# Supporting Information

## Benzothiadiazole based bolaamphiphiles: synthesis, self-assembly and white-light emissive property

Yulong Xiao,[‡[a]] Ruilin Zhang,[‡ [a, b]] Hongfei Gao,[[a]] Hongmei Zhao,[[a]] Xiaohong Cheng[*[a]]

[a] Key Laboratory of Medicinal Chemistry for Natural Resources, Chemistry Department, Yunnan University
Kunming,
Yunnan 650091,
P. R. China
Fax: (+86) 871 65032905
*E-mail: xhcheng@ynu.edu.cn

[b] Forensic Medicine of Kunming Medical University, Kunming, Yunnan 650500, P. R. China
‡Both authors contributed equally to this work

## Content

1. **Additional Experimental Data** ..... S2
2. **Syntheses and Analytical Data**..... S10
3. **References**..... S16

## 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 $min^{-1}$.

SEM experiments were carried out on a QUNT200 scanning electron microscopy (SEM, USA). All pictures were taken digitally. For the sample preparation, the gel was placed on an aluminium foil for some time until the gel became dry gel, then the sample was gold plated, finally the sample was put the sample into the scanning electron microscopy for observation.XRD measurement of xerogels was used the X-ray powder diffraction (XRD, Rigaku Co., Tokyo, Japan) analysis was conducted on a D/max-3B spectrometer with Cu Kα radiation.

Small-angle powder diffraction (SAXS) experiments were performed in transmission mode with synchrotron radiation at the 1W2A SAXS beamline at Beijing Accelerator Laboratory.[S1] A modified Linkam hot stage with a thermal stability within 0.2 ℃ was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. Samples were held in the poly(imide) (Kapton) film. A MarCCD 165 detector was used. $q$ calibration and linearization were verified using several orders of layer reflections from silver behemate. Positions and intensities of the diffraction peaks were measured using PeakSolve™ (Galactic).

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

$$E(xy) = \Sigma_{hk}\mathrm{sqrt}[I(hk)]\ \exp[i2\pi(hx+ky) + \phi_{hk}] \qquad (1)$$

For the centro-symmetric structures considered in this work the phase angle $\phi$ can take up the values of 0 or $\pi$. The choice of a phase combination was initially made on the merit of each reconstructed electron density map obtained using the most intense reflections, combined with the additional knowledge of the molecules (molecular shape, length, volume of each part and the distribution of electron density among the different moieties).

### 1.2 Molecular dynamics simulation

Annealing dynamics runs were carried out using the Universal Force Field (Material Studio, Accelrys). The structures in Fig. S7 was obtained with 4 or 2 molecules, respectively in a square prism 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 500 K, with a total annealing time of 30 ps.

### 1.3 Additional textures of LC phases, DSC traces and X-ray data

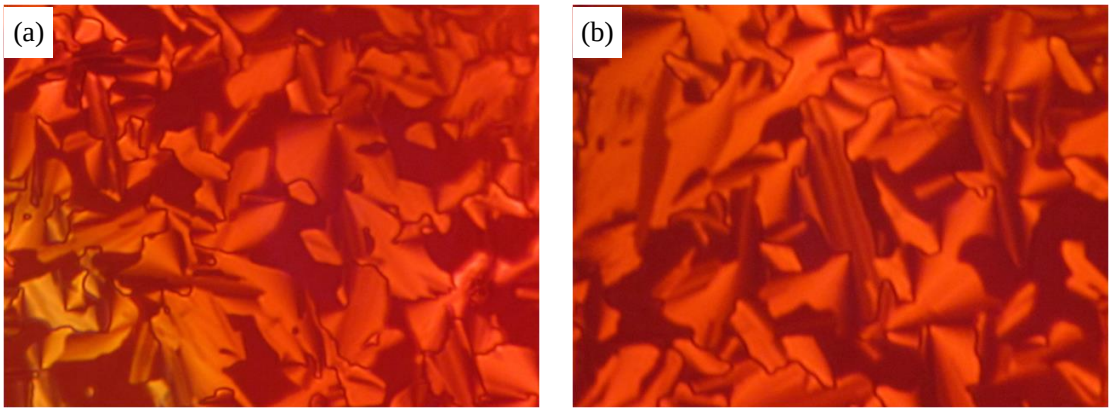



**Fig. S1** Representative textures between crossed polarizers: (a) the texture of $Col_{squ}/p4mm$ phase of **BTD/8** cooling at 80°C; (b) the texture of $Col_{squ}/p4mm$ phase of **BTD/12** cooling at 75°C.

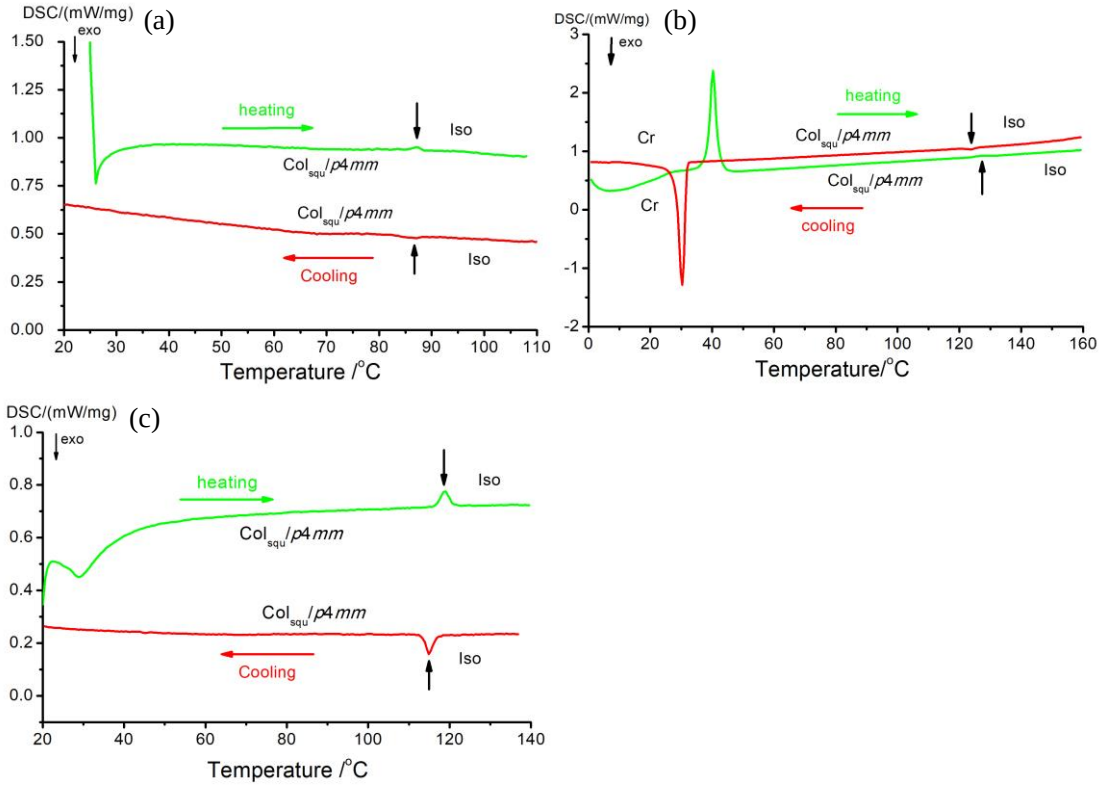



**Fig. S2** DSC heating and cooling scans (2 K $min^{-1}$) of (a) compound **BTD/8** (first scans); (b) compound **BTD/12** (second scans); (c) compound **BTD/16** (first scans).

**Table S1** Experimental and calculated *d*-spacings of the observed SAXS reflections of the square phase in compound **BTD/8** at 70 °C. All intensity values are Lorentz and multiplicity corrected.

| (*hk*) | $d_{obs.}$–spacing (nm) | $d_{cal.}$–spacing (nm) | *intensity* | *phase* |
|---|---|---|---|---|
| (10) | 3.17 | 3.17 | 100 | - |
| (11) | 2.24 | 2.24 | 0.20 | - |
| $a_{squ}$= 3.17 nm | | | | |

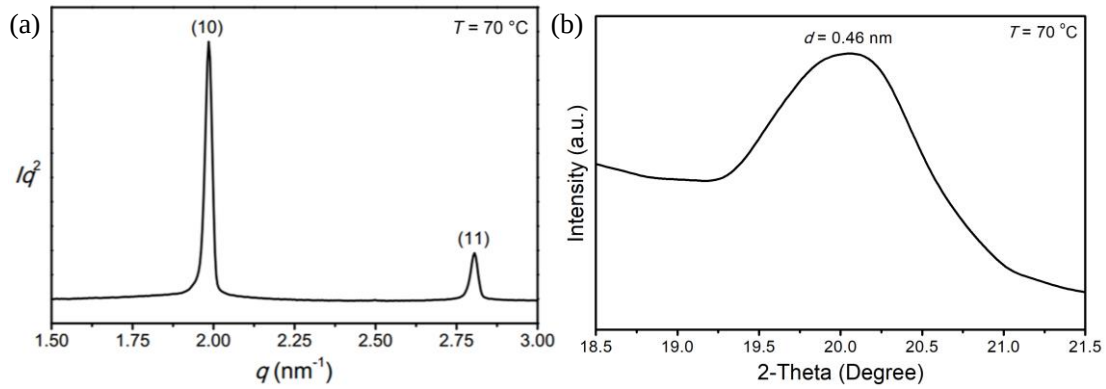



**Fig. S3** (a) SAXS diffraction pattern of $Col_{squ}/p4mm$ phase of compound **BTD/8** recorded at 70 °C; (b) Diffuse scattering in the wide angle region of the $Col_{squ}/p4mm$ phase of compound **BTD/8** at 70 °C.

**Table S2** Experimental and calculated *d*-spacings of the observed SAXS reflections of the square phase in compound **BTD/12** at 90 °C. All intensity values are Lorentz and multiplicity corrected.

| (*hk*) | $d_{obs.}$ – spacing (nm) | $d_{cal.}$ – spacing (nm) | *intensity* | *phase* |
|---|---|---|---|---|
| (10) | 3.20 | 3.19 | 100 | - |
| (11) | 2.25 | 2.26 | 0.09 | - |
| $a_{squ}$= 3.19 nm | | | | |

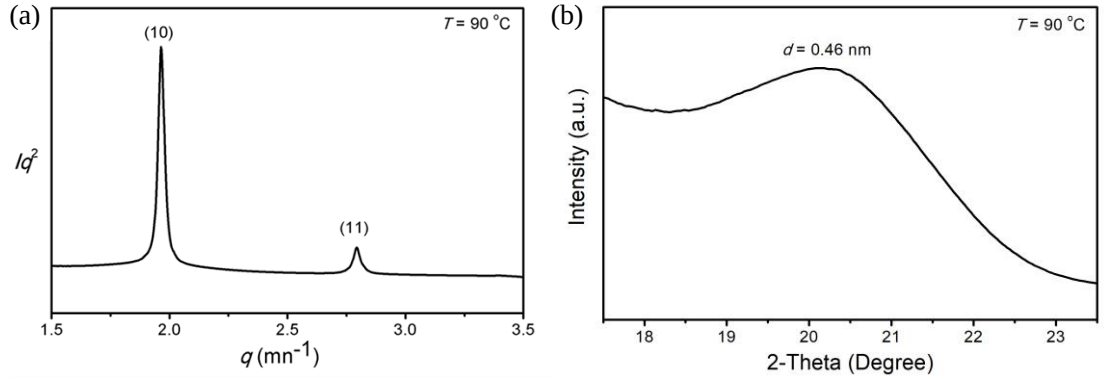



**Fig. S4** (a) SAXS diffraction pattern of $Col_{squ}/p4mm$ phase of compound **BTD/12** recorded at 90 °C; (b) Diffuse scattering in the wide angle region of the $Col_{squ}/p4mm$ phase of compound **BTD/12** at 90 °C.

**Table S3** Experimental and calculated *d*-spacings of the observed SAXS reflections of the square phase in compound **BTD/16** at 90 °C. All intensity values are Lorentz and multiplicity corrected.

| (*hk*) | $d_{obs.}$–spacing (nm) | $d_{cal.}$–spacing (nm) | *intensity* | *phase* |
|---|---|---|---|---|
| (10) | 3.18 | 3.19 | 100 | 0 |
| (11) | 2.26 | 2.26 | 0.11 | 0 |
| (20) | 1.60 | 1.60 | 0.01 | π |

| $a_{squ}$= 3.19 nm |
|---|

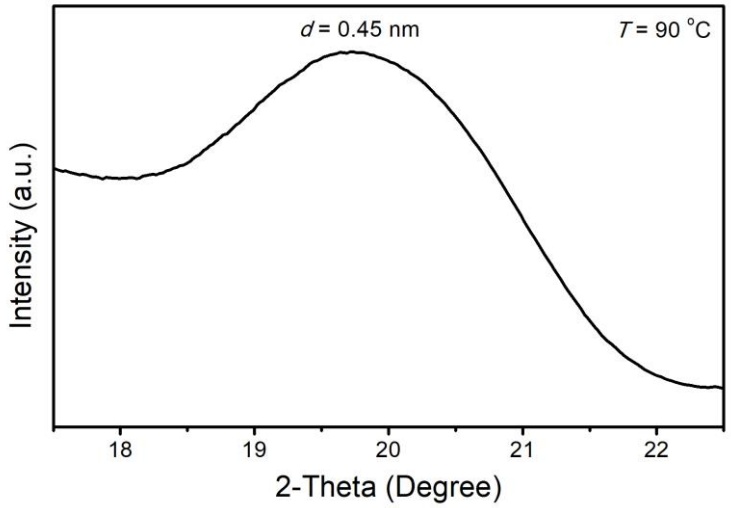



**Fig. S5** Diffuse scattering in the wide angle region of the $Col_{squ}/p4mm$ phase of compound **BTD/16** at 90 °C.

More details about the structure of the honeycomb LC phases were gained from the analysis of the molecular packing in the honeycombs based on the XRD data in Table S1-S3 and the calculated parameters collated in Table S4. The number of molecules in a hypothetical 3D unit cell was calculated from the volume of this unit cell ($V_{cell}$) and the volume of a molecule ($V_{mol}$, calculated using crystal volume increments[S2]) according to $n_{cell} = V_{cell}/V_{mol}$. $V_{cell}$ was estimated based on the experimental 2D lattice parameters and an assumed one-molecule thickness of $h$ = 0.45-0.46 nm corresponding to the experimentally determined maxima of the diffuse wide angle scatterings as shown in Fig. S3b, 4b and 5b.

The $n_{cell}$(average) values were corrected for an assumed packing density of 0.63 in the LC phase, which is intermediate between a crystal (0.7) and a liquid (0.55), see Table S4. The values $n_{cell}$(average) obtained in this way are in good agreement with those determined from the molecular mass ($M$), the Avagadro constant ($N$) and the density ($\rho$) according to $n_{cell}(\rho) = a^2hN\rho/M$ (Table S5); the density was determined for compounds **BTD/8** as $\rho$ = 1.167 g cm$^{-3}$, for compound **BTD/12** as $\rho$ = 1.124 g cm$^{-3}$ and for compound **BTD/16** as $\rho$= 1.095 g cm$^{-3}$ in the supercooled LC phase at 25 °C.

**Table S4** Calculations of molecular volumina ($V_{mol}$), volumina of the hypothetical unit cells ($V_{cell}$), number of molecules in these unit cells ($n_{cell}$) and calculated average numberof molecules in the cross section of the cylinder walls ($n_{wall}$) of compounds **2T/*n***,[S3] **BTD/*n*** and **4T/*n***.[S4a]

| Comp. | $a$/nm | $T$/°C | $V_{cell}$/nm$^3$ | $V_{mol}$/nm$^3$ | $f_R$ | $n_{cryst}$ | $n_{liq}$ | $n_{cell}$ (average) | $n_{wall}$ (average) |
|---|---|---|---|---|---|---|---|---|---|
| **2T/6** | 2.81 | - | 3.08 | 0.895 | 0.35 | 3.44 | 2.70 | 3.07 | 1.02 |
| **2T/7** | 2.80 | 50 | 3.06 | 0.945 | 0.38 | 3.24 | 2.55 | 2.90 | 0.97 |
| **2T/8** | - | - | - | 0.995 | 0.41 | - | - | - | - |
| **2T/12** | 2.78 | - | 3.48 | 1.193 | 0.51 | 2.92 | 2.29 | 2.60 | 1.30 |
| **BTD/8** | 3.17 | 70 | 4.52 | 1.15 | 0.36 | 3.93 | 3.09 | 3.51 | 1.78 |
| **BTD/12** | 3.19 | 90 | 4.58 | 1.35 | 0.45 | 3.40 | 2.67 | 3.04 | 1.54 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **BTD/16** | 3.19 | 90 | 4.58 | 1.55 | 0.53 | 2.96 | 2.33 | 2.65 | 1.33 |
| **4T/8** | 3.57 | 160 | 5.08 | 1.18 | 0.35 | 4.31 | 3.38 | 3.84 | 1.30 |
| **4T/12** | 3.25 | 130 | 4.86 | 1.38 | 0.44 | 3.53 | 2.77 | 3.15 | 1.60 |
| **4T/16** | 3.51 | 130 | 5.67 | 1.58 | 0.51 | 3.60 | 2.83 | 3.21 | 1.60 |

[a] $V_{cell}$ = volume of the unit cell defined by $a^2 \times h$ nm for square columnar phases; $V_{mol}$ = molecular volume as calculated using crystal volume increments;[S2] $n_{cryst}$ = number of molecules in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$; $n_{liqu}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{liqu} = 0.55/0.7 \times n_{cryst}$; $n_{cell}$ =number of molecules in the unit cell in the LC phase estimated as the average of that in the $n_{cryst}$ and $n_{liqu}$; $n_{wall}$ = number of molecules in the cross section of the cylinder walls as calculated from $n_{cell}$.

**Table S5**. Comparison of $n_{cell}$ (average), $n_{wall}$ (average), $n_{cell}(\rho)$ and $n_{wall}(\rho)$ values for compounds **BTD/*n***.

| Comp. | *T*/°C | $n_{cell}$ (average) | $n_{wall}$ (average) | $n_{cell}(\rho)$ | $n_{wall}$ $(\rho)$ |
|---|---|---|---|---|---|
| **BTD/8** | 70 | 3.56 | 1.78 | 3.80 | 1.90 |
| **BTD/12** | 90 | 3.08 | 1.54 | 3.27 | 1.63 |
| **BTD/16** | 90 | 2.33 | 1.33 | 2.55 | 1.27 |

$n_{cell}$ (average) = $V_{cell}/V_{mol}$; $n_{cell}$ $(\rho)$ was determined based on the measured density.

**Table S6**. Calculations of molecular volumina ($V_{mol}$), volumina of the hypothetical unit cells ($V_{cell}$), number of molecules in these unit cells ($n_{cell}$) and calculated average numberof molecules in the cross section of the cylinder walls ($n_{wall}$) of compounds **BTD/*n*** at different temperatures.

| Comp. | *a*/nm | *T*/°C | $V_{cell}$/nm$^3$ | $V_{mol}$/nm$^3$ | $f_R$ | $n_{cryst}$ | $n_{liq}$ | $n_{cell}$ (average) | $n_{wall}$ (average) |
|---|---|---|---|---|---|---|---|---|---|
| **BTD/8** | 3.37 | 50 | 5.11 | 1.15 | 0.36 | 4.44 | 3.49 | 3.97 | 1.99 |
| | 3.31 | 60 | 4.93 | 1.15 | 0.36 | 4.29 | 3.37 | 3.83 | 1.92 |
| | 3.17 | 70 | 4.52 | 1.15 | 0.36 | 3.93 | 3.09 | 3.51 | 1.78 |
| **BTD/12** | 3.33 | 70 | 4.99 | 1.35 | 0.45 | 3.70 | 2.91 | 3.31 | 1.65 |
| | 3.19 | 90 | 4.58 | 1.35 | 0.45 | 3.40 | 2.67 | 3.04 | 1.54 |
| **BTD/16** | 3.24 | 75 | 4.72 | 1.55 | 0.53 | 3.05 | 2.39 | 2.72 | 1.36 |
| | 3.19 | 90 | 4.58 | 1.55 | 0.53 | 2.96 | 2.33 | 2.65 | 1.33 |

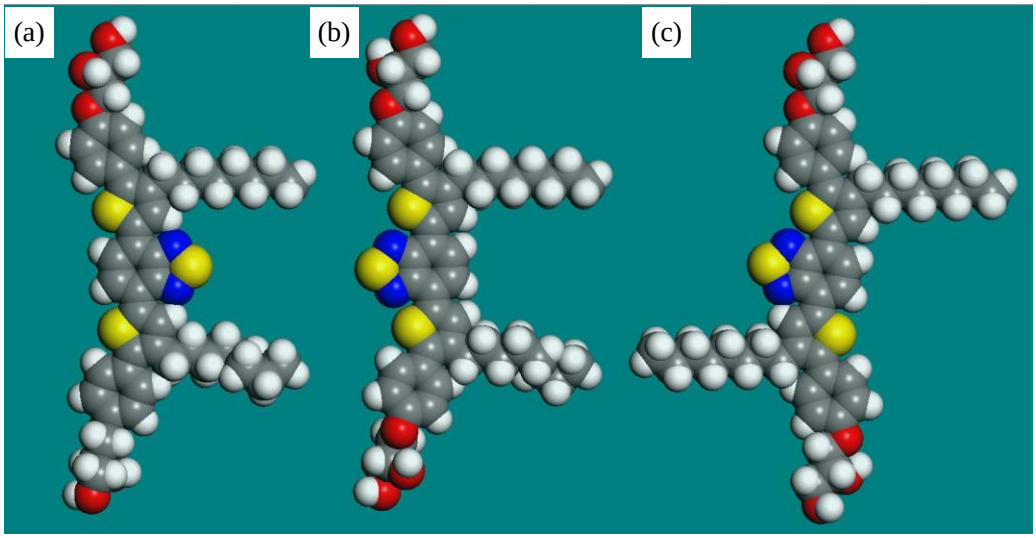



**Fig. S6** CPK molecular models showing compound **BTD/8** (a) and (b) in a bent conformation with parallel thiophene rings (both chains at one side, π-shape) and (c) in the most stretched conformation with antiparallel thiophene rings (X-shape).

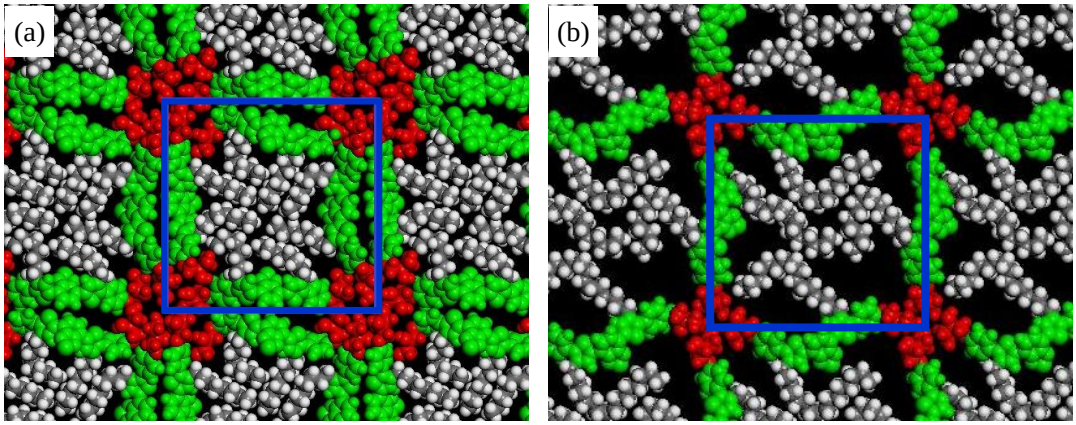



**Fig. S7** (a) Snapshot after molecular dynamics (MD) annealing of $Col_{squ}/p4mm$ phase with double-molecule wall of **BTD/8**,[S5] (b) Snapshot after molecular dynamics (MD) annealing of $Col_{squ}/p4mm$ phase with single-molecule wall of **BTD/16**.[S6]

**Table S7**. Calculated volumina of the hypothetical unit cells ($V_{cell}$) and number of molecules in these unit cells ($n_{cell}$) of compounds **BTD/*n*** according to the hypothesis that 4 molecules per cell.[a]

| Comp. | $a$/nm | $T$/°C | $c$/nm | $V_{cell}$/nm$^3$ | $V_{mol}$/nm$^3$ | $f_R$ | $n_{cryst}$ | $n_{liq}$ | $n_{cell}$ (average) | $n_{wall}$ (average) |
|---|---|---|---|---|---|---|---|---|---|---|
| **BTD/8** | 3.17 | 70 | 0.51 | 5.15 | 1.15 | 0.36 | 4.48 | 3.52 | 4.0 | 2.0 |
| **BTD/12** | 3.19 | 90 | 0.59 | 6.05 | 1.35 | 0.45 | 4.48 | 3.52 | 4.0 | 2.0 |
| **BTD/16** | 3.19 | 90 | 0.68 | 6.94 | 1.55 | 0.53 | 4.48 | 3.52 | 4.0 | 2.0 |

[a] $c = n_{cryst}V_{mol}/a^2$. $V_{cell}$/nm$^3$ was calculated using crystal volume increments.[S2]

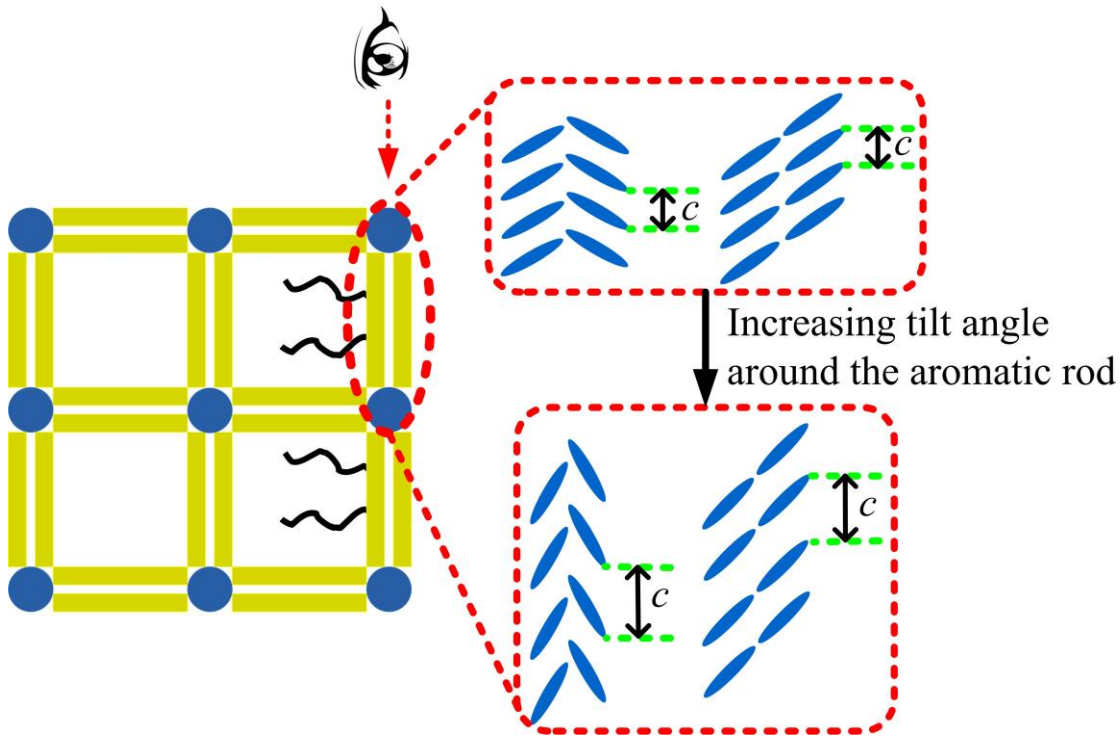



**Fig. S8** Possible molecular arrangement of double-molecule wall $Col_{squ}$/*p4mm* phase with tilted organization of rod-like aromatics. The inclination angle of the aromatic rod of **BTD/*n*** (rotation around its long axis) changed to fit the variable value of intermolecular distance along the column i.e. "*c*-parameter" from compound to compound. Since the aromatic cores are not cylindrical but are more or less like boards (not entirely planar, but the rings don't deviate too much from co-planarity because of hydrogen clashes. These are views along the molecular axis in a vertical wall. These are two possible stacking modes. The larger the tilt the larger is the intermolecular spacing along the column direction.

## 1.4 Additional gel, Photophysical, electrochemical and white emissive data

**Fig.S9** Image of gel of **BTD/16** obtained from *n*-butanol under daylight.

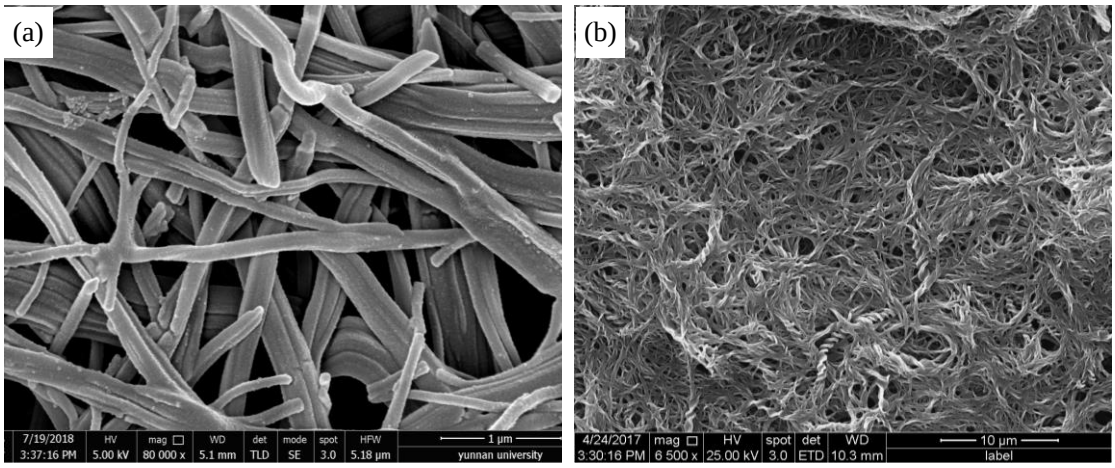



**Fig. S10** Another SEM images of xerogel formed by **BTD/16 (**a) in acetone; (b) in *n*-butanol.

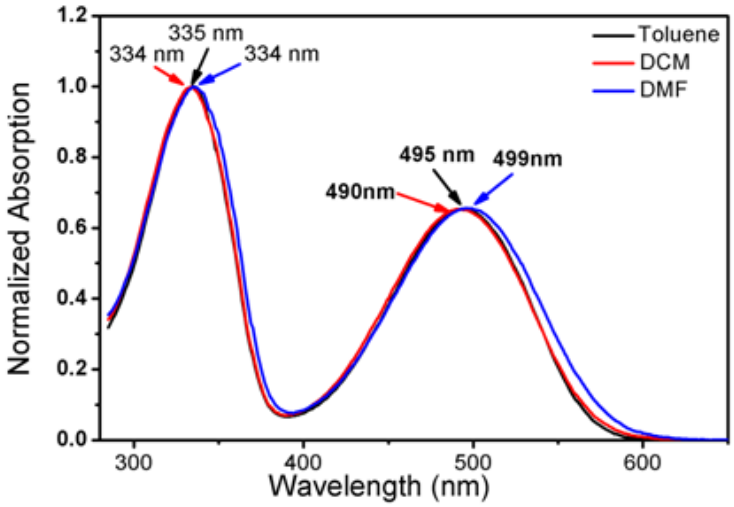



**Fig.S11** UV-vis spectra of **BTD/16** in toluene, DCM and DMF, respectively.

**Table S8** UV-vis absorption and fluorescence spectroscopy data of **BTD/16**.[a]

| Compd. | Solvent | $\lambda_{ex}$(nm) | $\lambda_{em}$(nm) | Stokes shift (nm) | $\Phi_{FL}$[b] |
|---|---|---|---|---|---|
| | Toluene | 335 | | | |
| | | 494 | 633 | 139 | 0.57 |
| | DCM | 334 | | | |
| **BTD/16** | | 490 | 655 | 165 | 0.45 |
| | DMF | 334 | | | |
| | | 499 | 685 | 186 | 0.38 |
| | Film | 342 | | | |
| | | 504 | 684 | 180 | -[c] |

[a] Stokes shifts = $\lambda_{em} - \lambda_{ex}$; [b] Relative to Rhodamine B in ethanol ($\Phi_{FL}$ = 0.65) as the standard; [c] not measured.

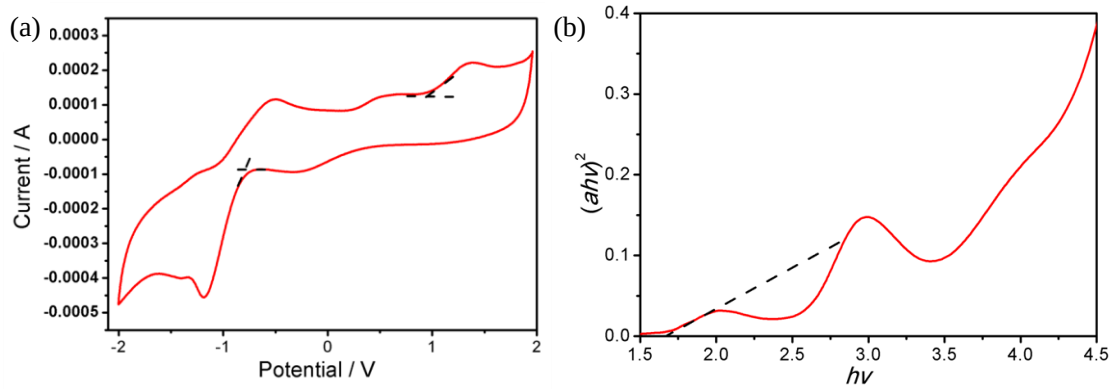



**Fig.S12** (a) Cyclic voltammogram of **BTD/16** film on glassy carbon electrode in 0.1 mol/L $Bu_4NBF_4$ in acetonitrile solution with a scan rate of 100 $mVs^{-1}$; (b) The calculation of energy band of **BTD/16** in film by UV-vis spectrum.

**Table S9** Electrochemical properties of **BTD/16** in $CH_3CN$ solution.

| Compd. | $E_{ox}$ (V)[a] | $E_{red}$(V)[a] | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $E_g$ (eV) |
|---|---|---|---|---|---|
| **I/16** | 1.00 | -0.75 | -5.80 | -4.05 | 1.75 |

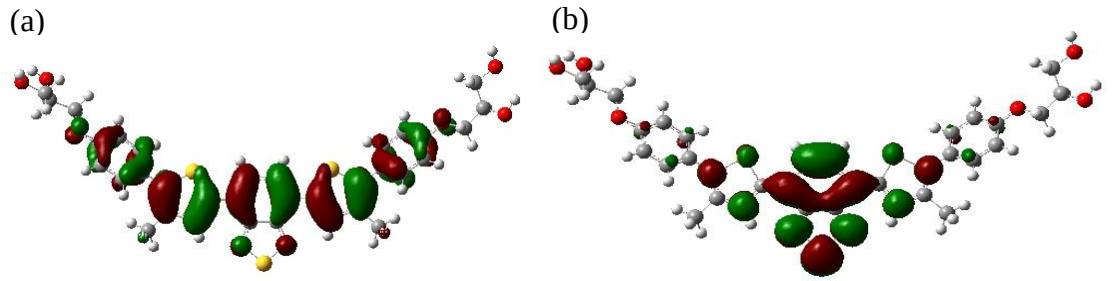



**Fig. S13** (a) HOMO orbital; (b) LUMO orbital of **BTD/16** (calculated using the DFT/B3LYP, 6-31G, d functional).

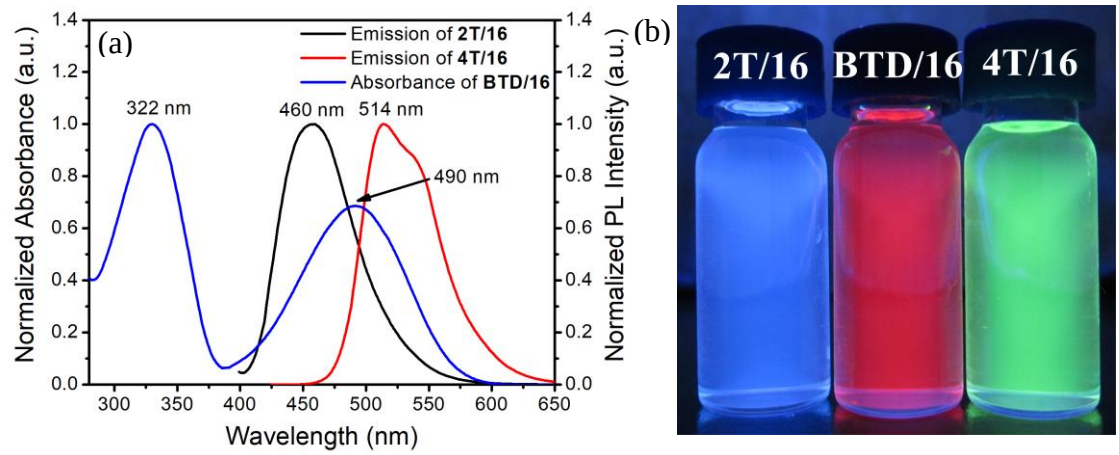
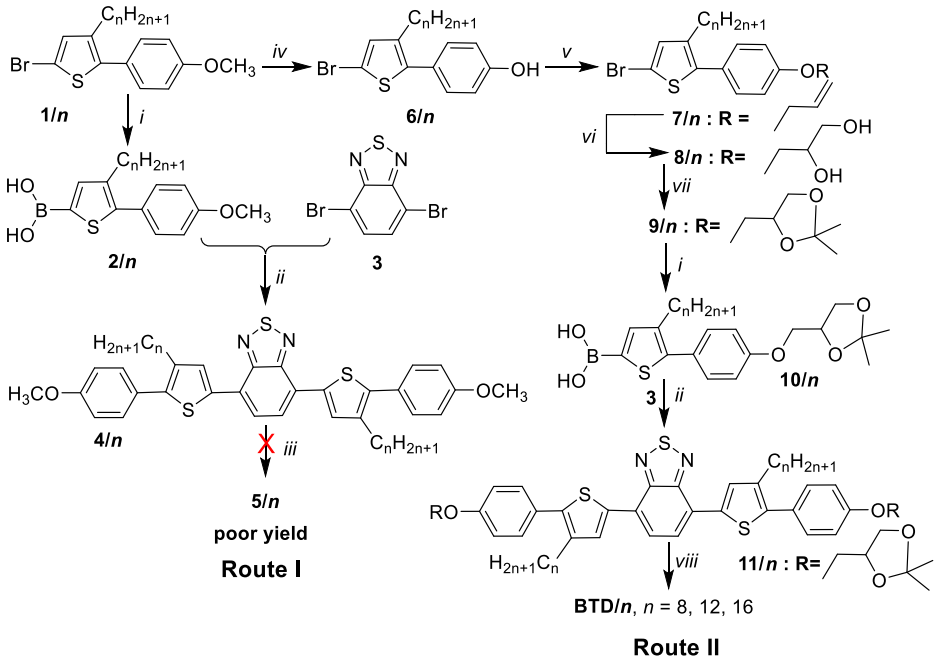



**Fig. S14** (a) UV-vis spectrum of **BTD/16** and fluorescence spectra of **2T/16** and **4T/16**; (b) Fluorescence images of their respective solutions under 365nm UV light irradiation.

## 1.3 Materials synthesis and analytical data

### 1.3.1 General

For the structures of the compounds see Scheme 1 in the main text. Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Tetrahydrofuran (THF) was distilled from sodium prior to use. Commercially available chemicals were used as received. $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker-DRX-400 spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Column chromatography was performed on Merck silica gel 60 (230-400 mesh).




**Scheme S1** Synthesis of compounds **BTD/*n***. *Reagents and conditions*: (*i*) (a) *n*-BuLi, THF, 1 h; (b) trimethylborate, -78 ºC, 6 h; (c) phosphate buffer, 0 ºC, 1 h; (*ii*) $Pd(PPh_3)_4$, $K_2CO_3$, THF, $H_2O$, reflux, 15 h; (*iii*) HBr, HOAc, reflux, 24 h; (*iv*) $BBr_3$, $CH_2Cl_2$, 12 h; (*v*) $K_2CO_3$, $CH_3CN$, allylbromide, reflux, 6 h; (*vi*) $OsO_4$, NMMNO, $H_2O$, acetone, RT; 5h; (*xii*) 2,2-dimethoxypropane, pyridinium *p*-toluene sulfonate, RT, 5 h; (*viii*) 10 % HCl, methanol, reflux, 12 h.

**General procedure for the synthesis of 5-Bromo-2-(4-methoxyphenyl)-3-alkylthiophenes 1/*n***

The synthesis of compounds 5-Bromo-2-(4-methoxyphenyl)-3-alkyl thiophenes **1/*n*** were carried out as described in ref.[S7]

**General procedure for the synthesis of 4-(5-bromo-3-alkylthiophen-2-yl)phenol 2/*n*[S8]**

5-Bromo-2-(4-methoxyphenyl)-3-alkylthiophene **1/*n*** (8.9 mmol) were dissolved in dry THF (20 mL) and this reaction mixture was cooled to –78 °C under $N_2$ atmosphere. Then *n*-BuLi (1.6 M solution in hexane, 7.8 mL) was added dropwise to the solution and stirred for 1 h at the same

temperature. Then trimethyl borate (5 mL, 44.5 mmol) was added dropwise at –78 °C. After stirring for 6 hours at the same temperature and then the mixture was warmed to 0 °C. And then the mixture was added to 200 mL of buffer solution composed of $NaH_2PO_4$-$Na_2HPO_4$ (pH = 4.5-5.0) and stirred at this temperature for 1 hour. Water (20 mL) and diethyl ether (50 mL) was added and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined exacts were washed with $H_2O$ (3 × 30 mL) and dried over anhydrous $Na_2SO_4$. After the solvent was evaporated in *vacuo*, the residue was crystallized once from petroleum ether. Additional purification steps do not enhance the purity, but drastically reduce the yield due to decomposition.

**General procedure for the synthesis of compounds 4/*n***

4,7-Dibromobenzo[c][1,2,5]thiadiazole **3**[S9] (147 mg, 0.5 mmol), compounds **2/*n*** (1.2 mmol), aqueous solution of $K_2CO_3$ (1M, 10 mL) were dissolved in THF (10 ml), then $Pd(PPh_3)_4$ (12.0 mg) was added under $N_2$ atmosphere. The mixture was refluxed at 78 °C and stirred for 15 h. After the reaction was complete (TLC), the mixture was cooled to RT and the mixture was extracted with ethyl acetate (3 × 40 mL). The combined extracts were washed with $H_2O$ (3 × 30 ml), dried over anhydrous $Na_2SO_4$, then the solvent was removed in *vacuo*. The residue was purified by column chromatography (petroleum ether: ethyl acetate = 7 : 1) to give a dark red solid.

**4,7-Bis(5-(4-methoxyphenyl)-4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole 4/8:** yield: 76%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.83 (s, 2 H, 2 Ar**H**), 7.47-7.44 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 6.99-6.96 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 3.87 (s, 6 H, 2ArOC**H**$_3$), 2.73-2.69 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.73-1.66 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.36-1.21 (m, 20 H, 10C**H**$_2$), 0.89-0.86 (t, *J* = 6.6 Hz, 6 H, 2C**H**$_3$); Elemental analysis calcd (%) for $C_{44}H_{52}N_2O_2S_3$ (737.09): C, 71.70; H, 7.11; N, 3.80; Found: C, 71.55; H, 7.01; N, 3.98.

**4,7-Bis(4-dodecyl-5-(4-methoxyphenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole 4/12:** yield: 75%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.83 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.8 Hz, 2 H, 2Ar**H**), 6.99-6.97 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 3.87 (s, 6 H, 2ArOC**H**$_3$), 2.72-2.68 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.72-1.65 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.36-1.21 (m,36 H, 18C**H**$_2$), 0.89-0.86 (t, *J* = 6.6 Hz, 6 H, 2C**H**$_3$); Elemental analysis calcd (%) for $C_{52}H_{68}N_2O_2S_3$ (849.31): C, 73.54; H, 8.07; N, 3.30; Found: C, 73.65; H, 8.24; N, 3.15.

**4,7-Bis(4-hexadecyl-5-(4-methoxyphenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole 4/16:** yield: 71%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.82 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 6.99-6.97 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 3.87 (s, 6 H, 2ArOC**H**$_3$), 2.73-2.69 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.73-1.64 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.36-1.20 (m,52 H, 26C**H**$_2$), 0.89-0.86 (t, *J* = 6.6 Hz, 6 H, 2C**H**$_3$); Elemental analysis calcd (%) for $C_{60}H_{84}N_2O_2S_3$ (961.52): C, 74.95; H, 8.81; N, 2.91; Found: C, 74.81; H, 8.60; N, 3.07.

**General procedure for the synthesis of compounds 5/*n***[S10]

Compounds **4/*n*** (0.3 mmol) and tetrabutylammonium bromide (96 mg, 0.3 mmol) were added to a 50 mL flask and HBr (33 % in HOAc, 2 mL) was added. The mixture was heated for 24 h at 100 °C, then the mixture was cooled to room temperature and water (100 mL) was added. The mixture was extracted with ethyl acetate (3 × 50 mL), and then organic solution was neutralized with NaOH (aq) and dilutes HCl (aq) in sequence. The organic solution was collected, dried over anhydrous $Na_2SO_4$ and filtrated, and then the solvent was evaporated in *vacuo*. The yields of the compounds **5/*n*** were relatively low, which made it impossible to reach the final step.

**General procedure for the synthesis of 4-(5-bromo-3-alkylthiophen-2-yl)phenol 6/*n***

5-Bromo-2-(4-methoxyphenyl)-3-alkylthiophene **1/*n*** (3.0 mmol) were dissolved in dry $CH_2Cl_2$ (20 mL) and cooled to –78 °C, $BBr_3$ (0.66 mL, 6.7 mmol) was added dropwise at that temperature and then the solution was stirred at room temperature for 12 hours. Water (50 mL) was added dropwise to quench the reaction and the mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic phases was dried over anhydrous $Na_2SO_4$ and filtrated. The solvent was evaporated in *vacuo*. The obtained product was used directly for the next step.

**General procedure for the synthesis of 2-(4-(allyloxy)phenyl)-5-bromo-3-alkylthiophene7/*n***

Allyl bromide (0.18 g, 1.5 mmol) was added to a mixture of **6/*n*** (2.0 mmol) and $K_2CO_3$ (0.82 g, 6.0 mmol) in dry $CH_3CN$ (15 mL) under $N_2$ atmosphere. The mixture was refluxed for 6 hours and then $CH_3CN$ was evaporated in *vacuo*. Water (50 mL) was added and organic compounds were extracted with ethyl acetate (3 × 50 mL). The combined organic phases was washed with water (3 ×50mL) and saturated NaCl solution (3 ×50mL), dried over anhydrous $Na_2SO_4$ and filtrated. The solvent was evaporated in *vacuo*. The crude product was purified by column chromatography (petroleum mether : ethyl acetate = 20 : 1).

**2-(4-(Allyloxy)phenyl)-5-bromo-3-octylthiophene7/8**: yield: 72%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.30-7.27 (d, $J$ = 8.8 Hz, 2 H, 2 Ar**H**), 6.96-6.94 (d, $J$ = 8.4 Hz, 2 H, 2Ar**H**), 6.91 (s, 1 H, Ar**H**), 6.13-6.04 (m, 1 H, $OCH_2C$**H**), 5.48-5.43 (m, 1 H, $OCH_2CHC$**H**$_2$), 5.34-5.30 (m, 1 H, $OCH_2CHC$**H**$_2$), 4.58-4.57 (t, $J$ = 2.6 Hz, 2 H, $OC$**H**$_2$), 2.64-2.53 (m, 2 H, $ArC$**H**$_2$), 1.57-1.54 (m, 2 H, $ArCH_2C$**H**$_2$), 1.33-1.20 (m, 10 H, $5C$**H**$_2$), 0.92-0.87 (t, $J$ = 6.8 Hz, 3 H, $C$**H**$_3$); Elemental analysis calcd (%) for $C_{21}H_{27}BrOS$ (407.41): C, 61.91; H, 6.68; Found: C, 61.70; H, 6.82.

**2-(4-(Allyloxy)phenyl)-5-bromo-3-dodecylthiophene7/12**: yield: 74%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.31-7.27 (d, $J$ = 8.8 Hz, 2 H, 2 Ar**H**), 6.96-6.93 (d, $J$ = 8.4 Hz, 2 H, 2Ar**H**), 6.91 (s, 1 H, Ar**H**), 6.13-6.04 (m, 1 H, $OCH_2C$**H**), 5.48-5.43 (m, 1 H, $OCH_2CHC$**H**$_2$), 5.34-5.30 (m, 1 H, $OCH_2CHC$**H**$_2$), 4.58-4.56 (t, $J$ = 2.6 Hz, 2 H, $OC$**H**$_2$), 2.64-2.53 (m, 2 H, $ArC$**H**$_2$), 1.57-1.54 (m, 2 H, $ArCH_2C$**H**$_2$), 1.33-1.19 (m, 18 H, $9C$**H**$_2$), 0.92-0.87 (t, $J$ = 6.8 Hz, 3 H, $C$**H**$_3$); Elemental analysis calcd (%) for $C_{25}H_{35}BrOS$ (463.52): C, 64.78; H, 7.61; Found: C, 64.89; H, 7.82.

**2-(4-(Allyloxy)phenyl)-5-bromo-3-hexadecylthiophene7/16**: yield: 77%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.30-7.26 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**),6.97-6.94 (d, *J* = 8.4 Hz, 2 H,2Ar**H**), 6.91 (s, 1 H, Ar**H**), 6.13-6.05 (m, 1 H, $OCH_2C\mathbf{H}$), 5.48-5.43(m, 1 H, $OCH_2CHC\mathbf{H}_2$), 5.34-5.31(m, 1 H, $OCH_2CHC\mathbf{H}_2$), 4.58-4.57(t, *J* = 2.6 Hz, 2 H, $OC\mathbf{H}_2$), 2.64-2.53 (m, 2 H, $ArC\mathbf{H}_2$), 1.57-1.54 (m, 2 H, $ArCH_2C\mathbf{H}_2$), 1.32-1.21 (m, 26 H, $13C\mathbf{H}_2$), 0.92-0.88 (t, *J* = 6.8 Hz, 3H, $C\mathbf{H}_3$); Elemental analysis calcd (%) for $C_{29}H_{43}BrOS$ (519.63): C, 67.03; H, 8.34; Found: C, 67.22; H, 8.15.

**General procedure for the synthesis of intermadiates 8/*n***

Compounds **7/*n*** (1.4 mmol) and NMMNO (1.0 mL, 60% solution in water) were dissolved inacetone. Osmium tetroxide (1.4 mL, 0.004 M solution in *tert*-butanol) was added, and the solution was refluxed for 5 hours at 50 ºC. Afterwards, saturated aqueous $Na_2SO_3$ (20 mL) was added, and the mixture was stirred for 30 min at room temperature. The mixture was filtered. Organic compounds were extracted with ethyl acetate (3 × 50 mL).The combined organic phases was washed with saturated aqueous $NaHCO_3$ (3 × 50 mL) and $H_2O$ (3 ×50mL), dried over anhydrous $Na_2SO_4$,and the solvent was evaporated in *vacuo*. The crude product was purified by column chromatography (petroleum mether : ethyl acetate = 5 : 1).

**Compound 8/8**: yield: 94%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz):$\delta$ = 7.29-7.27 (d, *J* = 8.0 Hz, 2 H, 2 Ar**H**), 6.95-6.93 (d, *J* = 8.0 Hz, 2 H, 2 Ar**H**), 6.91 (s, 1 H, Ar**H**), 4.14-4.12 (m, 1 H, $OCH_2C\mathbf{H}CH_2$), 4.08-4.07 (m, 2 H, $OC\mathbf{H}_2CHCH_2$), 3.80-3.75 (m, 2 H, $OCH_2CHC\mathbf{H}_2$), 2.61-2.51 (m, 2 H, $ArC\mathbf{H}_2$), 1.55-1.50 (m, 2 H, $ArCH_2C\mathbf{H}_2$), 1.33-1.19 (m, 10 H, 5 $C\mathbf{H}_2$), 0.93-0.86 (t, *J* = 6.6 Hz, 3 H, $C\mathbf{H}_3$); Elemental analysis calcd (%) for $C_{21}H_{29}BrO_3S$ (441.42): C, 57.14; H, 6.62; Found: C, 57.02; H, 6.77.

**Compound 8/12**: yield: 91 %; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz):$\delta$ = 7.29-7.27 (d, *J* = 8.0 Hz, 2 H, 2 Ar**H**), 6.95-6.93 (d, *J* = 8.0 Hz, 2 H, 2 Ar**H**), 6.90 (s, 1 H, Ar**H**), 4.14-4.13 (m, 1 H, $OCH_2C\mathbf{H}CH_2$), 4.08-4.07 (m, 2 H, $OC\mathbf{H}_2CHCH_2$), 3.78-3.74 (m, 2 H, $OCH_2CHC\mathbf{H}_2$), 2.61-2.51 (m, 2 H, $ArC\mathbf{H}_2$), 1.56-1.52 (m, 2 H, $ArCH_2C\mathbf{H}_2$), 1.32-1.20 (m, 18 H, 9 $C\mathbf{H}_2$), 0.93-0.86 (t, *J* = 6.6 Hz, 3 H, $C\mathbf{H}_3$); Elemental analysis calcd (%) for $C_{25}H_{37}BrO_3S$ (497.53): C, 60.35; H, 7.50; Found: C, 60.50; H, 7.36.

**Compound 8/16**: yield: 95 %; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz):$\delta$ = 7.29-7.27 (d, *J* = 8.0 Hz, 2 H, 2 Ar**H**), 6.96-6.93 (d, *J* = 8.0 Hz, 2 H, 2 Ar**H**), 6.90 (s, 1 H, Ar**H**), 4.14-4.13 (m, 1 H, $OCH_2C\mathbf{H}CH_2$), 4.09-4.07 (m, 2 H, $OC\mathbf{H}_2CHCH_2$), 3.79-3.74 (m, 2 H, $OCH_2CHC\mathbf{H}_2$), 2.61-2.51 (m, 2 H, $ArC\mathbf{H}_2$), 1.55-1.51 (m, 2 H, $ArCH_2C\mathbf{H}_2$), 1.32-1.20 (m, 26 H, 13 $C\mathbf{H}_2$), 0.92-0.86 (t, *J* = 6.6 Hz, 3 H, $C\mathbf{H}_3$); Elemental analysis calcd (%) for $C_{29}H_{45}BrO_3S$ (553.64): C, 62.91; H, 8.19; Found: C, 62.70; H, 8.29.

**General procedure for the synthesis of compounds 9/*n***

Compounds **8/*n*** (0.4 mmol) and 2,2-dimethoxypropane (5 mL) were dissolved in dry THF (20 mL). After addition of pyridium *p*-toluene solfonate (50 mg), the mixture was stirred at RT for 5

hours. The solvent was evaporated and water (50 mL) was added and organic compounds were extracted with ethyl acetate (3×50 mL). The combined organic phases was washed with saturated aqueous $NaHCO_3$ (3 × 50mL), $H_2O$ (3 × 50mL) and saturated aqueous NaCl (3 × 50mL) and the organic layer was dried with anhydrous $Na_2SO_4$ and the solvent was evaporated in *vacuo*. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1).

**Compound 9/8**: yield: 82%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz):$\delta$ = 7.28-7.26 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 6.94-6.92 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.90 (s, 1 H, Ar**H**), 4.52-4.47 (m, 1 H, $OCH_2CHCH_2$), 4.21-4.07 (m, 2 H, $OCH_2CHCH_2$), 3.94-3.90 (m, 2 H, $OCH_2CHCH_2$), 2.61-2.50 (m, 2 H, $ArCH_2$), 1.55-1.51 (m, 2 H, $ArCH_2CH_2$), 1.46 (s, 3 H, $CCH_3$), 1.41 (s, 3 H, $CCH_3$), 1.32-1.20 (m, 10 H, 5 $CH_2$), 0.90-0.86 (t, *J* = 6.8 Hz, 3 H, $CH_3$); Elemental analysis calcd (%) for $C_{24}H_{33}BrO_3S$ (481.49): C, 59.87; H, 6.91; Found: C, 59.97; H, 6.79.

**Compound 9/12**: yield: 87%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz):$\delta$ = 7.28-7.26 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 6.94-6.92 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.90 (s, 1 H, Ar**H**), 4.52-4.47 (m, 1 H, $OCH_2CHCH_2$), 4.20-4.07 (m, 2 H, $OCH_2CHCH_2$), 3.94-3.90 (m, 2 H, $OCH_2CHCH_2$), 2.61-2.51 (m, 2 H, $ArCH_2$), 1.55-1.51 (m, 2 H, $ArCH_2CH_2$), 1.47 (s, 3 H, $CCH_3$), 1.41(s, 3 H, $CCH_3$), 1.32-1.20 (m, 26 H, 13 $CH_2$), 0.90-0.86 (t, *J* = 6.8 Hz, 3 H, $CH_3$); Elemental analysis calcd (%) for $C_{28}H_{41}BrO_3S$ (537.60): C, 62.56; H, 7.69; Found: C, 62.67; H, 7.60.

**Compound 9/16**: yield: 80%; colourless liquid. $^1$H NMR ($CDCl_3$, 400 MHz):$\delta$ = 7.28-7.26 (d, *J* = 8.8 Hz, 2 H, 2 Ar**H**), 6.94-6.92 (d, *J* = 8.4 Hz, 2 H, 2 Ar**H**), 6.90 (s, 1 H, Ar**H**), 4.52-4.46 (m, 1 H, $OCH_2CHCH_2$), 4.20-4.08 (m, 2 H, $OCH_2CHCH_2$), 3.94-3.91 (m, 2 H, $OCH_2CHCH_2$), 2.61-2.50 (m, 2 H, $ArCH_2$), 1.55-1.51 (m, 2 H, $ArCH_2CH_2$), 1.47 (s, 3 H, $CCH_3$), 1.41(s, 3 H, $CCH_3$), 1.32-1.20 (m, 26 H, 13 $CH_2$), 0.90-0.86 (t, *J* = 6.8 Hz, 3 H, $CH_3$); Elemental analysis calcd (%) for $C_{32}H_{49}BrO_3S$ (593.71): C, 64.74; H, 8.32; Found: C, 64.88; H, 8.20.

**General procedure for the synthesis of compounds 10/*n***

**9/*n*** (1.2 mmol) was dissolved in anhydrous THF (20 mL) under an argon atmosphere. The solution was cooled to -78 °C and *n*-BuLi (1.6 M solution in hexane, 0.9 mL, 1.44 mmol) was added dropwise at this temperature. After stirring at -78 °C for 1 h, trimethyl borate (748.2 mg, 7.2 mmol), dissolved in 10 mL anhydrous THF, was added dropwise. After the mixture was stirred at -78 °C for 6 h, the mixture was warmed to 0 °C, and then the mixture was added to 200 mL of buffer solution composed of $NaH_2PO_4$-$Na_2HPO_4$ (pH = 4.5-5.0). After stirring for additional an hour, ethyl acetate (50 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (3 × 20 mL), brine (3 × 20 mL) and dried with anhydrous $Na_2SO_4$. After the solvent was evaporated in *vacuo*, the residue was crystallized once from petroleum ether. Additional purification steps do not enhance the purity, but drastically reduce the yield due to decomposition.

**General procedure for the synthesis of compounds 11/*n***

A mixture of compound **3** (147mg, 0.5mmol), boronic acids **10/*n*** (1.2mmol), $Pd(PPh_3)_4$, THF (10 mL) and aqueous solution of $K_2CO_3$ (1M, 10 mL) was refluxed for 15 hours under $N_2$ atmosphere, then cooled down to room temperature. Water (50 mL) was added and the mixture was extracted with ethyl acetate (3 × 50 mL).The combined organic phase was dried over anhydrous $Na_2SO_4$, and filtrated. The solvent was evaporated in *vacuo*. The crude product was purified by column chromatography (petroleum mether : ethyl acetate = 7 : 1) to give dark red solid.

**Compound 11/8:** yield: 76%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.83 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 6.99-6.97 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 4.52-3.85 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.73-2.69 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.72-1.65 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 CC**H**$_3$), 1.41(s, 6 H, 2 CC**H**$_3$), 1.36-1.20 (m, 20 H, 10C**H**$_2$), 0.90-0.86 (t, *J* = 6.6 Hz, 6 H, 2C**H**$_3$); Elemental analysis calcd (%) for $C_{54}H_{68}N_2O_6S_3$ (937.33): C, 69.20; H, 7.31; N, 2.99; Found: C, 69.10; H, 7.42; N, 3.11.

**Compound 11/12:** yield: 73%; dark red solid.$^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.83 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 6.99-6.96 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 4.55-3.84 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.73-2.69 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.72-1.64 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 CC**H**$_3$), 1.41 (s, 6 H, 2 CC**H**$_3$), 1.36-1.20 (m, 36 H, 18C**H**$_2$), 0.89-0.86 (t, *J* = 6.6 Hz, 6 H, 2C**H**$_3$); Elemental analysis calcd (%) for $C_{62}H_{84}N_2O_6S_3$ (1049.54): C, 70.95; H, 8.07; N, 2.67; Found: C, 70.85; H, 8.16; N, 2.83.

**Compound 11/16:** yield: 71%; dark red solid.$^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.83 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 6.99-6.97 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 4.51-3.85 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.73-2.69 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.72-1.65 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.47 (s, 6 H, 2 CC**H**$_3$), 1.41 (s, 6 H, 2 CC**H**$_3$), 1.36-1.20 (m, 52 H, 26C**H**$_2$), 0.89-0.86 (t, *J* = 6.6 Hz, 6 H, 2C**H**$_3$); Elemental analysis calcd (%) for $C_{70}H_{100}N_2O_6S_3$ (1161.76): C, 72.37; H, 8.68; N, 2.41; Found: C, 72.51; H, 8.58; N, 2.60.

**General procedure for the synthesis of target compounds BTD/*n***

A mixture of compounds **11/*n*** (0.3mmol) and 10% HCl (8 mL) in MeOH (30 mL) was refluxed for 12 hours and then cooled down to room temperature. The solvent was evaporated and saturated aqueous $NaHCO_3$ (50 mL) was added. The crude product was filtered and washed with water (3 × 20 mL) and then the crude product was purified by column chromatography (ethyl acetate).

**BTD/8**: yield: 84%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.00 (s, 2 H, 2 Ar**H**), 7.82 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 7.00-6.98 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 4.19-3.77 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.72-2.68 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.71-1.65 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.32-1.20 (m, 20 H, 10C**H**$_2$), 0.89-0.86 (t, *J* = 6.8 Hz, 6 H, 2C**H**$_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): 158.0 (2 C), 152.7 (2 C), 139.5 (2 C), 139.1 (2 C), 136.8 (2 C), 130.5 (4 C), 130.1 (2 C), 127.6 (2 C), 125.6 (2 C), 125.2 (2 C), 114.6 (4 C), 70.4 (2 C), 69.3 (2 C), 63.6 (2C), 31.9-28.9, 22.7, 14.1 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{48}H_{60}N_2O_6S_3$ (857.19): C, 67.26; H, 7.06; N, 3.27; Found: C, 67.15; H, 7.21; N, 3.16.

**BTD/12**: yield: 72%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.01 (s, 2 H, 2 Ar**H**), 7.83 (s, 2 H, 2 Ar**H**), 7.46-7.44 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 7.00-6.98 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 4.15-3.79 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.72-2.68 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.71-1.65 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.35-1.15 (m, 36 H, 18C**H**$_2$), 0.89-0.85 (t, *J* = 6.8 Hz, 6 H, 2C**H**$_3$). $^{13}$C NMR ($CDCl_3$, 100 MHz): 158 (2 C), 152.6 (2 C), 139.5 (2 C), 139.1 (2 C), 136.8 (2 C), 130.5 (4 C), 130.1 (2 C), 127.6 (2 C), 125.6 (2 C), 125.1 (2 C), 114.6 (4 C), 70.4 (2 C), 69.3 (2 C), 63.6 (2C), 31.9-28.9, 22.7, 14.1 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{56}H_{76}N_2O_6S_3$(969.41): C, 69.38; H, 7.90; N, 2.89; Found: C, 69.21; H, 7.78; N, 2.99.

**BTD/16**: yield: 79%; dark red solid. $^1$H NMR ($CDCl_3$; 400 MHz): $\delta$ = 8.06 (s, 2 H, 2 Ar**H**), 7.90 (s, 2 H, 2 Ar**H**), 7.47-7.44 (d, *J* = 8.4 Hz, 4 H, 4Ar**H**), 7.00-6.98 (d, *J* = 8.8 Hz, 4 H, 4Ar**H**), 4.20-3.77 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.70-2.68 (t, *J* = 8 Hz, 4 H, 2ArC**H**$_2$), 1.70-1.60 (m, 4 H, 2ArCH$_2$C**H**$_2$), 1.36-1.20 (m, 52 H, 26C**H**$_2$), 0.89-0.87 (t, *J* = 6.8 Hz, 6 H, 2C**H**$_3$).$^{13}$C NMR ($CDCl_3$, 100 MHz): 158 (2C), 152.6 (2 C), 139.5 (2 C), 139.1 (2 C), 136.8 (2 C), 130.5 (4 C), 130.1 (2 C), 127.6 (2 C), 125.6 (2 C),125.1 (2 C), 114.6 (4 C), 70.4 (2 C), 69.3 (2 C), 63.6 (2C), 31.9-28.9, 22.7, 14.1 (multicarbons in alkyl chains); Elemental analysis calcd (%) for $C_{64}H_{92}N_2O_6S_3$ (1080.61): C, 71.07; H, 8.57; N, 2.59; Found: C, 71.19; H, 8.45; N, 2.48.

## 3. References


[S1] Z. Li, Z. Wu, G. Mo, X. Xing and P. Liu, *Instrum. Sci. Technol.*, 2014, **42**, 128−141.

[S2] A. Immirzi and B. Perini, *Acta Crystallogr., Sect. A.*,1977, **33**, 216–218.

[S3] H. F. Gao, Y. F. Ye, L. Y. Kong, X. H. Cheng, M. Prehm, E. Ebert and C. Tschierske, *Soft Matter*., 2012, **8**, 10921–10931.

[S4] X. H. Cheng, H. F. Gao, X. P. Tan, X. Y. Yang, M. Prehm, H. Ebertb and C. Tschierske, *Chem. Sci*., 2013, **4**, 3317–3331.

[S5] M. Prehm, G. Götz, P. Bäuerle, F. Liu, X. B. Zeng, G. Ungar and C. Tschierske, *Angew. Chem. Int. Ed.*, 2007, **46**, 7856–7859.

[S6] R. Kieffer, M. Prehm, B. Glettner, K. Pelz, U. Baumeister, F. Liu, X. B. Zeng, G. Ungar and C. Tschierske, *Chem. Commun*., 2008, **33**, 3861–3863

[S7] X. H. Cheng, X. Dong, G. H. Wei, M. Prehm, C. Tschierske., *Angew. Chem. Int. Ed.*, 2009, 48, 8014–8017;

[S8] (a) M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain and S. Diele, *J. Am. Chem. Soc.* **2001**, *123*, 6809–6818; (b) X. H. Cheng, F. Liu, X. B. Zeng, G. Ungar, J. Kain, S. Diele, M. Prehm and C. Tschierske, *J. Am. Chem. Soc*. **2011**, *133*, 7872–7881.

[S9] D. X. Huang, M. Prehm, H. F. Gao,X. H. Cheng, Y. S. Liu, C. Tschierske, *RSC Adv*., 2016, **6**, 21387–21395.

[S10] (a) S. Y. Ku, K. T. Wong and A. J. Bard, *J. Am. Chem. Soc*., 2008, **130**, 2392–2393; (b) K. M. Omer, S. Y. Ku, K. T. Wong and A. J. Bard, *J. Am. Chem. Soc*., 2009, **131**, 10733–10741.