# Supporting Information

## Columnar mesophases of fluorescent polycatenar liquid crystals incorporating a 1,3-substituted benzene ring interconnecting two 1,3,4-oxadiazoles

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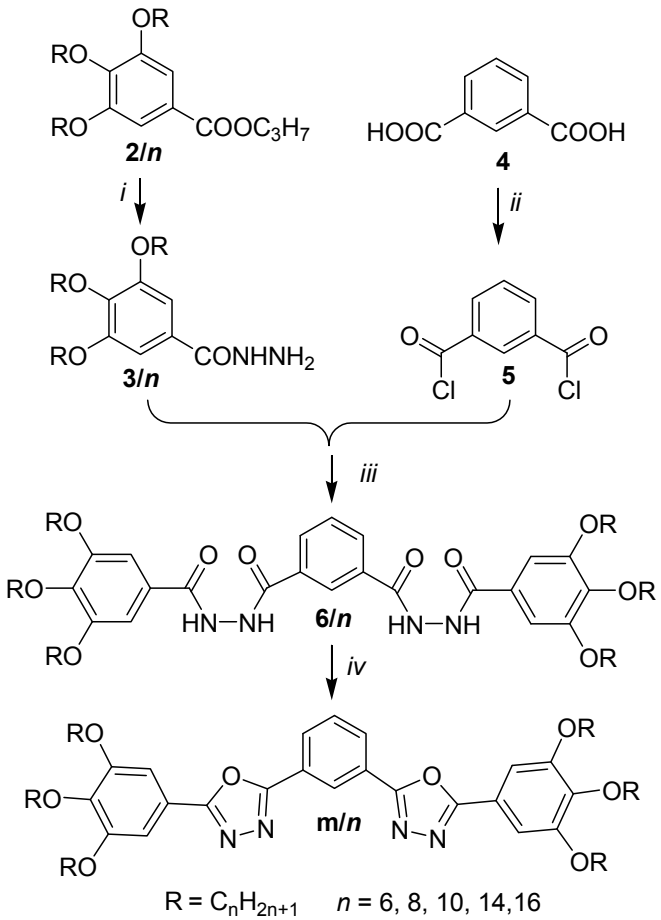
### 1. Synthesis of the materials.

#### 1.1 General

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Commercially available chemicals were used as received. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker–DRX-500 spectrometer. HRMS were performed on an Agilent 1100 LC/MSD TOF instrument. Column chromatography was performed with silica gel 60 (230-400 mesh) from Merck.




**Scheme S1**. Synthesis of compounds **m/*n***; *Reagents and conditions*: *i*) hydrazine hydrate, *n*-BuOH, 115 °C, 40 h; *ii*) $SOCl_2$, 70 °C, 6 h; *iii*) $Et_3N$, THF, 25 °C, 8 h; *iv*) $POCl_3$, reflux, 12 h.

## 1.2 Experimental procedures for compounds m/*n*

### 1.2.1 *n*-Propyl 3,4,5-tri-*n*-alkoxybenzoates 2/*n*:

To a mixture of $K_2CO_3$ (9.0 mmol), the appropriate propyl 3,4,5-trihydroxybenzoate (1.0 mmol) in dry DMF (20 mL), the appropriate *n*-bromoalkanes (3.3 mmol) was added under an argon atmosphere. The mixture was heated to 80 °C and stirred for 3 h. After the reaction was complete (TLC), the mixture was cooled to RT, poured into ice water (30 mL) and acidified with 10 % HCl to pH = 4-5. The mixture was extracted with $Et_2O$ (3 × 30 ml). The combined extracts were washed with $H_2O$ (5 × 20 mL), dried over $MgSO_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether: ethyl acetate = 15 : 1) to afford propyl 3,4,5-trialkoxylbenzoate **2/*n*.**

*n*-Propyl 3,4,5-tri-*n*-hexyloxybenzoate **2/*6*.** Yield: 86%; Colorless liquid. $^1$HNMR ($CDCl_3$, 500MHz): $\delta$ = 0.86-0.92 (t, 9H, $J$ = 6.7 Hz, 3C**H**$_3$), 1.00-1.02 (t, 3H, $J$ = 7.2 Hz, C**H**$_3$), 1.26-1.50 (m, 18H, 9C**H**$_2$), 1.80-1.87 (m, 8H, 4OCH$_2$C**H**$_2$), 4.03-4.11 (m, 6H, 3OC**H**$_2$), 4.25-4.28 (t, 2H, $J$ = 6.5 Hz, ArCOOC**H**$_2$ ), 7.26 (s, 2H, Ar**H**).

*n*-Propyl 3,4,5-tri-*n*-octyloxybenzoate **2/8**. Yield: 88%; Colorless liquid. $^1$HNMR ($CDCl_3$, 500MHz): $\delta$ = 0.88-0.90 (t, 9H, $J$ = 6.7 Hz, 3C**H**$_3$), 1.05-1.08 (t, 3H, $J$ = 7.2 Hz, C**H**$_3$), 1.27-1.51 (m, 30H, 15C**H**$_2$), 1.80-1.88 (m, 8H, 4OCH$_2$C**H**$_2$), 4.03-4.12 (m, 6H, 3OC**H**$_2$), 4.24-4.28 (t, 2H, $J$ = 6.5 Hz, ArCOOC**H**$_2$ ), 7.24 (s, 2H, Ar**H**).

*n*-Propyl 3,4,5-tri-*n*-decyloxybenzoate **2/10**. Yield: 94%; Colorless liquid. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.89-0.86 (t, $J$ = 6.7 Hz, 9H, 3C**H**$_3$)，1.00-1.02 (t, 3H, $J$ = 7.2 Hz, C**H**$_3$), 1.26-1.50 (m, 42H, 21C**H**$_2$), 1.80-1.87 (m, 8H, 4OCH$_2$C**H**$_2$), 4.37-4.33 (t, 2H, $J$ = 6.5 Hz, ArCOOC**H**$_2$ ), 7.25 (s, 2H, Ar**H**).

Compounds **2/14**, **2/16** and **2/18** were synthesized previously; the NMR data correspond to those reported in the references.[S1,S2]

### 1.2.2 3,4,5-Tri-*n*-alkoxybenzhydrazides 3/*n*[S3,S4]

A mixture of propyl 3,4,5-tri-*n*-alkoxybenzoate (2 mmol), excess hydrazine hydrate (2 mL), *n*-butanol (5 mL) and ethylene glycol ether (5 mL) was refluxed for 40 h. Water (25 mL) was added and the resulting precipitate was collected, dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure, the crude product was purified through a column chromatography (Dichloromethane : ethyl acetate = 10 : 1) to afford 3,4,5-trialkoxybenzhydrazide **3/*n***.

3,4,5-Tri-*n*-hexyloxybenzhydrazide **3/6**. Yield: 80%; white crystal, m.p. 90-92$^o$C. $^1$HNMR ($CDCl_3$, 500MHz): $\delta$ = 0.89-0.91 (t, 9H, $J$ = 6.5Hz, 3$CH_3$), 1.32-1.46 (m, 18H, 9$CH_2$), 1.73-1.79 (m, 6H, 3OCH$_2$C**H**$_2$), 3.98-4.00 (m, 6H, 3$OCH_2$), 6.95 (s, 2H, ArH), 7.77 (s, NH).

3,4,5-Tri-*n*-octyloxybenzhydrazide **3/8** was reported previously and the NMR data of **3/8** correspond to those reported in the literature.[S4]

3,4,5-Tri-*n*-decyloxybenzhydrazide **3/10**. Yield: 78%; colorless crystals, m.p.106-107 $^o$C. $^1$HNMR ($CDCl_3$, 500MHz): $\delta$ = 0.88-0.89 (t, 9H, $J$ = 6.5Hz, 3$CH_3$), 1.32-1.46 (m, 42H, 21$CH_2$), 1.73-1.79 (m, 6H, 3$OCH_2CH_2$), 3.97-3.98 (m, 6H, 3$OCH_2$), 7.04 (s, 2H, ArH), 7.54 (s, NH).

3,4,5-Tri-*n*-tetradecyloxybenzhydrazide **3/14**. Yield: 85%; colorless crystals, m.p.74-76 $^o$C. $^1$HNMR ($CDCl_3$, 500MHz): $\delta$ = 0.88-0.89 (t, 9H, $J$ = 6.5Hz, 3$CH_3$), 1.26-1.46 (m, 66H, 33$CH_2$), 1.73-1.81 (m, 6H, 3OCH$_2$C**H**$_2$), 3.97-4.00 (m, 6H, 3$OCH_2$), 6.93 (s, 2H, ArH), 7.35 (s, NH).

3,4,5-Tri-*n*-hexadecyloxybenzhydrazide **3/16**. Yield: 71%; colorless crystals, m.p.102-104 $^o$C. $^1$HNMR ($CDCl_3$, 500MHz): $\delta$ = 0.86-0.89 (t, 9H, $J$ = 6.5Hz, 3$CH_3$), 1.26-1.46 (m, 78H, 39$CH_2$), 1.71-1.81 (m, 6H, 3$OCH_2CH_2$), 3.99-4.00 (m, 6H,

3$OCH_2$), 6.93 (s, 2H, ArH), 7.29 (s, NH).

**Isophthaloyl dichloride 5**[S5]

Isophthalic acid (0.16 mmol) was solved in dry THF (10 mL) and DMF (1 drop) and thionyl chloride (10 mmol) was added. The mixture was heated to reflux for 10 h, then the solvent was removed *in vacuo,* the crude product (isophthaloyl dichloride) was dried *in vacuo* and used for the next reaction without further purification and characterization.

**1.2.3 1,3-Bis[5-(3,4,5-trialkoxyphenyl)-1,3,4-oxadiazol-2-yl]benzenes m/*n***

$N^{1'}$,$N^{3'}$-Bis(3,4,5-tri-*n*-alkoxybenzoyl)isophthaloyldihydrazines **6/*n***.

The isophthaloyl dichloride (1 mmol) was regularly injected into the THF (20 mL) solution of 3,4,5-trialkoxylbenzhydrazide (1 mmol) and triethylamine (1 mmol) under vigorous stirring at RT for 8h. The resulting crude products **6/*n*** were used directly for next step reaction.

1,3-Bis[5-(3,4,5-tri-*n*-alkoxyphenyl)-1,3,4-oxadiazol-2-yl]benzenes **m/*n***

**6/*n*** (1 mmol) was dissolved in phosphorous oxychloride ($POCl_3$, 5 mL) and refluxed for about 12h. Excess $POCl_3$ was removed through distillation and the residue was slowly added into ice water and extracted with dichloromethane. After removal of solvent in *vacuo*, the crude products were further purified through column chromatography (chloroform) to afford **m/*n*.**

1,3-Bis[5-(3,4,5-tri-*n*-hexyloxyphenyl)-1,3,4-oxadiazol-2-yl]benzene **m/6**. Colorless crystal. $^1$H-NMR ($CDCl_3$, 500MHz; *J*/Hz): $\delta$ = 0.87-0.90 (t, 18H, *J* = 6.5 Hz, 6$CH_3$), 1.29-1.51 (m, 36H, 18$CH_2$), 1.77-1.88 (m, 12H, 6$CH_2$), 4.04-4.07 (t, *J* = 6.3Hz, 4H, 2$OCH_2$), 4.09-4.10 (t, *J* = 6.5Hz, 8H, 4$OCH_2$), 7.36 (s, 4H, ArH), 7.72-7.75 (t, *J* = 7.8Hz, 1H, ArH), 8.31-8.33 (d, *J* = 7.6Hz, 2H, ArH), 8.91 (s, 1H, ArH). $^{13}$C NMR ( $CDCl_3$, 500 MHz): $\delta$ = 165.77 (2C), 163.96 (2C), 154.11 (4C), 142.27 (2C), 130.73 (2C), 130.53 (2C), 125.63 (2C), 118.52 (2C), 106.49 (4C), 74.11 (2C), 70.28 (4C), 32.14, 32.02, 30.73, 29.80, 26.23, 26.14, 23.05, 14.44 (multi carbons in alkyl chain). HRMS (TOF ES$^+$): *m/z* cacld for $C_{58}H_{86}N_4O_8$ $(M+Na)^+$: 989.6446 found: 989.6348.

1,3-Bis[5-(3,4,5-tri-*n*-octyloxyphenyl)-1,3,4-oxadiazol-2-yl]benzene **m/8**. Colorless crystal. $^1$H-NMR ($CDCl_3$, 500MHz; *J*/Hz): $\delta$ = 0.87-0.88 (t, 18H, *J* = 6.5 Hz, 6$CH_3$), 1.29-1.58 (m, 60H, 30$CH_2$) , 1.76-1.88 (m, 12H, 6$CH_2$), 4.04-4.07 (t, *J* = 6.2Hz, 4H, 2$OCH_2$), 4.09-4.11 (t, *J* = 6.1Hz, 8H, 4$OCH_2$),7.35 (s, 4H, ArH), 7.71-7.75 (t, *J* = 7.9 Hz, 1H, ArH), 8.31-8.34 (d, *J* = 7.8 Hz, 2H, ArH), 8.90 (s, 1H, ArH). $^{13}$C NMR ( $CDCl_3$, 500 MHz): $\delta$ = 165.76 (2C), 163.95 (2C), 154.11 (4C), 142.26 (2C), 130.72 (2C), 130.52 (2C), 125.62 (2C), 118.50 (2C), 106.47 (4C), 74.11 (2C), 70.28 (4C), 32.14, 32.02, 30.73, 29.80, 26.23, 26.14, 23.07, 14.48 (multi carbons in alkyl chain). HRMS (TOF ES$^+$): *m/z* cacld for $C_{70}H_{110}N_4O_8$ $(M+H)^+$: 1135.8324 found: 1135.8312

1,3-Bis[5-(3,4,5-tri-*n*-decyloxyphenyl)-1,3,4-oxadiazol-2-yl]benzene **m/10**. Colorless crystal. $^{1}$H-NMR ($CDCl_3$, 500MHz; *J*/Hz): $\delta$ = 0.87-0.90 (t, 18H, *J* = 6.5 Hz, $6CH_3$), 1.29-1.51 (m, 84H, $42CH_2$) , 1.77-1.88 (m, 12H, $6CH_2$), 4.04-4.07 (t, *J* = 6.5Hz, 4H, $2OCH_2$), 4.09-4.12 (t, *J* = 6.3Hz, 8H, $4OCH_2$), 7.36 (s, 4H, ArH), 7.72-7.75 (t, *J* = 7.8Hz, 1H, ArH), 8.31-8.33 (d, *J* = 7.6Hz, 2H, ArH), 8.91(s, 1H, ArH). $^{13}$C NMR ( $CDCl_3$, 500 MHz): $\delta$ = 165.73 (2C), 163.94 (2C), 154.12 (4C), 142.17 (2C), 130.73 (2C), 130.10 (2C), 125.59 (2C), 118.60 (2C), 106.09 (4C), 74.08 (2C), 69.93 (4C), 32.33, 30.77, 30.04, 30.00, 29.78, 26.52, 23.09, 14.49 (multi carbons in alkyl chain). HRMS (TOF ES$^+$): *m/z* cacld for $C_{82}H_{134}N_4O_8$ $(M+H)^+$: 1304.0202 found: 1304.0204.

1,3-Bis[2-(3,4,5-tri-*n*-tetradecyloxyphenyl)-1,3,4-oxadiazol-5-yl]benzene **m/14**. Colorless crystal. $^{1}$H-NMR ($CDCl_3$, 500MHz; *J*/Hz): $\delta$ = 0.86-0.89 (t, 18H, *J* = 6.5 Hz, $6CH_3$), 1.26-1.60 (m, 132H, $66CH_2$), 1.78-1.86 (m, 12H, $6CH_2$), 4.04-4.07 (t, *J* = 6.5Hz, 4H, $2OCH_2$), 4.10-4.12 (t, *J* = 6.3Hz, 8H, $4OCH_2$), 7.35 (s, 4H, ArH), 7.73-7.75 (t, 1H, *J* = 7.8 Hz, ArH), 8.31-8.33 (d, 2H, *J* = 7.7 Hz, ArH), 8.90 (s, 1H, ArH). $^{13}$C NMR ( $CDCl_3$, 500 MHz): $\delta$ = 165.73 (2C), 163.93 (2C), 154.12 (4C), 142.16 (2C), 130.31 (2C),, 130.10 (2C), 125.52 (2C), 118.58 (2C), 106.08 (4C), 74.08(2C), 69.93 (4C), 32.33, 3078, 30.12, 29.83, 29.78, 26.53, 23.09, 14.50 (multi carbons in alkyl chain). HRMS (TOF ES$^+$): *m/z* cacld for $C_{106}H_{182}N_4O_8$ $(M+Na)^+$: 1662.3958 found: 1662.3906

1,3-Bis[2-(3,4,5-tri-*n*-hexadecyloxyphenyl)-1,3,4-oxadiazol-5-yl]benzene **m/16**. Colorless crystal. $^{1}$H-NMR ($CDCl_3$, 500MHz; *J*/Hz): $\delta$ = 0.86-0.89 (t, 18H, *J* = 6.5 Hz, $6CH_3$), 1.27-1.59 (m, 156H, $78CH_2$) , 1.76-1.87 (m, 12H, $6CH_2$), 4.04-4.07 (t, *J* = 6.4Hz, 4H, $2OCH_2$), 4.10-4.12 (t, *J* = 6.2Hz, 8H, $4OCH_2$), 7.35 (s, 4H, ArH), 7.72-7.34 (t, 1H, *J* = 7.4Hz, ArH), 8.32-8.33 (d, 2H, *J* = 7.3Hz, ArH), 8.91 (s, 1H, ArH). $^{13}$C NMR ( $CDCl_3$, 500 MHz):$\delta$ = 165.73 (2C), 163.93 (2C), 154.12(4C), 142.16 (2C), 130.31 (2C), 130.10 (2C), 125.52 (2C), 118.58 (2C), 106.08 (4C), 74.08 (2C), 69.93 (4C), 32.33, 3078, 30.12, 29.83, 29.78, 26.53, 23.09, 14.50 (multi carbons in alkyl chain). HRMS (TOF ES$^+$): *m/z* cacld for $C_{118}H_{206}N_4O_8$ $(M+Na)^+$: 1830.5836 found: 1830.5786

### 1.3 Experimental procedures for compound p/*6*

1,4-Bis[5-(3,4,5-tri-*n*-hexyloxyphenyl)-1,3,4-oxadiazol-2-yl]benzene **p/6**. Synthesized in an analogous way as described for **m/6,** but using terepthaloylchloride instead of isophthaloylchloride. Colorless crystals, m.p. 140 °C [45.8 kJ/mol], crystallization temperature ($T_{cr}$): 127 °C. $^{1}$H-NMR ($CDCl_3$, 500MHz; *J*/Hz): $\delta$ = 0.74-0.92 (t, 18H, *J* = 6.4 Hz, $6CH_3$), 1.34-1.58 (m, 36H, $18CH_2$) , 1.75-1.88 (m, 12H, $6CH_2$), 4.04-4.07 (t, *J* = 6.3Hz, 4H, $2OCH_2$), 4.09-4.10 (t, *J* = 6.5Hz, 8H, $4OCH_2$), 7.35 (s, 4H, ArH), 8.31 (s, 4H, ArH). $^{13}$C NMR ( $CDCl_3$, 500 MHz): $\delta$ = 165.66 (2C),, 163.95 (2C), 154.12 (4C), 142.32 (2C), 127.86 (4C), 127.06 (2C), 118.58 (2C), 106.22 (4C), 74.08, 69.96, 32.32, 30.76, 30.04, 29.78, 26.50, 23.06, 14.45 (multi carbons in alkyl chain). HRMS

(TOF ES$^+$): *m/z* cacld for $C_{58}H_{86}N_4O_8$ $(M+H)^+$: 966.6446 found: 966.6442.

## 2. Additional data

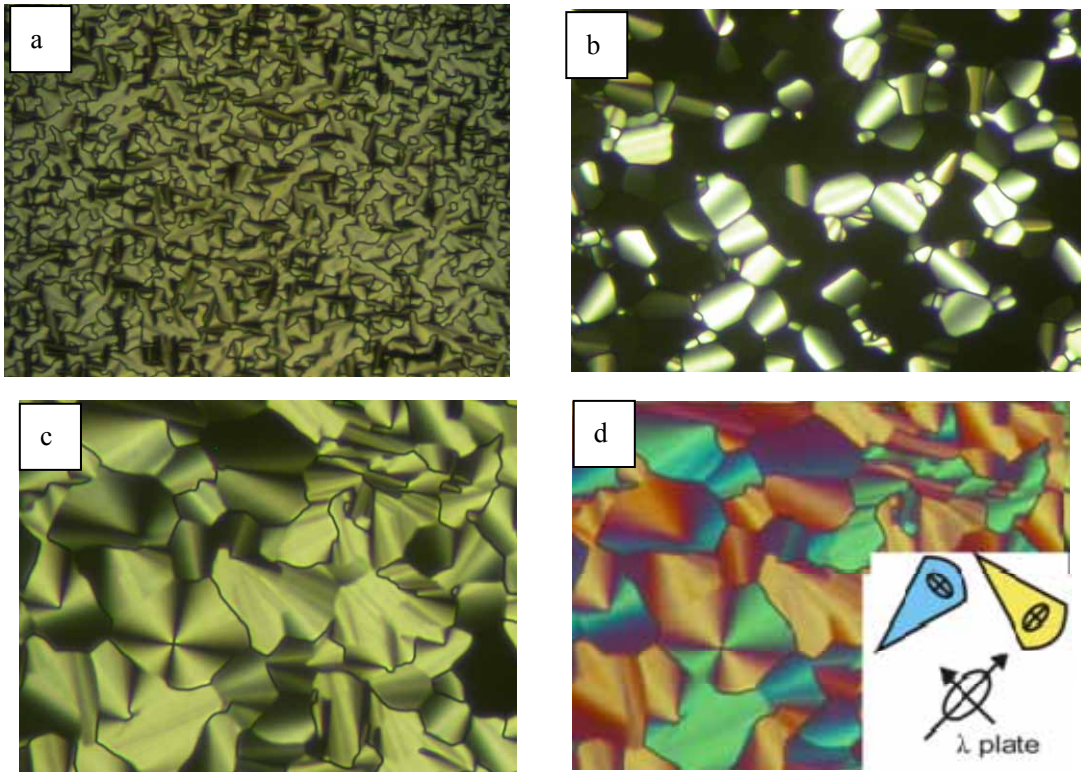



**Fig. S1** Optical textures of the hexagonal columnar mesophases of **(**a) **m/6** as seen between crossed polarizers at $T$ = 76 °C ; (b) **m/10** as seen between crossed polarizers at $T$ = 78 °C; (c) **m/16** as seen between crossed polarizers at $T$ = 83 °C; (d) texture of **m/16** with λ-plate in the same area and indicatrix orientation in the compensator.

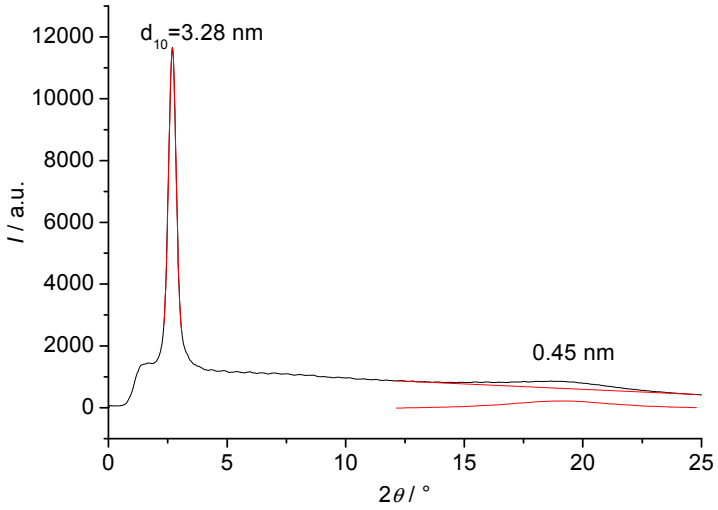


**Fig. S2** X-ray diffraction pattern of **m/14** at $T$ = 78 °C.

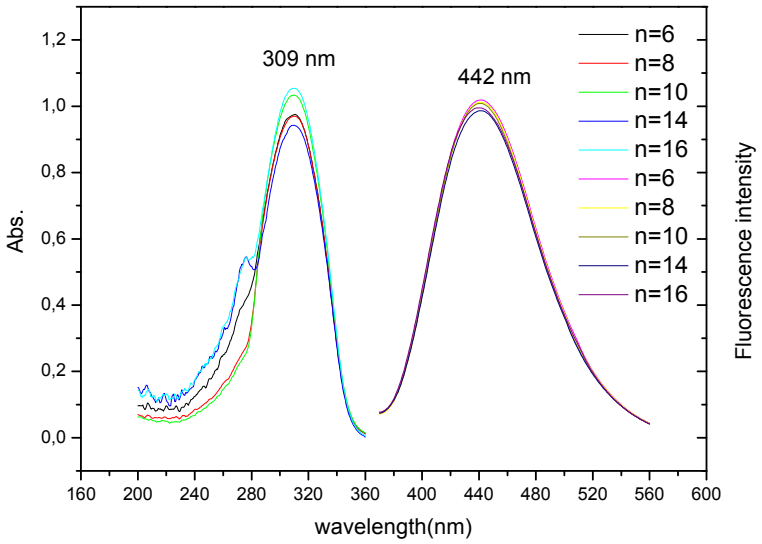



**Fig. S3** Normalized absorption spectra (left) and photoluminescence spectra (right) of compounds **m/*n*** ($n$ = 6-16) recorded in $CH_2Cl_2$ solution ($c$ = $10^{-6}$ mol $l^{-1}$) at room temperature.

## 3. References

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