Supporting Information

For

Transforming a C_3-Symmetrical Liquid Crystal to a π-Gelator by Alkoxy Chain Variation

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1. Materials and Methods

1.1. Synthesis-General Procedures

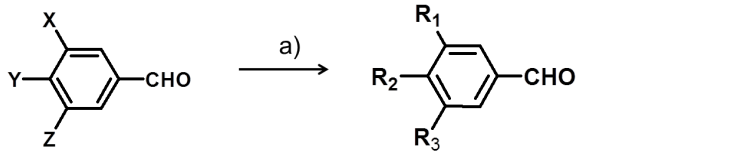
Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. The solvents were purified and dried by standard methods prior to use. The reactions were monitored using thin layer chromatography (TLC) on silica gel 60 F_{254} (0.2 mm; Merck). Visualization was accomplished using UV lamp (365 nm). Column chromatography was performed on glass columns of different sizes hand packed with silica gel 60 (particle size 0.040–0.063 mm, Merck).

1.2. Synthesis-Characterization Techniques

NMR spectra were measured on a 300 or 500 MHz Bruker Avance DPX spectrometer. Chemical shifts are reported in parts per million (ppm) using tetramethylsilane (TMS) (δ_H = 0 ppm) as an internal reference. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet) and m (multiplet). Mass spectra (MS) were recorded on a JEOL JSM 600 fast atom bombardment (FAB) high-resolution mass spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu AXIMA-CFR PLUS spectrometer using α-cyano-4-hydroxycinnamic acid as the matrix.

1.3. Scheme for the Synthesis

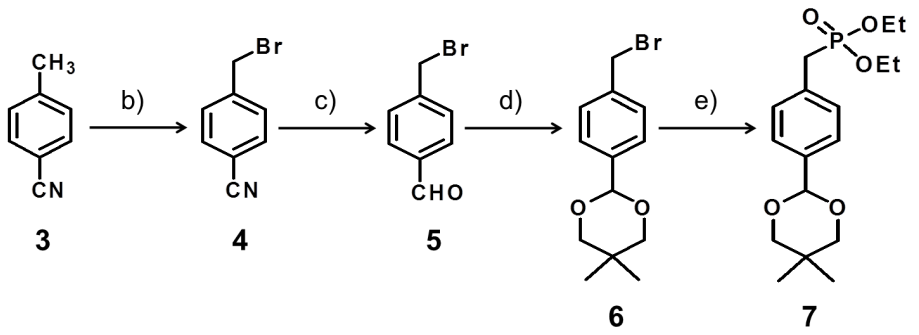
1.3.1. Synthesis



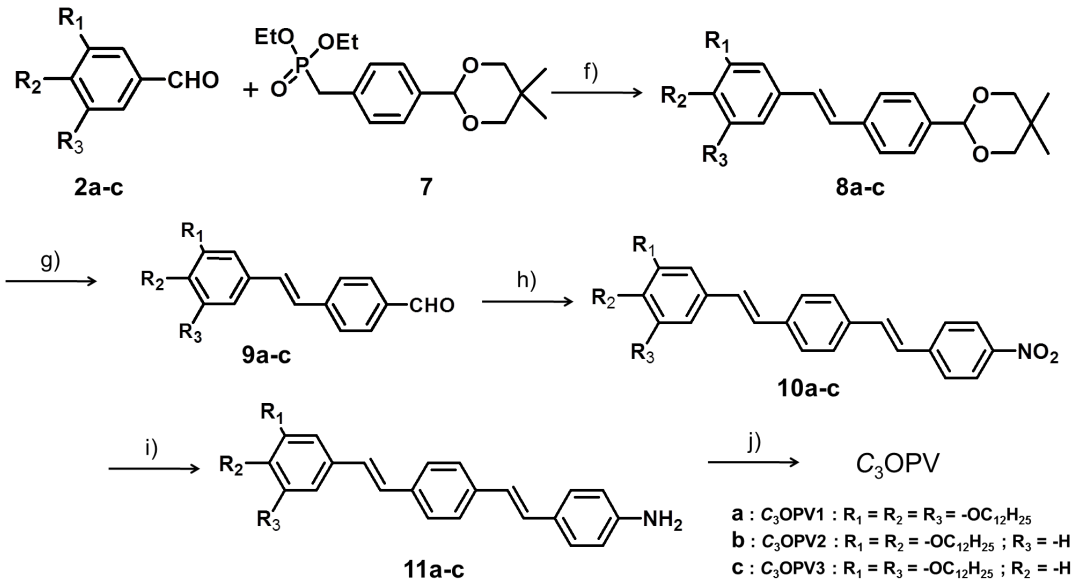
1 **a : X = Y = Z = OH**
b : X = Y = OH ; Z = H
c : X = Z = OH ; Y = H

2 **a : $R_1 = R_2 = R_3 = -OC_{12}H_{25}$**
b : $R_1 = R_2 = -OC_{12}H_{25}$; $R_3 = -H$
c : $R_1 = R_3 = -OC_{12}H_{25}$; $R_2 = -H$

Scheme S1. Reagent and conditions: (a) 1-bromododecane, K_2CO_3, DMF, 70 ºC, 14 h, 90-95%.



Scheme S2. Reagent and conditions: (b) *N*-bromosuccinimide, AIBN, CCl_4, 80 ºC, 12 h, 90%;[S1,S2] (c) DIBALH, dry toluene, 0 ºC, 1 h, 70%;[S1,S2] (d) 2,2-dimethyl 1,3-propanediol, dry benzene, pyridinium hydrochloride (catalytic amount) 100 ºC, 10 h, 80%;[S3] (e) triethylphosphite, 160 ºC, 8 h, 90%.[S1]



Scheme S3. Reagents and conditions: (f) NaH, dry THF, rt, 5 h; (g) trifluoroacetic acid, CH_2Cl_2, rt, 2 h; (h) diethyl(4-nitrobenzyl)phosphonate, NaH, dry THF, rt, 5 h; (i) stannous chloride, dry THF, 70 ºC, 4 h; (j) trimesic acid chloride, Et_3N, dry CH_2Cl_2, rt, 6 h, 45% (***C*$_3$OPV1**), 50% (***C*$_3$OPV2**) and 42% (***C*$_3$OPV3**).

Preparation of 3,4,5-tris-dodecyloxy-benzaldehyde (2a): A mixture of 3,4,5-trihydroxy benzaldehyde (2 g, 13 mmol), potassium carbonate (5 g) was mixed well in dry DMF (60 ml). The 1-bromododecane (11.00 g, 10.50 mL, 44 mmol) was added drop wise and the reaction mixture was stirred at 70 ºC for 14 h. After checking the completion of the reaction using TLC, the reaction mixture was cooled to room temperature and poured to ice water. The precipitate thus formed was filtered. The crude product was then purified by silica gel column chromatography using 5% ethyl acetate-*n*-hexane as the eluent. The product was then precipitated by adding methanol into a concentrated solution of dichloromethane. Yield: 94% ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.83 (s, 1H), 7.08 (s, 2H), 4.06-4.01 (m, 6H), 1.83- 1.75 (m, 6H),

1.48-1.26 (m, 54H), 0.88-0.86 (t, 9H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{43}H_{78}O_4$ is 659.59; found 659.48.

Preparation of 4-bromomethyl-benzonitrile (4):[S1,S2] To a solution of 4-methyl-benzonitrile (**3**) (1 g, 8.32 mmol) in 30 mL of dry carbon tetrachloride was added *N*-bromosuccinimide (1.77 g, 10 mmol) and AIBN. The reaction mixture was refluxed for 12 h. The hot solution was then filtered, concentrated and kept overnight for recrystallization and the product obtained filtered and dried. Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63-7.68 (m, 2H), 7.26-7.51 (m, 2H), 4.48 (s, 1H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for C_8H_6BrN is 197.04; found 196.07.

Preparation of 4-bromomethyl-benzaldehyde (5):[S1,S2] Compound **4** (4-(bromomethyl)benzonitrile) (1 g, 5.1 mmol) was dissolved in 10 ml of toluene and cooled at 0 ºC. A portion of 1.08 M DIBAL-H in *n*-hexane (2 equiv.) was added drop wise under nitrogen atmosphere. The solution was stirred for another hour at 0 ºC. Chloroform (75 ml) was added then followed by 10% hydrochloric acid (150 ml) and the solution was stirred at room temperature for another hour. The organic layer was separated washed with distilled water and dried over anhydrous Na_2SO_4 and filtered. The solvent was almost completely removed from the filtrate under reduced pressure and the residue was cooled, filtered and washed with cold *n*-hexane and dried at 50 ºC under vacuum. Yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 7.86 (m, 2H), 7.57 (m, 2H), 4.52 (s, 2H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for C_8H_7BrO is 200.04; found 200.76.

Preparation of 2-(4-bromomethyl-phenyl)-5,5-dimethyl-[1,3]dioxane (6):[S3] Compound **5** (4-(bromomethyl)benzaldehyde) (0.5 g, 1 mmol), 2,2-dimethyl-1,3-propandiol (0.3 g, 2.88 mmol) and catalytic amount of pyridinium hydrochloride were dissolved in dry benzene. The solution is then refluxed for 10 h at 100 ºC. The side product water was separated from benzene using a dean-stark. After the completion of the reaction the excess benzene was distilled off and the residue is dissolved in dichloromethane. The compound was then extracted, dried over anhydrous Na_2SO_4. The product was then further purified using column chromatography over silica gel (30% $CHCl_3$-*n*-hexane). Yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61-7.49 (m, 2H), 7.41-7.38 (m, 2H), 5.39 (s, 1H), 4.59 (s, 2H), 3.79-3.63 (dd, 4H), 1.29 (s, 3H), 0.80 (s, 3H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{13}H_{17}BrO_2$: 286.18; found 287.5.

Preparation of [4-(5,5-dimethyl-[1,3]dioxan-2-yl)-benzyl]-phosphonic acid diethyl ester (7):[S1] A mixture of triethyl phosphite (2.0 mL, 1.94 g, 11.6 mmol) and **6** (1.25 g, 5.1 mmol) was heated at 160 °C. The generated bromoethane was distilled off, as was the excess triethyl phosphite after a reaction time of 8 h, and the residue was purified by column chromatography over basic alumina using ethylacetate as an eluent. Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46-7.43 (d, 2H), 7.31-7.28 (d, 2H), 5.37 (s, 1H), 4.13-3.96 (q, 4H), 3.78-3.62 (m, 4H), 3.18-3.11 (d, 2H), 1.36-1.21 (t, 6H), 0.79 (s, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{17}H_{27}O_5P$ is 343.37; found 343.16.

Preparation of 5,5-Dimethyl-2-{4-[2-(3,4,5-tris-dodecyloxy-phenyl)-vinyl]-phenyl}-[1,3]dioxane (8a): Both the compound **2a** (0.4 g, 0.65 mmol) and compound **7** (diethyl 4-(2, 2-dimethyl-1, 3-dioxan-5-yl)benzylphosphate) (0.35 g, 1.2 mmol) was taken in a two neck round bottom flask purged with argon. Dry THF was then added to the flask using a pressure equalizer. Small amount of sodium hydride was then added to the reaction mixture. The mixture was stirred for 5 h at room temperature. The reaction mixture was then extracted with chloroform and dried over anhydrous Na_2SO_4. The product thus obtained was purified by reprecipitation by adding excess methanol into chloroform solution. The resulting product was then further purified by column chromatography over silica gel using 40% $CHCl_3$-*n*-hexane as an eluent. Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46-7.16 (m, 4H), 6.96-6.84 (m, 2H), 6.6 (s, 2H), 5.32 (s, 1H), 3.95-3.86 (m, 6H), 3.7-3.45 (m, 4H), 1.64-1.21 (m, 60H), 0.82-0.81 (t, 9H), 0.79 (s, 3H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{56}H_{94}O_5$ is 848.34; found 847.70.

Preparation of 4-[2-(3,4,5-tris-dodecyloxy-phenyl)-vinyl]-benzaldehyde (9a): Compound **8a** (0.4 g, 0.47 mmol) and trifluoroacetic acid in dichloromethane was stirred at room temperature for 2 h. The organic layer was then washed with water dried and evaporated to dryness. The product was then purified by column chromatography over silica gel using 30% $CHCl_3$-*n*-hexane as an eluent. Yield: 92%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.88-7.85 (d, 2H), 7.65-7.62 (d, 2H), 7.19-6.98 (m, 2H), 6.74 (s, 2H), 4.05-3.96 (t, 6H), 1.83-1.75 (m, 6H), 1.48-1.26 (m, 58H), 0.88-0.86 (t, 9H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{51}H_{84}O_4$ is 762.21; found 762.40.

Preparation of 1,2,3-tris-dodecyloxy-5-(2-{4-[2-(4-nitro-phenyl)-vinyl]-phenyl}-vinyl)-benzene (10a): The compound **9a** (0.080 g, 0.1 mmol) and the compound (diethyl 4-nitrobenzylphosphonate) (0.082 g, 0.3 mmol) were mixed in a two-necked round bottom flask purged with argon. The compounds were then dissolved in dry THF and sodium hydride was added. The reaction mixture was then stirred for 5 h. After the completion of the reaction checked by TLC, the reaction mixture was extracted using chloroform and washed with water for several times. The combined extracts were then dried over anhydrous Na_2SO_4. The product thus obtained was purified by reprecipitation by adding excess methanol into chloroform solution. The resulting product was then further purified by column chromatography over silica gel using 30% $CHCl_3$-*n*-hexane as an eluent. Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28-8.21 (m, 2H), 7.71-7.63 (m, 2H), 7.53 (s, 4H), 7.18-7.1 (m, 2H), 7.04-6.95 (m, 2H), 6.73 (s, 2H), 4.05-3.98 (t, 6H), 1.83-1.76 (t, 6H), 1.56-1.27 (m, 57H), 0.88-0.86 (t, 9H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{58}H_{89}NO_5$ is 881.33; found 882.10.

Preparation of 4-(2-{4-[2-(3,4,5-tris-dodecyloxy-phenyl)-vinyl]-phenyl}-vinyl)-phenylamine (11a): The OPV nitro compound **10a** (0.10 g, 0.11 mmol), stannous chloride in THF containing four drops of 37% hydrochloric acid was refluxed at around 70 °C for 4 h. The reaction mixture was then diluted with 50 ml dichloromethane and washed once with 0.1 M sodium bicarbonate solution and two times with water. The organic layer was then filtered through a silica pad using

dichloromethane as the eluent to afford the corresponding amino derivative. The product thus obtained was purified by reprecipitation by adding excess methanol into dichloromethane solution. Yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5-7.28 (m, 4H), 7.19-7.07 (m, 2H), 7.04-6.88 (m, 3H), 6.81-6.79 (m, 3H), 6.4-6.38 (d, 2H), 4.69 (s, 2H), 3.99-3.9 (t, 6H), 1.83-1.76 (t, 6H), 1.51-1.3 (m, 57H), 0.88-0.87 (t, 9H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{58}H_{91}NO_3$ is 851.35; found 852.10.

Preparation of 3,4-bis-dodecyloxy-benzaldehyde (2b): Synthesis of **1b** is carried out by following the same procedure for the synthesis of compound **2a**. Yield: 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.83 (s, 1H), 7.42-7.40 (m, 2H), 6.96-6.95 (d, 1H), 4.13-4.06 (m, 4H), 1.83- 1.75 (m, 4H), 1.48-1.26 (m, 36H), 0.88-0.86 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{31}H_{54}O_3$ is 475.76; found 474.31.

Preparation of 2-{4-[2-(3,4-bis-dodecyloxy-phenyl)-vinyl]-phenyl}-5,5-dimethyl-[1,3]dioxane (8b): Synthesis of **8b** is carried out by following the same procedure for the synthesis of compound **8a**. Yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92-7.91 (m, 2H), 7.6-7.45 (m, 4H), 6.89-6.86 (m, 3H), 5.32 (s, 1H), 3.95-3.86 (m, 4H), 3.7-3.45 (m, 4H), 1.64-1.21 (m, 40H), 0.82-0.81 (t, 9H), 0.79 (s, 3H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{56}H_{94}O_5$ is 664.02; found 663.45.

Preparation of 4-[2-(3,4-bis-dodecyloxy-phenyl)-vinyl]-benzaldehyde (9b): Synthesis of **9b** is carried out by following the same procedure for the synthesis of compound **9a**. Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.92-7.91 (m, 2H), 7.7- 7.54 (m, 4H), 6.89-6.86 (m, 3H), 4.05-3.96 (t, 4 H), 1.83-1.75 (m, 4H), 1.48-1.26 (m, 36H), 0.88-0.86 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{51}H_{84}O_4$ is 577.89; found 577.90.

Preparation of 1,2-Bis-dodecyloxy-4-(2-{4-[2-(4-nitro-phenyl)-vinyl]-phenyl}-vinyl)-benzene (10b): Synthesis of **10b** is carried out by following the same procedure for the synthesis of compound **10a**. Yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28-8.21 (m, 2H), 7.71-7.63 (m, 2H), 7.53 (s, 4H), 7.18-7.1 (m, 2H), 7.04-6.95 (m, 2H), 6.95- 6.73 (m, 3H), 4.05-3.98 (t, 4H), 1.83-1.76 (t, 4H), 1.56-1.27 (m, 37H), 0.88-0.86 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{58}H_{89}NO_5$ is 697.01; found 698.10.

Preparation of 4-(2-{4-[2-(3,4-bis-dodecyloxy-phenyl)-vinyl]-phenyl}-vinyl)-phenylamine Compound (11b): Synthesis of **11b** is carried out by following the same procedure for the synthesis of compound **11a**. Yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5-7.28 (m, 4H), 7.19-7.07 (m, 2H), 7.04-6.88 (m, 3H), 6.81-6.79 (m, 3H), 6.4-6.38 (d, 3H), 4.69 (s, 2H), 3.99-3.9 (t, 4H), 1.83-1.76 (t, 4H), 1.51-1.3 (m, 37H), 0.88-0.87 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{58}H_{91}NO_3$ is 851.35; found 852.10.

Preparation of 3,4-bis-dodecyloxy-benzaldehyde (2c): Synthesis of **2c** is carried out by following the same procedure for the synthesis of compound **2a**. Yield: 92%; ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 9.89 (s, 1H), 6.99-6.98 (d, 2H), 6.96 (s, 1H), 3.99-3.97 (t, 4H), 1.81- 1.75 (m, 4H), 1.48-1.42 (m, 36H), 0.89-0.88 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{31}H_{54}O_3$ is 475.76; found 475.01.

Preparation of 2-{4-[2-(3,4-bis-dodecyloxy-phenyl)-vinyl]-phenyl}-5,5-dimethyl-[1,3]dioxane (8c): Synthesis of **8c** is carried out by following the same procedure for the synthesis of compound **8a**. Yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53-7.51 (m, 2H), 7.23-7.18 (m, 4H), 6.96-6.93 (m, 3H), 5.31 (s, 1H), 3.99-3.97 (t, 4H), 3.7-3.45 (m, 4H), 1.64-1.21 (m, 40H), 0.89-0.87 (t, 9H), 0.79 (s, 3H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{56}H_{94}O_5$ is 664.02; found 663.64.

Preparation of 4-[2-(3,4-bis-dodecyloxy-phenyl)-vinyl]-benzaldehyde (9c): Synthesis of **9c** is carried out by following the same procedure for the synthesis of compound **9a**. Yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.53-7.51 (m, 2H), 7.31-7.28 (m, 4H), 6.96-6.93 (m, 3H), 3.99-3.96 (t, 4 H), 1.83-1.75 (m, 4H), 1.48-1.41 (m, 36H), 0.89-0.88 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{51}H_{84}O_4$ is 577.89; found 577.73.

Preparation of 1,2-Bis-dodecyloxy-4-(2-{4-[2-(4-nitro-phenyl)-vinyl]-phenyl}-vinyl)-benzene (10c): Synthesis of **10c** is carried out by following the same procedure for the synthesis of compound **10a**. Yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15-8.09 (m, 2H), 7.73-7.61 (m, 2H), 7.53-7.47 (m, 4H), 7.23-7.18 (m, 4H), 6.96-6.92 (m, 3H), 3.99-3.95 (t, 4 H), 1.83-1.75 (m, 4H), 1.48-1.39 (m, 36H), 0.89-0.88 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{58}H_{89}NO_5$ is 697.01; found 698.10.

Preparation of 4-(2-{4-[2-(3,4-bis-dodecyloxy-phenyl)-vinyl]-phenyl}-vinyl)-phenylamine Compound (11c): Synthesis of **11c** is carried out by following the same procedure for the synthesis of compound **11a**. Yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52-7.27 (m, 4H), 7.25-7.19 (m, 2H), 6.96-6.92 (m, 3H), 6.8-6.79 (m, 4H), 6.53-6.51 (m, 2H), 4.54 (s, 2H), 3.99-3.9 (t, 4H), 1.83-1.76 (t, 4H), 1.49-1.37 (m, 37H), 0.88-0.87 (t, 6H) ppm; MS-FAB (m/z): $[M+H]^+$ calculated for $C_{58}H_{91}NO_3$ is 851.35; found 851.41.

2. Supporting Information Tables

Table S1. Temperature-dependent XRD data of the columnar LC phase of ***C*$_3$OPV1**, presenting the measured and calculated spacing, miller indices and lattice parameters.

Temp. (°C)	d_{meas} (Å)	d_{calc} (Å)	hk	Columnar Rectangular Parameters
250 Col_h	47.03	47.03	(10)	a = 54.31
	17.84	17.78	(21)	
	17.69*			
	4.77*			
200 Col_h	47.67	47.67	(10)	a = 55.04
	18.05	18.02	(21)	
	17.38*			
	4.77*			
100 Col_r	51.36	51.36	(11)	a = 59.84 b = 100.08
	50.04	50.04	(02)	
	25.59	25.68	(22)	
	18.97	18.98	(15)	
	17.34*			
50 Col_r	51.05	51.05	(10)	a = 59.49 b = 99.44
	49.72	49.72	(02)	
	25.46	25.53	(22)	
	18.88	18.86	(15)	
	17.29*			
28 Col_r	51.26	51.26	(10)	a = 59.78 b = 99.62
	49.81	49.81	(02)	
	25.76	25.63	(22)	
	18.92	18.90	(15)	
	17.27*			
	4.43*			

*diffuse peak

Table S2. The absorption and emission spectral details of ***C*$_3$OPV1-3** (1 x 10^{-4} M).

Solvent	***C*$_3$OPV1** (λ_{max} in nm)		***C*$_3$OPV2** (λ_{max} in nm)		***C*$_3$OPV3** (λ_{max} in nm)	
	Abs.	Em.	Abs.	Em.	Abs.	Em.
THF	380	435	380	431	370	436
Toluene	380	435	370	504	360	436

Table S3. The gelation details of ***C*$_3$OPV1-3** with minimal gelation concentration (mM) in bracket.

Molecule	**Cyclohexane**	**Methylcyclohexane**	***n*-Decane**	**Toluene**
***C*$_3$OPV1**	S	S	S	S
***C*$_3$OPV2**	G (14.86)	G (13.94)	G (9.29)	G (4.65)
***C*$_3$OPV3**	S	S	S	S

S = solution; G = gel

3. Supporting Information Figures

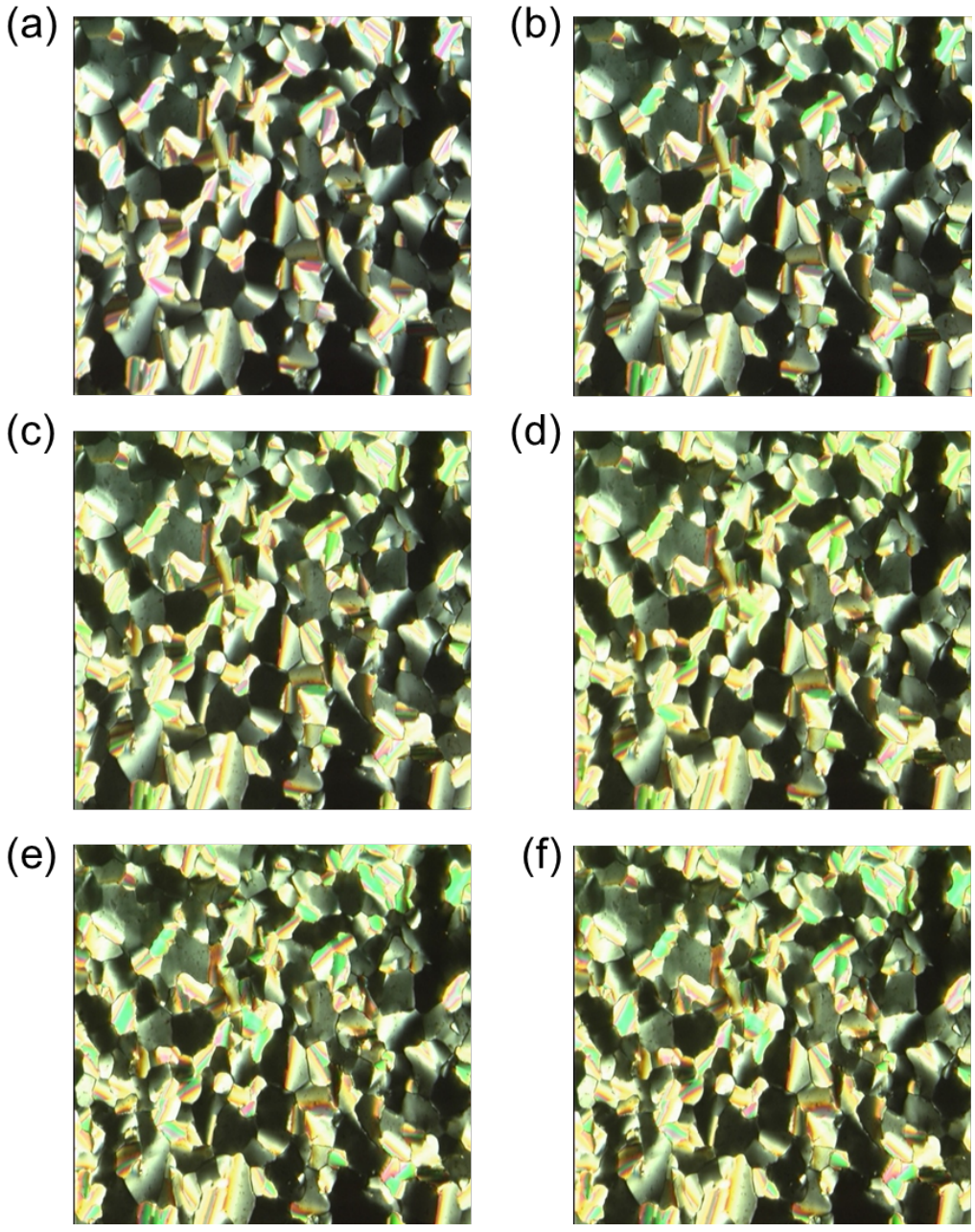


Figure S1. OPM images of ***C*$_3$OPV1** at (a) 218, (b) 200, (c) 165, (d) 118, (e) 65 and (f) 40 °C upon cooling the sample from higher temperature (260 °C).

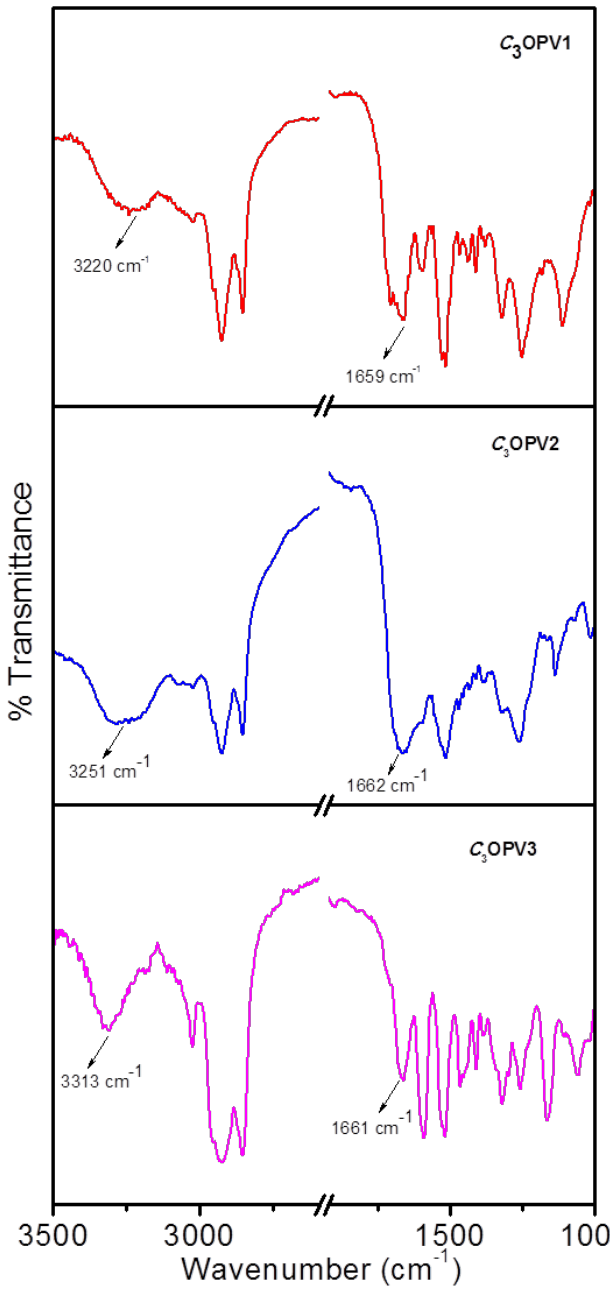


Figure S2. FT-IR spectra of ***C*$_3$OPV1-3** in solid state.

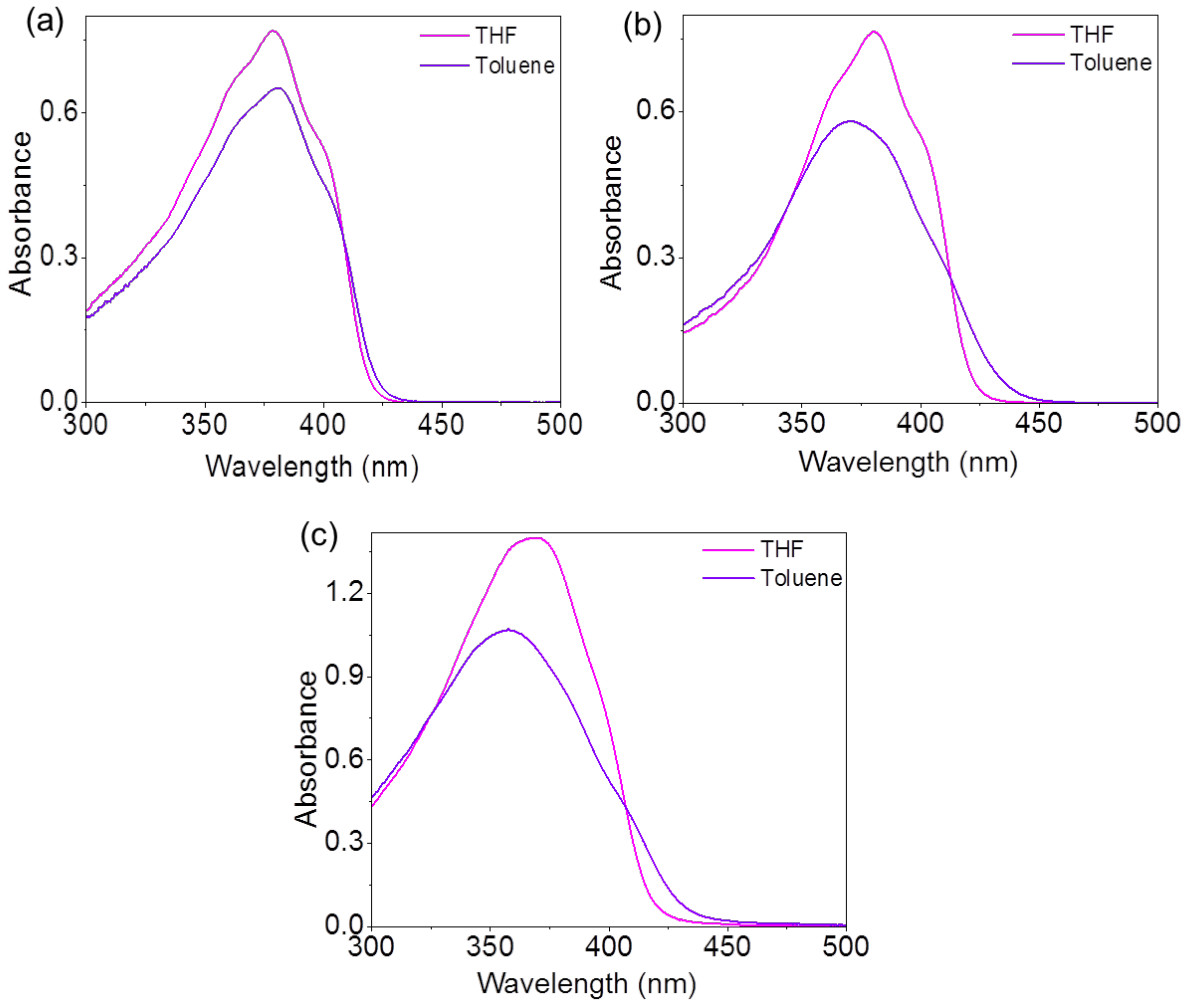


Figure S3. Absorption spectra of (a) ***C*$_3$OPV1**, (b) ***C*$_3$OPV2** and (c) ***C*$_3$OPV3** in THF and toluene (1 x 10^{-4} M).

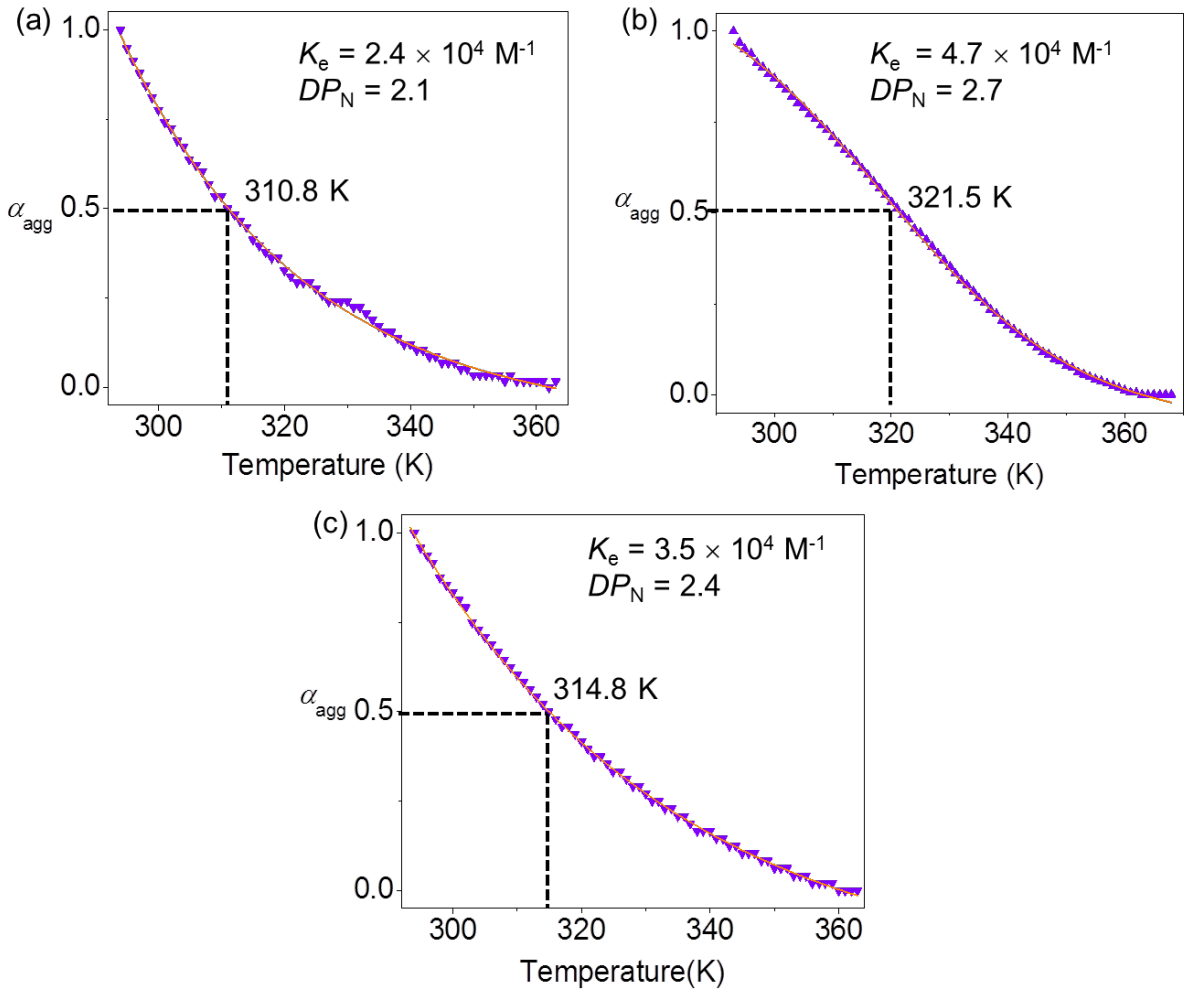


Figure S4. Plot of the fraction of aggregates (α_{agg}) *versus* temperature for (a) ***C*$_3$OPV1**, (b) ***C*$_3$OPV2** and (c) 10% (v/v) of ***C*$_3$OPV2** in ***C*$_3$OPV1**. Absorbance was monitored at 425 nm with a rate of cooling of 1 K min^{-1}. (▲ is the normalized spectra and — is the curve fit). The value of association constant (K_e) and degree of polymerization (DP_N) are given in the inset.

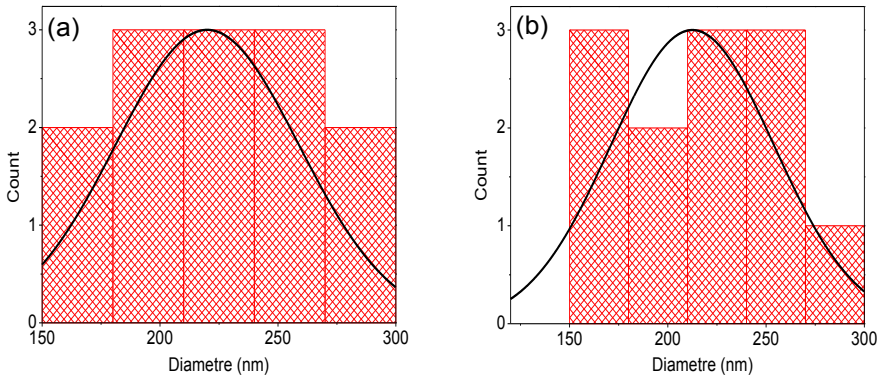


Figure S5. Histogram showing the size distribution of spherical particles formed by (a) ***C*$_3$OPV1** and (b) ***C*$_3$OPV3**.

4. Supporting Information References

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