

Supporting Information

Mesogenic D-A fluorophores based on cyanovinyl and benzothiadiazole

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1. Additional experimental data

1.1 Experimental techniques

A Mettler heating stage (FP 82 HT) was used for polarizing optical microscopy (POM, Optiphot 2, Nikon) and DSC were recorded with a DSC 200 F3 Maia calorimeter (NETZSCH) at 5 K min⁻¹. Their optical properties (UV-vis and fluorescent emission) were done on a UNIC UV2600A and HITACHI F-7000 spectrophotometers. Cyclic voltammograms (CV) were recorded on a CHI 660E Electrochemical Workstation from Shanghai Chenhua Instrument (Shanghai, China) and conducted using a three electrode system, with the modified GCE as working electrode, a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode with nitrogen-saturated solution of 0.1 mol/L tetra-*n*-butylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile. SEM experiments were carried out on a QUNT200 scanning electron microscopy (SEM, USA). Picture was taken digitally. For the sample preparation, the gel was placed on an aluminium foil for some time until the gel become dry gel. After the gold plating, the sample was finally put into the scanning electron microscopy for observation.

Small-angle X-ray scattering experiments were recorded on the beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). Samples were held in evacuated 1 mm capillaries. A Linkam hot stage with a thermal stability within 0.2 °C was used, with a hole for the capillary drilled through the silver heating block. A MarCCD detector was used. q calibration and linearization were verified using several orders of layer reflections from silver behemate.

For electron density reconstruction, Fourier reconstruction of the electron density was carried out using the general formula for 2D periodic systems:

$$\rho_{xy} = \sum_{hk} \frac{1}{m_{hk}} \cdot |F_{hk}| \cdot \cos(\varphi_{hkl}) \cdot (\cos(2\pi \cdot (hx + ky))) \quad (1)$$

here m being the multiplicity, F the structure factor, which is proportional to the intensity and φ the phase of the reflex.

1.2 Molecular dynamics simulation

Annealing dynamics runs were carried out using the Universal Force Field (Material Studio, Accelrys). The structure in Fig. 1d was obtained with 11 molecules in a 42 degree parallelogram box with the short side and long side equal to 5.83 and 9.10 nm, respectively, and a height of 0.45 nm, with 3D periodic boundary conditions. 30 temperature cycles of NVT dynamics were run between 300 and 700 K, with a total annealing time of 30 ps. The structure in Fig. 2d was obtained with three molecules in a 60 degree rhombicprism box with the side equal to the unit cell length and a height of 0.45 nm, with 3D periodic boundary conditions. 30 temperature cycles of NVT dynamics were run between 300 and 700 K, with a total annealing time of 30 ps.

1.3 Additional textures of LC phases and DSC traces

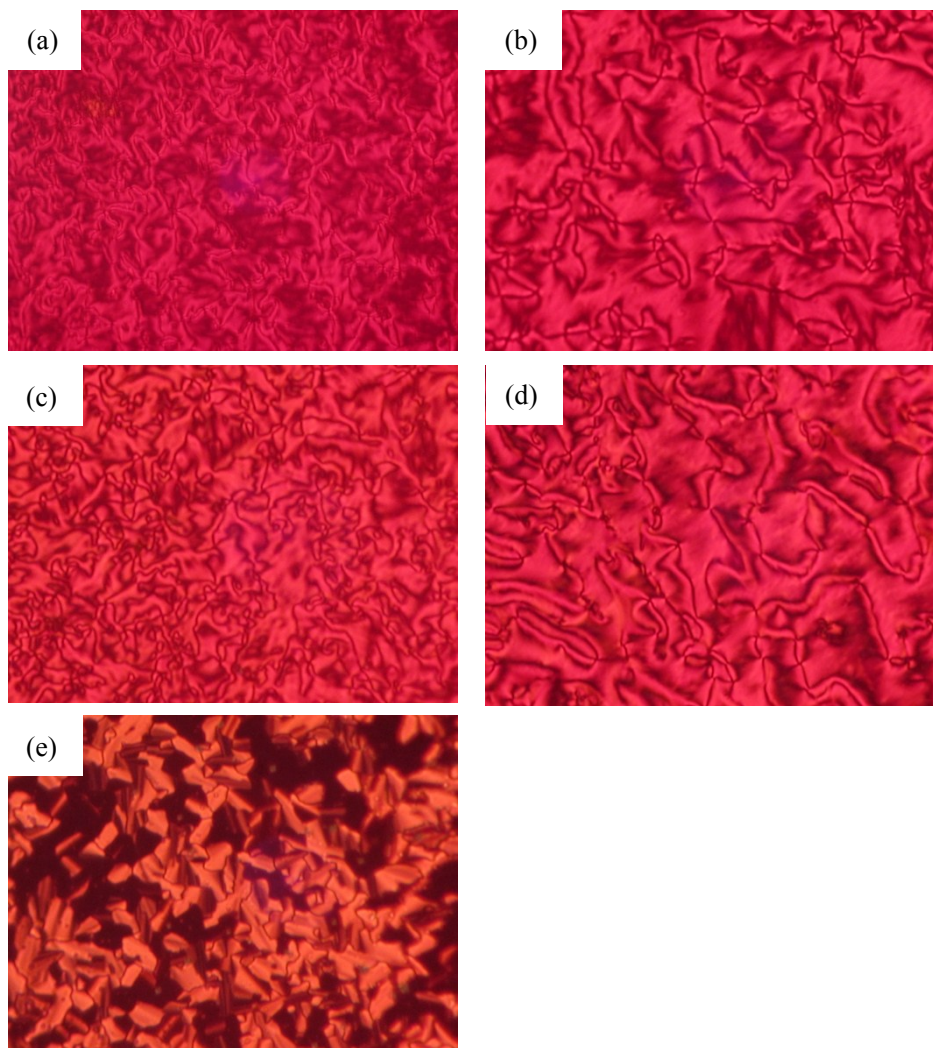


Fig. S1 Representative textures between crossed polarizers: a) SmC of **I¹/10** cooling at 205 °C; b) SmC of **I¹/12** cooling at 210 °C; c) SmC of **I¹/16** cooling at 200 °C; d) SmC of **I¹/18** cooling at 200 °C; e) Col_{hex} phase of **I³/16** cooling at 110 °C.

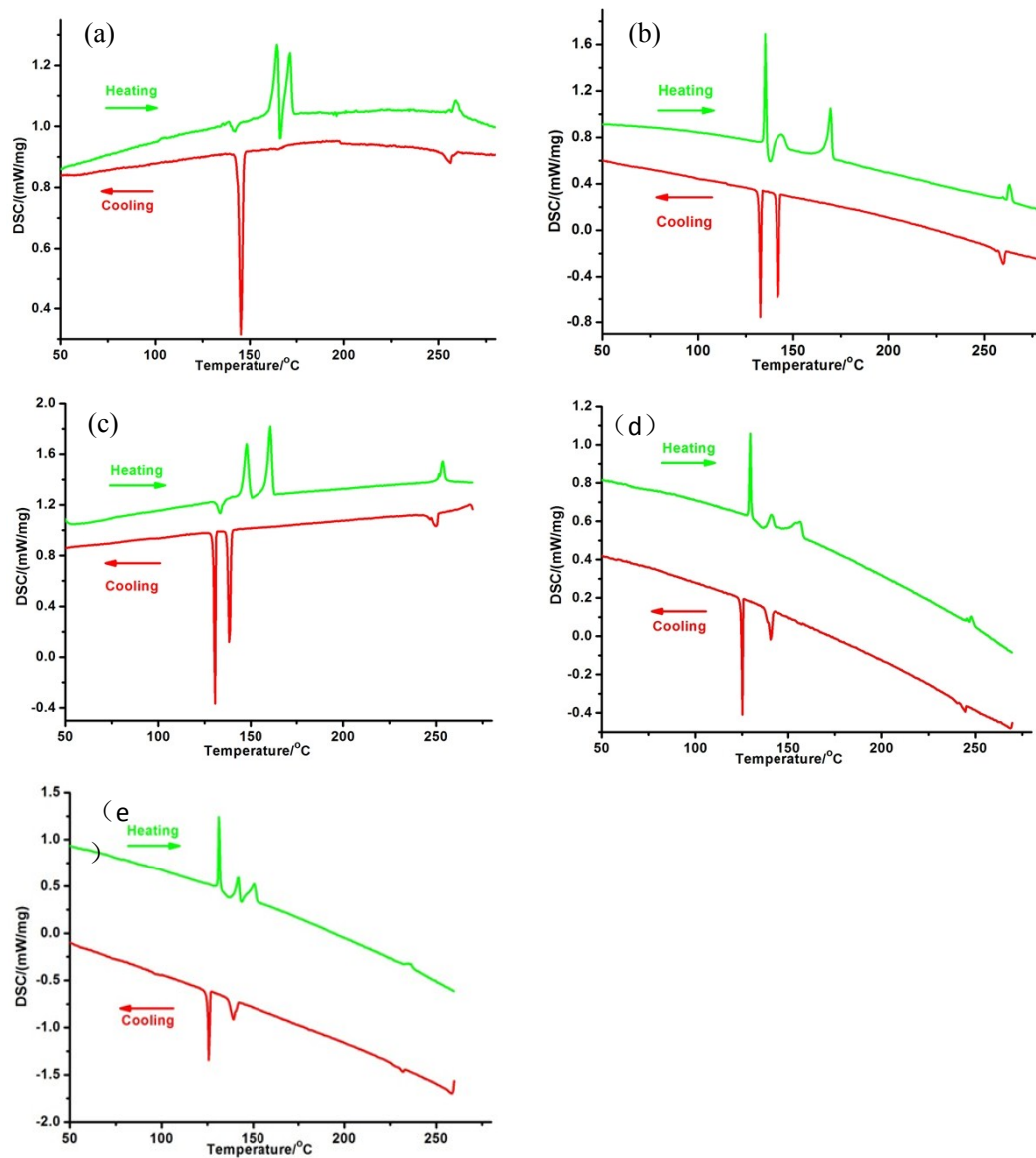


Fig. S2 DSC traces of a) compound **I¹/10** (3 K min⁻¹, second scans); b) compound **I¹/12** (3 K min⁻¹, second scans); c) compound **I¹/14** (3 K min⁻¹, second scans); d) compound **I¹/16** (3 K min⁻¹, second scans); e) compound **I¹/18** (3 K min⁻¹, second scans).

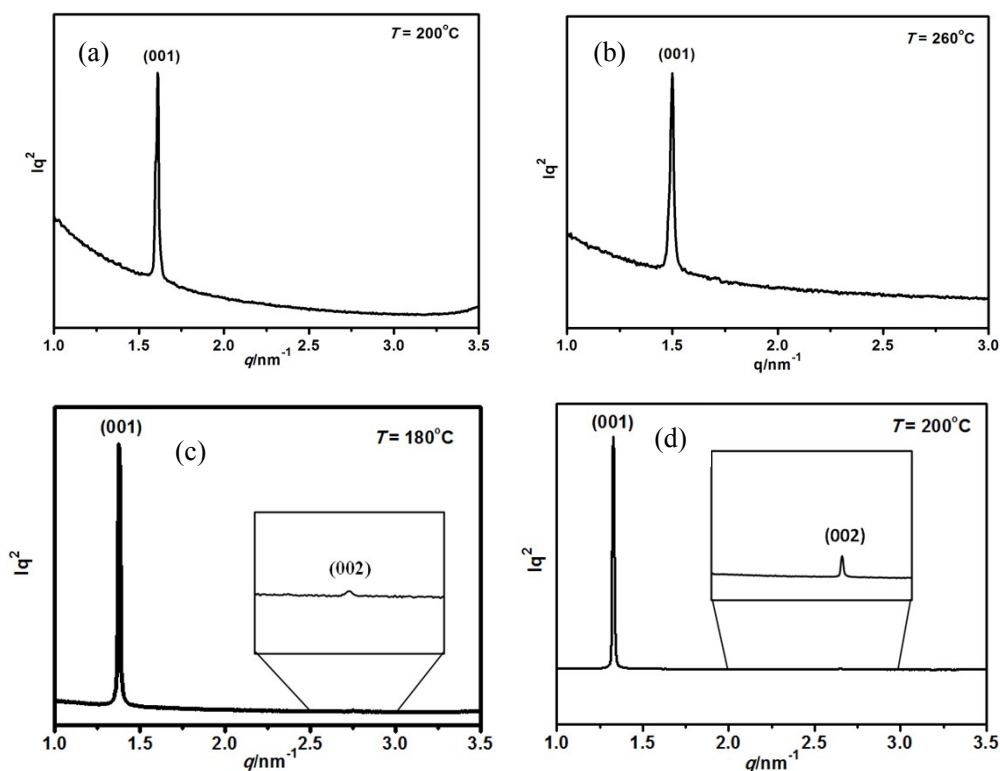


Fig. S3 SAXS diffraction patterns of SmC phase of a) compound **I¹/10** recorded at 200 °C; b) compound **I¹/12** recorded at 260 °C; c) compound **I¹/16** recorded at 180 °C; d) compound **I¹/18** recorded at 200 °C.

Table S1 Experimental and calculated d-spacings of the observed SAXS reflections of the SmC phase in compound **I¹/10** at 200 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\text{obs}}\text{-spacing}(\text{nm})$	$d_{\text{cal}}\text{-spacing}(\text{nm})$
001	3.90	3.90
$d = 3.90 \text{ nm}$		

Table S2 Experimental and calculated d-spacings of the observed SAXS reflections of the SmC phase in compound **I¹/12** at 260 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\text{obs}}\text{-spacing}(\text{nm})$	$d_{\text{cal}}\text{-spacing}(\text{nm})$
001	4.19	4.19
$d = 4.19 \text{ nm}$		

Table S3 Experimental and calculated d-spacings of the observed SAXS reflections of the SmC phase in compound **I¹/14** at 247 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\text{obs}}\text{-spacing}(\text{nm})$	$d_{\text{cal}}\text{-spacing}(\text{nm})$
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001	4.34	4.34
002	2.17	2.17
$d = 4.34 \text{ nm}$		

Table S4 Experimental and calculated d-spacings of the observed SAXS reflections of the SmC phase in compound **I¹/16** at 180 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\text{obs}}\text{-spacing}(\text{nm})$	$d_{\text{cal}}\text{-spacing}(\text{nm})$
001	4.57	4.58
002	2.29	2.29
$d = 4.58 \text{ nm}$		

Table S5 Experimental and calculated d-spacings of the observed SAXS reflections of the SmC phase in compound **I¹/18** at 200 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\text{obs}}\text{-spacing}(\text{nm})$	$d_{\text{cal}}\text{-spacing}(\text{nm})$
001	4.73	4.74
002	2.37	2.37
$d = 4.74 \text{ nm}$		

Table S6 Experimental and calculated d-spacings of the observed SAXS reflections of the Col_{hex} phase in compound **I³/16** at 110 °C. All intensity values are Lorentz and multiplicity corrected.

(hk)	$d_{\text{obs}}\text{-spacing}(\text{nm})$	$d_{\text{cal}}\text{-spacing}(\text{nm})$	$intensity$	$phase$
10	4.70	4.71	100	0
11	2.72	2.72	0.38	π
20	2.37	2.36	0.62	π
$a_{\text{hex}} = 5.44 \text{ nm}$				

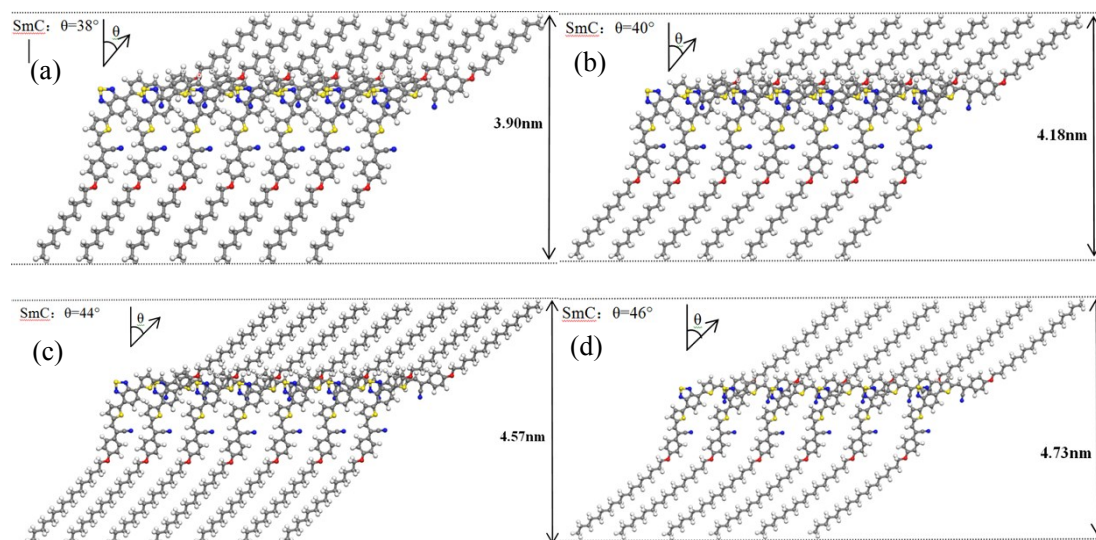


Fig. S4 (a) Model for molecular packing of compound **I**¹/**10** in SmC phase; (b) Model for molecular packing of compound **I**¹/**12** in SmC phase; (c) Model for molecular packing of compound **I**¹/**16** in SmC phase; (d) Model for molecular packing of compound **I**¹/**18** in SmC phase.

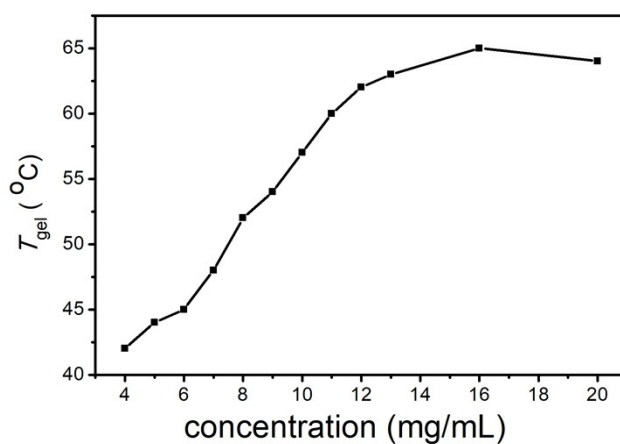


Fig. S5 Plots of T_{gel} vs concentration of **I**³/**16** in ethyl acetate: petroleum ether = 1 : 1 (v : v).

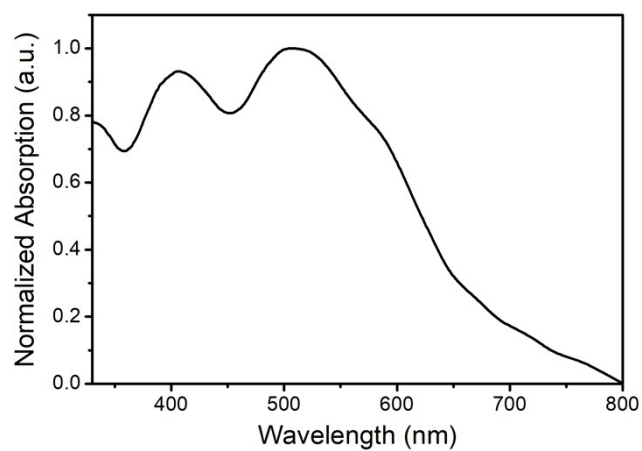


Fig. S6 UV-vis spectrum of the gel of **I**³/**16** in ethyl acetate: petroleum ether = 1 : 1 (v : v).

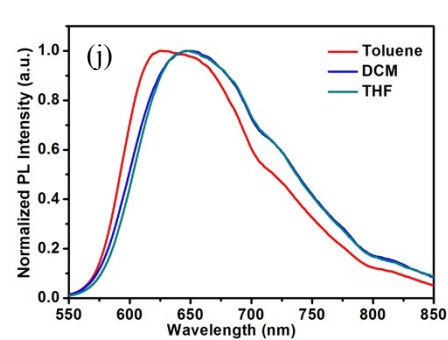
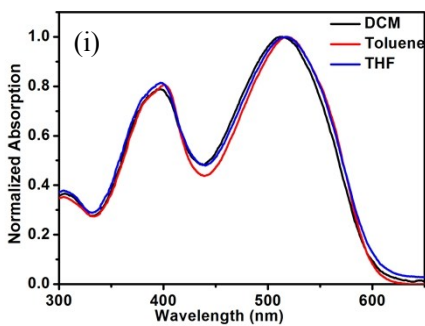
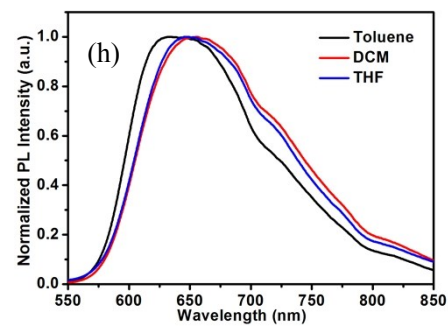
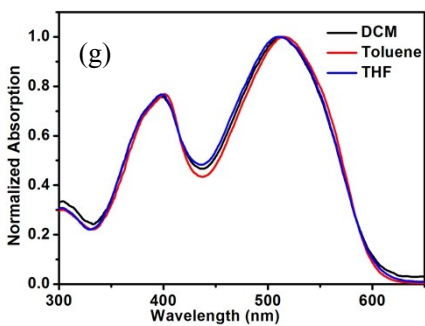
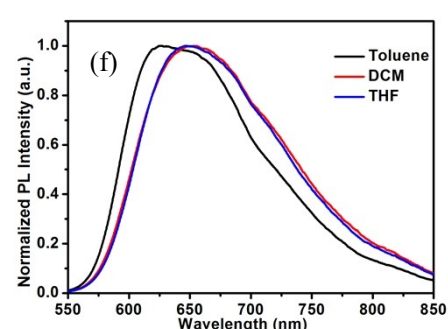
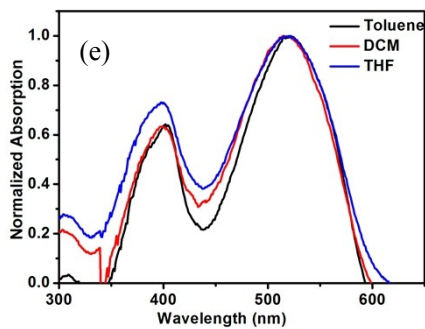
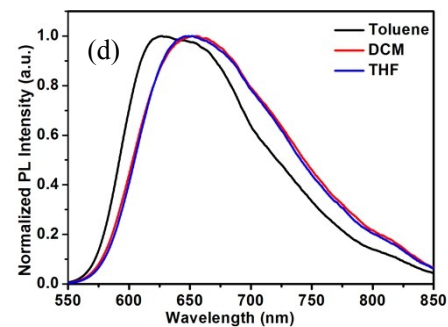
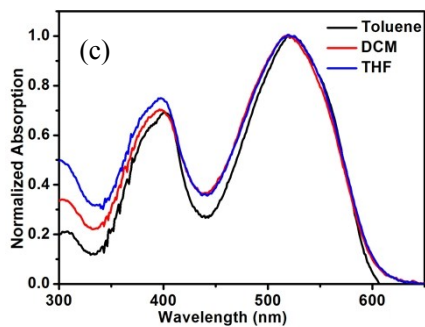
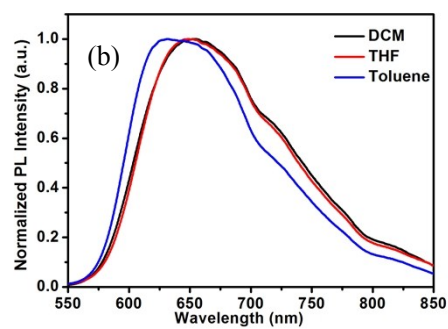
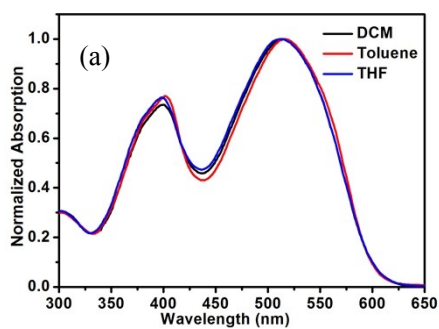


Fig. S7 a) UV-vis spectra of compound **I¹/10**; b) Fluorescence spectra of compound **I¹/10**; c) UV-vis spectra of compound **I¹/12**; d) Fluorescence spectra of compound **I¹/12**; e) UV-vis spectra of compound **I¹/14**; f) Fluorescence spectra of compound **I¹/14**; g) UV-vis spectra of compound **I¹/18**; h) Fluorescence spectra of compound **I¹/18**; i) UV-vis spectra of compound **I³/16**; j) Fluorescence spectra of compound **I³/16**.

Table S7 UV-vis absorption and fluorescence spectroscopy data of compound **I^m/n** (10⁻⁶ M) at 20 °C.

Compd.	Solvent	λ_{ex} (nm)	λ_{em} (nm)	Stokes shifts (nm) ^a
I¹/10	THF	398, 513	650	137
	DCM	400, 514	653	139
	Toluene	401, 516	632	116
I¹/12	THF	400, 522	652	130
	DCM	398, 519	656	137
	Toluene	400, 522	631	109
I¹/14	THF	398, 520	649	129
	DCM	398, 520	655	135
	Toluene	402, 522	627	105
I¹/16	THF	398, 519	653	134
	DCM	398, 517	653	136
	Toluene	400, 521	632	111
I¹/18	THF	398, 510	651	141
	DCM	400, 513	656	143
	Toluene	401, 516	634	118
I³/16	THF	397, 518	648	130
	DCM	394, 512	648	136
	Toluene	401, 518	620	102

^a Stokes shifts = $\lambda_{\text{em}} - \lambda_{\text{ex}}$.

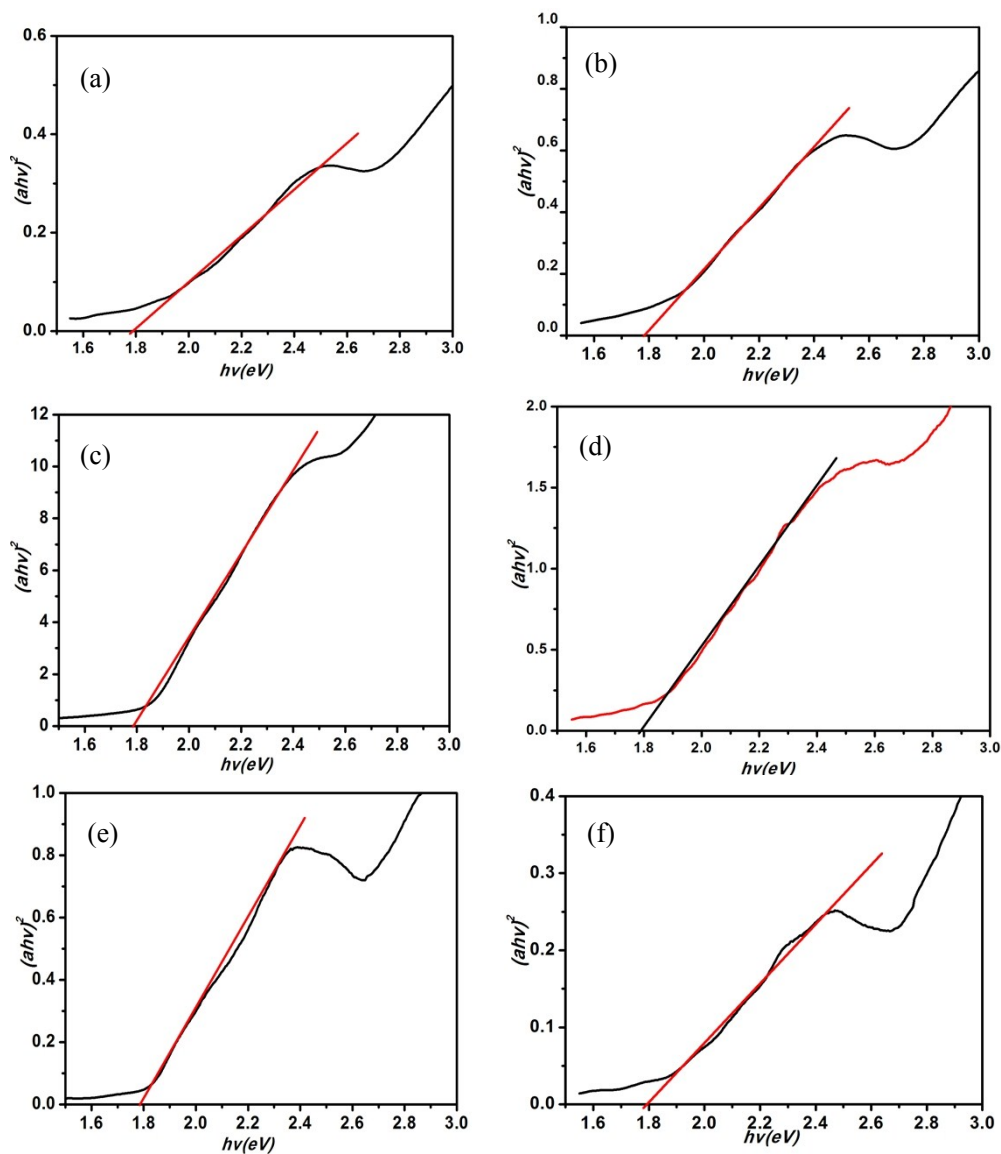


Fig. S8 The calculation of energy band of **I¹/10** a); **I¹/12** b); **I¹/14** c); **I¹/16** d); **I¹/18** e); **I³/16** f) in film by UV-vis spectrum.

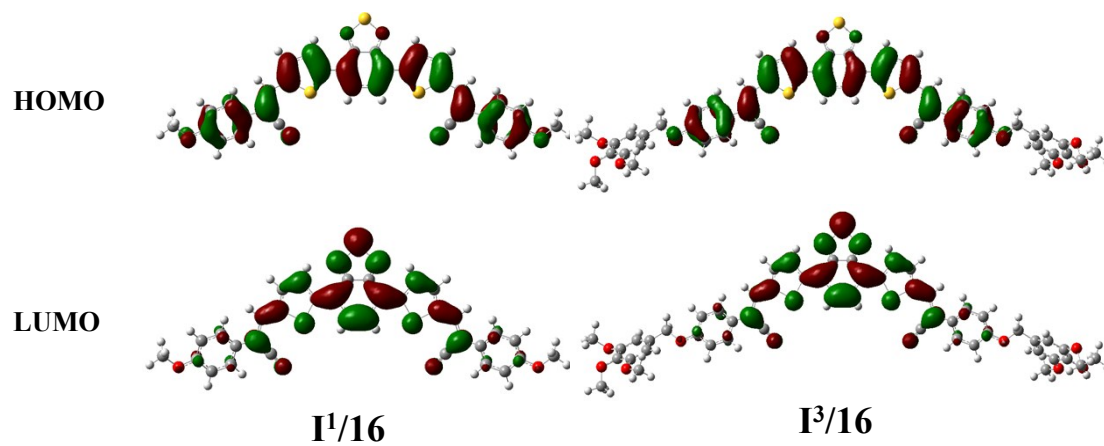
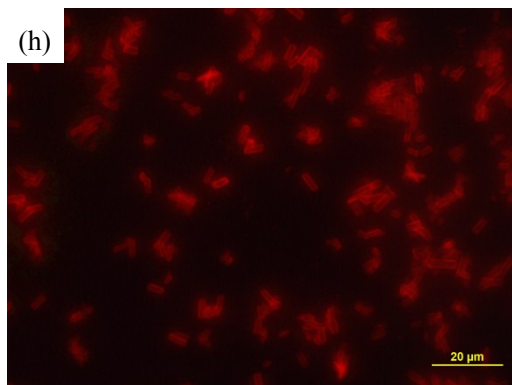
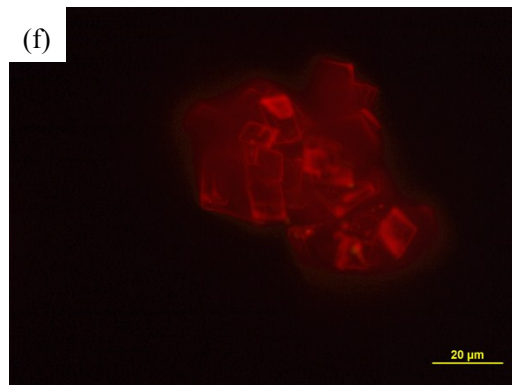
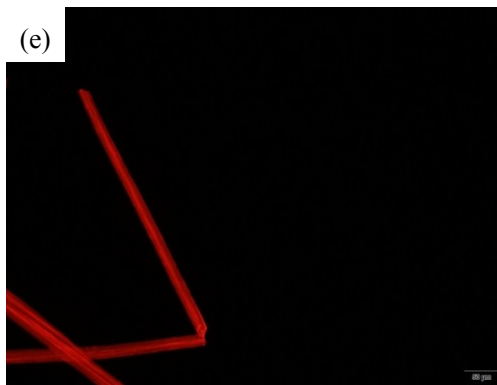
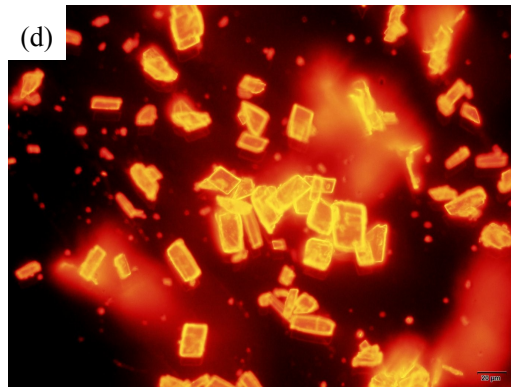
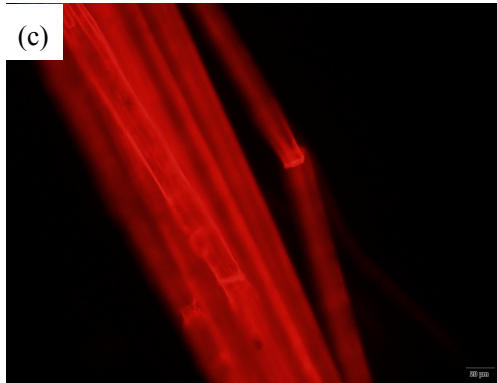
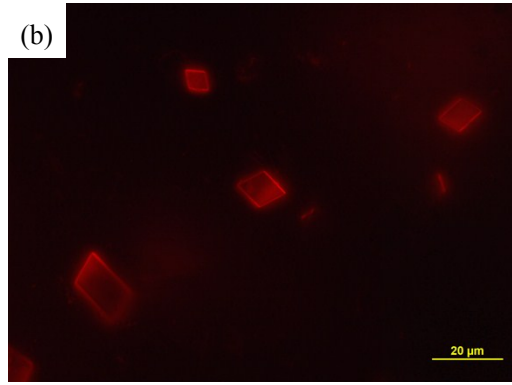
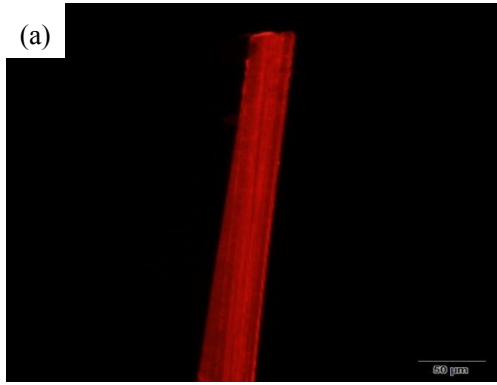


Fig. S9 Molecular structures and calculated frontier orbitals distributions of **I¹/16**, **I³/16**. (calculated using the

DFT/B3LYP, 6-31G, d functional).



Fig. S10 Fluorescence of **I¹/16** without and with **C₇₀** in **CHCl₃** under irradiation (365 nm).



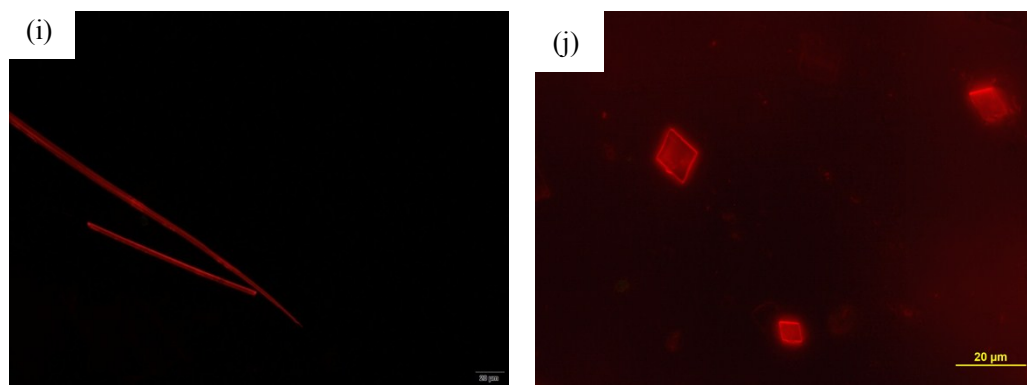


Fig. S11 PL microscopy images of the crystalline aggregates at 540-560 nm of **I¹/10** a) **I¹/12** c), **I¹/14** e), **I¹/16** g) and **I¹/18** i) produced in DCM/MeOH mixed solution; **I¹/10** b) **I¹/12** d), **I¹/14** f), **I¹/16** h) and **I¹/18** j) produced in THF/PE mixed solution.

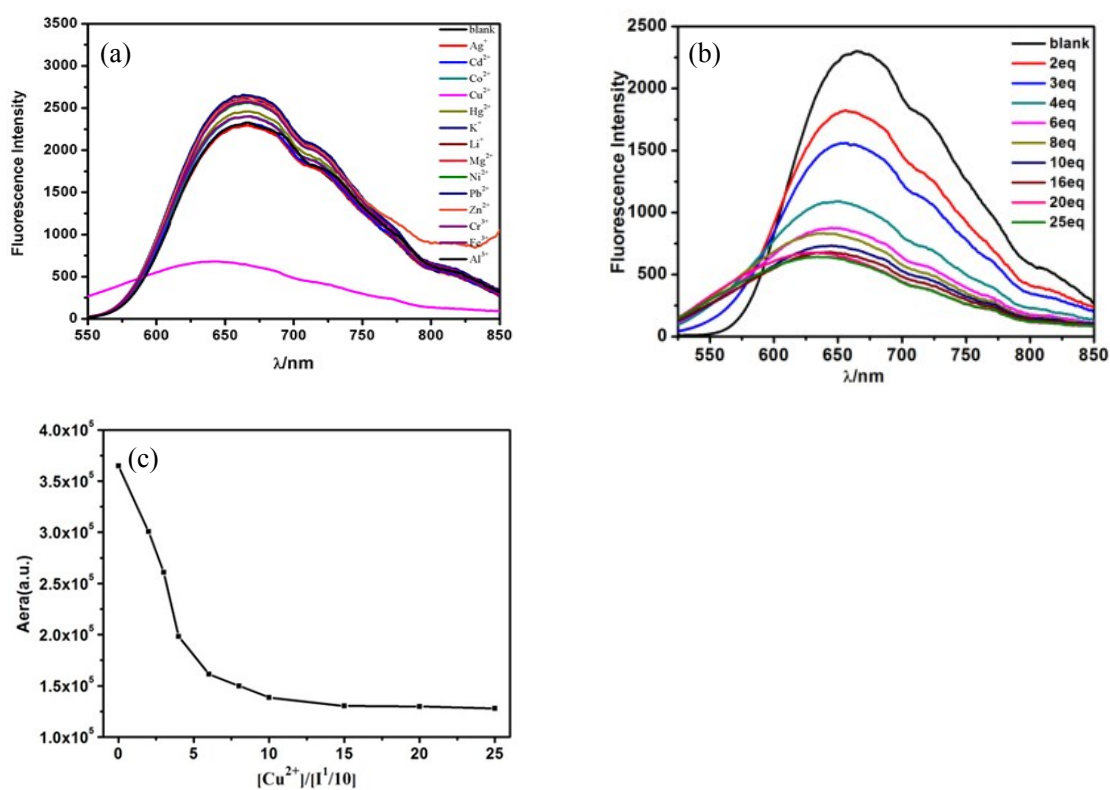


Fig. S12 a) The fluorescence response of **I¹/10** (10^{-6} M, $\text{CH}_3\text{CN} : \text{DCM} = 2 : 1$) upon addition of different metal ions (20 equiv.) at pH = 7.0 ($\lambda_{\text{ex}} = 510$ nm); b) Fluorescence spectra of compound **I¹/10** (10^{-6} M), upon addition of an increasing concentration of Cu^{2+} ions (0-26 equiv.) measured in $\text{CH}_3\text{CN} : \text{DCM} = 2 : 1$ ($\lambda_{\text{ex}} = 660$ nm) at room temperature; c) Titration curve of the integrated fluorescence as a function of Cu^{2+} concentration.

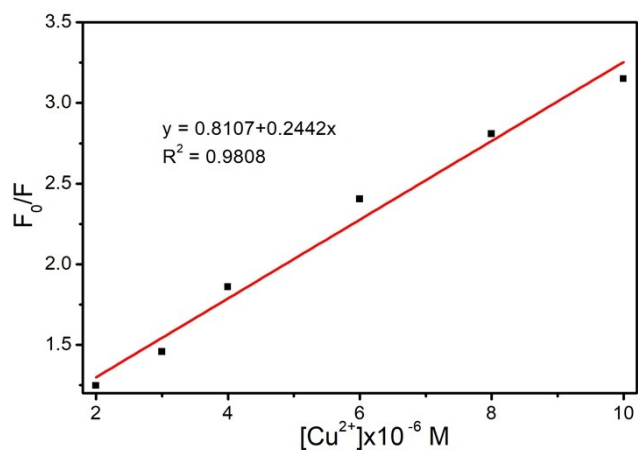


Fig. S13 Plots of the detection limit for Cu^{2+} evaluated from the fluorescence emission of **I**¹/**10**.

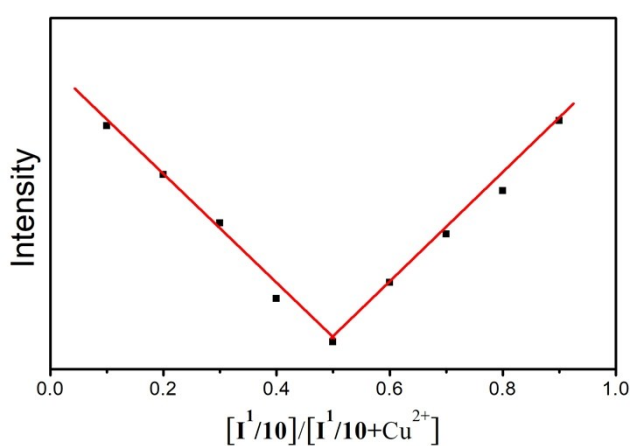


Fig. S14 Job's plot for determining the stoichiometry of **I**¹/**10** and Cu^{2+} . The total concentration of **I**¹/**10** and Cu^{2+} was 10 μM .

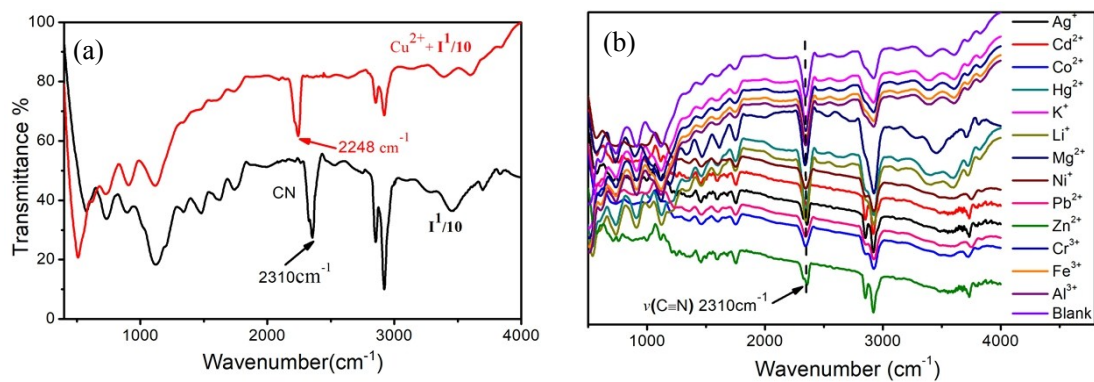
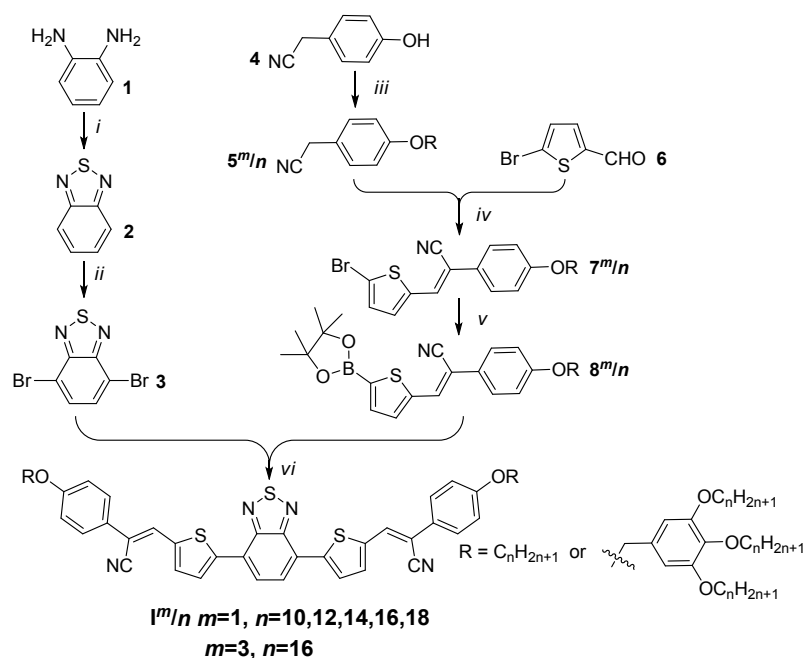


Fig. S15 a) FTIR spectra of **I**¹/**10** (blank line) and **I**¹/**10**+ Cu^{2+} (red line); b) The FTIR spectra of **I**¹/**10**+different metal ions.

2. Synthesis and analytical data

2.1 General

All reagents, unless otherwise specified, were obtained from Energy Chemical Company and used as received. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-DRX-400 spectrometer and Bruker-DRX-800 spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Column chromatography was performed with merck silica gel 60 (230-400 mesh). The intermediates were purified by column chromatography, their structures were confirmed by ^1H NMR and the purity was checked by TLC. Full analytic characterization was provided for all final compounds.



Scheme S1 Synthetic route to afford compounds **I^{m/n}**: *Reagents and conditions*: (i) SOCl_2 , Et_3N , CH_2Cl_2 , 40°C , 7 h; (ii) Br_2 , HBr , 90°C , 12 h; (iii) DMF , K_2CO_3 , RBr ($\text{R} = \text{C}_n\text{H}_{2n+1}$) or 5-(chloromethyl)-1,2,3-tris(hexadecyloxy)benzene, 90°C , 5 h; (iv) EtOH , MeONa , room temperature, 1 h; (v) Toluene , AcOK , $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, Ph_3P , bis(pinacolato)diboron, 120°C , 24 h; (vi) Na_2CO_3 , H_2O , EtOH , toluene , $\text{Pd}(\text{PPh}_3)_4$, 110°C , 36 h.

Synthesis of 2,1,3-benzothiadiazole (2) and 4,7-dibromo-2,1,3-benzothiadiazole (3)

2,1,3-Benzothiadiazole (**2**) [S1] and 4,7-dibromobenzothiadiazole (**3**) [S2], were synthesized according to the literatures and the corresponding data are consistent with those reported in literatures.

General procedures for the synthesis of 5¹/10, 5¹/12, 5¹/14, 5¹/16, 5¹/18 and 5³/16.

To a mixture of K₂CO₃ (11.6 mmol, 1.61 g), 4-hydroxybenzyl cyanide **4** (6.0 mmol, 0.68 mg) in dry DMF (20 mL), the appropriate halide (6 mmol) was added. The mixture was heated to 90 °C and stirred for 5 h. After the reaction was complete (monitored by TLC), the mixture was cooled to RT, H₂O (15 mL) was added to dissolve the precipitate and then the reaction mixture was extracted with ethyl acetate (3 × 60 mL). The combined organic phase was dried by anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and reaction mixture was purified by column chromatography on silica gel using petroleum ether : ethyl acetate (30 : 1) as the eluent to afford compounds.

2-(4-(Decyloxy)phenyl)acetonitrile **5¹/10**: White solid. Yield: 80% (1.45 g, 4.8 mmol). m.p. 40-42 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.20 (d, 2H, J = 8.4 Hz, 2×PhH), 6.88 (d, J = 8.8 Hz, 2H, 2×PhH), 3.93 (t, J = 6.6 Hz, 2H, OCH₂), 3.66 (s, 2H, CH₂), 1.82-1.74 (m, 2H, OCH₂CH₂), 1.45-1.40 (m, 2H, OCH₂CH₂CH₂), 1.42-1.24 (m, 12H, 6×CH₂), 0.89 (t, J = 6.6 Hz, 3H, CH₃).

2-(4-(Dodecyloxy)phenyl)acetonitrile **5¹/12**: White solid. Yield: 77% (1.39 g, 4.6 mmol). m.p. 47-49 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.21 (d, 2H, J = 8.4 Hz, 2×PhH), 6.89 (d, J = 8.8 Hz, 2H, 2×PhH), 3.94 (t, J = 6.6 Hz, 2H, OCH₂), 3.67 (s, 2H, CH₂), 1.83-1.74 (m, 2H, OCH₂CH₂), 1.47-1.42 (m, 2H, OCH₂CH₂CH₂), 1.46-1.24 (m, 16H, 8×CH₂), 0.89 (t, J = 6.6 Hz, 3H, CH₃).

2-(4-(Tetradecyloxy)phenyl)acetonitrile **5¹/14**: White solid. Yield: 84% (1.65 g, 5.0 mmol). m.p. 59-61 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.22 (d, 2H, J = 8.4 Hz, 2×PhH), 6.89 (d, J = 8.8 Hz, 2H, 2×PhH), 3.93 (t, J = 6.6 Hz, 2H, OCH₂), 3.67 (s, 2H, CH₂), 1.81-1.72 (m, 2H, OCH₂CH₂), 1.46-1.41 (m, 2H, OCH₂CH₂CH₂), 1.40-1.23 (m, 20H, 10×CH₂), 0.89 (t, J = 6.6 Hz, 3H, CH₃).

2-(4-(Hexadecyloxy)phenyl)acetonitrile **5¹/16**: White solid. Yield: 82% (1.75 g, 4.9 mmol). m.p. 66-67 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.21 (d, 2H, J = 8.4 Hz, 2×PhH), 6.89 (d, J = 8.8 Hz, 2H, 2×PhH), 3.94 (t, J = 6.6 Hz, 2H, OCH₂), 3.67 (s, 2H, CH₂), 1.85-1.73 (m, 2H, OCH₂CH₂), 1.48-1.42 (m, 2H, OCH₂CH₂CH₂), 1.39-1.20 (m, 24H, 12×CH₂), 0.88 (t, J = 6.6 Hz, 3H, CH₃).

2-(4-(Octadecyloxy)phenyl)acetonitrile **5¹/18**: White solid. Yield: 75% (1.74 g, 4.5 mmol). m.p.

70-72 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.23 (d, 2H, *J* = 8.4 Hz, 2×PhH), 6.70 (d, *J* = 8.8 Hz, 2H, 2×PhH), 3.95 (t, *J* = 6.6 Hz, 2H, OCH₂), 3.68 (s, 2H, CH₂), 1.87-1.74 (m, 2H, OCH₂CH₂), 1.49-1.42 (m, 2H, OCH₂CH₂CH₂), 1.40-1.21 (m, 28H, 14×CH₂), 0.89 (t, *J* = 6.6 Hz, 3H, CH₃).

2-(4-((3,4,5-Tris(hexadecyloxy)benzyl)oxy)phenyl)acetonitrile **5³/16**: White solid. Yield: 79% (4.48 g, 4.74 mmol). m.p. 57-59 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.24 (d, 2H, *J* = 8.4 Hz, 2×PhH), 6.98-6.96 (m, 2H, 2×PhH), 6.60 (s, 2H, 2×PhH), 4.94 (s, 2H, OCH₂), 3.99-3.93 (m, 6H, 3×OCH₂), 3.69 (s, 2H, CH₂), 1.82-1.70 (m, 6H, 3×OCH₂CH₂), 1.46-1.42 (m, 6H, 3×OCH₂CH₂CH₂), 1.38-1.21 (m, 72H, 36×CH₂), 0.88 (t, *J* = 6.8 Hz, 3×CH₃).

General procedures for the synthesis of 7¹/10, 7¹/12, 7¹/14, 7¹/16, 7¹/18 and 7³/16.

A solution of the 5-bromothiophene-2-carbaldehyde **6** (4 mmol, 764.0 mg) and **5^m/n** (4 mmol) in absolute EtOH (20 mL) was treated with NaOMe (4 mmol, 272.2 mg) portionwise, stirred at room temperature for 1 h. After the reaction was complete (TLC), the mixture was cooled to 0 °C, and filtered. The precipitate was washed with EtOH.

3-(5-Bromothiophen-2-yl)-2-(4-(decyloxy)phenyl)acrylonitrile **7¹/10**: Yellow solid. Yield: 87% (1.55 g, 3.48 mmol). m.p. 85-87 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.55 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.41 (s, 1H, CH), 7.29 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.09 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 6.94 (d, 2H, *J* = 8.8 Hz, 2×PhH), 3.99 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.80-1.75 (m, 2H, OCH₂CH₂), 1.50-1.43 (m, 2H, OCH₂CH₂CH₂), 1.35-1.26 (m, 12H, 6×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-Bromothiophen-2-yl)-2-(4-(dodecyloxy)phenyl)acrylonitrile **7¹/12**: Yellow solid. Yield: 84% (1.59 g, 3.36 mmol). m.p. 87-89 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.54 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.40 (s, 1H, CH), 7.28 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.08 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 6.93 (d, 2H, *J* = 8.8 Hz, 2×PhH), 3.98 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.82-1.76 (m, 2H, OCH₂CH₂), 1.49-1.42 (m, 2H, OCH₂CH₂CH₂), 1.34-1.25 (m, 16H, 8×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-Bromothiophen-2-yl)-2-(4-(tetradecyloxy)phenyl)acrylonitrile **7¹/14**: Yellow solid. Yield: 86% (1.73 g, 3.44 mmol). m.p. 91-93 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.54 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.40 (s, 1H, CH), 7.28 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.08 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 6.93 (d, 2H, *J* = 8.8 Hz, 2×PhH), 3.98 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.81-1.74 (m, 2H, OCH₂CH₂), 1.45-1.41 (m, 2H, OCH₂CH₂CH₂), 1.32-1.21 (m, 20H, 10×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-Bromothiophen-2-yl)-2-(4-(hexadecyloxy)phenyl)acrylonitrile **7¹/16**: Yellow solid. Yield: 87% (1.85 g, 3.48 mmol). m.p. 95-96 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.53 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.39 (s, 1H, CH), 7.27 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.07 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 6.92 (d, 2H, *J* = 8.8 Hz, 2×PhH), 3.97 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.83-1.72 (m, 2H, OCH₂CH₂), 1.46-1.40 (m, 2H, OCH₂CH₂CH₂), 1.34-1.21 (m, 24H, 12×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-Bromothiophen-2-yl)-2-(4-(octadecyloxy)phenyl)acrylonitrile **7¹/18**: Yellow solid. Yield: 83% (1.91 g, 3.32 mmol). m.p. 99-101 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.54 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.40 (s, 1H, CH), 7.27 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.07 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 6.93 (d, 2H, *J* = 8.8 Hz, 2×PhH), 3.99 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.80-1.74 (m, 2H, OCH₂CH₂), 1.47-1.43 (m, 2H, OCH₂CH₂CH₂), 1.35-1.21 (m, 28H, 14×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-Bromothiophen-2-yl)-2-(4-((3,4,5-tris(hexadecyloxy)benzyl)oxy)phenyl)acrylonitrile **7³/16**: Yellow solid. Yield: 80% (3.58 g, 3.20 mmol). m.p. 74-75 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.56 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.42 (s, 1H, CH), 7.29 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.09 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.01 (d, 2H, *J* = 9.2 Hz, 2×PhH), 6.61 (s, 2H, 2×PhH), 4.98 (s, 2H, OCH₂), 3.99-3.93 (m, 6H, 3×OCH₂), 1.83-1.71 (m, 6H, 3×OCH₂CH₂), 1.46-1.42 (m, 6H, 3×OCH₂CH₂CH₂), 1.29-1.23 (m, 72H, 36×CH₂), 0.88 (t, 9H, *J* = 6.8 Hz, 3×CH₃).

General procedures for the synthesis of **8^{1/10}**, **8^{1/12}**, **8^{1/14}**, **8^{1/16}**, **8^{1/18}** and **8^{3/16}**.

A solution of compound **8^{m/n}** (3.0 mmol), bis(pinacolato) diborane (4.0 mmol, 1.02 g), KOAc (9 mmol, 0.88 g), Pd(PPh₃)₂Cl₂ (0.02 mmol, 14.0 mg) in dry toluene (25 mL) was refluxed at 120 °C under nitrogen atmosphere for 24 h. After the reaction was complete (TLC), the mixture was cooled to RT. The mixture was poured into water (30 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic layers were dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by silica column chromatography eluting with petroleum ether : ethyl acetate (20 : 1) to afford compounds.

2-(4-(Decyloxy)phenyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)

acrylonitrile **8^{1/10}**: Yellow solid. Yield: 78% (1.15 g, 2.34 mmol). m.p. 89-101 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.69 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.60 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.57 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.53 (s, 1H, CH), 6.93 (d, 2H, *J* = 9.2 Hz, 2×PhH), 3.98 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.82-1.77 (m, 2H, OCH₂CH₂), 1.46-1.44 (m, 2H, OCH₂CH₂CH₂), 1.36 (s, 12H, CH₃), 1.30-1.22 (m, 12H, 6×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

2-(4-(Dodecyloxy)phenyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-

yl)acrylonitrile **8^{1/12}**: Yellow solid. Yield: 76% (1.19 g, 2.28 mmol). m.p. 88-98 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.70 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.61 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.58 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.54 (s, 1H, CH), 6.94 (d, 2H, *J* = 9.2 Hz, 2×PhH), 3.99 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.83-1.76 (m, 2H, OCH₂CH₂), 1.48-1.43 (m, 2H, OCH₂CH₂CH₂), 1.36 (s, 12H, CH₃), 1.29-1.23 (m, 16H, 8×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

2-(4-(Tetradecyloxy)phenyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-

yl)acrylonitrile **8^{1/14}**: Yellow solid. Yield: 75% (1.24 g, 2.25 mmol). m.p. 95-100 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.69 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.61 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.57 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.54 (s, 1H, CH), 6.94 (d, 2H, *J* = 9.2 Hz, 2×PhH), 3.98 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.84-1.75 (m, 2H, OCH₂CH₂), 1.47-1.44 (m, 2H, OCH₂CH₂CH₂),

1.36 (s, 12H, CH₃), 1.31-1.22 (m, 20H, 10×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

2-(4-(Hexadecyloxy)phenyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)acrylonitrile **8¹/16**: Yellow solid. Yield: 78% (1.40 g, 2.34 mmol). m.p. 99-104 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.70 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.62 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.58 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.54 (s, 1H, CH), 6.93 (d, 2H, *J* = 9.2 Hz, 2×PhH), 3.99 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.83-1.76 (m, 2H, OCH₂CH₂), 1.48-1.43 (m, 2H, OCH₂CH₂CH₂), 1.35 (s, 12H, CH₃), 1.30-1.20 (m, 24H, 12×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

2-(4-(Octadecyloxy)phenyl)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)acrylonitrile **8¹/18**: Yellow solid. Yield: 77% (2.80 g, 2.31 mmol). m.p. 102-107 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.70 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.62 (d, 1H, *J* = 4.0 Hz, ThiopheneH), 7.58 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.54 (s, 1H, CH), 6.93 (d, 2H, *J* = 9.2 Hz, 2×PhH), 3.99 (t, 2H, *J* = 6.6 Hz, OCH₂), 1.83-1.76 (m, 2H, OCH₂CH₂), 1.48-1.43 (m, 2H, OCH₂CH₂CH₂), 1.35 (s, 12H, CH₃), 1.30-1.20 (m, 28H, 14×CH₂), 0.88 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-2-(4-((3,4,5-tris(hexadecyloxy)benzyl)oxy)phenyl)acrylonitrile **8³/16**: Yellow solid. Yield: 80% (2.80 g, 2.40 mmol). m.p. 100-109 °C. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.59 (d, 2H, *J* = 8.8 Hz, 2×PhH), 7.50 (s, 1H, CH), 7.48 (d, 1H, *J* = 3.6 Hz, ThiopheneH), 7.31 (d, 1H, *J* = 3.6 Hz, ThiopheneH), 7.03 (d, 2H, *J* = 8.4 Hz, 2×PhH), 6.62 (s, 2H, 2×PhH), 4.99 (s, 2H, OCH₂), 4.00-3.93 (m, 6H, 3×OCH₂), 1.81-1.73 (m, 6H, 3×OCH₂CH₂), 1.49-1.43 (m, 6H, 3×OCH₂CH₂CH₂), 1.33 (s, 12H, CH₃), 1.28-1.25 (m, 72H, 36×CH₂), 0.88 (t, 9H, *J* = 6.6 Hz, 3×CH₃).

General procedures for the synthesis of I¹/10, I¹/12, I¹/14, I¹/16, I¹/18 and I³/16.

Dry toluene (20 mL), 4,7-dibromobenzothiadiazole **3** (0.25 mmol, 73.49 mg), **8^m/n** (0.50 mmol), PPh₃ (0.02 mmol), Pd(PPh₃)₂Cl₂ (0.02 mmol), 2 mL ethanol and 3 mL Na₂CO₃ aqueous (2 M) were placed in a flask and degassed with nitrogen, and the mixture was maintained at 110 °C for 36 h. After the reaction was complete (TLC), the mixture was cooled to RT. And then the solvent was evaporated to dryness, and the crude product was purified by column chromatography on

silica gel using petroleum ether : dichloromethane (1 : 1) as the eluent to afford compounds.

3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2-(4-(decyloxy)phenyl)acrylonitrile) **I¹/10**: Brown solid. Yield: 83% (0.182 g, 0.21 mmol). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.22 (d, 2H, $J = 4.0$ Hz, 2 \times ThiopheneH), 7.98 (s, 2H, 2 \times PhH), 7.70 (d, 2H, $J = 4.0$ Hz, 2 \times ThiopheneH), 7.60 (d, 4H, $J = 8.8$ Hz, 4 \times PhH), 7.56 (s, 2H, 2 \times CH), 6.96 (d, 4H, $J = 8.8$ Hz, 4 \times PhH), 4.00 (t, 4H, $J = 6.4$ Hz, 2 \times OCH₂), 1.84-1.77 (m, 4H, 2 \times OCH₂CH₂), 1.48-1.43 (m, 4H, 2 \times OCH₂CH₂CH₂), 1.34-1.27 (m, 24H, 12 \times CH₂), 0.89 (t, 6H, $J = 6.6$ Hz, 2 \times CH₃). ¹³C NMR (CDCl₃, 200 MHz), δ (ppm): 160.1 (2 C), 152.5 (2 C), 142.6 (2 C), 139.4 (2 C), 132.7 (2 C), 131.5 (2 C), 128.6 (2 C), 127.1 (4 C), 126.3 (2 C), 126.1 (2 C), 125.9 (2 C), 118.4 (2 C), 115.1 (4 C), 108.4 (2 C), 68.3 (2 C), 31.9-14.1 (multi-carbon in alkyl chain). Elemental Analysis (%), found: C, 72.21; H, 6.89; N, 6.68; molecular formula C₅₂H₅₈N₄O₂S₃ requires C, 72.02; H, 6.74; N, 6.46.

3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2-(4-(dodecyloxy)phenyl)acrylonitrile) **I¹/12**: Brown solid. Yield: 80% (0.185 g, 0.20 mmol). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.18 (d, 2H, $J = 4.0$ Hz, 2 \times ThiopheneH), 7.93 (s, 2H, 2 \times PhH), 7.66 (d, 2H, $J = 4.0$ Hz, 2 \times ThiopheneH), 7.58 (d, 4H, $J = 8.8$ Hz, 4 \times PhH), 7.51 (s, 2H, 2 \times CH), 6.94 (d, 4H, $J = 8.4$ Hz, 4 \times PhH), 3.98 (t, 4H, $J = 6.6$ Hz, 2 \times OCH₂), 1.83-1.76 (m, 4H, 2 \times OCH₂CH₂), 1.46-1.42 (m, 4H, 2 \times OCH₂CH₂CH₂), 1.34-1.25 (m, 32H, 16 \times CH₂), 0.88 (t, 6H, $J = 6.8$ Hz, 2 \times CH₃). ¹³C NMR (CDCl₃, 200 MHz), δ (ppm): 160.1 (2 C), 152.4 (2 C), 142.6 (2 C), 139.4 (2 C), 132.7 (2 C), 131.5 (2 C), 128.5 (2 C), 127.1 (4 C), 126.3 (2 C), 126.1 (2 C), 125.9 (2 C), 118.4 (2 C), 115.1 (4 C), 108.5 (2 C), 68.3 (2 C), 29.7-14.1 (multi-carbon in alkyl chain). Elemental Analysis (%), found: C, 73.04; H, 7.39; N, 6.26; molecular formula C₅₆H₆₆N₄O₂S₃ requires C, 72.85; H, 7.21; N, 6.07.

3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2-(4-(tetradecyloxy)phenyl)acrylonitrile) **I¹/14**: Brown solid. Yield: 76% (0.186 g, 0.19 mmol). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.20 (d, 2H, $J = 3.6$ Hz, 2 \times ThiopheneH), 7.92 (d, 2H, $J = 4.0$ Hz, 2 \times PhH), 7.68 (d, 2H, $J = 4.0$ Hz, 2 \times ThiopheneH), 7.59 (d, 4H, $J = 8.8$ Hz, 4 \times PhH), 7.53 (s, 2H, 2 \times CH), 6.95 (d, 4H, $J = 7.6$ Hz, 4 \times PhH), 3.98 (t, 4H, $J = 6.6$ Hz, 2 \times OCH₂), 1.82-1.78 (m, 4H,

2×OCH₂CH₂), 1.48-1.42 (m, 4H, 2×OCH₂CH₂CH₂), 1.34-1.25 (m, 40H, 20×CH₂), 0.88 (t, 6H, *J* = 6.8 Hz, 2×CH₃). ¹³C NMR (CDCl₃, 200 MHz), δ (ppm): 160.0 (2 C), 152.7 (2 C), 142.7 (2 C), 139.6 (2 C), 132.9 (2 C), 131.7 (2 C), 128.7 (2 C), 127.3 (4 C), 126.4 (2 C), 126.3 (2 C), 126.0 (2 C) 118.6 (2 C), 115.3(4 C), 108.6 (2 C), 68.4 (2 C), 29.8-14.3 (multi-carbon in alkyl chain). Elemental Analysis (%), found: C, 73.40; H, 7.45; N, 5.61; molecular formula C₆₀H₇₄N₄O₂S₃ requires C, 73.58; H, 7.62; N, 5.72.

3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2-(4-(hexadecyloxy)phenyl)acrylonitrile) **I**/**16**: Brown solid. Yield: 79% (0.205 g, 0.20 mmol). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.18 (d, 2H, *J* = 4.0 Hz, 2×ThiopheneH), 7.94 (s, 2H, 2×PhH), 7.67 (d, 2H, *J* = 4.0 Hz, 2×ThiopheneH), 7.58 (d, 4H, *J* = 8.4 Hz, 4×PhH), 7.52 (s, 2H, 2×CH), 6.94 (d, 4H, *J* = 8.8 Hz, 4×PhH), 3.98 (t, 4H, *J* = 6.4 Hz, 2×OCH₂), 1.83-1.76 (m, 4H, 2×OCH₂CH₂), 1.46-1.43 (m, 4H, 2×OCH₂CH₂CH₂), 1.31-1.25 (m, 48H, 24×CH₂), 0.88 (t, 6H, *J* = 6.6 Hz, 2×CH₃). ¹³C NMR (CDCl₃, 200 MHz), δ (ppm): 160.0 (2 C), 152.0 (2 C), 142.2 (2 C), 139.4 (2 C), 132.7 (2 C), 131.5 (2 C), 128.5 (2 C), 127.1 (4 C), 126.3 (2 C), 126.2 (2 C), 125.9 (2 C) 118.5 (2 C), 115.1(4 C), 108.7 (2 C), 68.3 (2 C), 29.7-14.3 (multi-carbon in alkyl chain). Elemental Analysis (%), found: C, 74.01; H, 7.80; N, 5.32; molecular formula C₆₄H₈₂N₄O₂S₃ requires C, 74.23; H, 7.98; N, 5.41.

3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2-(4-(octadecyloxy)phenyl)acrylonitrile) **I**/**18**: Brown solid. Yield: 82% (0.224 g, 0.21 mmol). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.22 (d, 2H, *J* = 4.0 Hz, 2×ThiopheneH), 7.98 (s, 2H, 2×PhH), 7.71 (d, 2H, *J* = 3.6 Hz, 2×ThiopheneH), 7.60 (d, 4H, *J* = 8.8 Hz, 4×PhH), 7.56 (s, 2H, 2×CH), 6.96 (d, 4H, *J* = 8.8 Hz, 4×PhH), 4.00 (t, 4H, *J* = 6.4 Hz, 2×OCH₂), 1.82-1.78 (m, 4H, 2×OCH₂CH₂), 1.47-1.45 (m, 4H, 2×OCH₂CH₂CH₂), 1.28-1.23 (m, 56H, 28×CH₂), 0.88 (t, 6H, *J* = 6.6 Hz, 2×CH₃). ¹³C NMR (CDCl₃, 200 MHz), δ (ppm): 159.8 (2 C), 151.7 (2 C), 142.0 (2 C), 139.2 (2 C), 132.5 (2 C), 131.3 (2 C), 128.3 (2 C), 126.9 (4 C), 126.0 (2 C), 125.9 (2 C), 125.7 (2 C) 118.3 (2 C), 114.9(4 C), 108.5 (2 C), 68.0 (2 C), 31.7-14.0 (multi-carbon in alkyl chain). Elemental Analysis (%), found: C, 74.99; H, 8.50; N, 5.29; molecular formula C₆₈H₉₀N₄O₂S₃ requires C, 74.82; H, 8.31; N, 5.13.

3,3'-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2-(4-((3,4,5-tris(hexadecyloxy)benzyl)oxy)phenyl)acrylonitrile) **1³/16**: Brown solid. Yield: 60 % (0.331 g, 0.15 mmol). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.22 (d, 2H, *J* = 4.0 Hz, 2×ThiopheneH), 7.98 (s, 2H, 2×PhH), 7.70 (d, 2H, *J* = 3.6 Hz, 2×ThiopheneH), 7.61 (d, 4H, *J* = 8.4 Hz, 4×PhH), 7.57 (s, 2H, 2×CH), 7.04 (d, 4H, *J* = 8.8 Hz, 4×PhH), 6.62 (s, 4H, 4×PhH), 4.99 (s, 4H, 2×OCH₂), 4.00-3.94 (m, 12H, 6×OCH₂), 1.83-1.71 (m, 12H, 6×OCH₂CH₂), 1.53-1.47 (m, 12H, 6×OCH₂CH₂CH₂), 1.28-1.23 (m, 144H, 72×CH₂), 0.87 (t, 18H, *J* = 6.4 Hz, 6×CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 158.6 (2 C), 152.4 (4 C), 151.4 (2 C), 141.7 (2 C), 138.3 (2 C), 137.2 (2 C), 131.8 (2 C), 130.7 (2 C), 130.3 (2 C), 127.5 (2 C), 126.1 (4 C), 125.7 (2 C), 125.2 (2 C), 124.8 (2 C), 117.3 (2 C), 114.7 (4 C), 107.3 (2 C), 105.2 (4 C), 72.4 (2 C), 69.6 (2 C), 68.2 (4 C), 30.9-13.1 (multi-carbon in alkyl chain). Elemental Analysis (%), found: C, 77.35; H, 10.32; N, 2.65; molecular formula C₁₄₂H₂₂₂N₄O₈S₃ requires C, 77.19; H, 10.13; N, 2.54.

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