26	1.25			
(10)	2.37	2.37			
(02)	2.49	2.49			
(-11)	2.69	2.73			
(13)	4.32	4.31			
(04)	4.98	4.99			
$a = 3.74$ nm, $b = 7.10$ nm, $\gamma = 86.9$ °					

at

Table S6. Experimental and calculated 2θ for the Colhd phase of the **bis-C10Si3** at 432.3 K.

(<i>hk</i>)	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °			
(10)	2.553	2.553			
(11)	4.423	4.422			
(20)	5.109	5.107			
<i>a</i> =3.996 nm					



Fig. S8. Schematic illustration for molecular aggregations in (a) Col_{obd} and (b) Col_{hd} phases of the **bis-C10Si3**.

6. Electron Density Map Construction

The small-angle X-ray diffraction (XRD) measurements were made using a Rigaku NANO-Viewer Imaging Plate (IP) system. The CuK α radiation (wavelength $\lambda = 0.154$ nm) was focused with a Conforcal Max-Flux mirror and collimated into the sample position in a home-made heated cell using a three-slit system. The powder sample was inserted into a drilled hole in a brass plate, sealed with Kapton windows at both sides, which was placed in the above heated cell, and the temperature was controlled within ±0.1 K by a Rigaku Thermo Plus 2 system. The diffracted X-rays were recorded on an IP camera with an effective area of 11.5 x 11.5 cm² (2300 x 2300 pixel²). The distance between the sample and the IP was 45 cm. After the absence of preferred orientation was ascertained, the intensities were radially integrated and averaged, and redistributed when converting the pixel number into the corresponding diffraction angle 2θ to produce a circularly averaged pattern. The 2θ values (or the reciprocal spacings) of the pattern were calibrated using standard materials (α -stearic acid and silver behenate at 298 K). All the detected peaks were reasonably approximated to a Gaussian line shape and so that the peak area intensities and their errors were estimated through curve fitting using the graph software Sma4Win ver. 1.54 (produced and distributed by T. Suzuki). The Lorentz correction on them yielded the final intensities. The experimental magnitude of structure factors ($|F_{obs}|$) and errors ($\sigma(F_{obs})$) thus estimated are tabulated together with the estimated ones (F_{calc}) via maximum entropy method (MEM) analyses described below in Table S5.

The reconstruction of electron density maps for the *Ia3d* phases was performed using the structure factors $|F_{obs}|$. The symmetry *Ia3d* brings the situation where the sign of one half of the structure factors belonging to general $\{hkl\}$ is opposite to that of the other half. Moreover, the Landau theory of freezing for the *Ia3d* phase formation [S3] requires the same signs of the structure factors for the two strongest reflections (+2,+1,+1) and (+2,+2,0). In our MEM analyses, the signs were assumed to be both –, while those of the others are automatically determined by the symmetry. The signs of the structure factors other than $\{2,1,1\}$ and $\{2,2,0\}$ were estimated during the optimization process between F_{obs} 's and F_{calc} 's on the basis of the MEM analyses. The analyses were performed using a laboratory-made code and the space of the unit cell was divided into 128×128×128 pixels. The detailed procedure was already published [S4,S5]. The electron density distribution in a molecule for the bis-C10Si2 was calculated quantum-mechanically on the basis of the density functional theory at the B3LYP/3-21G level using a Gaussian package [S6]. The obtained result is shown in Figure S8. This offers a clue to obtaining deeper insights from the reconstructed electron density and considering the positions of core parts in the unit cell.

Table S7. Experimental and calculated *F* and $\sigma(F)$ values for the *Ia3d*-Cub_{bi} phase of **bis**-**C10Si2** (a) at 298 K after annealed at room temperature for several days and (b) at 374 K on heating. "-" indicates nonobserved reflections within the experimental 2θ ranges. The (211) in the first column stands for (+2, +1, +1), for example. *F*(*hkl*) with other combinations of signs (to *h*, *k*, and *l*) may have an opposite sign.

•

(11)		298 K			374 K	
(hkl)		a = 9.26 m	m	a	l = 8.61 nm	n
	$ F_{\rm obs} $	F_{calc}	$\sigma(F_{\rm obs})$	$ F_{obs} $	F_{calc}	$\sigma(F_{obs})$
(211)	1.000	-1.000	0.005	1.000	-1.000	0.004
(220)	0.492	-0.492	0.003	0.476	-0.476	0.003
(321)	0.053	-0.054	0.004	0.019	-0.030	0.006
(400)	0.205	-0.160	0.008	0.176	-0.166	0.004
(420)	0.144	0.143	0.003	0.158	0.157	0.003
(332)	0.197	-0.197	0.003	0.212	-0.212	0.002
(422)	0.235	-0.234	0.003	0.190	-0.189	0.001
(431)	0.135	-0.135	0.002	0.101	-0.101	0.002
(521)	-	-	-	0.026	0.024	0.006
(440)	-	-	-	-	-	-
(620)	-	-	-	0.016	0.016	0.004
(541)	0.034	-0.033	0.005	0.024	-0.020	0.008



Fig. S9. Electron density of **bis-C10Si2**. (Top) Molecular structure optimized and (bottom) electron density map integrated within a plane normal to the molecular long axis (sold curve) and its step approximation (red dashed curve), both of which were obtained from the quantum chemical (DFT) calculation by Gaussian09 at B3LYP/6-31G* level.



Fig. S10. Electron density reconstructed by MEM analyses [green (low) to red (high)] for the *Ia*3*d*-Cub_{bi} phase of **bis-C10Si2** at (a) 298 K and (b) 374 K. The region with a smaller density than the average is shown transparent.



Fig. S11. Electron density recovered by MEM analyses along the body diagonal of the unit cell of the *Ia3d*-Cub_{bi} phase for the **bis-C10Si2** at 298 K (black) and 374 K (red). They are normalized to 0.5 for maximum value and 0 for average.

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