# **Supporting Information for**

# Molecular Design of Anti-spindle-like Molecules by Use of Siloxanyl

# Terminals for Thermotropic Bicontinuous Cubic Phase

Akane Kawafuchi,<sup>a</sup> Shoichi Kutsumizu,<sup>b,\*</sup> Yuki Kawase,<sup>c</sup> Issei Tokiwa,<sup>a</sup> Taro Udagawa,<sup>b</sup>

and Yohei Miwa<sup>b</sup>

<sup>*a</sup></sup><i>Applied Chemistry Division, Graduate School of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan.*</sup>

<sup>b</sup>Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan.

<sup>c</sup>Materials Chemistry Course, Department of Materials Science and Processing, Graduate School of Natural Science and Technology, Gifu University, Yanagido, Gifu 501-1193, Japan.



**Figure S1.** DSC thermograms of (a) **Bis-B6Si2**, (b) **Bis-B8Si2**, (c) **Bis-B11Si2**, (d) **Bis-B10** <sup>*i*</sup>**Si3**, (e) **Bis-N10Si2**, (f) **Bis-N10Si3**, and (g) **Bis-N11Si3** on 1<sup>st</sup> and 2<sup>nd</sup> heating (1H and 2H, red curves) and on 1<sup>st</sup> and 2<sup>nd</sup> cooling (1C and 2C, blue curves) at a rate of 5 K min<sup>-1</sup>. The DSC scan started after room-temperature aging for the indicated days for the compounds not showing enantiotropic behavior.

# 2. POM data

## (a) Bis-B6Si2



**Figure S2.** Textures of **Bis-B6Si2** (a) at 315 K (Cr), (b) at 354 K ( $Col_r1$ ), (c) at 373 K ( $Col_r1$ ), (d) at 403 K ( $Col_h$ ), and (e) at 423 K (Iso) on heating after cooling from the isotropic melt and storing at 296 K for 2 d; (f) at 413 K ( $Col_h$ ), (g) at 358 K ( $Col_r1$ ), and (h) at 313 K ( $Col_r2$ ) on the subsequent cooling.

### (b) Bis-B8Si2



**Figure S3.** Textures of **Bis-C8Si2** (a) at 349 K (M) and (b) at 406 K  $(Col_h)$  on 1<sup>st</sup> heating; (c) at 421 K  $(Col_h)$ , (d) at 364 K (Ia3d (major)+M), (e) at 348 K (M), and (f) at 318 K (M) on the subsequent cooling: in the M phase temperature region, we could not observe the presence of two domains of different brightness under uncrossed polarizers.

## (c) Bis-B11Si2



**Figure S4.** Textures of **Bis-B11Si2** (a) at 385 K (*Ia3d*) and (b) at 428 K (Col<sub>h</sub>) on  $2^{nd}$  heating; (c) at 373 K (*Ia3d*) and (d) at 426 K (Col<sub>h</sub>) on the subsequent cooling.

## (d) Bis-B10<sup>*i*</sup>Si3



**Figure S5.** Textures of **Bis-C10** <sup>*i*</sup>**Si3** (a) at 304 K (Cr), (b) at 379 K (Col<sub>ob</sub>), and (c) at 443 K (Iso) on heating after quenching from the isotropic melt and storing at 296 K for 43 h; (d) at 423 K (Col<sub>b</sub>), and (e) at 323 K (Col<sub>ob</sub>) on the subsequent cooling.

## (e) Bis-N10Si2



**Figure S6.** Textures of **Bis-N10Si2** (a) at 373 K (Cr) and (b) at 453 K (*Ia3d*) on  $2^{nd}$  heating; (c) at 453 K (*Ia3d*) and (d) at 373 K (Cr) on  $3^{rd}$  cooling (after  $3^{rd}$  heating).

## (f) Bis-N10Si3



**Figure S7.** Textures of **Bis-N10Si3** (a) at 299 K (Sm) and (b) at 443 K (Col<sub>h</sub>) on  $1^{st}$  heating; (c) at 313 K (Col<sub>h</sub>) and (d) at 453 K (Col<sub>h</sub>) on  $1^{st}$  cooling; (e) at 350 K (Sm) and (f) at 401 K (Col<sub>h</sub>) on  $2^{nd}$  heating.

## (g) Bis-N11Si3



**Figure S8.** Textures of **Bis-N11Si3** (a) at 303 K (Sm), (b) at 440 K (Col<sub>h</sub>), and (c) at 490 K (Iso) on  $1^{st}$  heating; (d) at 490 K, (e) at 462 K (Col<sub>h</sub>), and (f) at 302 K (Col<sub>h</sub>) on the subsequent cooling.

## 3. XRD data

### (a) Bis-B6Si2



Figure S9. XRD patterns for bis-B6Si2 on (a) heating and (b) cooling.

**Table S1.** Experimental and calculated  $2\theta$  for the Col<sub>rec</sub>1 phase of **Bis-B6Si2** at 374 K on heating.

$Col_{rec}1$ with $a = 6.83$ nm and $b = 4.87$ nm at 374 K on cooling					
( <i>hk</i> )	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm	
(20)	2.586	2.586	3.416	3.416	
(21)	3.124	3.160	2.828	2.796	
(02)	3.632	3.632	2.433	2.433	
(41)	5.447	5.483	1.622	1.612	
(03)	5.447	5.449	1.622	1.622	
(13)	5.724	5.601	1.543	1.578	
(42)	6.262	6.322	1.411	1.398	
(50)	6.508	6.468	1.357	1.367	

$\operatorname{Col}_{h}$ with $a = 3.267 \pm 0.001$ nm at 408 K on heating					
( <i>hk</i> ) $2\theta_{obs} / \circ 2\theta_{calc} / \circ d_{obs} / nm d_{calc} / nm$					
(10)	3.122	3.123	2.830	2.829	
(11)	5.413	5.410	1.633	1.633	
(20)	6.246	6.248	1.415	1.415	

**Table S2.** Experimental and calculated  $2\theta$  for the Col<sub>h</sub> phase of **Bis-B6Si2** at 408 K on heating.

**Table S3.** Experimental and calculated  $2\theta$  for the Col<sub>rec</sub>2 phase of **Bis-B6Si2** at 313 K on cooling.

$Col_{rec}2$ with $a = 14.00$ nm and $b = 8.11$ nm at 313 K on cooling				
( <i>hk</i> )	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm
(30)	1.893	1.893	4.666	4.667
(02)	2.180	2.180	4.053	4.053
(22)	2.466	2.519	3.582	3.507
(41)	2.709	2.749	3.261	3.213
(32)	2.986	2.887	2.959	3.060
(50)	3.142	3.155	2.812	2.800
(23)	3.659	3.505	2.415	2.521
(33)	3.898	3.779	2.267	2.338
(44)	5.037	5.039	1.755	1.754
(81)	5.220	5.166	1.693	1.711
(54)	5.457	5.383	1.619	1.642
(74)	6.288	6.209	1.406	1.423
(06)	6.519	6.542	1.356	1.351

## (b) Bis-B8Si2



Figure S10. XRD patterns for Bis-B8Si2 on (a) heating and (b) cooling.

**Table S4.** Experimental and calculated  $2\theta$  for an un-identified isotropic M phase reminiscent of the *I*432-Cub<sup>[\*]</sup> phase in **Bis-B8Si2** at 354.3 K on heating.

$a_{\rm Cub} = 12.81 \pm 0.03$ nm at 354.3 K on heating						
$\{hkl\}$	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$2\theta_{\rm calc}$ – $2\theta_{\rm obs}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm	
{222}	2.352	2.389	0.037	3.756	3.689	
{321}	2.592	2.581	-0.011	3.408	3.423	
{400}	2.778	2.759	-0.019	3.180	3.202	
{420}	3.066	3.085	0.019	2.882	2.864	
{332}	3.270	3.235	-0.035	2.702	2.731	
{620}	4.374	4.363	-0.011	2.020	2.025	
{631}	4.644	4.679	0.035	1.903	1.889	
{710},{550},{543}	4.872	4.878	0.006	1.814	1.811	
{642}	5.166	5.163	-0.003	1.711	1.712	
{800}	5.550	5.519	-0.031	1.592	1.601	

**Table S5.** Experimental and calculated  $2\theta$  for the *Ia3d*-Cub phase of **Bis-B8Si2** at 370.0 K on heating.

$a_{\text{Cub}} = 7.994 \pm 0.002 \text{ nm at } 370.0 \text{ K} \text{ on heating}$					
$\{hkl\}$	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm	
{211}	2.708	2.707	3.262	3.263	
{220}	3.126	3.126	2.826	2.826	
{400}	4.422	4.421	1.998	1.998	
{420}	4.938	4.944	1.790	1.787	
{332}	5.184	5.185	1.705	1.704	
{422}	5.412	5.416	1.633	1.632	
{431}	5.646	5.637	1.565	1.568	

**Table S6.** Experimental and calculated  $2\theta$  for the Col<sub>h</sub> phase of **Bis-B8Si2** at 411.3 K on heating.

$\operatorname{Col}_{h}$ with $a = 3.567 \pm 0.002$ nm at 411.3 K on heating					
( <i>hk</i> ) $2\theta_{obs} / \circ = 2\theta_{calc} / \circ = d_{obs} / nm = d_{calc} / nm$					
(10)	2.862	2.860	3.087	3.089	
(11)	4.950	4.955	1.785	1.783	
(20)	5.724	5.722	1.544	1.544	

## (c) Bis-B11Si2



Figure S11. XRD patterns for Bis-B11Si2 on (a) heating and (b) cooling.

Fable S7.	Experimental and calculated $2\theta$ for the <i>Ia</i> 3 <i>d</i> -Cub phase of <b>Bis-B11Si2</b> at 412 K.
	(Different data scan from those in Figure S11)

$a_{\rm Cub} = 8.637 \pm 0.002$ nm at 412 K					
$\{hkl\}$	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm	
{211}	2.507	2.506	3.524	3.526	
{220}	2.894	2.893	3.053	3.053	
{400}	4.092	4.092	2.159	2.159	
{420}	4.578	4.576	1.930	1.931	
{332}	4.794	4.799	1.843	1.841	
{422}	5.010	5.013	1.764	1.763	
{431}	5.220	5.217	1.693	1.694	

**Table S8.** Experimental and calculated  $2\theta$  for the Col<sub>h</sub> phase of **Bis-B11Si2** at 433 K.

$\operatorname{Col}_{h}$ with $a = 3.925 \pm 0.002$ nm at 433 K on heating						
( <i>hk</i> ) $2\theta_{obs} / \circ = 2\theta_{calc} / \circ = d_{obs} / nm = d_{calc} / nm$						
(10)	2.601	2.599	3.397	3.399		
(11)	4.502	4.502	1.963	1.963		
(20)	5.196	5.199	1.701	1.700		

## (d) Bis-B10<sup>*i*</sup>Si3



Figure S12. XRD patterns for Bis-B10 <sup>*i*</sup>Si3 on (a) heating and (b) cooling.

Col <sub>ob</sub> with $a = 3.74$ nm, $b = 6.80$ nm, and $\gamma = 88.51$ ° at 338.8 K on heating							
( <i>hk</i> )	( <i>hk</i> ) $2\theta_{obs} / \circ 2\theta_{calc} / \circ d_{obs} / nm d_{calc} / nm$						
(10)	2.361	2.631	3.742	3.742			
(02)	2.601	2.601	3.397	3.397			
(13)	4.508	4.508	1.960	1.960			
(20)	(20) 4.739 4.723 1.864 1.871						
(04)	5.205	5.203	1.698	1.698			

**Table S9.** Experimental and calculated  $2\theta$  for the Col<sub>ob</sub> phase of **Bis-B10 'Si3** at 338.8 K.

**Table S10.** Experimental and calculated  $2\theta$  for the Col<sub>h</sub> phase of **Bis-B10** iSi3 at 423.3 K.

$Col_h$ with $a = 3.952$ nm at 423.3 K on heating						
( <i>hk</i> )	( <i>hk</i> ) $2\theta_{obs} / \circ 2\theta_{calc} / \circ d_{obs} / nm d_{calc} / n$					
(10)	2.581	2.581	3.423	3.423		
(11)	4.470	4.474	1.977	1.975		
(20)	5.163	5.167	1.712	1.710		
(21)	6.836	6.836	1.293	1.293		





Figure S13. XRD patterns for the Bis-N10Si2 on (a) heating and (b) cooling.

**Table S11.** Experimental and calculated  $2\theta$  for the *Ia*3*d*-Cub phase of **Bis-N10Si2** at 418 K.

$a_{\text{Cub}} = 9.531 \pm 0.005 \text{ nm at } 418 \text{ K}$					
$\{hkl\}$	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm	
{211}	2.270	2.271	3.892	3.891	
{220}	2.621	2.622	3.371	3.370	
{321}	3.481	3.469	2.538	2.547	
{400}	3.705	3.708	2.385	2.383	
{420}	4.147	4.146	2.131	2.131	
{332}	4.347	4.349	2.033	2.032	
{422}	4.538	4.542	1.947	1.945	
{431}	4.725	4.728	1.870	1.869	



**Figure S14.** XRD patterns for **Bis-N10Si3** on (a) heating, (b) cooling, and (c)  $2^{nd}$  heating; blue broken lines in (a) indicate the positions of the (001) and (003) reflections assumed on the basis of the plausible layered thickness. (d) WAXS patterns at 293 K, immediately after cooling from the melt and after aging at 296 K for 1 year, the latter of which shows the complete replacement of metastable Col<sub>h</sub> with stable Sm phases.

	$\operatorname{Col}_{h}$ with $a = 4.480 \pm 0.001$ nm at 403 K on heating						
ſ	( <i>hk</i> )	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm		
	(10)	2.278	2.277	3.878	3.879		
	(11)	3.945	3.945	2.240	2.240		
	(20)	4.554	4.555	1.940	1.940		

**Table S12.** Experimental and calculated  $2\theta$  for the Col<sub>h</sub> phase of **Bis-N10Si3** at 403 K.

## (g) Bis-N11Si3



Figure S15. XRD patterns for Bis-N11Si3 on (a) heating and (b) cooling.

**Table S13.** Experimental and calculated  $2\theta$  for the Col<sub>h</sub> phase of **Bis-N11Si3** at 412.6 K.

$\operatorname{Col}_{h}$ with $a = 4.646 \pm 0.002$ nm at 412.6 K on heating							
( <i>hk</i> )	$2 heta_{ m obs}$ / °	$2 heta_{ m calc}$ / °	$d_{\rm obs}$ / nm	$d_{\rm calc}$ / nm			
(10)	2.196	2.196	4.023	4.023			
(11)	3.804	3.804	2.322	2.323			
(20)	4.396	4.393	2.010	2.012			
(30)	6.584	6.591	1.342	1.341			

(h) Ia3d-Cub and Colh phases of Bis-BnSi2 series



**Figure S16.** Plots of (a) the lattice dimension of the *Ia3d* Cub phase  $(a(I_{Ia3d}))$  versus temperature (*T*) for three **Bis-BnSi2** compounds with n = 8, 10, and 11 on heating. Vertical thin broken lines represent the temperatures of the phase boundaries. The  $a(I_{Ia3d})$  values at 420 K for n = 8 and 11 were evaluated using the linear least-squares fit for the  $a(I_{Ia3d})$  versus *T* variation, the equations of which are given in the figure.



**Figure S17.** Plots of the lattice parameter of the *Ia*3*d* Cub phase at 380 K (a(la3d at 380 K)) versus alkyl spacer length *n* for three **Bis-BnSi2** compounds with n = 8, 10, and 11 on heating; the a(la3d at 380 K) was determined by using the the linear least-squares fit for the a(la3d) versus *T* variation in Figure S16. The estimation errors are of the magnitude of  $\pm (0.001-0.007)$  nm, within the symbol size.



**Figure S18.** Plots of the lattice parameter of the Col<sub>h</sub> phase (a(Col<sub>h</sub>)) versus alkyl spacer length n for four **Bis-BnSi2** compounds with n = 6, 8, 10, and 11 on heating; the recorded temperatures are 408, 411, 425, and 433 K, respectively. The estimation errors are of the magnitude of ±(0.001–0.002) nm, within the symbol size.

# 4. IR data



Figure S19. IR spectra for six siloxane-terminated compounds, Bis-B10Si3, Bis-B10Si2, Bis-B8Si2, Bis-B6Si2 Bis-N10Si3, and Bis-N10Si2, at LC phase temperatures.

## 5. Computational procedures

To investigate the flexibility of alkyl spacer in Bis-B6Si2, -B8Si2 and -B10Si2, we calculated rotational barrier of the individual C-C bonds. First, geometries of **Bis-B6Si2**, -B8Si2 and -B10Si2 were fully optimized using HF/3-21G and M06/6-31G methods. To calculate rotational barrier at nth C-C bond, the molecular geometry was optimized within the constraint of HC<sub>*n*-1</sub>-C<sub>*n*</sub>H dihedral angle =  $0^{\circ}$ .

We also performed NVT ab initio molecular dynamics (MD) simulation at three temperatures (T = 300 K, 400 K, and 420 K) for the single molecule (N = 1). The force acting on atoms was evaluated by HF/3-21G method. The velocity Verlet algorithm and Nose-Hoover chain method were used for the MD simulation. Initial velocities were obtained from a random Maxwell-Boltzmann ensemble. The time evolutions of CCCC dihedral angles and molecular length were shown in Figs. S20 and S21, respectively. The molecular length is defined as the distance of the farthest atom pair in the initial geometry.



Figure S20. MD calculations for (A) Bis-B6Si2 and (B) Bis-B10Si2 single molecules under vacuum. Dihedral angle is the angle between two planes on which  $C_{n-1}-C_n-C_{n+1}$  and  $C_n-C_{n+1}-C_{n+2}$  $(1 \le n \le 5 \text{ in } (A) \text{ and } 1 \le n \le 9 \text{ in } (B), C_0 \text{ corresponds to } O, \text{ and } C_7 \text{ for } (A) \text{ and } C_{10} \text{ for } (B) \text{ correspond}$ to Si) are embedded, respectively, and 180° represents trans conformer, whereas 60° and 300° represent gauche conformers. The plots for the dihedral angles are colored with different colors respectively.



Figure S21. The time variation of the molecular length of (A) **Bis-B6Si2** and (B) -**B10Si2** obtained by HF/3-21G MD simulation at T = 300 K, 400 K, and 420 K. The molecular length is defined as the distance of the farthest atom pair in the initial geometry.

## 6. Sample preparation

### 6.1.General

All starting materials and solvents were purchased from commercial sources and used without further purification unless otherwise noted. The purity and characterization of all intermediary compounds and the final compounds were checked by a combination of thin-layer chromatography (TLC: on silica gel coated glass plates (Merck) with fluorescent indicator), NMR spectroscopy, and elemental analysis. <sup>1</sup>H NMR (400 MHz) spectra were recorded on either of two JEOL FT-NMR spectrometers  $\alpha$ -400 and JMN-ECS400, and CDCl<sub>3</sub> was as solvents and tetramethysilane (TMS) was used as internal standard ( $\delta$ = 0.00). Chemical shifts are reported as  $\delta$  in parts per million downfield from TMS. Elemental analyses were performed using a J-Science Labo micro corder JM10 at Division Instrumental Analysis, Life Science Research Center, Gifu University.

### 6.2. Detailed synthesis procedures and characterization data

## (a) Synthesis of 1,2-bis(4'-(6''-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-*n*-hex-1''yloxy)benzoyl)hydrazine (Bis-B6Si2)

### a-1. Preparation of 6-bromo-1-n-hexene<sup>[S1]</sup>

Carbon tetrabromide (20.00 g, 60.4 mmol ) was dissolved in dichloromethane (20 mL) and the solution was cooled to 0 °C, to which 5-*n*-hexen-1-ol (6.0 mL, 50.0 mmol) was added while stirring. Then, to the solution was added a dichloromethane (25 mL) solution of triphenylphosphine (15.80 g, 60.2 mmol) dropwise while stirring. The solution was further stirred at 0 °C for 1h and then at room temperature for 24 h. After that, *N*,*N*-diisopropylethylamine (DIPEA) was added to neutralize the solution. After the evaporation of the solvent, a large amount of *n*-hexane was added and the precipitate was removed by filtration. The yellow transparent filtrate was evaporated to remove the solvent and the resulting solution was purified by column chromatography (eluent: *n*-hexane). From the obtained pale yellow solution, the solvent was removed by evaporation, dried in vacuum, to give a liquid (6.69 g, 41.0 mmol, 82.0%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.53 (quin, *J* = 7.6 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*Br*), 1.87 (quin, *J* = 7.3 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*Br*), 2.07 (q, *J* = 7.1 Hz, 2H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 3.34 (t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>Br), 4.91 – 5.06 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.72 – 5.84 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>).

### a-2. Preparation of Ethyl 4-(n-hex-5'-en-1'-yloxy)benzoate

Ethyl 4-hydroxybenzoate (6.84 g, 41.2 mmol) and 6-bromo-1-*n*-hexene (6.69 g, 41.0 mmol) were dissolved in dimethylformaide (DMF) (50 mL) at 60 °C while stirring, to which KI (6.86 g, 41.3 mmol) and K<sub>2</sub>CO<sub>3</sub> (10.33 g, 74.7 mmol) were added and stirred at 60 °C for 10 h. After that, ethyl acetate and NaCl saturated aqueous solution were added and the organic layer was separated. The solvent was removed by evaporation. The obtained orange solution was purified by chromatography (eluent: *n*-hexane : ethyl acetate = 2 : 1) to give a yellow solution, from which the solvent was removed. The product was dried under vacuum, to give the final one (9.13 g, 36.8 mmol, 89.3%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.36 (t, *J*<sub>1</sub> = 7.2 Hz, 3H, *COOCH*<sub>2</sub>CH<sub>3</sub>), 1.56 (quin, *J* = 7.9 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*O*), 1.80 (quin, *J* = 7.2 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.11 (q, *J* = 8.1 Hz, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 3.99 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>O), 4.32 (q, *J* = 7.1 Hz, 2H, *COO*CH<sub>2</sub>*CH*<sub>3</sub>), 4.95 – 5.06 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.76 – 5.87 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>), 6.88 (d, *J* = 8.9 Hz, 2H, Ar-H).

#### a-3. Preparation of 4-(n-hex-5'-en-1'-yloxy)benzoic acid

Ethyl 4-(*n*-hex-5'-en-1'-yloxy)benzoate (9.13 g, 15.7 mmol) was dissolved in methanol (40 mL), to which NaOH (1.79 g, 44.8 mmol) dissolved in water (40 mL) was slowly added and the resulting mixture was refluxed for 15 h. After cooled to room temperature, the solution was acidified with 12 N HCl and further stirred at room temperature for 1 h. The precipitate was collected and washed with water. The final crystalline solid was dried under vacuum to give 5.35 g (24.3 mmol, 66.0 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.58 (quin, *J* = 7.6 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*O*), 1.83 (quin, *J* = 7.0 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.13 (q, *J* = 7.2 Hz, 2H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 4.03 (t, *J* = 6.4 Hz, 2H, CH<sub>2</sub>O), 4.94 – 5.07 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.77 – 5.88 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>), 6.92 (dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 1.8 Hz, 2H, Ar–H), 8.04 (dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 1.8 Hz, 2H, Ar–H).

### a-4. Preparation of 1,2-bis(4-(n-hex-5'-en-1'-yloxy)benzoyl)hydrazine<sup>[S2]</sup>

Under a nitrogen atmosphere, 4-(*n*-hex-5'-en-1'-yloxy)benzoic acid (2.01 g, 9.13 mmol) was dissolved in 25 mL of distilled tetrahydrofuran (THF) containing a catalytic amount (3 drops) of distilled DMF and thionyl chloride (2 mL, 27.5 mmol). The mixture was stirred at 45 °C for 2 h. After that, the remaining thionyl chloride and the solvent were removed under a reduced pressure to give the acid chloride, to which 10 mL of distilled THF was added to give a pale yellow solution. This solution was slowly added dropwise to 10 mL of distilled THF containing hydrazine monohydrate (0.24 g, 4.79 mmol) and DIPEA (3.54 g, 27.4 mmol) while stirring at room temperature to give a while precipitate. The solution was further stirred for 45 min, and after that, a large amount of water was

added to quench the reaction. The precipitate was collected, washed with water and ethanol, dried under vacuum, to give a while solid (1.82 g, 4.17 mmol, 91.3 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.58 (quin, *J* = 7.6 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*O*), 1.82 (quin, *J* = 7.0 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.13 (q, *J* = 7.2 Hz, 4H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 4.01 (t, *J* = 6.4 Hz, 4H, CH<sub>2</sub>O), 4.97 – 5.07 (m, 4H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.77 – 5.87 (m, 2H, *H*<sub>2</sub>*C*=*CHCH*<sub>2</sub>), 6.93 (dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 1.8 Hz, 4H, Ar–H), 7.81 (dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 1.8 Hz, 4H, Ar–H), 9.14 (s, 2H, NH).

### a-5. Preparation of Pt catalyst composition for hydrosilylation<sup>[S3]</sup>

Under a reduced nitrogen atmosphere, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.51 g, 098 mmol) in ethanol (4 mL) was mixed with 1,9-decadience (1.1 mL, 6.0 mmol) while stirring at room temperature to give an orange solution, to which NaHCO<sub>3</sub> (0.68 g, 8.1 mmol) was slowly added. After termination of bubble generation, the solution was further stirred at 333 K for 4 h to give a black solution. After that, insoluble residues were removed by filtration and the obtained filtrate was condensed. Distilled toluene was added to the solution and insoluble residues produced were removed by filtration. This procedure was repeated 6 times to produce the objective product (0.34 g, 1.0 mmol), to which toluene was added to give a 0.1 M solution.

# *a-6.* Preparation of 1,2-bis(4'-(6''-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-n-hex-1''yloxy)benzoyl)hydrazine (Bis-B6Si2)<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(4-(*n*-hex-5'-en-1'-yloxy)benzoyl)hydrazine (0.93 g, 2.13 mmol), 1,1,1,3,3-pentamethyldisiloxane (1.8 mL, 9.16 mmol), and three drops of the Pt catalyst solution were dissolved in 12 mL of dry toluene. After that, the mixture was stirred at 65 °C for 17 h. After cooling to room temperature, the solvent was removed with a rotary evaporator to give a brown solid. The crude product was purified by chromatography three times (1<sup>st</sup> and 2<sup>nd</sup> eluent: *n*-hexane : ethylacetate = 2 : 1, 3<sup>rd</sup> eluents: *n*-hexane : ethylacetate = 4 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid. The solid was dried under vacuum to give the final product (0.49 g, 0.67 mmol, 31.5%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta = 0 - 0.09$  (m, 30H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.49 (t, J = 7.5 Hz, 4H, SiCH<sub>2</sub>), 1.20 - 1.49 (m, 12H, (CH<sub>2</sub>)<sub>3</sub>), 1.79 (quin, J = 7.1 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 3.98 (t, J = 6.5 Hz, 4H, CH<sub>2</sub>O), 6.91 (d, J = 8.6 Hz, 4H, Ar-H), 7.81 (d, J = 9.0 Hz, 4H, Ar-H), 9.23 (s, 2H, NH). Elemental Anal. Calcd for Si<sub>4</sub>C<sub>36</sub>H<sub>64</sub>N<sub>2</sub>O<sub>6</sub>: C, 58.97; H, 8.80; N, 3.82. Found: C, 58.80; H, 8.82; N, 3.83 %.

## (b) Synthesis of 1,2-bis(4'-(8"-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-*n*-oct-1"yloxy)benzoyl)hydrazine (Bis-B8Si2)

### b-1. Preparation of Ethyl 4-(n-oct-7'-en-1'-yloxy)benzoate

Ethyl 4-hydroxybenzoate (3.48 g, 20.9 mmol) and 8-bromo-1-*n*-octene (13.9 g, 13.9 mmol) were dissolved in acetone (30 mL) at 60 °C while stirring, to which KI (3.52 g, 21.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.97 g, 21.5 mmol) were added and stirred at 60 °C for 21 h. The solvent was removed by evaporation. After that, CHCl<sub>3</sub> and NaCl saturated aqueous solution were added and the organic layer was separated and dried with MgSO<sub>4</sub>. After removal of MgSO<sub>4</sub>, the solvent was removed by evaporation. The obtained colorless transparent solution was purified by chromatography (eluent: *n*-hexane : ethyl acetate = 9 : 1) to give a colorless transparent solution, from which the solvent was removed. The obtained product was a colorless transparent liquid (1.38 g, 5.0 mmol, 36.0%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.36-1.52 (m, 11H, *COOCH*<sub>2</sub>CH<sub>3</sub> and *H*<sub>2</sub>*C*=*CH*(CH<sub>2</sub>)<sub>4</sub>) 1.80 (quin, *J* = 7.0 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.05 (q, *J* = 6.9 Hz, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 3.99 (t, *J* = 6.5 Hz, 2H, CH<sub>2</sub>O), 4.33 (q, *J* = 7.2 Hz, 2H, *COO*CH<sub>2</sub>*CH*<sub>3</sub>), 4.91 – 5.02 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.75 – 5.85 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>), 6.88 (dt, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 2.7 Hz, 2H, Ar–H), 7.97 (dt, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 2.5 Hz, 2H, Ar–H).

### b-2. Preparation of 4-(n-oct-7'-en-1'-yloxy)benzoic acid

Ethyl 4-(*n*-oct-7'-en-1'-yloxy)benzoate (1.38 g, 5.0 mmol) was dissolved in methanol (25 mL), to which NaOH (0.41 g, 10.3 mmol) dissolved in water (4 mL) was slowly added and the resulting mixture was refluxed for 21 h. After cooled to room temperature in 2 h, the solution was acidified with 12 N HCl (0.9 mL, 10.8 mmol) and further stirred at room temperature for 0.8 h. The precipitate was collected and washed with water. The final white solid was dried under vacuum to give 1.18 g (4.8 mmol, 96.0 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.34 - 1.50$  (m, 6H,  $H_2C = CHCH_2$ (CH<sub>2</sub>)<sub>3</sub>), 1.80 (quin, J = 7.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>O), 2.05 (q, J = 6.9 Hz, 2H,  $H_2C = CHCH_2$ ), 4.01 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>O), 4.92 - 5.02 (m, 2H, H<sub>2</sub>C = CHCH<sub>2</sub>), 5.75 - 5.86 (m, 1H,  $H_2C = CHCH_2$ ), 6.91 (dt,  $J_1 = 9.0$  Hz,  $J_2 = 2.3$  Hz, 2H, Ar–H), 8.02 (dt,  $J_1 = 9.0$  Hz,  $J_2 = 2.3$  Hz, 2H, Ar–H).

### b-3. Preparation of 1,2-bis(4-(n-oct-7'-en-1'-yloxy)benzoyl)hydrazine<sup>[S2]</sup>

Under a nitrogen atmosphere, 4-(*n*-oct-7'-en-1'-yloxy)benzoic acid (1.34 g, 5.4 mmol) was dissolved in 15 mL of distilled tetrahydrofuran (THF) containing a catalytic amount (4 drops) of distilled DMF and thionyl chloride (0.8 mL, 11.0 mmol). The mixture was stirred at 45 °C for 4 h. After that, the remaining thionyl chloride and the solvent were

removed under a reduced pressure to give a viscus yellowish brown solution. This solution was slowly added dropwise to 15 mL of distilled THF containing hydrazine monohydrate (0.14 g, 2.9 mmol) and DIPEA (1.47 g, 11.4 mmol) while cooled with iced bath to give a solid. The solution was further stirred for 2 h, and after that, a large amount of water and *n*-hexane was added to quench the reaction. The precipitate was collected, dried under vacuum, to give a while solid (0.88 g, 0.18 mmol, 33.1 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.36 – 1.51 (m, 12H,  $H_2C$ =*CHCH*<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>), 1.80 (quin, J = 7.0 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.06 (q, J = 6.9 Hz, 4H,  $H_2C$ =*CH*CH<sub>2</sub>), 4.00 (t, J = 6.7 Hz, 4H, CH<sub>2</sub>O), 4.92 – 5.02 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.75 – 5.86 (m, 2H,  $H_2C$ =CH*CH*<sub>2</sub>), 6.93 (dt,  $J_1$  = 9.0 Hz,  $J_2$  = 2.4 Hz, 2H, Ar–H), 7.81 (dt,  $J_1$  = 9.0 Hz,  $J_2$  = 2.4 Hz, 2H, Ar–H), 9.11 (s, 2H, NH).

# *b-4.* Preparation of 1,2-bis(4'-(8''-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-n-oct-1''yloxy)benzoyl)hydrazine (Bis-B8Si2)<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(4-(*n*-oct-7'-en-1'-yloxy)benzoyl)hydrazine (0.51 g, 1.0 mmol), 1,1,1,3,3-pentamethyldisiloxane (0.5 mL, 2.5 mmol), and 4 drops of the Pt catalyst solution were dissolved in 20 mL of distilled toluene. After that, the mixture was stirred at 60 °C for 7 h. After cooling to room temperature, the solvent was removed with a rotary evaporator and the obtained solution was purified by chromatography (eluent: *n*-hexane : ethylacetate = 2 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid. The solid was dried under vacuum to give the final product (0.18 g, 0.2 mmol, 21.5%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.01 – 0.06 (m, 30H, SiCH<sub>3</sub>), 0.50 (t, *J* = 7.6 Hz, 4H, SiCH<sub>2</sub>), 1.24 – 1.31 (m, 20H, (CH<sub>2</sub>)<sub>5</sub>), 1.79 (quin, *J* = 7.1 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 4.00 (t, *J* = 6.5 Hz, 4H, CH<sub>2</sub>O), 6.93 (dt, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 2.4 Hz, 2H, Ar–H), 7.81 (dt, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 2.5 Hz, 2H, Ar–H), 9.11 (s, 2H, NH). Elemental Anal. Calcd for Si<sub>4</sub>C<sub>40</sub>H<sub>72</sub>N<sub>2</sub>O<sub>6</sub>: C, 60.86; H, 9.19; N, 3.55. Found: C, 61.05; H, 9.15; N, 3.60 %. 2019/9/29 15:59

# (c) Synthesis of 1,2-bis(4'-(11"-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-*n*-undec-1"-yloxy)benzoyl)hydrazine (Bis-B11Si2)

### *c-1. Preparation of 11-bromo-1-n-undecene*<sup>[S1]</sup>

Carbon tetrabromide (16.06 g, 48.4 mmol ) was dissolved in dichloromethane (20 mL) and the solution was cooled to 0 °C, to which 10-*n*-undecen-1-ol (8.0 mL, 39.9 mmol) was added while stirring. Then, to the solution was added a dichloromethane (10 mL) solution of triphenylphosphine (10.71 g, 40.8 mmol) dropwise while stirring. The solution

was further stirred at 0 °C for 1h and then at room temperature for 23 h. After that, DIPEA was added to neutralize the solution. After the evaporation of the solvent, a large amount of *n*-hexane was added and the precipitate was removed by filtration. The yellow transparent filtrate was evaporated to remove the solvent and the resulting solution was purified by column chromatography (eluent: *n*-hexane). From the obtained colorless transparent solution, the solvent was removed by evaporation, dried in vacuum, to give a liquid (11.29 g, 48.4 mmol,100%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.19 – 1.46 (m, 12H, (CH<sub>2</sub>)<sub>6</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*Br*), 1.84 (quin, *J* = 7.1 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*Br*), 2.03 (q, *J* = 7.1 Hz, 2H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 3.40 (t, *J* = 7.1 Hz, 2H, CH<sub>2</sub>Br), 4.86 – 5.04 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.73 – 5.86 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>).

## c-2. Preparation of Ethyl 4-(n-undec-10'-en-1'-yloxy)benzoate

Ethyl 4-hydroxybenzoate (10.07 g, 60.6 mmol) and 11-bromo-1-*n*-undecene (11.29 g, 48.4 mmol) were dissolved in acetone (80 mL), to which KI (8.12 g, 48.9 mmol) and K<sub>2</sub>CO<sub>3</sub> (7.22 g, 52.2 mmol) were added and refluxed for 16 h while stirring. The solvent was removed by evaporation. After that, CHCl<sub>3</sub> and NaCl saturated aqueous solution were added and the organic layer was separated and dried with MgSO<sub>4</sub>. After removal of MgSO<sub>4</sub>, the solvent was removed by evaporation. The obtained orange transparent solution was purified by chromatography (eluent: *n*-hexane : ethyl acetate = 9 : 1) to give an orange transparent solution, from which the solvent was removed to obtain the product (11.38 g, 35.7 mmol, 73.8%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.20-1.54 (m, 15H, *COOCH*<sub>2</sub>CH<sub>3</sub> and *H*<sub>2</sub>*C*=*CHCH*<sub>2</sub>CH<sub>2</sub>O<sub>6</sub>), 1.79 (quin, *J* = 7.2 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>O), 2.03 (q, *J* = 6.7 Hz, *H*<sub>2</sub>*C*=*CHC*H<sub>2</sub>), 3.99 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>O), 4.34 (q, *J* = 8.5 Hz, 2H, *COOC*H<sub>2</sub>*CH*<sub>3</sub>), 4.90 - 5.00 (m, 2H, H<sub>2</sub>C=*CHC*H<sub>2</sub>), 5.74 - 5.85 (m, 1H, *H*<sub>2</sub>C=CH*C*H<sub>2</sub>), 6.88 (d, *J* = 6.8 Hz, 2H, Ar-H), 7.96 (d, *J* = 9.0 Hz, 2H, Ar-H).

#### c-3. Preparation of 4-(n-undec-10'-en-1'-yloxy)benzoic acid

Ethyl 4-(*n*-undec-10'-en-1'-yloxy)benzoate (11.38 g, 35.7 mmol) was dissolved in ethanol (60 mL), to which NaOH (3.01 g, 75.3 mmol) dissolved in water (10 mL) was slowly added and the resulting mixture was refluxed for 16 h. After cooled to room temperature, the solution was acidified with 12 N HCl (9 mL, 100 mmol) and further stirred at room temperature for 0.5 h. The precipitate was collected and washed with water. The final white solid was dried under vacuum to give a solid of 5.54 g (19.1 mmol, 53.5 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.23 - 1.40$  (m, 10H,  $H_2C = CHCH_2$ (CH<sub>2</sub>)5, 1.45 (quin,

J = 7.3 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*O*), 1.79 (quin, J = 7.0 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.03 (q, J = 7.1 Hz, 2H,  $H_2C=CHCH_2$ ), 4.01 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>O), 4.88 – 5.02 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.74 – 5.86 (m, 1H,  $H_2C=CHCH_2$ ), 6.92 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.4$  Hz, 2H, Ar–H), 8.03 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.3$  Hz, 2H, Ar–H).

### c-4. Preparation of 1,2-bis(4-(n-undec-10'-en-1'-yloxy)benzoyl)hydrazine<sup>[S2]</sup>

Under a nitrogen atmosphere, 4-(*n*-undec-10'-en-1'-yloxy)benzoic acid (2.08 g, 7.2 mmol) was dissolved in 14 mL of distilled tetrahydrofuran (THF) containing a catalytic amount (3 drops) of distilled DMF and thionyl chloride (1.2 mL, 16.5 mmol). The mixture was stirred at 70 °C for 2 h. After that, the remaining thionyl chloride and the solvent were removed under a reduced pressure, to which 10 mL of distilled THF was added to give a pale yellow solution. This solution was slowly added dropwise to 10 mL of distilled THF containing hydrazine monohydrate (0.26 g, 5.2 mmol) and DIPEA (4.95 g, 38.3 mmol) at room temperature. The solution was further stirred for 1 h, and after that, a large amount of water was added to quench the reaction. The white precipitate was collected, washed with water and ethanol, dried under vacuum, to give a while solid (1.80 g, 3.12 mmol, 86.0 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.23 – 1.40 (m, 20H,  $H_2C$ =*CHCH*<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>), 1.45 (quin, J = 7.4 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*O*), 1.79 (quin, J = 7.0 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.03 (q, J = 6.9 Hz, 4H,  $H_2C$ =*CH*CH<sub>2</sub>), 3.99 (t, J = 6.5 Hz, 4H, CH<sub>2</sub>O), 4.89 – 5.02 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.74 – 5.86 (m, 2H,  $H_2C$ =CH*CH*<sub>2</sub>), 6.93 (dt,  $J_1$  = 9.0 Hz,  $J_2$  = 2.5 Hz, 2H, Ar–H), 7.81 (dt,  $J_1$  = 8.6 Hz,  $J_2$  = 1.8 Hz, 2H, Ar–H), 9.10 (s, 2H, NH).

# *c-5.* Preparation of 1,2-bis(4'-(11"-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-n-undec-1"yloxy)benzoyl)hydrazine (Bis-B11Si2)<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(4-(*n*-undec-10'-en-1'-yloxy)benzoyl)hydrazine (0.96 g, 1.66 mmol), 1,1,1,3,3-pentamethyldisiloxane (1.5 mL, 7.63 mmol), and four drops of the Pt catalyst solution were dissolved in 15 mL of distilled toluene. After that, the mixture was stirred at 60 °C for 2.75 h. After cooling to room temperature, the solvent was removed with a rotary evaporator to obtain brown solid. The product was purified by chromatography three times (1<sup>st</sup> and 2<sup>nd</sup> eluent: *n*-hexane : ethylacetate = 2 : 1, 3<sup>rd</sup> eluents: *n*-hexane : ethylacetate = 4 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid. The solid was dried under vacuum to give the final product (0.20 g, 0.29 mmol, 17.5%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$ = 0 – 0.10 (m, 30H, SiCH<sub>3</sub>), 0.49 (t, *J* = 7.4 Hz, 4H, SiCH<sub>2</sub>), 1.28 – 1.54 (m, 32H, (CH<sub>2</sub>)<sub>8</sub>), 1.79 (quin, *J* = 7.0 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 4.00 (t, *J* = 6.9 Hz, 4H, CH<sub>2</sub>O), 6.93 (d, J = 9.0 Hz, 4H, Ar-H), 7.81 (d, J = 8.6 Hz, 4H, Ar-H), 9.12 (s, 2H, NH). Elemental Anal. Calcd for Si<sub>4</sub>C<sub>40</sub>H<sub>72</sub>N<sub>2</sub>O<sub>6</sub>: C, 63.25; H, 9.69; N, 3.21. Found: C, 62.97; H, 9.91; N, 3.14 %.

# (d) Synthesis of 1,2-bis(4'-(10"-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-*n*-dec-1"-yloxy)benzoyl)hydrazine (Bis-B10<sup>i</sup>Si3)

### d-1. Preparation of 1,2-bis(4-(n-dec-9'-en-1'-yloxy)benzoyl)hydrazine<sup>[S2]</sup>

1,2-bis(4-(*n*-dec-9'-en-1'-yloxy)benzoyl)hydrazine was prepared according to the method described in ref<sup>[S2]</sup>.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.31 – 1.39 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.45 (tt, *J*<sub>1</sub> = 13.5 Hz, *J*<sub>2</sub> = 7.18 Hz, 2H, C*H*<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.79 (tt, *J*<sub>1</sub> = 13.9 Hz, *J*<sub>2</sub> = 7.06 Hz, 2H, C*H*<sub>2</sub>CH<sub>2</sub>O), 2.04 (dt, *J*<sub>1</sub> = 14.4 Hz, *J*<sub>2</sub> = 7.04 Hz, 2H, H<sub>2</sub>C=CHCH<sub>2</sub>), 4.01 (t, *J* = 6.50 Hz, 2H, CH<sub>2</sub>O), 4.91 – 5.01 (m, 2H, *H*<sub>2</sub>C=CHCH<sub>2</sub>), 5.75 – 5.84 (m, 1H, H<sub>2</sub>C=CHCH<sub>2</sub>), 6.92 (d, *J* = 8.97 Hz, 2H, Ar-H), 8.04 (d, *J* = 8.97 Hz, 2H, Ar-H).

# *d-2. Preparation of 1,2-bis(4'-(10"-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-n-dec-1"-yloxy)benzoyl)hydrazine (Bis-B10<sup>i</sup>Si3)*<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(4-(*n*-dec-9'-en-1'-yloxy)benzoyl)hydrazine (0.55 g, 1.0 mmol) was dissolved in 10 mL of dry toluene while heating at 65 °, to which, bis(trimethylsiloxy)methylsilane (0.5 mL, 2.5 mmol) and the Pt-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 2 h. After cooling to room temperature, the solvent was removed with a rotary evaporator and the obtained solution was purified by chromatography (eluent: *n*-hexane : ethylacetate = 3 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid (0.32 g, 0.32 mmol, 32%). The product was further purified using acetonitrile and activated carbon.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.018 (s, 6H, Si(*OSi*(*CH*<sub>3</sub>)<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 0.071 (s, 36H, Si(OSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>)), 0.435 (t, *J* = 7.64 Hz, 4H, SiCH<sub>2</sub>), 1.27 – 1.40 (m, 24H, (CH<sub>2</sub>)<sub>6</sub>), 1.45 (tt, *J*<sub>1</sub> = 13.9 Hz, *J*<sub>2</sub> = 7.18 Hz, 4H, CH<sub>2</sub> *CH*<sub>2</sub>*CH*<sub>2</sub>*O*), 1.79 (tt, *J*<sub>1</sub> = 13.4 Hz, *J*<sub>2</sub> = 6.95 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 3.99 (t, *J* = 6.52 Hz, 4H, CH<sub>2</sub>O), 6.93 (d, *J* = 8.97 Hz, 4H, Ar-H), 7.81 (d, *J* = 8.97 Hz, 4H, Ar-H), 9.14 (s, 2H, NH). Elemental Anal. Calcd for Si<sub>6</sub>C<sub>48</sub>H<sub>92</sub>N<sub>2</sub>O<sub>8</sub>: C, 58.01; H, 9.33; N, 2.82. Found: C, 58.02; H, 9.49; N, 2.80 %.

# (e) Synthesis of 1,2-bis(6'-(10"-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-*n*-dec-1"-yloxy)-2'-naphthoyl)hydrazine (Bis-N10Si2)

### e-1. Preparation of 10-bromo-1-n-decene<sup>[S1]</sup>

Carbon tetrabromide (7.96 g, 24.0 mmol ) was dissolved in dichloromethane (20 mL) and the solution was cooled to 0 °C, to which 9-*n*-decen-1-ol (4.1 mL, 22.3 mmol) was added while stirring. Then, to the solution was added a dichloromethane (10 mL) solution of triphenylphosphine (5.25 g, 20.2 mmol) dropwise while stirring. The solution was further stirred at 0 °C for 1h and then at room temperature for 24 h. After that, DIPEA was added to neutralize the solution. After evaporation of the solvent, a large amount of *n*-hexane was added and the precipitate was removed by filtration. The yellow solution was evaporated to remove the solvent, which was purified by column chromatography (eluent: *n*-hexane). The solvent was removed from the obtained pale yellow solution by evaporation, dried in vacuum, to give the final product (4.81 g, 21.9 mmol, 98.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.20 – 1.49 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>), 1.84 (quin, *J* = 7.7 Hz,

2H, CH<sub>2</sub>*CH*<sub>2</sub>*Br*), 2.03 (q, J = 7.5 Hz, 2H,  $H_2C = CHCH_2$ ), 3.39 (t, J = 7.0 Hz, 2H, CH<sub>2</sub>Br), 4.88 – 5.02 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.74 – 5.85 (m, 1H,  $H_2C = CHCH_2$ ).

### e-2. Preparation of ethyl 6-hydroxy-2-naphthoate

6-hydroxy-2-naphthoic acid (5.65 g, 30.0 mmol) was dissolved in ethanol (100 mL), to which concentrated H<sub>2</sub>SO<sub>4</sub> (2.0 mL, 36.0 mmol) was added dropwise. The mixture was then refluxed at 85 °C for 20 h. After cooled, the solvent was removed with a rotary evaporator. The product in the organic layer was extracted with CHCl<sub>3</sub> and NaCl saturated aqueous solution. After the solution was dried with MgSO<sub>4</sub>, the resulting filtrate was evaporated to remove the solvent. The obtained pale yellow solution was purified by column chromatography (eluent: *n*-hexane/ethyl acetate (9/1) and then ethyl acetate). After the solvent was removed from the obtained colorless transparent solution by evaporation, the product was dried in vacuum, to give the final white solid (5.03 g, 22.9 mmol, 76.3%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.44 (t, *J* = 7.1 Hz, 3H, *COOCH*<sub>2</sub>CH<sub>3</sub>), 4.43 (q, *J* = 7.3 Hz, 2H, COOCH<sub>2</sub>), 7.15 (d, *J* = 1.9 Hz, 1H, Ar–H), 7.17 (d, *J* = 1.5 Hz, 1H, Ar–H), 7.70 (d, *J* = 8.3 Hz, 1H, Ar–H), 7.87 (d, *J* = 8.3 Hz, 1H, Ar–H), 8.02 (d, *J* = 8.8 Hz, 1H, Ar–H), 8.52 (s, 1H, Ar–H).

### e-3. Preparation of ethyl 6-(n-dec-9'-en-1'-yloxy)-2-naphthoate

Ethyl 6-hydroxy-2-naphthoate (5.03 g, 22.9 mmol), 10-bromo-1-n-decene (4.81 g, 21.9

mmol), K<sub>2</sub>CO<sub>3</sub> (4.56 g, 33.0 mmol), and KI (4.07 g, 24.5mmol) were dissolved in acetone (50 mL), and refluxed at 75 °C for 24 h. After cooled, the solvent was removed with a rotary evaporator. The product in the organic layer was extracted with CHCl<sub>3</sub> and NaCl saturated aqueous solution, and dried with MgSO<sub>4</sub>. After filtration, the solvent was removed with a rotary evaporator and the resulting orange solution was purified by column chromatography (eluent: *n*-hexane/ethyl acetate (9/1)). The solvent was removed with a rotary evaporator and the product was dried under vacuum to give the final product (4.90 g, 13.8 mmol, 63.0 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, r.t.):  $\delta = 1.19 - 1.54$  (m, 11H, (CH<sub>2</sub>)<sub>4</sub> and *COOCH*<sub>2</sub>CH<sub>3</sub>), 1.83 (quin, J = 7.1 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.04 (q, J = 6.4 Hz, 2H,  $H_2C=CHCH_2$ ), 4.05 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>O), 4.41 (q, J = 7.0 Hz, 2H, COOCH<sub>2</sub>), 4.92 - 5.01 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.77 - 5.82 (m, 1H,  $H_2C=CHCH_2$ ), 7.11 (s, 1H, Ar–H), 7.17 (d, J = 8.8 Hz, 1H, Ar–H), 7.71 (d, J = 8.8 Hz, 1H, Ar–H), 7.81 (d, J = 9.2 Hz, 1H, Ar–H), 8.01 (d, J = 8.8 Hz, 1H, Ar–H), 8.51 (s, 1H, Ar–H).

### e-4. Preparation of 6-(n-dec-9'-en-1'-yloxy)-2-naphthoic acid

Ethyl 6-(*n*-dec-9'-en-1'-yloxy)-2-naphthoate (4.90 g, 13.8 mmol) was dissolved in ethanol (30 mL), to which NaOH (0.81 g, 20.0 mmol) dissolved in water (5 mL) was slowly added and the resulting mixture was refluxed for 6 h. After cooled to room temperature, the solution was acidified with 12 N HCl (2 mL, 24.0 mmol) and further stirred at room temperature for 1 h. The precipitate was collected and washed with water. The final crystalline solid was dried under vacuum to give 3.75 g (11.5 mmol, 83.3 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.27 - 1.55$  (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.85 (quin, J = 6.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>O), 2.05 (q, J = 6.8 Hz, 2H,  $H_2C=CHCH_2$ ), 4.11 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>O), 4.92 – 5.02 (m, 2H, H<sub>2</sub>C=CHCH<sub>2</sub>), 5.77 – 5.85 (m, 1H,  $H_2C=CHCH_2$ ), 7.16 (s, 1H, Ar–H), 7.21 (d, J = 8.8 Hz, 1H, Ar–H), 7.77 (d, J = 8.8 Hz, 1H, Ar–H), 7.87 (d, J = 8.8 Hz, 1H, Ar–H), 8.06 (d, J = 8.8 Hz, 1H, Ar–H), 8.61 (s, 1H, Ar–H).

### e-5. Preparation of 1,2-bis(6'-(n-dec-9"-en-1"-yloxy)-2'- naphthoyl)hydrazine<sup>[S2]</sup>

Under a nitrogen atmosphere, 6-(n-dec-9'-en-1'-yloxy)-2-naphthoic acid (3.75 g, 11.5 mmol) was dissolved in 50 mL of distilled THF containing a catalytic amount (5 drops) of distilled DMF and thionyl chloride (1.25 mL, 17.2 mmol). The mixture was stirred at 70 °C for 3 h. After that, the remaining thionyl chloride and the solvent were removed under a reduced pressure to give the acid chloride, to which 30 mL of distilled THF was added to give a pale yellow solution. Hydrazine monohydrate (0.28 g, 5.6 mmol) and DIPEA (2.67 g, 20.7 mmol) were dissolved in 20 mL of distilled THF, to which the above

pale yellow solution was slowly added dropwise while stirring at room temperature to give a while precipitate. The solution was further refluxed at 60 °C for 1 h. After cooling to room temperature, 60 mL of water was added dropwise to produce a while precipitate. The precipitate was collected, washed with water, ethanol, and CHCl<sub>3</sub>, dried under vacuum, to give a while solid (1.90 g, 2.9 mmol, 52.3 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 1.30 - 1.55$  (m, 20H, (CH<sub>2</sub>)<sub>5</sub>), 1.87 (quin, J = 7.5 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.06 (q, J = 7.3 Hz, 4H,  $H_2C = CHCH_2$ ), 4.10 (t, J = 6.6 Hz, 4H, CH<sub>2</sub>*OAr*), 4.92 - 5.03 (m, 4H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.77 - 5.86 (m, 2H,  $H_2C = CHCH_2$ ), 7.16 (d, J = 2.4Hz, 2H, Ar–H), 7.21 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 2H, Ar–H), 7.79 (d, J = 8.8 Hz, 2H, Ar–H), 7.83 (d, J = 8.8 Hz, 2H, Ar–H), 7.88 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.7$  Hz, 2H, Ar–H), 8.36 (s, 2H, Ar–H), 9.46 (s, 2H, NH). Elemental Anal. Calcd for C<sub>42</sub>H<sub>52</sub>N<sub>2</sub>O<sub>4</sub>: C, 77.56; H, 8.23; N, 4.28. Found: C, 77.74; H, 8.03; N, 4.32 %.

# e-6. Preparation of 1,2-bis(6'-(10"-(1,1,3,3,3-pentamethyldisiloxan-1-yl)-n-dec-1"yloxy)-2'-naphthoyl)hydrazine (Bis-N10Si2)<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(6'-(*n*-dec-9"-en-1"-yloxy)-2'-naphthoyl)hydrazine (0.20 g, 0.30 mmol), 1,1,1,3,3-pentamethyldisiloxane (0.25 mL, 1.3 mmol), and 0.2 mL of the Pt catalyst solution were dissolved in 3 mL of dry toluene. After that, the mixture was stirred at 80 °C for 1 h. After cooling to room temperature, the solvent was removed with a rotary evaporator to give a brown solid. The crude product was purified by chromatography twice (1<sup>st</sup> eluent: *n*-hexane : ethylacetate = 2 : 1, 2<sup>nd</sup> eluents: *n*-hexane : ethylacetate = 3 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid. The solid was dried under vacuum to give the final product (0.055 g, 0.052 mmol, 17.0%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta = 0 - 0.21$  (m, 30H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.49 (t, J = 7.2 Hz, 4H, SiCH<sub>2</sub>), 1.29 - 1.53 (m, 28H, (CH<sub>2</sub>)<sub>7</sub>), 1.86 (quin, J = 7.2 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 4.09 (t, J = 6.5 Hz, 4H, CH<sub>2</sub>O), 7.15 (d, J = 2.2 Hz, 2H, Ar–H), 7.22 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.5$  Hz, 2H, Ar–H), 7.79 (d, J = 8.8 Hz, 2H, Ar–H), 7.83 (d, J = 9.4 Hz, 2H, Ar–H), 7.87 (d, J = 9.2 Hz, 2H, Ar–H), 8.35 (s, 2H, Ar–H), 9.40 (s, 2H, NH). Elemental Anal. Calcd for Si<sub>4</sub>C<sub>52</sub>H<sub>84</sub>N<sub>2</sub>O<sub>6</sub>: C, 66.05; H, 8.95; N, 2.96. Found: C, 65.80; H, 9.17; N, 2.94 %.

(f) Synthesis of 1,2-bis(6'-(10"-(1,1,3,3,5,5,5-heptamethyldisiloxan-1-yl)-*n*-dec-1"-yloxy)-2'-naphthoyl)hydrazine (Bis-N10Si3)

### *f-1. Preparation of 10-bromo-1-n-decene*<sup>[S1]</sup>

According to the same procedure described in e-l, from 9-n-decen-1-ol (3.64 g, 23.3 mmol) and carbon tetrabromide (8.02 g, 24.2 mmol), yielding 5.08 g (23.2 mmol, 99.6 %) of the final product.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.21 – 1.47 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>), 1.84 (quin, *J* = 7.3 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*Br*), 2.03 (q, *J* = 7.2 Hz, 2H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 3.39 (t, *J* = 7.0 Hz, 2H, CH<sub>2</sub>Br), 4.88 – 5.04 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.72 – 5.87 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>).

### f-2. Preparation of ethyl 6-hydroxy-2-naphthoate

According to the same procedure described in *e-2*, from 6-hydroxy-2-naphthoic acid (6.94 g, 36.9 mmol), yielding the final product (6.73 g, 31.1 mmol, 84.3%).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.43 (t, *J* = 7.2 Hz, 3H, *COOCH*<sub>2</sub>CH<sub>3</sub>), 4.42 (q, *J* = 7.2 Hz, 2H, COOCH<sub>2</sub>), 5.27 (s, 1H, OH), 7.14 (d, *J* = 2.3 Hz, 1H, Ar–H), 7.17 (q, *J* = 2.3 Hz, 1H, Ar–H), 7.69 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.86 (d, *J* = 8.5 Hz, 1H, Ar–H), 8.01 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H, Ar–H), 8.52 (s, 1H, Ar-H).

### f-3. Preparation of ethyl 6-(n-dec-9'-en-1'-yloxy)-2-naphthoate

According to the same procedure described in *e-3*, from ethyl 4-hydroxybenzoate (3.30 g, 15.3 mmol) and 10-Bromo-1-*n*-decene (5.08 g, 23.2 mmol), yielding the final product (3.15 g, 8.9 mmol, 38.4 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, r.t.):  $\delta = 1.23 - 1.55$  (m, 11H, (CH<sub>2</sub>)<sub>4</sub> and *COOCH*<sub>2</sub>CH<sub>3</sub>), 1.84 (quin, J = 7.1 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.04 (q, J = 7.0 Hz, 2H,  $H_2C=CHCH_2$ ), 4.07 (t, J = 6.7 Hz, 2H, CH<sub>2</sub>O), 4.41 (q, J = 7.0 Hz, 2H, COOCH<sub>2</sub>), 4.89 - 5.05 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.74 - 5.88 (m, 1H,  $H_2C=CHCH_2$ ), 7.09 - 7.22 (m, 2H, Ar–H), 7.71 (d, J = 9.0 Hz, 1H, Ar–H), 7.82 (d, J = 9.0 Hz, 1H, Ar–H), 8.02 (dd,  $J_1 = 9.9$  Hz,  $J_2 = 1.3$  Hz, 1H, Ar–H), 8.51 (s, 1H, Ar-H).

### f-4. Preparation of 6-(n-dec-9'-en-1'-yloxy)-2-naphthoic acid

According to the same procedure described in e-4, from ethyl 6-(n-dec-9'-en-1'-yloxy)-2-naphthoate (3.15 g, 8.9 mmol), yielding 1.87 g (5.7 mmol, 64.0 %) of the final crystalline solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.26 – 1.71 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.86 (quin, *J* = 6.9 Hz, 2H, CH<sub>2</sub>*CH<sub>2</sub>O*), 2.04 (q, *J* = 7.0 Hz, 2H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 4.10 (q, *J* = 6.4 Hz, 2H, CH<sub>2</sub>O), 4.88

- 5.04 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.73 – 5.87 (m, 1H, *H*<sub>2</sub>C=CH*CH*<sub>2</sub>), 7.14 – 7.22 (m, 2H, Ar–H), 7.76 (d, *J* = 8.7 Hz, 1H, Ar–H), 7.85 (d, *J* = 9.2 Hz, 1H, Ar–H), 8.04 (dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H, Ar–H), 8.58 (s, 1H, Ar-H).

### f-5. Preparation of 1,2-bis(6'-(n-dec-9"-en-1"-yloxy)-2'- naphthoyl)hydrazine<sup>[S2]</sup>

According to the same procedure described in *e*-5, from 6-(n-dec-9'-en-1'-yloxy)-2- naphthoic acid (1.14 g, 3.5 mmol), yielding 1,2-bis(6'-(n-dec-9''-en-1''-yloxy)-2'- naphthoyl)hydrazine (0.48 g, 0.74 mmol, 42.6 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta = 1.29 - 1.54$  (m, 16H, (CH<sub>2</sub>)<sub>4</sub>), 1.86 (quin, J = 7.1 Hz, 4H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.04 (q, J = 6.9 Hz, 4H,  $H_2C = CHCH_2$ ), 4.09 (t, J = 6.5 Hz, 4H, CH<sub>2</sub>*OAr*), 4.89 - 5.04 (m, 4H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.75 - 5.88 (m, 2H,  $H_2C = CHCH_2$ ), 7.14 (d, J = 2.4Hz, 2H, Ar–H), 7.21 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.4$  Hz, 2H, Ar–H), 7.78 (d, J = 8.6 Hz, 2H, Ar–H), 7.82 (d, J = 9.0 Hz, 2H, Ar–H), 7.87 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 2.0$  Hz, 2H, 2H, Ar–H), 8.35 (s, 2H, Ar–H), 9.43 (s, 2H, NH).

# *f-6. Preparation of 1,2-bis(6'-(10''-(1,1,3,3,5,5,5-heptamethyldisiloxan-1-yl)-n-dec-1''-yloxy)-2'-naphthoyl)hydrazine (Bis-N10Si3)*<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(6'-(*n*-dec-9''-en-1''-yloxy)-2'- naphthoyl)hydrazine (0.85 g, 1.3 mmol), 1,1,1,3,3,5,5-heptamethyltrisiloxane (1.5 mL, 5.5 mmol), and three drops of the Pt catalyst solution were dissolved in 5 mL of distilled toluene. The mixture was stirred at 60 °C for 2 h, and then, the temperature was raised to 358 K, and 5 mL of distilled toluene was further added and stirred at 60 °C for 16.5 h. After cooling to room temperature, the solvent was removed with a rotary evaporator to give a brown solid. The crude product was purified by chromatography twice (1<sup>st</sup> eluent: *n*-hexane : ethylacetate =  $2 : 1, 2^{nd}$  and  $3^{rd}$  eluents: *n*-hexane : ethylacetate = 4 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid, which was dried under vacuum to give the final product (0.18 g, 0.2 mmol, 15.4 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta = 0 - 0.11$  (m, 42H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.52 (t, J = 7.6 Hz, 4H, Si(CH<sub>2</sub>), 1.22 - 1.55 (m, 32H, (CH<sub>2</sub>)<sub>8</sub>), 1.86 (quin, J = 7.1 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 4.09 (t, J = 6.5 Hz, 4H, CH<sub>2</sub>O), 7.14 (d, J = 2.4 Hz, 2H, Ar–H), 7.20 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.7$  Hz, 2H, Ar–H), 7.78 (d, J = 8.6 Hz, 2H, Ar–H), 7.82 (d, J = 9.4 Hz, 2H, Ar–H), 7.86 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 1.6$  Hz, 2H, Ar–H), 8.34 (s, 2H, Ar-H), 9.46 (s, 2H, NH). Elemental Anal. Calcd for Si<sub>6</sub>C<sub>56</sub>H<sub>96</sub>N<sub>2</sub>O<sub>8</sub>: C, 61.48; H, 8.85; N, 2.56. Found: C, 61.22; H, 8.92; N, 2.60 %.

(g) Synthesis of 1,2-bis(6'-(11"-(1,1,3,3,5,5,5-heptamethyldisiloxan-1-yl)-*n*-undec-1"-yloxy)-2'-naphthoyl)hydrazine (Bis-N11Si3)

### g-1. Preparation of 11-bromo-1-n-undecene<sup>[S1]</sup>

According to the same procedure described in *c*-*1*, from 10-*n*-undecen-1-ol (8.0 mL, 39.9 mmol), yielding11-bromo-1-*n*-undecene (8.10 g, 34.7 mmol, 87.0 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.27 – 1.43 (m, 12H, (CH<sub>2</sub>)<sub>6</sub>*CH*<sub>2</sub>*CH*<sub>2</sub>*Br*), 1.84 (quin, *J* = 7.2 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*Br*), 2.03 (q, *J* = 7.7 Hz, 2H, *H*<sub>2</sub>*C*=*CH*CH<sub>2</sub>), 3.40 (t, *J* = 6.7 Hz, 2H, CH<sub>2</sub>Br), 4.90 – 5.01 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.74 – 5.85 (m, 1H, *H*<sub>2</sub>*C*=CH*CH*<sub>2</sub>).

#### g-2. Preparation of ethyl 6-(n-undec-10'-en-1'-yloxy)-2-naphthoate

According to the same procedure described in *e-3*, from ethyl 4-hydroxybenzoate (4.64 g, 21.5 mmol) and 11-Bromo-1-*n*-decene (6.09 g, 26.1 mmol), yielding the final product (3.89 g, 10.6 mmol, 49.3 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, r.t.):  $\delta = 1.20 - 1.48$  (m, 15H, (CH<sub>2</sub>)<sub>6</sub> and *COOCH*<sub>2</sub>CH<sub>3</sub>), 1.79 (quin, J = 7.1 Hz, 2H, CH<sub>2</sub>*CH*<sub>2</sub>*O*), 2.02 (q, J = 7.5 Hz, 2H,  $H_2C = CHCH_2$ ), 3.99 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>O), 4.39 (q, J = 7.2 Hz, 2H, COOCH<sub>2</sub>), 4.90 - 5.01 (m, 2H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.73 - 5.84 (m, 1H,  $H_2C = CHCH_2$ ), 7.06 (d, J = 2.0 Hz, 1H, Ar–H), 7.14 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.7$  Hz, 1H, Ar–H), 7.67 (d, J = 8.5 Hz, 1H, Ar–H), 7.77 (d, J = 9.0 Hz, 1H, Ar–H), 8.00 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.8$  Hz, 1H, Ar–H), 8.48 (s, 1H, Ar-H).

### g-3. Preparation of 6-(n-undec-10'-en-1'-yloxy)-2-naphthoic acid

According to the same procedure described in e-4, from ethyl 6-(*n*-undec-10'-en-1'-yloxy)-2-naphthoate (3.86 g, 10.6 mmol), yielding 3.03 g (8.9 mmol, 84.0 %) of the final crystalline solid.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>):  $\delta = 1.19 - 1.55$  (m, 12H, (CH<sub>2</sub>)<sub>6</sub>), 1.85 (quin, J = 7.1 Hz, 2H, CH<sub>2</sub>*CH<sub>2</sub>O*), 2.03 (q, J = 7.5 Hz, 2H,  $H_2C = CHCH_2$ ), 4.09 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>O), 4.90 - 5.01 (m, 2H, H<sub>2</sub>C=*CHCH<sub>2</sub>*), 5.75 - 5.86 (m, 1H,  $H_2C = CHCH_2$ ), 7.15 (d, J = 2.2 Hz, 1H, Ar–H), 7.20 (dd,  $J_1 = 9.0$  Hz,  $J_2 = 2.7$  Hz, 1H, Ar–H), 7.75 (d, J = 8.5 Hz, 1H, Ar–H), 7.85 (d, J = 9.4 Hz, 1H, Ar–H), 8.04 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.8$  Hz, 1H, Ar–H), 8.59 (s, 1H, Ar–H).

### g-4. Preparation of 1,2-bis(6'-(n-undec-10"-en-1"-yloxy)-2'-naphthoyl)hydra-zine<sup>[S2]</sup>

According to the same procedure described in e-5, from 6-(n-undec-10'-en-1'-yloxy)-2-naphthoic acid (3.03 g, 8.9 mmol), yielding 0.92 g (1.4 mmol, 15.7 %) of the final crystalline solid.

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta = 1.31 - 1.50$  (m, 24H, (CH<sub>2</sub>)<sub>6</sub>), 1.86 (quin, J = 7.1 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 2.04 (q, J = 7.0 Hz, 4H,  $H_2C = CHCH_2$ ), 4.09 (t, J = 6.5 Hz, 4H, CH<sub>2</sub>*OAr*), 4.91 - 5.02 (m, 4H, H<sub>2</sub>C=*CHCH*<sub>2</sub>), 5.76 - 5.86 (m, 2H,  $H_2C = CHCH_2$ ), 7.15 (d, J = 2.5 Hz, 2H, Ar–H), 7.21 (dd,  $J_1 = 6.5$  Hz,  $J_2 = 2.5$  Hz, 2H, Ar–H), 7.78 (d, J = 9.0 Hz, 2H, Ar–H), 7.83 (d, J = 9.0 Hz, 2H, Ar–H), 7.88 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.8$  Hz, 2H, Ar–H), 8.35 (s, 1H, Ar–H), 9.41 (s, 2H, NH).

## g-5. Preparation of 1,2-bis(6'-(11"-(1,1,3,3,5,5,5-heptamethyldisiloxan-1-yl)-n-undec-1"-yloxy)-2'-naphthoyl)hydrazine (Bis-N11Si3)<sup>[S2]</sup>

Under a nitrogen atmosphere, 1,2-bis(6'-(*n*-undec-10"-en-1"-yloxy)-2'naphthoyl)hydrazine (0.92 g, 1.4 mmol), 1,1,1,3,3,5,5-heptamethyltrisiloxane (0.5 mL, 1.8 mmol), and 3 drops of the Pt catalyst solution were dissolved in 17 mL of distilled toluene. The mixture was stirred at 60 °C for 22 h. After cooling to room temperature, the solvent was removed with a rotary evaporator to give a solid. The crude product was purified by chromatography twice (eluent: *n*-hexane : ethylacetate = 4 : 1) to give a colorless transparent solution. The solvent was removed to give a white solid, which was dissolved in CH<sub>3</sub>CN and refluxed for 30 min. The obtained solid was recrystallized from THF, dried under vacuum to give the final white solid (0.011 g, 0.010 mmol, 0.7 %).

<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.05 – 0.07 (m, 42H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.50 – 0.52 (m, 4H, SiCH<sub>2</sub>), 1.18 – 1.51 (m, 32H, (CH<sub>2</sub>)<sub>8</sub>), 1.86 (quin, *J* = 7.1 Hz, 4H, CH<sub>2</sub>*CH<sub>2</sub>O*), 4.09 (t, *J* = 6.5 Hz, 4H, CH<sub>2</sub>O), 7.15 (d, *J* = 2.9 Hz, 2H, Ar–H), 7.22 (q, *J* = 3.0 Hz, 2H, Ar–H), 7.80 (d, *J* = 9.0 Hz, 2H, Ar–H), 7.84 (d, *J* = 9.0 Hz, 2H, Ar–H), 7.88 (s, 2H, Ar–H), 8.35 (s, 2H, Ar-H), 9.35 (s, 2H, NH).

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