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Supporting Information

Synthesis and self-assembly of photoresponsive and luminescent polycatenar liquid crystals incorporating an azobenzene unit interconnecting two 1,3,4-thiadiazoles

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Content

1. Additional Experimental Data

1.1 Additional textures of LC phases and DSC traces

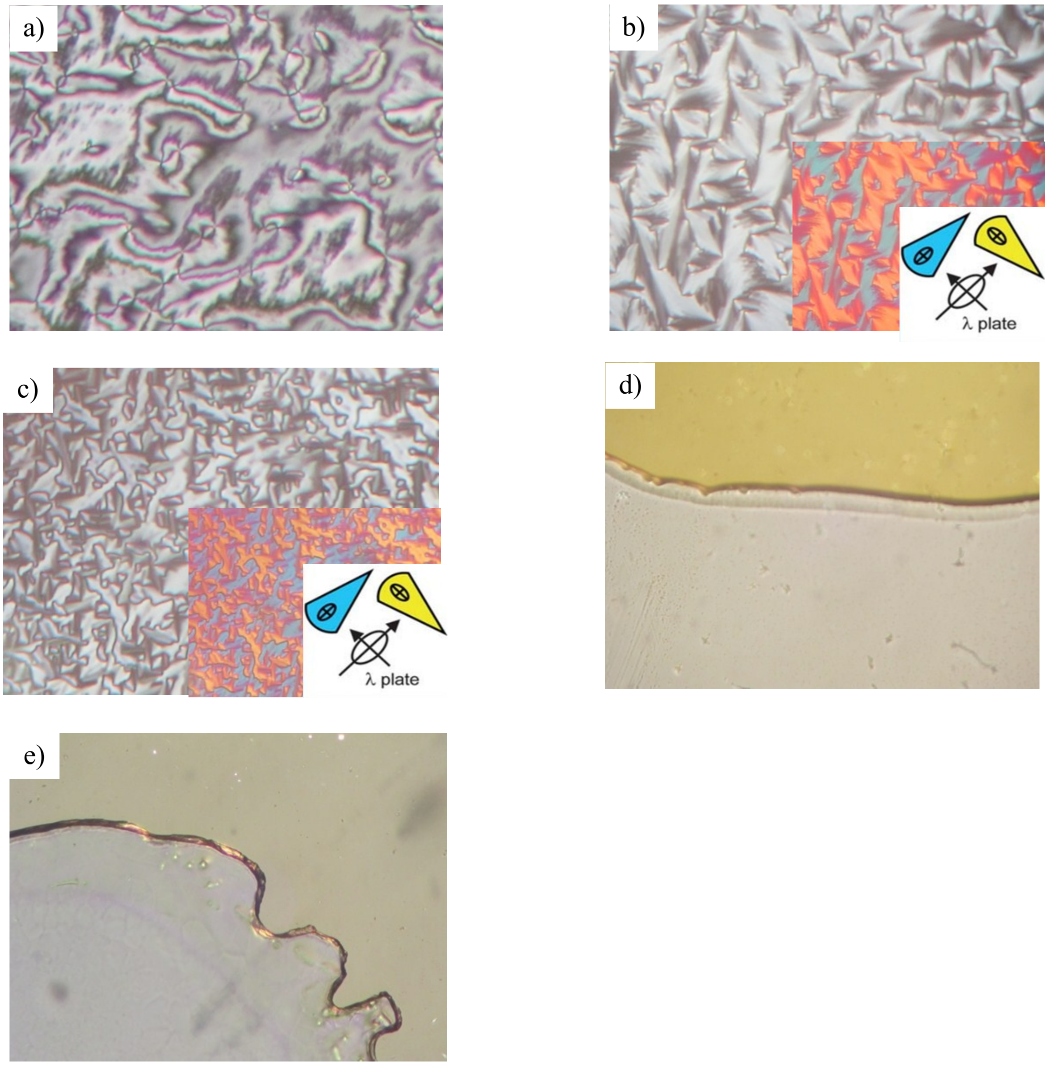

Fig. S1 Representative textures between crossed polarizers: (a) SmC phase of **$\mathbf{I}^1$/14** cooling at 130 °C; (b) Col$_{hex}$/*p6mm* phase of ***o*-$\mathbf{I}^2$/12** (inset shows the same region with λ-plate) cooling at 90 °C; (c) Col$_{hex}$/*p6mm* phase of ***o*-$\mathbf{I}^2$/8** (inset shows the same region with λ-plate) cooling at 94 °C; (d) textures of the Cub$_I$/ $Pm\bar{3}n$ phases of compounds **$\mathbf{I}^3$/12** cooling at 68 °C; (e)textures of the Cub$_I$/ $Pm\bar{3}n$ phases of compounds **$\mathbf{I}^3$/14** cooling at 62 °C.

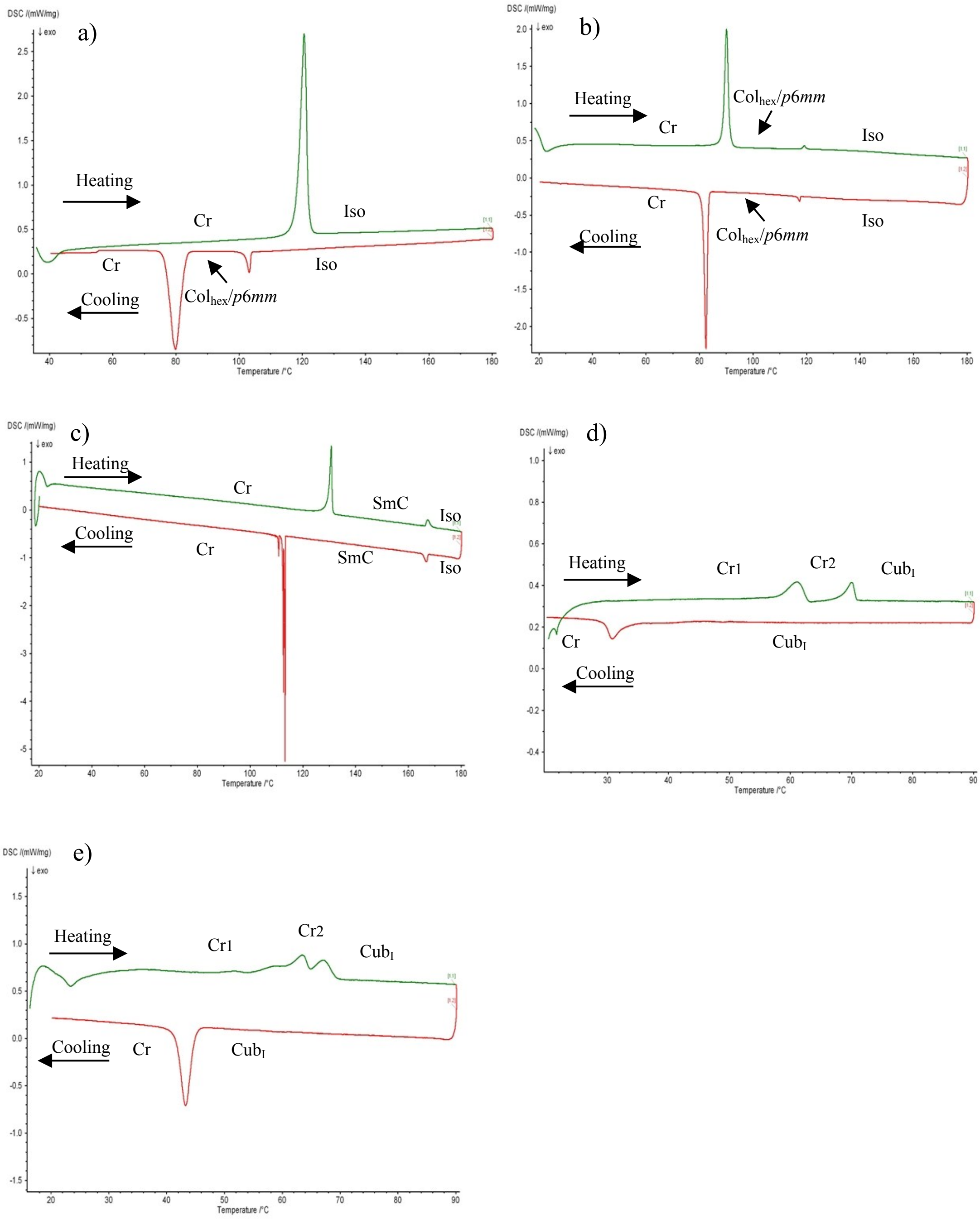

Fig. S2 DSC traces of (a) compound ***o*-I^2/8** (5 K min^{-1}, second scans); (b) compound ***o*-I^2/12** (5 K min^{-1}, second scans); (c) compound **I^1/14**, (2 K min^{-1}, second scans); (d) compound **I^3/12**, (1 K min^{-1}, first scans); (e) compound **I^3/14**, (1 K min^{-1}, first scans).

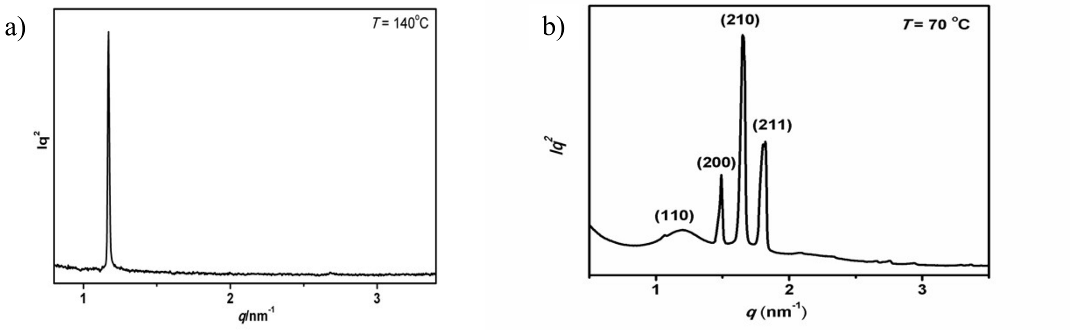

Fig. S3 (a) SAXS diffraction patterns of SmC phase of compound **$\mathbf{I}^1$/14** recorded at 140 °C; (b) SAXS diffraction patterns of Cub$_I$/ $Pm\bar{3}n$ phase of compound **$\mathbf{I}^3$/12** recorded at 70 °C

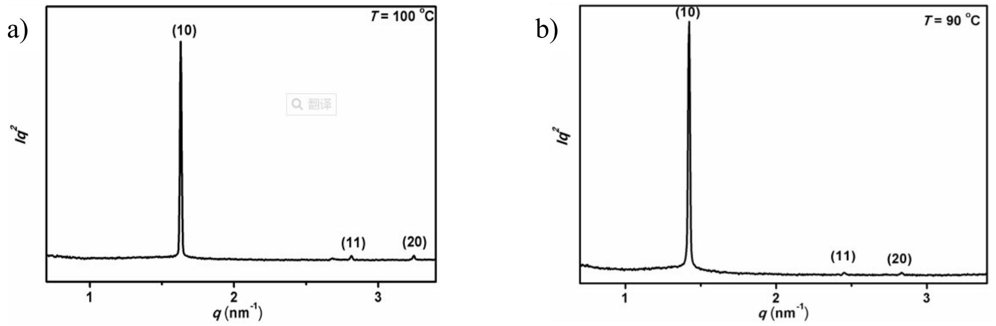

Fig. S4 (a) SAXS diffraction patterns of hexagonal phase of compound ***o*-$\mathbf{I}^2$/8** recorded at 100 °C; (b) SAXS diffraction patterns of hexagonal phase of compound ***o*-$\mathbf{I}^2$/12** recorded at 90 °C.

Table S1 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound ***o*-$\mathbf{I}^2$/8** at 100 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{\mathrm{obs.}}$ – spacing (nm)	$d_{\mathrm{cal.}}$ – spacing (nm)	*intensity*	*phase*
(10)	3.97	3.95	100	0
(11)	2.27	2.28	2.2	0
(20)	1.97	1.97	1.1	0
a_{hex} = 4.56 nm				

Table S2 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound ***o*-$\mathbf{I}^2$/12** at 90 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{\mathrm{obs.}}$ – spacing (nm)	$d_{\mathrm{cal.}}$ – spacing (nm)	*intensity*	*phase*
(10)	4.57	4.57	100	0
(11)	2.61	2.64	0.6	0
(20)	2.32	2.29	1.1	π
a_{hex} = 5.28 nm				

Table S3 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound ***o*-$\mathbf{I}^2$/14** at 105 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{\mathrm{obs.}}$ – spacing (nm)	$d_{\mathrm{cal.}}$ – spacing (nm)	*intensity*	*phase*
(10)	4.49	4.50	100	0
(11)	2.61	2.60	0.42	0
(20)	2.25	2.25	0.78	π
a_{hex} = 5.20 nm				

Table S4 Experimental and calculated *d*-spacings of the observed SAXS reflections of the Cub$_I$/ $Pm\overline{3}n$ phase in compound **I^3/14** at 65 °C. All intensity values are Lorentz and multiplicity corrected.

(*hkl*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*phase*
(200)	4.32	4.33	19.1	0
(211)	3.87	3.87	100	0
(220)	3.53	3.53	52.4	0
a_{cub} = 8.65 nm				

Table S5 Experimental and calculated *d*-spacings of the observed SAXS reflections of the Cub$_I$/ $Pm\overline{3}n$ phase in compound **I^3/12** at 70 °C. All intensity values are Lorentz and multiplicity corrected.

(*hkl*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*phase*
(110)	5.87	5.87	0.04	0
(200)	4.21	4.23	25.1	0
(211)	3.81	3.78	100	0
(220)	3.45	3.45	58.2	0
a_{cub} = 8.46 nm				

Table S6 Calculations of molecular volume (V_{mol}), volume of the (hypothetical) unit cells (V_{cell}) and number of molecules in these unit cells (n_{cell}).[a]

Comp.	phase	*a*/nm (T/°C)	V_{mol} [nm^3]	micelle size *D*/nm	V_{cell} [nm^3]	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell}	*n*
***o*-I^2/8**	Col$_{hex}$/*p6mm*	4.56(100)	1.38	/	8.09	5.86	4.61	5.28	5.28
***o*-I^2/12**	Col$_{hex}$/*p6mm*	5.28(90)	1.88	/	10.85	5.62	4.41	5.15	5.15
***o*-I^2/14**	Col$_{hex}$/*p6mm*	5.20(105)	1.98	/	10.53	5.26	4.13	4.70	4.70
I^3/12	Cub$_I$/ $Pm\overline{3}n$	8.46(70)	2.39	4.23(70)	605.50	253.35	199.01	226.20	28.3
I^3/14	Cub$_I$/ $Pm\overline{3}n$	8.65(65)	2.69	4.33(65)	647.21	240.60	189.04	214.82	26.8

[a] $D = 0.5 \times a_{cub}$ for $Pm\overline{3}n$; V_{cell} = volume of the unit cell defined by the dimensions $a_{hex}^2 \times \sin(60^\circ) \times 0.45$ nm for hexagonal phases and a_{cub}^3 for the cubic phases; V_{mol} = volume for a single molecule as calculated using the crystal volume increments,[S1] $n_{cell,cryst}$ = number of molecules in the unit cell, calculated according to $n_{cell,cryst} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$;[S2] $n_{cell,liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{cell,liq} = 0.55/0.7 \times n_{cell,cryst}$; n_{cell} = in the LC phase estimated as the average of that in the $n_{cell,cryst}$ and $n_{cell,liq}$. $n = n_{cell}/8$ for the $Pm\overline{3}n$ phase.

1.2 Additional UV-vis and Fluorescence Data, HOMO and LUMO orbital etc.

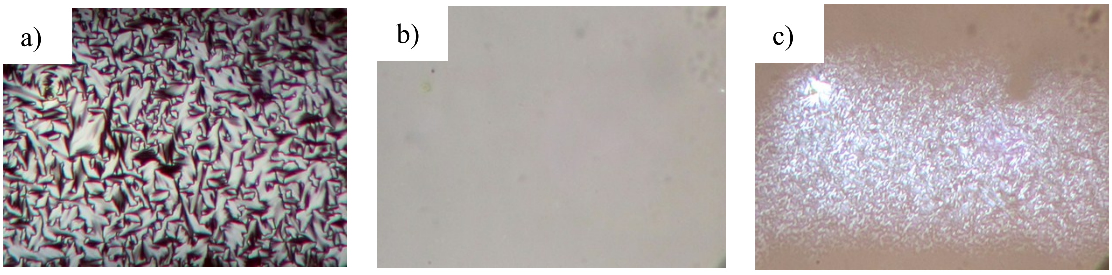

Fig. S5 Textural changes as observed by POM at the photoinduced Col$_{hex}$/*p6mm*-Iso transition and the relaxation Iso-Col$_{hex}$/*p6mm* as observed for compound ***o*-I^2/14** at 100 °C: (a) before UV irradiation; (b) after UV irradiation for 1 s; (c) after visible light irradiation for 1 s.

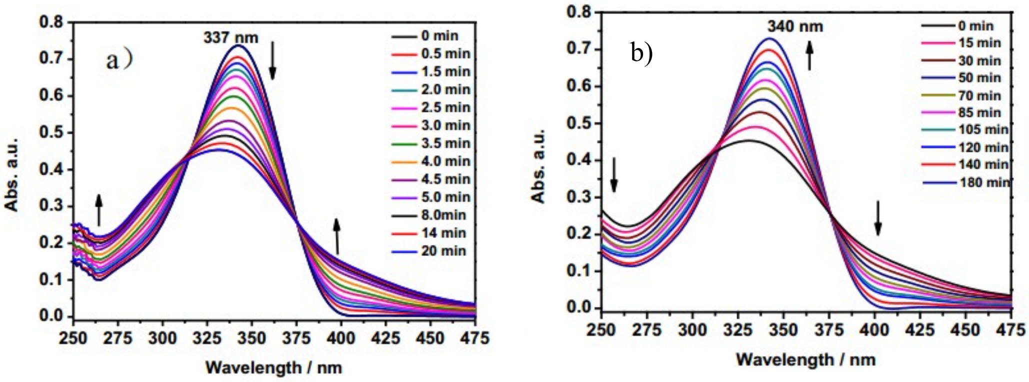

Fig. S6 Time dependent UV spectra of **I^1/14** in CH$_2$Cl$_2$ solution (c = 10^{-5} mol·L^{-1}) (a) from *E*- to *Z*- azobenzene under irradiation with 365 nm light; (b) from *Z*- to *E*-azobenzene under irradiation with visible light.

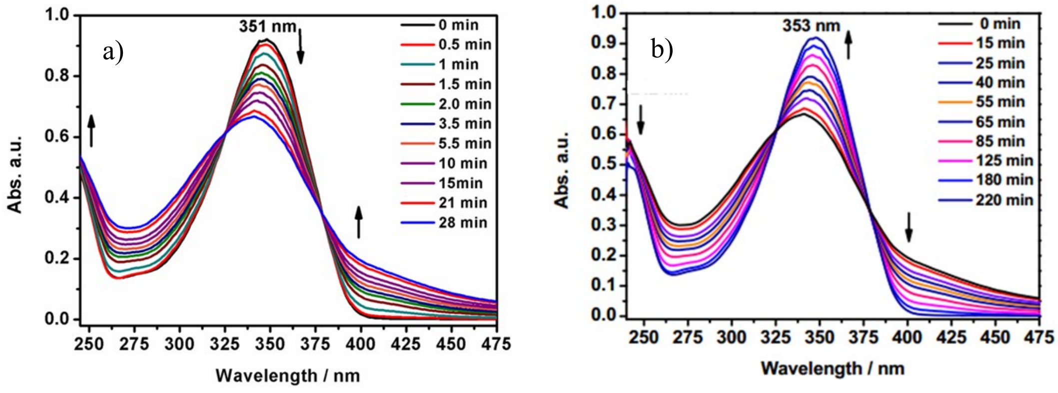

Fig. S7 Time dependent UV spectra of ***o*-I^2/14** in CH$_2$Cl$_2$ solution (c = 10^{-5} mol·L^{-1}) (a) from *E*- to *Z*- azobenzene under irradiation with 365 nm light; (b) from *Z*- to *E*-azobenzene under irradiation with visible light.

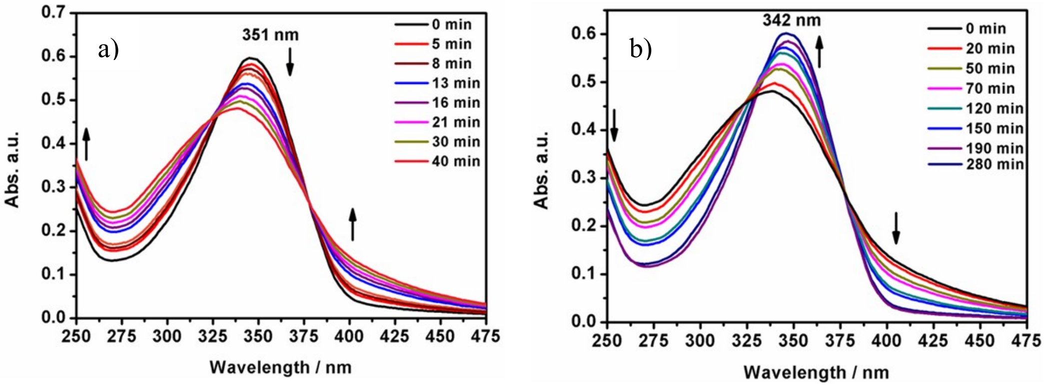

Fig. S8 Time dependent UV spectra of **I^3/14** in CH_2Cl_2 solution (c = 10^{-5} mol·L^{-1}) (a) from *E*- to *Z*- azobenzene under irradiation with 365 nm light; (b) from *Z*- to *E*-azobenzene under irradiation with visible light.

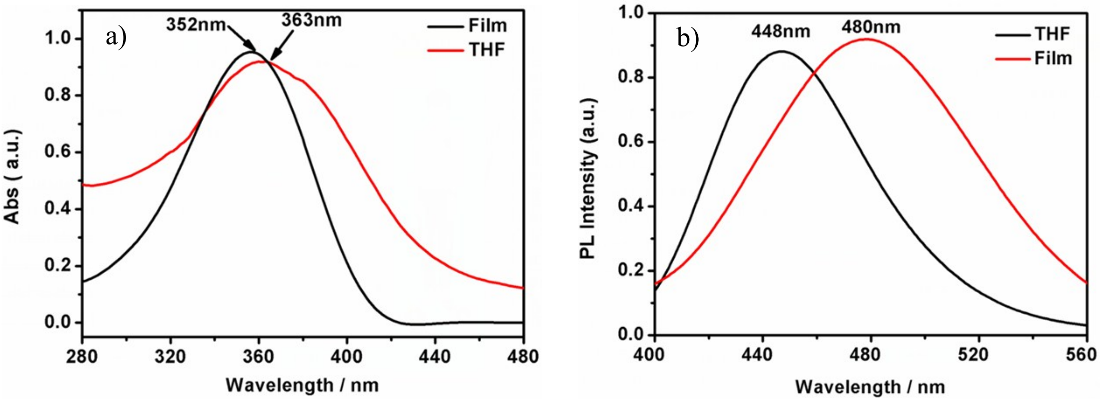

Fig. S9 (a) UV-vis absorption spectra and (b) photoluminescence spectra of compound **I^3/14** in THF solution (10^{-6} M) (red line) and in a solid thin film (black line).

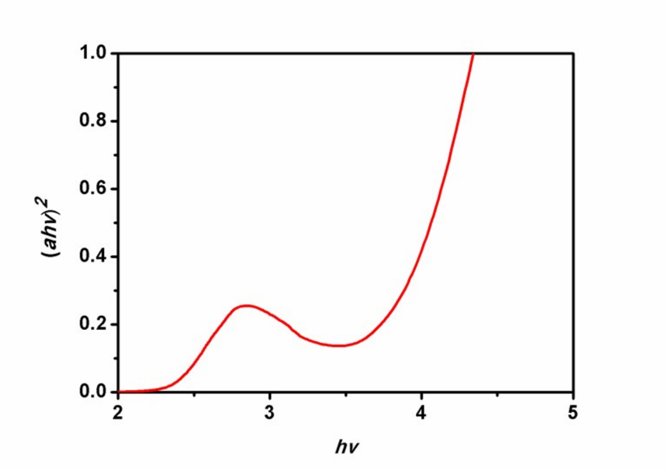

Fig. S10 The calculation of energy band of **I^3/14** in film by UV-vis spectrum.

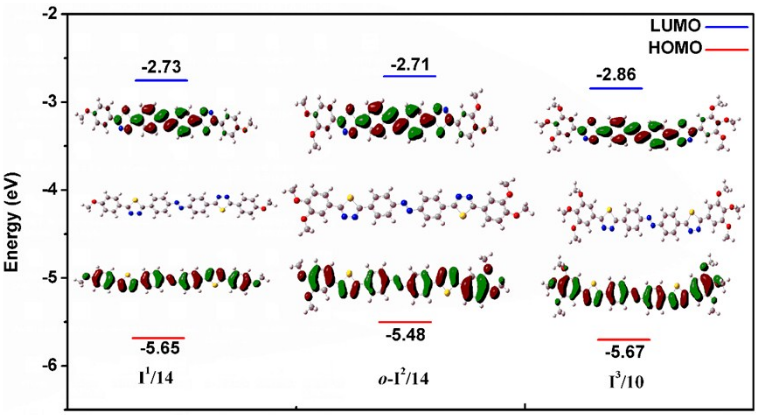

Fig. S11 HOMO orbital and LUMO orbital of **I^1/14**, ***o*-I^2/14**, **I^3/10** calculated using the DFT/B3LYP, 6-31G, d functional.

Table S7 Photophysical properties of the compounds **I^3/10** and **T^3/10$^{[S3]}$**

Comp.	λ_{max}(nm)	λ_{em}(nm)	Stokes shift(nm)
I^3/10	355	448	103
T^3/10	365	480	115

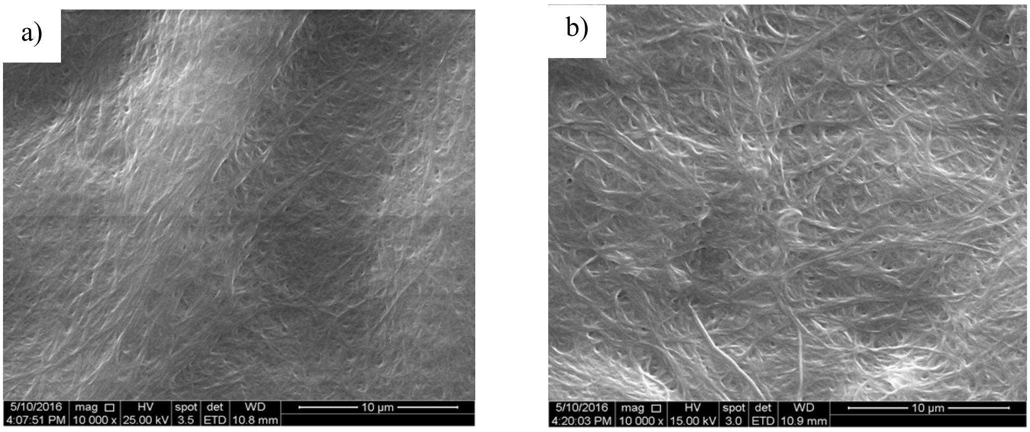

Fig. S12 Selected SEM images of xerogel formed by **I^3/10** in ethanol: a) scale bar is 10 μm; b) scale bar is 10 μm.

2. Synthesis and analytical date

2.1 General procedures for the synthesis of 4-(alkoxy)benzohydrazide (1a/*n*), 3,5-bis(alkoxy) benzohydrazide (1b/*n*), 3,4-bis(alkoxy)benzohydrazide (1c/*n*) and 3,4,5-tris(alkoxy) benzohydrazide (1d/*n*)

Compound **1**was prepared with a modified condition according to the literature procedure.[S3] The appropriate alkoxybenzoate (2.50 mmol) was dissolved in 2-methoxyethanol (20 mL). Then excess hydrazine hydrate (20 mL) was added. The mixture was stirred at 100 °C for 12 h. After cooling, water (40 mL) was added and the resulting white precipitate was collected. The crude product was purified by recrystallized from ethanol.

4-(tetradecyloxy)benzohydrazide 1a/14: R_f = 0.20 (petroleum ether: ethyl acetate = 1:1); colorless solid, m.p.: 98-99°C; yield: 0.73 g, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71-7.68 (d, J = 8.8 Hz, 2 H, 2 Ar**H**), 7.41 (s, 1 H, N**H**), 6.92-6.90 (d, J = 8.8 Hz, 2 H, 2 Ar**H**), 4.11 (s, 2 H, N**H**$_2$), 4.00-3.96 (t, J = 6.8 Hz, 2 H, OC**H**$_2$), 1.82-1.75 (m, 2 H, C**H**$_2$), 1.48-1.41 (m, 2 H, C**H**$_2$). 1.40-1.20 (m, 20 H, 10 C**H**$_2$), 0.89-0.86 (t, J = 6.8 Hz, 3 H, C**H**$_3$).

3,5-bis(octyloxy)benzohydrazide 1b/8: R_f = 0.45 (petroleum ether: ethyl acetate = 1:1); colorless solid, m.p.: 78-79°C; yield: 1.35 g, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.24 (s, 1 H, N**H**), 6.82-6.81 (d, J = 2.0 Hz, 2 H, 2 Ar**H**), 6.58-6.57 (t, J = 2.0 Hz, 1 H, Ar**H**), 4.08 (s, 2 H, N**H**$_2$), 3.97-3.94 (t, J = 6.4 Hz, 4 H, 2 OC**H**$_2$), 1.80-1.73 (m, 4 H, 2 OC**H**$_2$), 1.47-1.40 (m, 4 H, 2 C**H**$_2$), 1.38-1.24 (m, 16 H, 8 C**H**$_2$), 0.90-0.87 (t, J = 6.8 Hz, 6 H, 2 C**H**$_3$).

3,5-bis(dodecyloxy)benzohydrazide 1b/12: R_f = 0.55 (petroleum ether: ethyl acetate = 1:1); colorless solid; yield: 0.94 g, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.25 (s, 1 H, N**H**), 6.82-6.81 (d, J = 2.0 Hz, 2 H, Ar**H**), 6.58-6.57 (d, J = 2.4 Hz, 1 H, Ar**H**), 4.09 (s, 2 H, N**H**$_2$), 3.97-3.94 (t, J = 6.4 Hz, 4 H, 2 OC**H**$_2$), 1.80-1.73 (m, 4 H, 2 OC**H**$_2$), 1.47-1.40 (m, 4 H, 2 C**H**$_2$), 1.38-

1.25 (m, 32 H, 16 C**H**$_2$), 0.90-0.87 (t, *J* = 6.8 Hz, 6 H, 2 C**H**$_3$).

3,4-bis(octyloxy)benzohydrazide 1c/8: R$_f$ = 0.31 (petroleum ether: ethyl acetate = 1:15); colorless solid, m.p.: 103-104 °C (ref.[S4] 100 °C); yield: 0.84 g, 86%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.55 (s, 1 H, N**H**), 7.35-7.34 (d, *J* = 2.0 Hz, 1 H, Ar**H**), 7.25-7.23 (d, *J* = 8.4 Hz, 1 H, Ar**H**), 6.85-6.83 (d, *J* = 8.4 Hz, 1 H, Ar**H**), 4.03-3.99 (t, *J* = 6.8 Hz, 4 H, 2 OC**H**$_2$), 3.72 (s, 2 H, N**H**$_2$), 1.84-1.79 (m, 4 H, 2 C**H**$_2$), 1.49-1.41 (m, 4 H, 2 C**H**$_2$), 1.39-1.23 (t, 16 H, 8 C**H**$_2$), 0.90-0.87 (t, *J* = 6.8 Hz, 6 H, 2 C**H**$_3$).

3,4-bis(dodecyloxy)benzohydrazide 1c/12: R$_f$ = 0.35 (petroleum ether: ethyl acetate = 1:1) ; colorless solid, m.p.: 101-102 °C (ref.[S5] 101 °C); yield: 1.00 g, 89%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.55 (s, 1 H, N**H**), 7.35-7.34 (d, *J* = 2.0 Hz, 1 H, Ar**H**), 7.25-7.23 (d, *J* = 6.4 Hz, 1 H, Ar**H**), 6.85-6.83 (d, *J* = 8.4 Hz, 1 H, Ar**H**), 4.03-4.00 (t, *J* = 8.4 Hz, 4 H, 2 OC**H**$_2$), 3.72 (s, 2 H, N**H**$_2$), 1.84-1.79 (m, 4 H, 2 C**H**$_2$), 1.45-1.44 (m, 4 H, 2 C**H**$_2$), 1.40-1.24 (t, 32 H, 16 C**H**$_2$). 0.90-0.87 (t, *J* = 6.8 Hz, 6H, 2 C**H**$_3$).

3,4-bis(tetradecyloxy) benzohydrazide 1c/14: R$_f$ = 0.40 (petroleum ether: ethyl acetate = 1:1); colorless solid, m.p.: 100-101 °C (ref.[S5] 100 °C); yield: 1.13 g, 85%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.55 (s, 1 H, N**H**), 7.35-7.34 (d, *J* = 2.0 Hz, 1 H, Ar**H**), 7.25-7.23 (d, *J* = 6.4 Hz, 1 H, Ar**H**), 6.85-6.83 (d, *J* = 8.4 Hz, 1 H, Ar**H**), 4.03-4.00 (t, *J* = 8.4 Hz, 4 H, 2 OC**H**$_2$), 3.72 (s, 2 H, N**H**$_2$), 1.84-1.79 (m, 4 H, 2 C**H**$_2$), 1.45-1.44 (m, 4H, 2 C**H**$_2$), 1.40-1.22 (t, 40 H, 20 C**H**$_2$). 0.90-0.87 (t, *J* = 6.8 Hz, 6 H, 2 C**H**$_3$).

3,4,5-tris(octyloxy)benzohydrazide (1d/8): R$_f$ = 0.38 (petroleum ether: ethyl acetate = 1:15); colorless solid, m.p.: 109-111 °C; yield: 1.30 g, 90%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.41 (s, 1 H, N**H**), 6.93 (s, 2 H, 2 Ar**H**), 4.14 (s, 2 H, **NH$_2$**), 4.00-3.96 (t, *J* = 6.8 Hz, 6 H, 3 OC**H**$_2$), 1.83-1.71 (m, 6 H, 3 C**H$_2$**), 1.51-1.42 (m, 6 H, 3 C**H$_2$**), 1.26 (s, 24 H, 12 C**H$_2$**), 0.89-0.86 (t, *J* = 6.8 Hz, 9H, 3 C**H$_3$**).

3,4,5-tris(decyloxy)benzohydrazide (1d/10): R$_f$ = 0.40 (petroleum ether: ethyl acetate = 1:1); colorless solid, m.p.: 113-114 °C (ref.[S3] 113-115 °C); yield: 1.31 g, 87%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.41 (s, 1 H, N**H**), 6.93 (s, 2 H, 2 Ar**H**), 4.14 (s, 2 H, **NH$_2$**), 4.00-3.96 (t, *J* = 6.8 Hz, 6 H, 3 OC**H**$_2$), 1.83-1.70 (m, 6 H, 3 C**H$_2$**), 1.48-1.42 (m, 6 H, 3 C**H$_2$**), 1.38-1.23 (s, 36 H, 18 C**H$_2$**), 0.89-0.86 (t, *J* = 6.8 Hz, 9H, 3 C**H$_3$**).

3,4,5-tris(dodecyloxy)benzohydrazide (1d/12): R$_f$ = 0.45 (petroleum ether: ethyl acetate = 1:1); colorless solid, m.p.: 114-115 °C (ref.[S3] 114-116 °C); yield: 1.50 g, 87%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.41 (s, 1 H, N**H**), 6.93 (s, 2 H, 2 Ar**H**), 4.14 (s, 2 H, **NH$_2$**), 4.00-3.96 (t, *J* = 6.8 Hz, 6 H, 3 OC**H**$_2$), 1.83-1.69 (m, 6 H, 3 C**H$_2$**), 1.48-1.42 (m, 6 H, 3 C**H$_2$**), 1.39-1.22 (s, 48 H, 24 C**H$_2$**), 0.89-0.86 (t, *J* = 6.8 Hz, 9 H, 3 C**H$_3$**).

3,4,5-tris(tetradecyloxy)benzohydrazide (1d/14): R$_f$ = 0.48 (petroleum ether: ethyl acetate = 1:1); colorless solid, m.p.: 109-110 °C; yield: 1.64 g, 85%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.41 (s, 1 H, N**H**), 6.93 (s, 2 H, 2 Ar**H**), 4.14 (s, 2 H, **NH$_2$**), 4.00-3.96 (t, *J* = 6.8 Hz, 6 H, 3

OCH_2), 1.83-1.71 (m, 6 H, 3 CH_2), 1.48-1.42 (m, 6 H, 3 CH_2), 1.40-1.23 (s, 60 H, 30 CH_2), 0.89-0.86 (t, $J = 6.8$ Hz, 9 H, 3 CH_3).

2.2 Procedure for the synthesis of azobenzene-4,4-dicarboxylic acid (2)[S5]

4-Nitrobenzoic acid (4.0 g, 24 mmol) and NaOH (11.5 g, 288 mmol) were added in 50 mL of water and heated until the solid dissolved. Glucose (26.0 g, 144 mmol) in aqueous solution (30 mL) was added dropwise at 70 °C, initially yielding a yellow precipitate and subsequently a brown solution upon further addition of glucose. The mixture was stirred at 70 °C for 12 h and then acetic acid was used to adjust the pH of the solution in the range of 5 to 6, resulting in a light brown precipitate. The precipitate was filtered and then washed with 20 mL of distilled water. Approximately 2.12 g azobenzene-4,4-dicarboxylic acid **2** as light pink powder was obtained and finally dried to constant weight in an oven at 80 °C.
$R_f = 0.46$ (petroleum ether: ethyl acetate = 1:6); light pink soli; yield: 3.24g, 81%; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.46 (s, 2 H, 2 COO**H**), 7.71-7.69 (d, $J = 8.4$ Hz, 4 H, 4 Ar**H**), 6.71-6.69 (d, $J = 8.4$ Hz, 4 H, 4 Ar**H**).

2.3 Procedure for the synthesis of 4,4-bis (chlorocarbonyl) azobenzene (3)[S6]

Azobenzene-4,4-dicarboxylic acid **2** (2.7 g, 10 mmol) was dissolved in 20 mL of thionyl chloride, then the mixture was refluxed at 70 °C for 5 h, yielding a clear red solution. Excess thionyl chloride was removed by distillation, and approximately 2.0 g of crude 4,4-bis(chlorocarbonyl) azobenzene **3** as a red solid was obtained. The obtained product was used directly for the next step without further purification.

2.4 General procedure for the synthesis of 1,2-bis(4-(5-(4-(alkoxy)phenyl)-1,3,4- thiadiazol-2-yl)phenyl)diazene (I^1/n), 1,2-bis(4-(5-(3,5-bis(alkoxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (*m*-I^2/n), 1,2-bis(4-(5-(3,4-bis(alkoxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl) diazene (*o*-I^2/n) and 1,2-bis(4-(5-(3,4,5-tris(alkoxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl) diazene (I^3/n)[S3]

4,4-Bis(chlorocarbonyl)azobenzene **3** (0.27g, 0.90 mmol) was firstly dissolved in dry THF (4 mL) and then added dropwise to a mixture of alkoxybenzohydrazide **1** (2.25 mmol), dry triethylamine (0.18g, 1.80 mmol) and dry THF (20 mL). The reaction mixture was stirred at 70 °C for 12 h. After cooling, THF was evaporated in vacuo and 20 mL water was added to the residue. The mixture was extracted with dichloromethane (3 × 30 mL). The combined extract was washed with water (10 mL) and brine (10 mL), then dried over by anhydrous Na_2SO_4 and concentrated. The resulting crude product **4a/*n*** was directly used for the next reaction. The solution of crude product **4a/*n*** (0.4 mmol) in dry toluene (10 mL) was added to P_2S_5 (3.2 mmol) at room temperature, then heated to 100 °C and refluxed for 12 h. After cooling, NaOH saturated solution was added dropwise to the mixture until the excess P_2S_5 disappeared. Then the mixture was extracted with dichloromethane (3 × 30 mL). The combined extract was washed with water (10 mL) and brine (10 mL), then dried over by anhydrous Na_2SO_4 and concentrated. The crude products were further purified through column chromatography (petroleum ether: dichloromethane = 3:1).

1,2-bis(4-(5-(4-(tetradecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (I^1/14): R_f = 0.31 (petroleum ether: ethyl acetate = 2:1); pale yellow solid, yield: 0.19 g, 21%; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.91-7.89 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 7.81-7.79 (d, *J* = 8.0 Hz, 4 H, 4 Ar**H**), 6.98-6.96 (d, *J* = 8.8 Hz, 4 H, 4 Ar**H**). 6.74-6.72 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 4.03-4.00 (t, *J* = 6.4 Hz, 4 H, 2 OC**H$_2$**), 1.84-1.77 (m, 4 H, 2 OCH$_2$C**H**$_2$), 1.48-1.43 (m, 4 H, 2 OCH$_2$CH$_2$C**H**$_2$), 1.37-1.23 (m, 40 H, 20 C**H**$_2$), 0.89-0.86 (t, *J* = 6.4 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm) = 167.6 (2 C), 166.4 (2 C), 161.2 (2 C), 149.0 (2 C), 129.3 (4 C), 129.2 (4 C), 122.9 (2 C), 120.5 (2 C), 114.9 (4 C), 114.8 (4 C), 68.2 (2 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (2 C). Elemental Analysis calcd (%) for $C_{56}H_{74}N_6O_2S_2$ (927.36): C 72.53, H 8.04, N 9.06; found: C 72.35, H 8.02, N 9.04.

1,2-bis(4-(5-(3,5-bis(octyloxy) phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (*m*-I^2/8): R_f = 0.38 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.29 g, 32%; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.82-7.81 (dd, *J* = 1.6, 1.6 Hz, 4 H, 4 Ar**H**), 7.12-7.11 (d, *J* = 2.0 Hz, 4 H, 4 Ar**H**), 6.75-6.73 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**). 6.56-6.55 (t, *J* = 2.4 Hz,,2 H, 2 Ar**H**), 4.03-3.99 (t, *J* = 6.4 Hz, 8 H, 4 OC**H**$_2$), 1.83-1.76 (m, 8 H, 4 OCH$_2$C**H**$_2$), 1.50-1.43 (m, 8 H, 4 OCH$_2$CH$_2$C**H**$_2$), 1.38-1.26 (m, 32 H, 16 C**H**$_2$), 0.91-0.87 (t, *J* = 6.4 Hz, 12 H, 4 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$); δ (ppm) = 168.5 (2 C), 166.7 (2 C), 160.6 (4 C), 149.3 (2 C), 131.9 (2 C), 129.5 (4 C), 120.3 (2 C), 114.9 (4 C), 106.2 (4 C), 104.0 (2 C), 68.4 (4 C), 31.8 - 22.7 (multi-carbon in alkyl chain), 14.1 (4 C). Elemental Analysis calcd (%) for $C_{60}H_{82}N_6O_4S_2$ (1015.46): C 70.97, H 8.14, N 8.28; found: C 70.79, H 8.12, N 8.26.

1,2-bis(4-(5-(3,5-bis(dodecyloxy) phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (*m*-I^2/12): R_f = 0.40 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.40 g, 35%; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.81-7.79 (dd, *J* = 1.6, 2.0 Hz, 4 H, 4 Ar**H**), 7.12-7.11 (d, *J* = 2.0 Hz, 4 H, 4 Ar**H**), 6.75-6.72 (d, *J* = 8.8 Hz, 4 H, 4 Ar**H**). 6.56-6.55 (t, *J* = 2.4 Hz, 2 H, 2 Ar**H**), 4.02-3.99 (t, *J* = 6.4 Hz, 8 H, 4 OC**H**$_2$), 1.82-1.76 (m, 8 H, 4 OCH$_2$C**H**$_2$), 1.48-1.42 (m, 8 H, 4 OCH$_2$CH$_2$C**H**$_2$), 1.33-1.22 (m, 64 H, 32 C**H**$_2$), 0.89-0.86 (t, *J* = 6.4 Hz, 12 H, 4 C**H**$_3$). ^{13}C NMR (100 MHz, CDCl$_3$); δ (ppm) = 168.5 (2 C), 166.7 (2 C), 160.6 (4 C), 149.2 (2 C), 131.9 (2 C), 129.5 (4 C), 120.4 (2 C), 114.9 (4 C), 106.1 (4 C), 104.0 (2 C), 68.4 (4 C), 31.8-22.7 (multi-carbon in alkyl chain), 14.1 (4 C). Elemental Analysis calcd (%) for $C_{76}H_{114}N_6O_4S_2$ (1239.89): C 73.62, H 9.27, N 6.78; found: C 73.79, H 9.29, N 6.80.

1,2-bis(4-(5-(3,4-bis (octyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (*o*-I^2/8): R_f = 0.40 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.39 g, 43%; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.81-7.79 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 7.63-7.62 (d, *J* = 2.0 Hz, 2 H, 2 Ar**H**), 7.42-7.40 (dd, *J* = 2.0, 1.6 Hz, 2 H, 2 Ar**H**), 6.92-6.90 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.75-6.73 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 4.11-4.04 (m, 8 H, 4 OC**H**$_2$), 1.88-1.83 (m, 8 H, 4 OCH$_2$C**H**$_2$), 1.50-1.47 (t, *J* = 6.4 Hz, 8 H, 4 OCH$_2$CH$_2$C**H**$_2$), 1.39-1.26 (m, 32 H, 16 C**H**$_2$), 0.90-0.87 (t, *J* = 6.4 Hz, 12 H, 4 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm) = 167.7 (2 C), 166.7 (2 C), 151.5 (2 C), 149.4 (2 C), 149.1 (2 C), 129.4 (4 C), 123.2 (2 C), 121.4 (2 C), 120.6 (2 C), 114.9 (4 C), 113.1 (2 C), 112.0 (2 C), 69.4 (2 C), 69.2 (2 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (4 C). Elemental Analysis calcd (%) for $C_{60}H_{82}N_6O_4S_2$ (1015.46): C 70.97, H 8.14, N 8.28; found: C 71.15, H 8.16, N 8.30.

1,2-bis(4-(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (*o*-I^2/12): R_f = 0.43 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.41 g, 37%; ^{1}H NMR (400 MHz, CDCl$_3$) *δ* (ppm) = 7.80-7.78 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 7.63-7.62 (d, *J* = 2.0 Hz, 2 H, 2 Ar**H**), 7.41-7.38 (dd, *J* = 2.0, 2.0 Hz, 2 H, 2 Ar**H**), 6.92-6.90 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.75-6.73 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 4.10-4.03 (m, 8 H, 4 OC**H**$_2$), 1.87-1.83 (m, 8 H, 4 OCH$_2$C**H**$_2$), 1.50-1.46 (t, *J* = 6.4 Hz, 8 H, 4 OCH$_2$CH$_2$C**H**$_2$), 1.50-1.20 (m, 64 H, 32 C**H**$_2$), 0.89-0.86 (t, *J* = 6.4 Hz, 12 H, 4 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$); *δ* (ppm) = 167.7 (2 C), 166.5 (2 C), 151.5 (2 C), 149.4 (2 C), 149.1 (2 C), 129.4 (4 C), 123.2 (2 C), 121.4 (2 C), 120.6 (2 C), 114.9 (4 C), 113.1 (2 C), 112.0 (2 C), 69.3 (2 C), 69.2 (2 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (4 C). Elemental Analysis calcd (%) for $C_{76}H_{114}N_6O_4S_2$ (1239.89): C 73.62, H 9.27, N 6.78; found: C 73.78, H 9.29, N 6.79.

1,2-bis(4-(5-(3,4-bis(tetradecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (*o*-I^2/14): R_f = 0.46 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.54 g, 43%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.80-7.78 (d, *J* = 8.0 Hz, 4 H, 4 Ar**H**), 7.63 (s, 2 H, 2 Ar**H**), 7.41-7.39 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.92-6.90 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.74-6.72 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 4.11-4.03 (m, 8 H, 4 OC**H**$_2$), 1.85-1.81 (m, 8 H, 4 OCH$_2$C**H**$_2$), 1.51-1.47 (m, 8 H, 4 CH$_2$CH$_2$C**H**$_2$), 1.38-1.23 (m, 80 H, 40 C**H**$_2$), 0.89-0.86 (t, *J* = 6.4 Hz, 12 H, 4 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$); *δ* (ppm) = 167.7 (2 C), 166.5 (2 C), 151.5 (2 C), 149.4 (2 C), 149.1 (2 C), 129.4 (4 C), 123.2 (2 C), 121.4 (2 C), 120.6 (2 C), 114.9 (4 C), 113.1 (2 C), 112.0 (2 C), 69.3 (2 C), 69.2 (2 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (4 C). Elemental Analysis calcd (%) for $C_{84}H_{130}N_6O_4S_2$ (1352.10): C 74.62, H 9.69, N 6.22; found: C 74.79, H 9.71, N 6.23.

1,2-bis(4-(5-(3,4,5-tris(octyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (I^3/8): R_f = 0.47 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.30 g, 26%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.81-7.79 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 7.18 (s, 4 H, 4 Ar**H**), 6.75-6.73 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 4.07-4.00 (m, 12 H, 6 OC**H**$_2$), 1.87-1.72 (m, 12 H, 6 OCH$_2$C**H**$_2$), 1.50-1.45 (m, 12 H, 6 OCH$_2$CH$_2$C**H**$_2$), 1.39-1.23 (s, 48 H, 24 C**H**$_2$), 0.89-0.85 (t, *J* = 6.4 Hz, 18 H, 6 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$); *δ* (ppm) = 168.1 (2 C), 166.7 (2 C), 153.5 (4 C), 149.2 (2 C), 140.5 (2 C), 129.4 (4 C), 125.3 (2 C), 120.4 (2 C), 114.9 (4 C), 106.3 (4 C), 73.6 (2 C), 69.4 (4 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (6 C). Elemental Analysis calcd (%) for $C_{76}H_{114}N_6O_6S_2$ (1271.89): C 71.77, H 9.03, N 6.61; found: C 71.89, H 9.01, N 6.60.

1,2-bis(4-(5-(3,4,5-tris(decyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (I^3/10): R_f = 0.48 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.39 g, 30%; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) = 7.80-7.78 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 7.17 (s, 4 H, 4 Ar**H**), 6.74-6.72 (d, *J* = 8.4 Hz, 4 H, 4 Ar**H**), 4.06-4.01 (m, 12 H, 6 OC**H**$_2$), 1.85-1.73 (m, 12 H, 6 OCH$_2$C**H**$_2$), 1.50-1.44 (m, 12 H, 6 OCH$_2$CH$_2$C**H**$_2$), 1.38-1.20 (s, 72 H, 36 C**H**$_2$), 0.89-0.86 (t, 18 H, *J* = 6.4 Hz, 6 C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$), *δ* (ppm) = 168.1 (2 C), 166.7 (2 C), 153.5 (4 C), 149.2 (2 C), 140.5 (2 C), 129.4 (4 C), 125.3 (2 C), 120.4 (2 C), 114.9 (4 C), 106.3 (4 C), 73.6 (2 C), 69.4 (4 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (6 C). Elemental Analysis calcd (%) for $C_{88}H_{138}N_6O_6S_2$ (1440.20): C 73.39, H 9.66, N 5.84; found: C 73.20, H 9.64, N 5.82.

1,2-bis(4-(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (I^3/12): R_f = 0.50 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.43 g, 30%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.80-7.78 (d, J = 8.4 Hz, 4 H, 4 Ar**H**), 7.18 (s, 4 H, 4 Ar**H**), 6.74-6.72 (d, J = 8.4 Hz, 4 H, 4 Ar**H**), 4.07-4.00 (m, 12 H, 6 $OC\mathbf{H}_2$), 1.85-1.72 (m, 12 H, 6 $OCH_2C\mathbf{H}_2$), 1.52-1.45 (m, 12 H, 6 $OCH_2CH_2C\mathbf{H}_2$), 1.35-1.20 (m, 96 H, 48 $C\mathbf{H}_2$), 0.89-0.86 (t, J = 6.4 Hz, 18 H, 6 $C\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) = 168.1 (2 C), 166.7 (2 C), 153.5 (4 C), 149.2 (2 C), 140.6 (2 C), 129.4 (4 C), 125.3 (2 C), 120.4 (2 C), 114.9 (4 C), 106.4 (4 C), 73.6 (2 C), 69.4 (4 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (6 C). Elemental Analysis calcd (%) for $C_{100}H_{162}N_6O_6S_2$ (1608.52): C 74.67, H 10.15, N 5.22; found: C 74.46, H 10.13, N 5.21.

1,2-bis(4-(5-(3,4,5-tris(tetradecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)diazene (I^3/14): R_f = 0.52 (petroleum ether: ethyl acetate = 2:1); faint yellow solid, yield: 0.37 g, 25%; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.81-7.79 (d, J = 6.0 Hz, 4 H, 4 Ar**H**), 7.18 (s, 4 H, 4 Ar**H**), 6.74-6.73 (d, J = 5.6 Hz, 4 H, 4 Ar**H**), 4.07-4.01 (m, 12 H, 6 $OC\mathbf{H_2}$), 1.85-1.76 (m, 12 H, 6 $OCH_2C\mathbf{H_2}$), 1.65-1.44 (m, 12 H, 6 $CH_2CH_2C\mathbf{H_2}$), 1.38-1.22 (s, 120 H, 60 $C\mathbf{H_2}$), 0.88-0.87 (t, J = 6.4 Hz, 18 H, 6 $C\mathbf{H_3}$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) = 168.1 (2 C), 166.7 (2 C), 153.5 (4 C), 149.2 (2 C), 140.5 (2 C), 129.4 (4 C), 125.3 (2 C), 120.4 (2 C), 114.9 (4 C), 106.3 (4 C), 73.6 (2 C), 69.4 (4 C), 31.9-22.7 (multi-carbon in alkyl chain), 14.1 (6 C). Elemental Analysis calcd (%) for $C_{112}H_{186}N_6O_6S_2$ (1776.84): C 75.71, H 10.55, N 4.73; found: C 75.55, H 10.53, N 4.72.

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