SUPPORTING INFORMATION (PART A)

# Facile Bottom-up Synthesis of Coronene-based 3-Fold Symmetrical and Highly Substituted Nanographenes from Simple Aromatics

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# 1 General

Unless otherwise mentioned, all commercials were used as received without further purification. THF were distilled from sodium with benzophenone as an indicator. $CH_2Cl_2$ and DMF were distilled from $CaH_2$. The reactions were monitored using analytical thin layer chromatography (TLC, GF-254). Flash chromatography was performed using silica gel (200−300 mesh) with freshly distilled solvents.

$^1$H NMR (300 MHz), $^1$H NMR (400 MHz) spectra were recorded on a Bruker Avance spectrometers using DSMO-$d_6$ or $CDCl_3$ as a solvent. $^{13}$C NMR (75 MHz), $^{13}$C NMR (100 MHz) and $^{13}$C NMR (150 MHz) spectra were recorded on Bruker Avance spectrometers using DSMO-$d_6$ or $CDCl_3$ as a solvent. Chemical shifts ($\delta$) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad), coupling constant $J$ (Hz) and integration. The mass spectra of the starting materials and the intermediates were recorded on a Bruker Avance Mass Spectrometer (maXis, ESI), the mass spectra of the termimal products were recorded on a Bruker Avance spectrometer (microflex, MALDI-TOF). Melting points were uncorrected.

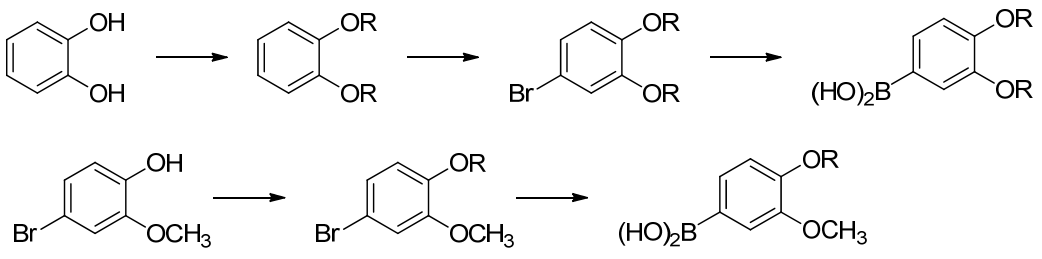
The crystal structure was recorded on an X-ray single crystal diffraction spectrometer (SuperNova) for **4b** and **5c**, or an X-ray single crystal diffraction spectrometer (GEMINIE) for **3a** and **3t**. Ultraviolet and visible spectra were obtained with an ultraviolet and visible spectrometer (TU-1900) in $CH_2Cl_2$. Fluorescence spectra were performed on a fluorescence spectrophotometer (CARY ECLIPSE). TG analyses were performed on athermal gravimetric analyzer (Q600-SDT) with a heating rate of 20 ºC/min under $N_2$.

# 2 Preparation of arylboronic acids and arylaldehydes

The starting material 1,3,5-tri(bromomethyl)benzene, some benzenebornic acids and most benzaldehydes are commercial availible or preparable according to the literature method. The arylboronic acids and arylaldehydes that are not commercial available or too expensive were synthesized here.

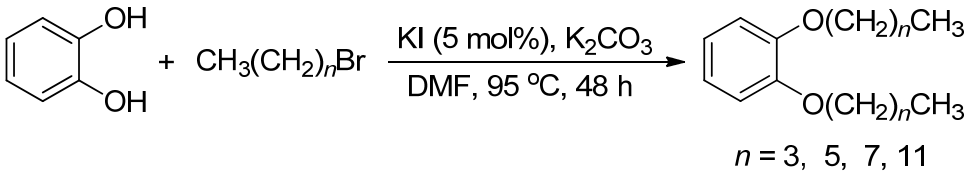
## 2.1 Preparation of arylboronic acids

Synthetic routes of arylboronic acids:



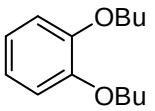

**Scheme S1:** Routes used for the preparation of arylboronic acids

### 2.1.1 The preparation of 1,2-dialkoxybenzenes

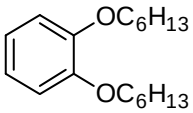



**Scheme S2:** The synthesis of 1,2-dialkoxybenzenes

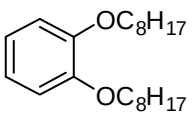
1,2-Dialkoxybenzenes were prepared by alkylation of catechol with appropriate alkylbromides according to the literature method[1] A mixture of catechol (11 g, 100 mmol), anhydrous $K_2CO_3$ (4.0 equiv), KI (5 mol %), and 1-bromoalkane (2.2 equiv) in 100 mL dry *N, N*-dimethylformide (DMF) was stirred at 95 ºC (oil temperature) under Ar atmosphere for 72 h. After cooling to room temperature, the resulting mixture was poured into 500 mL $H_2O$ and was extracted with petroleum ether (PE). The combined organic layer was washed by water and dried by $Na_2SO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography.




**1,2-Dibutoxybenzene** was prepared from catechol and 1-bromobutane and purified by flash column chromatography (silica gel, PE:DCM = 6:1, v/v) to give a colorless liquid (yield 82 %). The observed characterization data was consistent with that previously reported in the literature.[2] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.89 (s, 4H), 4.02-3.97 (t, $J$ = 7.5 Hz, 4H), 1.77-1.85 (m, $J$ = 7.5 Hz, 4H), 1.45−1.55 (m, $J$ = 7.4 Hz, 4H), 0.94−1.00 (t, $J$ = 7.4 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.3, 121.0, 114.2, 69.0, 31.4, 19.3, 13.9.

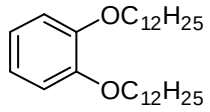



**1,2-Bis(hexyloxy)benzene** was prepared from catechol and 1-bromohexane and purified by flash column chromatography (silica gel, PE:DCM = 6:1, v/v); Colorless oil (yield 89 %). The observed characterization data was consistent with that previously reported in the literature. [2] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.89 (s, 4H), 4.04-3.98 (t, $J$ = 6.6 Hz, 4H), 1.87−1.77 (m, 4H), 1.46−1.33 (brs, 12H), 0.94−0.88 (t, $J$ = 6.0 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.3, 121.0, 114.2, 69.3, 31.6, 29.3, 25.7, 22.6, 14.0.




**1,2-Bis(octyloxy)benzene** was prepared from catechol and 1-bromooctane and purified by flash column chromatography (silica gel, PE:DCM = 6:1, v/v); Colorless oil (yield 90 %). The observed characterization data was consistent with that previously reported in the literature.[2] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.90 (s, 4H), 4.03-3.99 (t, $J$ = 6.6 Hz, 4H), 1.88−1.81 (m, 4H), 1.50−1.31 (brs, 20H),

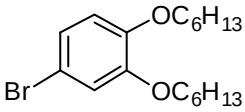
0.91−0.88 (brs, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.3, 121.0, 114.2, 69.3, 31.9, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1.



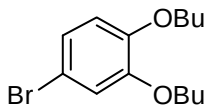

**1,2-Bis(dodecyloxy)benzene** was prepared from catechol and 1-bromododecane and purified by column chromatography (silica gel, PE then PE:DCM = 6:1, v/v). Waxy solid (yield 87 %); Mp 44–46 ºC (Mp 47–49 ºC, lit.[5]); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.89 (brs, 4H), 4.01−3.97 (t, $J$ = 6.6 Hz, 4H), 1.86−1.76 (m, 4H), 1.49−1.26 (brs, 36H), 0.91−0.88 (t, $J$ = 6.0 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.3, 121.0, 114.2, 69.3, 31.9, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1.

### 2.1.2 The preparation of the aryl bromides with two identical alkoxy groups

The aryl bromides with two identical alkoxy groups were prepared by bromination of the 1,2-dialkoxybenzenes with NBS according to the literature method.[3]

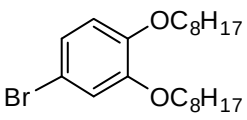



**4-Bromo-1,2-bis(hexyloxy)benzene**. A 500 mL three necked round-bottom flask equipped with a magnetic stirrer, $SiO_2$ (9.00 g) and NBS (3.36 g, 18.86 mmol) were added to a solution of 1,2-bis(hexyloxy)benzene (4.99 g, 17.92 mmol) in dry DCM (180 mL). After vigorous stirring at room temperature for 8 h, this mixture was filtered to remove $SiO_2$, concentrated under reduced pressure to *ca*. 50 mL, and washed with saturated aqueous $Na_2S_2O_5$ (50 mL). The aqueous layer was extracted with DCM and the combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, PE:DCM = 6:1, v/v) to give a colorless oil (yield 97 %). The observed characterization data was consistent with that previously reported in the literature.[3] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.00−6.96 (m, 2 H), 6.74−6.71 (m, 1 H), 3.97−3.92 (m, 4H), 1.80−1.27 (m, 16H), 0.86−0.89 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.1, 148.4, 123.5, 117.0, 115.2, 112.8, 69.6, 69.4, 31.6, 31.5, 29.2, 29.1, 25.7, 22.6, 14.0. HR-MS (ESI): *m/z* calcd for ($C_{18}H_{29}BrO_2$ + Na), 379.1249, found: 379.1251.

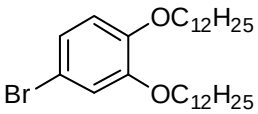



**4-Bromo-1,2-dibutoxybenzene** was prepared from 1,2-bis(octyloxy)benzene according to the similar procedure to 4-Bromo-1,2-bis(hexyloxy)benzene. The resulting residue was purified by column chromatography (silica gel, PE) to give a colorless oil (yield 96 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.99−6.97 (m, 2H), 6.75−6.73 (m, 1H), 3.99−3.95 (m, 4H), 1.81−1.76 (m, 4H), 1.54−1.48 (m, 4H), 1.00−0.95 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.1, 148.5, 123.5, 117.0, 115.3, 112.8, 69.2, 69.1, 31.3, 31.2, 19.2, 13.86.

HR-MS (ESI): *m/z* calcd for ($C_{14}H_{21}BrO_2$ + Na), 323.0623, found: 323.0625.

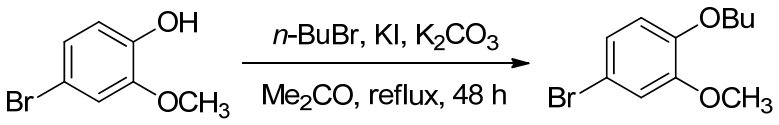


**4-Bromo-1,2-bis(octyloxy)benzene** was prepared from 1,2-bis(octyloxy)benzene according to the similar procedure to 4-bromo-1,2-bis(hexyloxy)benzene. The resulting residue was purified by column chromatography (silica gel, PE:DCM = 6:1, v/v) to give a colorless oil (yield 92 %). The observed characterization data was consistent with that previously reported in the literature.[4] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.06−6.89 (m, 2H), 6.75−6.73 (m, 1H), 4.02−3.97 (m, 4H), 1.84−1.29 (m, 24H), 0.87−0.89 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.1, 148.4, 123.5, 117.0, 115.2, 112.8, 69.6, 69.4, 31.6, 31.5, 29.2, 29.1, 25.7, 22.6, 14.0. HR-MS (ESI): *m/z* calcd for ($C_{22}H_{37}BrO_2$ + Na), 435.1875, found: 435.1878.



**4-Bromo-1,2-bis(dodecyloxy)benzene** was prepared according to the similar procedure from 1,2-bis(dodecyloxy)benzene to 4-bromo-1,2-bis(hexyloxy)benzene. The crude product was purified by column chromatography (silica gel, PE:DCM = 15:1, v/v) to give a needlelike solid (yield 91 %); Mp 27–28 ºC; The observed characterization data as consistent with that previously reported in the literature.[1] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.00−6.96 (m, 2H), 6.71−6.75 (m, 1H), 3.98−3.92 (m, 4H), 1.85−1.74 (m, 4H) 1.48−1.33 (brs, 36H), 0.90−0.86 (t, $J$ = 6.5 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.1, 148.4, 123.5, 117.0, 115.2, 112.8, 69.6, 69.4, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; HR-MS (ESI): *m/z* calcd for ($C_{30}H_{53}BrO_2$ + Na), 547.3127, found: 547.3124.

### 2.1.2 The preparation of aryl bromide with two different alkoxy groups: 4-bromo-1-butoxy-2-methoxybenzene



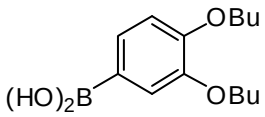

**Scheme S3:** The synthesis of 4-bromo-1-butoxy-2-methoxybenzene

A 500 mL three necked round-bottom flask equipped with a magnetic stirrer, a T-shaped $N_2$ inlet and a condenser was charged with 4-bromo-2-methoxyphenol (20.3 g, 0.10 mol), $K_2CO_3$ (20.7 g, 150 mmol), KI (0.85 g, 5 mmol), 1-bromobutane (16.3 g, 0.12 mol) and 300 mL dry acetone. The mixture was refluxed for 48 h with stirring under Ar atmosphere. The resulting mixture was filtered, concentrated to 1/3 volume and poured into water and extracted with PE (3 × 150 mL). The combined organic layer was washed by water and dried with $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, PE:DCM = 20:1,

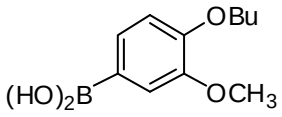
v/v) to give a light yellow oil (22.3 g, yield 86 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.06−6.97 (m, 2H), 6.75−6.72 (m, 1H), 4.00−3.95 (t, $J$ = 6.6 Hz, 2H), 3.84 (s, 3H), 1.83−1.78 (m, 2H), 1.60−1.41 (m, 2H), 0.99−0.94 (t, $J$ = 7.4 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.3, 147.9, 123.3, 115.2, 114.3, 112.6, 69.0, 56.2, 31.2, 19.2, 13.8; HR-MS (ESI): *m/z* calcd for ($C_{11}H_{15}BrO_2$ + Na), 281.0153, found: 281.0148.

### 2.1.3 The preparation of arylboronic acids

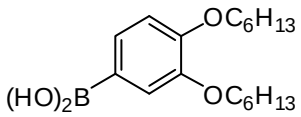
Substituted phenylboronic acids were synthesized from the corresponding arylbromides and triisopropyl borate according to the literature procedure[5] with a slight modification.



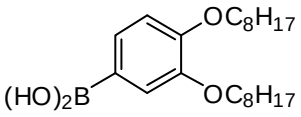

**3,4-Dibutoxyphenylboronic acid**. To a 500 mL three necked, round bottomed flask were fitted with a thermometer, a magnetic stirrer, and a pressure equalizing dropping funnel. The flask was charged with 4-bromo-1,2- bis(butoxy)benzene (30.1 g, 100 mmol), triisopropyl borate (30.0 mL, 130 mmol) and dry THF (350 mL) under Ar atomosphere. The reaction mixture was cooled to *ca.* – 80 ºC and *n*-BuLi/hexane (2.5 M, 52 mL, 130 mmol) was added dropwise over 1.5 h. Upon completion of the addition, the reaction mixture was stirred at – 80 ºC for 2 h and then allowed to warm to room temperature over 8 h. The resulting mixture was acidified with 6 N HCl (26 mL) and stirred for overnight. After being concentrated to 1/3 volume, the mixture was poured into water, extracted with diethyl ether and washed with water, dried over $MgSO_4$, followed by filtration under rotary evaporation. Then, cold hexane was added and the precipitate filtered to give a white solid (22.9 g, yield 86 %). The product was used without further purification in the next step; The analytical sample was obtained by recrystallization from water with a few drops of ethyl ether to give a white solid; Mp 160−162 ºC; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.83 (brs, 2 H), 7.37−7.33 (m, 2 H), 6.92−6.88 (m, 1H), 3.96−3.94 (m, 4 H), 1.70−1.60 (m, 4H), 1.46−1.43 (m, 4H), 0.93 (t, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 155.7, 152.9, 133.1, 124.8, 117.9, 73.3, 72.9, 36.2, 36.1, 24.0, 18.9.



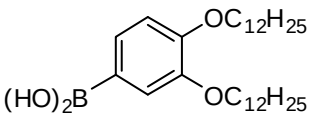

**4-Butoxy-3-methoxyphenylboronic acid** was obtained as a white solid according to the general procedure from 4-bromo-1-butoxy-2-methoxybenzene, triisopropyl borate, n-BuLi/hexane (2.5 M) in dry THF. The product was used without further purification; The analytical sample was obtained by recrystallization from water/ethyl ether (yield 83 %); Mp 161−163 ºC. $^1$H NMR (300 MHz, DMSO−$d_6$): $\delta$ 7.84 (s, 2H), 7.36−7.33 (m, 2H), 6.91−6.89 (d, $J$ = 6.0 Hz, 1H), 3.95 (t, $J$ = 6.5 Hz, 2H), 3.75 (s, 3H), 1.71−1.67 (m, 2H), 1.45−1.40 (m, 2H), 0.95−0.91 (t, $J$ = 5.6 Hz, 3H); $^{13}$C NMR (75 MHz, DMSO−$d_6$): $\delta$ 150.1, 148.1, 127.7, 117.6, 112.1, 67.6, 55.4, 30.8, 18.7, 13.7.



**3,4-Bis(hexyloxy)phenylboronic acid** was prepared according to the same procedure to 3,4-dibutoxyphenylboronic acid from 4-bromo-1,2-bis(hexyloxy) benzene, triisopropyl borate, *n*-BuLi/hexane (2.5 M) in dry THF. The product was used without further purification; The analytical sample was recrystallized from water/ethyl ether to give a white solid ( yield 83 %); Mp 126–128 ºC; $^1$H NMR (300 MHz, DMSO−$d_6$): $\delta$ 7.85 (s, 2 H), 7.41−7.37 (m, 2 H), 6.93−6.96 (m, 1 H), 4.02−3.98 (m, 4 H), 1.77−1.72 (m, 4H), 1.51−1.30 (m, 12H), 0.93 (brs, 6 H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 153.3, 148.4, 130.0, 120.7, 112.6, 69.6, 68.8, 31.6, 31.5, 29.4, 29.1, 25.8, 25.7, 22.6, 14.0.



**3,4-Bis(octyloxy)phenylboronic acid**[6] The above procedure was failed to obtain the arylboronic acids in pure form from arylbromides with long-aliphatic chains. We therefore revised the synthetic procedure by changing the loading sequence of the reactants and succeeded in access this compound. The detailed preparation is as follows: To a 500 mL three necked, round bottomed flask were fitted with a thermometer, a magnetic stirrer, and a pressure equalizing dropping funnel. The flask was charged with dry THF (300 mL) and cooled to – 80 ºC under Ar atmosphere with stirring. Then, *n*-BuLi/hexane (2.5 M, 26 mL, 65 mmol) was added dropwise and the resulting mixture was allowed to stir at – 80 ºC for 30 min. To the resulting solution maintained at – 80 ºC were added dropwise a solution of 4-bromo-1,2-bis(octyloxy)benzene (10.3 g, 25 mmol) and triisopropyl borate (7.5 mL, 6.1 g, 32.5 mmol) in dry THF (50 mL) over 2 h from the dropping funnel. After the addition was complete, the reaction mixture was stirred at – 80 ºC for 2 h and then allowed to warm to room temperature over 8-10 h. The resulting mixture was acidified with 6 N HCl (26 mL) and stirred for overnight. Similar workup gave a white solid (6.5 g, yield 69 %). The product was used without further purification; analytical sample was recrystallized from water/ethyl ether; Mp 120–122 ºC; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.81 (s, 2 H), 7.36−7.33 (m, 2 H), 6.90−6.88 (m, 1H), 3.95−3.92 (m, 4 H) 1.70−1.60 (m, 4H), 1.46−1.23 (m, 20H), 0.96−0.91 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 153.3, 148.4, 130.0, 120.9, 112.7, 69.6, 68.9, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1.

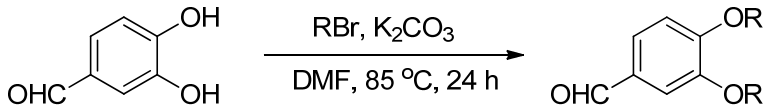


**3,4-Bis(dodecyloxy)phenylboronic acid**[7] was prepared according to the revised procedure for 3,4-bis(octyloxy)phenylboronic acid. The crude product was purified by column chromatography (silica gel, PE:EA = 3:1). White solid (yield 57 %); Mp 124–126 ºC; $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.81 (s, 2 H), 7.35−7.32 (m, 2 H), 6.90−6.87 (m, 1H), 3.94−3.92 (m, 4 H), 1.70-1.60 (m, 4H), 1.46−1.27 (m, 36H), 0.96−0.91 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 153.3, 148.5, 130.0, 120.6, 112.6, 69.6, 68.9, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1.

## 2.2 The synthesis of 3,4-dialkoxybenzaldehydes

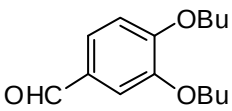
3,4-Dialkoxybenzaldehydes used here were conveniently prepared via a alkylation of 3,4-dihydroxy-benzaldehyde or 4-hydroxy-3-methoxybenzaldehyde according to the literature procedure.[8]

### 2.2.1 General procedure for the synthesis of 3,4-dialkoxybenzaldehyde

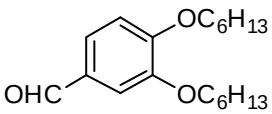



**Scheme S4:** The synthesis of 3,4-dialkoxybenzaldehyde

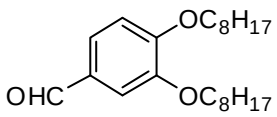
A mixture of 3,4-dihydroxybenzaldehyde (1.38 g, 10 mmol), anhyd. $K_2CO_3$ (5.52 g, 40 mmol), and the appropriate *n*-bromoalkane (22 mmol) were taken in dry DMF (20 mL) and heated at 85 ºC for 24 h under nitrogen atmosphere. The reaction mixture was poured into ice–water and extracted with dichloromethane. The combined extracts were washed with water and brine, dried over anhyd $Na_2SO_4$, and concentrated. The crude product was purified by column chromatography (silica gel, PE/DCM) to give the desired product.



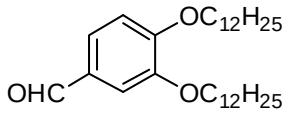

**3,4-Dibutoxybenzaldehyde** was prepared according to the general procedure described above using 3,4-dihydroxybenzaldehyde and 1-bromobutane and purified by flash column chromatography (silica gel, PE:DCM = 6:1, v/v). Colorless solid (89 % yield); Mp 34–36 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.83 (s, 1H), 7.44−7.40 (d, $J$ = 9.0 Hz, 1H), 7.43 (s, 1H), 6.97−6.94 (d, $J$ = 9.0 Hz, 1H); 4.11−4.03 (m, 4H), 1.88-1.80 (m, 4H), 1.56−1.48 (m, 4H), 1.02−0.96 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 191.0, 154.7, 149.5, 129.9, 126.6, 111.8, 110.9, 68.8, 31.1, 31.0, 19.2, 13.8; HR-MS (ESI): *m/z* calcd for ($C_{15}H_{22}O_3$ + Na), 273.1467, found: 273.1470.




**3,4-Bis(hexyloxy)benzaldehyde** was prepared according to the general procedure described above using 3,4-dihydroxybenzaldehyde and 1-bromohexane and purified by flash column chromatography (silica gel, PE/DCM = 6:1, v/v). Colorless solid (yield 91 %); Mp 43–44 ºC (lit.[9] 40–42 ºC); The observed characterization data was consistent with that previously reported in the literature.[10] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.83 (s, 1H), 7.43−7.40 (d, $J$ = 9.0 Hz, 1H), 7.40 (s, 1H), 6.96−6.93 (d, $J$ = 9.0 Hz, 1H); 4.10−4.03 (m, 4H), 1.88−1.82 (m, 4H), 1.49−1.35 (m, 12H), 0.91 (brs, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 191.0, 154.7, 149.5, 129.9, 126.6, 1118, 111.0, 69.1, 31.5, 29.0, 28.9, 25.7, 25.6, 22.6, 14.0. HR-MS (ESI) *m/z*: calcd for ($C_{15}H_{22}O_3$ + Na), 329.2093, found: 329.2096.

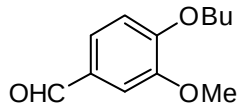


**3,4-Bis(octyloxy)benzaldehyde** was prepared according to the general procedure described above using 3,4-dihydroxybenzaldehyde with 1-bromooctane and purified by flash column chromatography (silica gel, PE:DCM = 6:1, v/v). Colorless solid (yield 87 %); The observed characterization data was consistent with that previously reported in the literature.[11] Mp 48–50 ºC (lit.[9] 48–51 ºC); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.83 (s, 1H), 7.43−7.39 (m, 2H), 7.00−6.93 (m, 1H), 4.10-4.00 (m, 4H), 1.87−1.83 (m, 4H), 1.50−1.53 (m, 16H), 0.91−0.88 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 190.4, 154.2, 149.0, 129.4, 126.0, 111.3, 110.6, 68.7, 68.6, 31.3, 28.8, 28.7, 28.6, 28.5, 25.5, 25.4, 22.2. 13.6. HR-MS (ESI) *m/z*: calcd for ($C_{15}H_{22}O_3$ + Na), 385.2719, found: 385.2719.



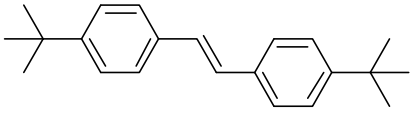
**3,4-Bis(dodecyloxy)benzaldehyde** was prepared according to the general procedure described above using 3,4-dihydroxybenzaldehyde with 1-bromooctane and purified by flash column chromatography (silica gel, PE:EA = 4:1, v/v). Colorless solid (yield 87 %); The observed characterization data was consistent with that previously reported in the literature.[11] Mp 69–70 ºC (lit.[9] 62–65 ºC); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.83 (s, 1H), 7.42−7.37 (m, 2H), 6.96−6.94 (d, $J$ = 8.1Hz, 1H), 4.09−4.03 (m, 4H), 1.89−1.80 (m, 4H), 1.49−1.44 (m, 4H), 1.35−1.26 (m, 32 H), 0.90−0.86 (t, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.0, 154.7, 149.5, 129.9,126.5, 111.8, 111.1, 69.2, 32.1, 29.9, 29.8, 29.7, 29.6, 29.4, 29.1, 29.0, 26.2, 26.0, 25.9, 22.7, 14.1; HR-MS (ESI) *m/z*: calcd for ($C_{99}H_{168}O_6$ + Na), 1476.2739 found: 1476.2697.

### 2.2.2 The preparation of 3,4-dialkoxybenzaldehyde with different alkoxy groups



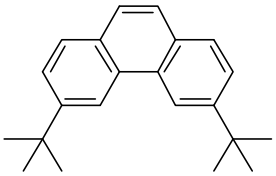
**4-Butoxy-3-methoxybenzaldehyde** was prepared according to the general procedure described above using 4-hydroxy-3-methoxybenzaldehyde (vanillin) (7.6 g, 50 mmol), 1-bromobutane (10.2 g, 75 mmol), $K_2CO_3$ (10.4 g, 75 mmol) and in dry $Me_2CO$ (200 mL), and purified by flash column chromatography (silica gel, PE:DCM = 10:1, v/v) to give a colorless solid (9.68 g, yield 93 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.84 (s, 1H), 7.46−7.41 (m, 2H), 6.98−6.95 (m, 1H); 4.14−4.00 (m, 2H), 3.93 (s, 3H), 1.90−1.82 (m, 2H), 1.56−1.47 (m, 2H), 1.02−0.96 (t, $J$ = 7.4 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 190.9, 154.2, 149.9, 129.9, 126.8, 111.4, 109.3, 68.9, 56.0, 31.0, 19.1, 13.8; HR-MS (ESI): *m/z* calcd for ($C_{12}H_{16}O_3$ + Na), 231.0992, found: 231.0997.

### 2.2.3 The synthesis of 3,6-di-*tert*-butylphenanthrene-9-carbaldehyde

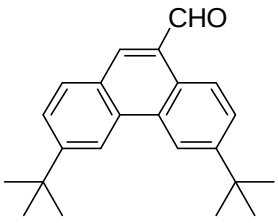


**(*E*)-1,2-Bis(4-*tert*-butylphenyl)ethane** was prepared via McMurry

coupling reaction of 4-*tert*-butylbenzaldehyde following the procedure of Thallaplly, P. K. et al[12].To a stirred suspension of zinc powder (147.2 g, 2.25 mol) in dry THF (700 mL), $TiCl_4$ (98.3 mL, 0.9 mol) was added slowly at -10ºC. Then, a solution of 4-*tert*-butylbenzaldehyde (48.6 g, 0.3 mol) in of dry THF (100 mL) was added dropwise at 0 ºC, and then the mixture was refluxed for 20 h. The solution was quenched with 2 L water, HCl (12 N, 50 mL) was added, filtered, the residue was extracted with $CHCl_3$ (300 mL) using Soxhlet extractor. And concentrated and washed with EtOH to afford a white solid (yield 39.9 g, 91%); Mp 181 ºC; $^1$HNMR ($CDCl_3$, 400 MHz): $\delta$ 7.47−7.45 (d, $J$ = 8.4 Hz, 4H), 7.40−7.38 (d, $J$ = 8.4 Hz, 4H), 7.08 (s, 2H), 1.35 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 150.6, 134.8, 127.7, 126.1, 125.6, 34.6, 31.3; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{22}H_{28}$: 292.0 ($M^+$), found: 292.2.



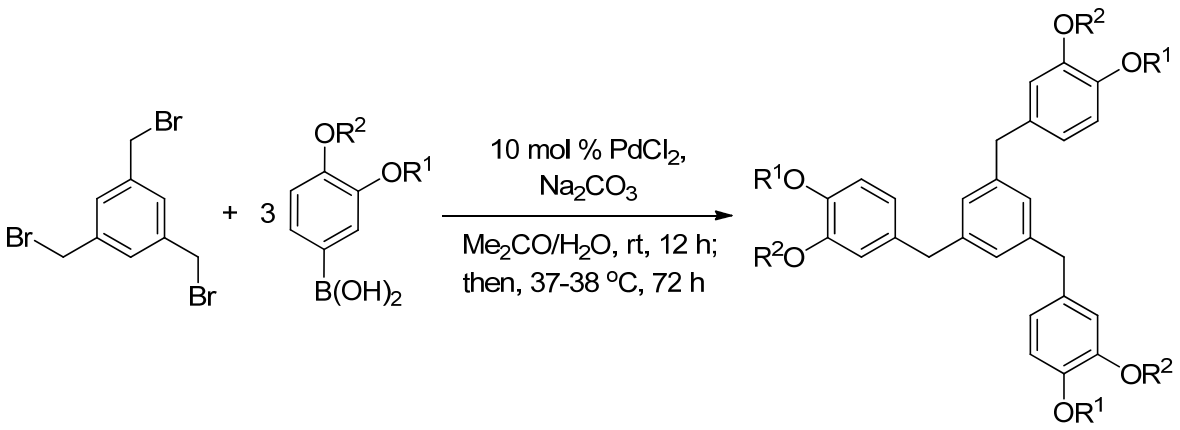
**3,6-Di-*tert*-butylphenanthrene.**[13] To a large immersion photolysis vessel equipped with a magnetic stir bar were added cyclohexane (900 mL), *trans*-4,4'-di-*t*-butylstilbene (876 mg, 3.0 mmol), and iodine (914 mg, 3.6 mmol). This solution was purged with Ar for 20 min. Propylene oxide (80 mL) was added to the purged mixture, and the immersion lamp was inserted into the photolysis vessel. The reaction mixture was subjected to UV light for 4 h. The reaction mixture was washed with 10% $Na_2S_2O_3$ (3×80 mL), deionized water (3×50 mL) and brine (40 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude solied was absorbed onto silica gel purified using column chromatography with hexanes as the eluent. The desired product was obtained as a white solid (509 mg, yield 88%); Mp 94–95 ºC (lit. 93–94 ºC [14]); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.72 (s, 2H), 7.86−7.68(m, 6H), 1.54 (s, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 149.0, 130.2, 130.0, 128.3, 125.8, 124.7, 117.9, 35.2, 31.5; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{22}H_{26}$: 290.2 ($M^+$), found: 290.2.




**3,6-Di-*tert*-butylphenanthrene-9-carbaldehyde.** A 250 mL flask equipped with a magnetic stirrer was charged with 3,6-di-*tert*-butylphenanthrene (3.63 g, 12.5 mmol) and 150 mL of dry DCM. The solution was cooled to – 5 ºC with stirring. After 15 min, $TiCl_4$ (2.75 mL, 25 mmol) was added. Then dichloromethyl methyl ether (1.13 mL, 15 mmol) in 50 mL dry DCM was added dropwise and stirred at – 5 ºC for 2 h and at room temperature for 20 h. Upon addition of 50 mL cold water, the resulting mixture was stirred for 2 h and extracted with DCM. The organic layer was washed with water and saturated $NaHCO_3$, dried over anhyd. $MgSO_4$, filtered, and rotoevaporated to dryness. The residue was purified by column chromatography (PE:DCM = 3:1) to give a brown oil (3.56 g, yield 89 %) and further recrystallized from EtOH to give a light yellow solid (3.1 g, yield 78 %); Mp 112–114 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.17 (s, 1H), 9.17−9.15 (d, 1H), 8.57 (t, 2 H), 7.96 (s, 1H), 7.78−7.56 (m, 3 H), 1.39 (s, 18H); $^{13}$C

NMR (100 MHz, $CDCl_3$): $\delta$ 193.5, 153.2, 150.0, 140.1, 130.1, 126.3, 1254, 118.3, 118.0, 35.5, 35.1, 31.3, 31.2; HR-MS (ESI): *m/z* calcd for ($C_{23}H_{26}O$ + Na): 341.1881, found: 341.1859.

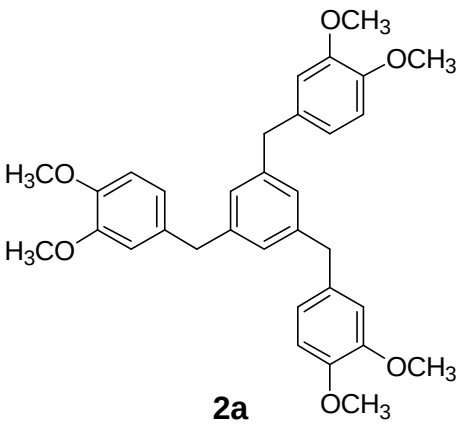
# 3 Synthesis and characterization of the intermediates and the products




**Scheme S5:** The synthesis of TBBs

## 3.1 The synthesis of 1,3,5-tri(3,4-dialkoxybenzyl)benzenes (TBBs)[15]

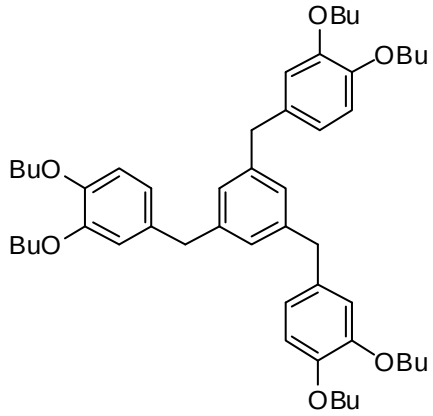
A mixture of arylboronic acid, $Na_2CO_3$ in 40 mL acetone–water (1:1) was stirred at room temperature until it became homogeneous. Then, it was cooled in an ice bath and degassed by bubbling Ar for 15 min. To this mixture 1,3,5-tris(bromomethyl)benzene and $PdCl_2$ was added at 0 ºC and stirred at room temperature for 12 h and 37–38 ºC for 3 days under argon atmosphere. After completion of the reaction (monitored by TLC), acetone was removed under reduced pressure and the product was extracted with diethyl ether, dried with anhydrous $Na_2SO_4$. Removal of the ether on a rotory evaporator furnished the crude product, which was further purified by column chromatography (silica gel).




**2a**

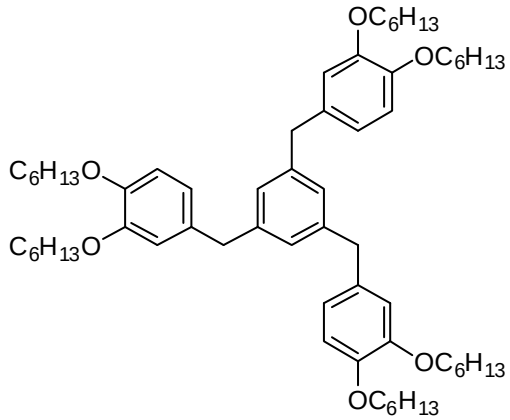
**1,3,5-Tris(3,4-dimethoxybenzyl)benzene (TBB 2a)** was prepared from 3,4-dimethoxyphenylboronic acid and 1,3,5-tris-(bromomethyl)benzene and purified by column chromatography (silica gel, PE:EA = 2:1, v/v). White solid (yield 83 %); Mp 112–114 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.85 (s, 3H), 6.79−6.76 (d, $J$ = 9.0 Hz, 3H), 6.70−6.67 (d, $J$ = 9.0 Hz, 3H), 6.65 (s, 3H), 3.84 (s, 18H), 3.78 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.8, 147.3, 141.5, 133.7, 127.1, 120.7,

112.2, 111.2, 55.8, 55.7, 41.3; HR-MS (ESI): *m/z* calcd for ($C_{33}H_{36}O_6$ + Na) 551.2410, found 551.2398.



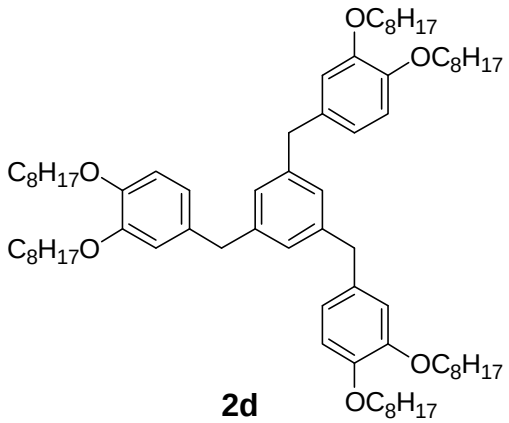

**2b**

**1,3,5-Tris(3,4-dibutoxybenzyl)benzene (2b)** was prepared from 3,4-dibutoxyphenylboronic acid and 1,3,5-tris(bromomethyl)benzene and purified by column chromatography (silica gel, PE:DCM = 2:1, v/v). White solid (yield 81%); Mp 57–58 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.84 (s, 3H), 6.79−6.77 (d, $J$ = 8.0 Hz, 3H), 6.68 (s, 3H), 6.65−6.63 (d, $J$ = 8.0 Hz, 3H), 3.98−3.90 (m, 12H), 3.82 (s, 6H), 1.82−1.73 (m, 12H), 1.55−1.46 (m, 12H), 0.99−0.95 (m, 18H); $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 149.1, 147.5, 141.5, 134.0, 127.2, 121.0, 115.0, 114.1, 69.2, 68.9, 41.3, 31.5, 19.3, 13.9; HR-MS (ESI): *m/z* calcd for ($C_{51}H_{72}O_6$ + Na) 803.5214, found 803.5210.




**2c**

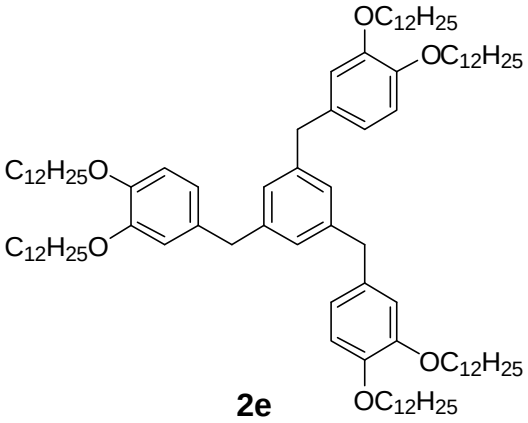
**1,3,5-Tris(3,4-bis(hexyloxy)benzyl)benzene (2c)** was prepared from 3,4-bis(hexyloxy)phenylboronic acid and 1,3,5-tris(bromomethyl)benzene and purified by column chromatography (silica gel, PE:EA = 20:1, v/v). White solid (yield 78 %); Mp 58–59 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.84 (s, 3H), 6.79-6.76 (d, $J$ = 8.0 Hz, 3H), 6.68 (s, 3H), 6.65−6.62 (d, $J$ = 8.0 Hz, 3H), 3.98−3.89 (m, 12H), 3.82 (s, 6H), 1.82−1.75 (m, 12H), 1.35−1.33 (m, 24H), 0.93−0.88 (m, 18H); $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 149.1, 147.5, 141.5, 134.0, 127.2, 121.0, 115.0, 114.1, 69.5, 69.2, 41.3, 31.7, 29.4, 25.8, 22.6, 14.0; HR-MS (ESI): *m/z* calcd for ($C_{63}H_{96}O_6$ + Na) 971.7105, found 971.7085.




**2d**

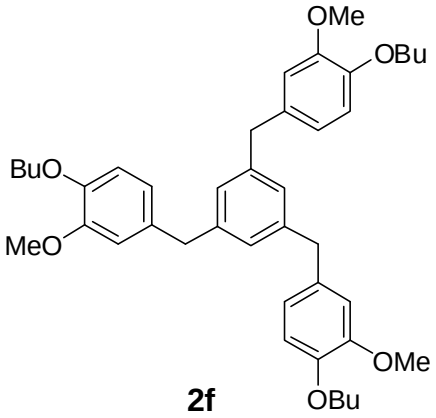
**1,3,5-Tris(3,4-bis(octyloxy)benzyl)benzene (2d)** was prepared from 3,4-bis(octyloxy)phenylboronic acid and 1,3,5-tri(bromomethyl)benzene and purified by column chromatography (silica gel, PE:EA = 30:1, v/v) to give a white solid (yield 72 %); Mp 53–54 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.83 (s, 3H), 6.78−6.74 (d, $J$ = 8.0 Hz, 3H), 6.67 (s, 3H) 6.64−6.62 (d, $J$ = 8.0 Hz, 6H), 3.97−3.89 (m, 12H), 3.81 (s, 6H), 1.83−1.74 (m, 12H), 1.33−1.28 (m, 48H), 0.90−0.87 (m, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.2, 147.6, 141.5, 134.0, 127.2, 121.1, 115.1, 114.3, 69.5, 69.3, 41.3,

31.8, 29.5, 29.3, 26.1, 22.7, 14.1; HR-MS (ESI): *m/z* calcd for ($C_{75}H_{120}O_6$ + Na) 1139.8983, found 1139.8961.



**2e**

**1,3,5-tris(3,4-bis(dodecoxy)benzyl)benzene (2e)** was prepared from 3,4-bis(dodecyloxy)phenylboronic acid and 1,3,5-tris(bromomethyl)benzene and purified by column chromatography (silica gel, PE:EA = 10:1, v/v) and recrystallization from EtOH. Brownish solid (64 %); Mp 54–55 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.83 (s, 3H), 6.78−6.76 (d, *J* = 8.0 Hz, 3H), 6.67 (s, 3H), 6.63−6.61 (d, *J* = 8.0 Hz, 6H), 3.97−3.87 (m, 12H), 3.80 (s, 6H), 1.81−1.74 (m, 12H), 1.40−1.26 (m, 108H), 0.90−0.86 (t, *J* = 6.6 Hz, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.1, 147.5, 141.5, 134.0, 127.2, 121.0, 115.0, 114.1, 69.5, 69.3, 41.3, 40.0, 29.7, 29.5, 26.1, 22.7, 14.1; HR-MS(ESI): *m/z* calcd for ($C_{99}H_{168}O_6$ + Na) 1476.2739, found 1476.2697.

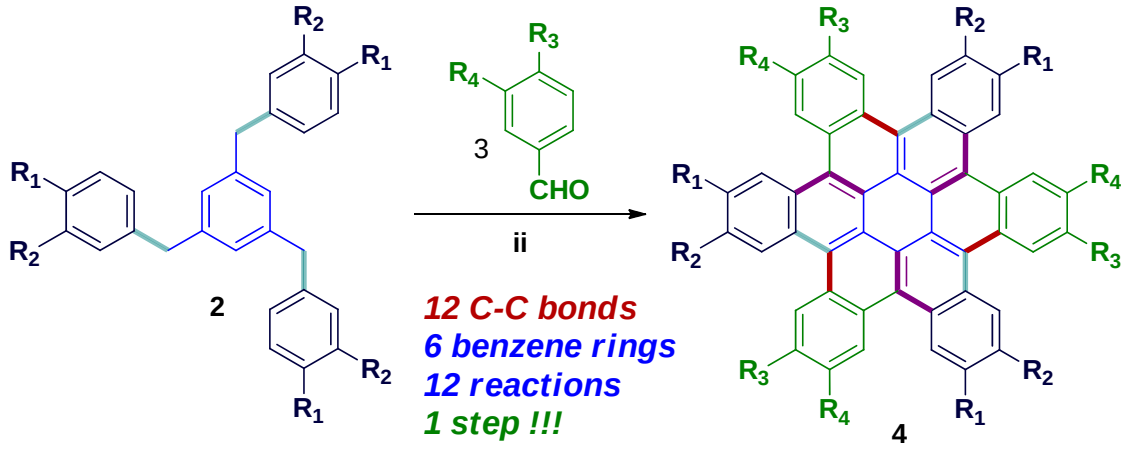


**2f**

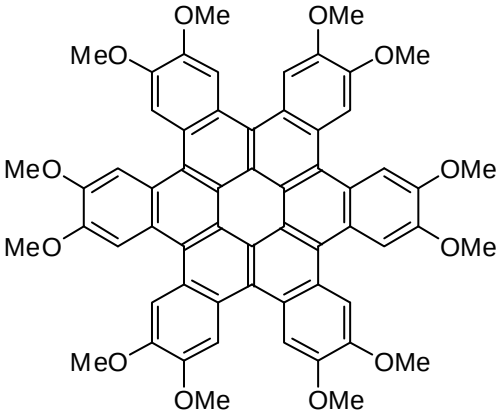
**1,3,5-Tris(4-butoxy-3-methoxybenzyl)benzene (2f)** was prepared from 4-butoxy-3-methoxyphenylboronic acid and 1,3,5-tris(bromomethyl)benzene and purified by chromatography (silica gel, PE:EA = 10:1, v/v); White solid (yield 81 %); Mp 73–75 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 6.86 (s, 3H), 6.78−6.76 (d, *J* = 8.0 Hz, 2H), 6.67−6.69 (d, *J* = 8.0 Hz, 2H), 4.00-3.96(m, 12H), 3.84 (s, 6H), 3.76 (s, 9H), 1.83−1.79 (t, *J* = 7.4 Hz, 2H), 1.52-1.46 (q, *J* = 7.4 Hz, 2H), 0.99−0.95 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.3, 146.9, 141.6, 133.8, 127.2, 120.8, 113.0, 112.7, 55.9, 41.4, 31.3, 19.3, 13.9; HR-MS(ESI): *m/z* calcd for ($C_{42}H_{54}O_6$ + Na) 677.3818, found 677.3819.

## 3.2 The synthesis of the substituted *c*-HBCs

### 3.2.1 The synthesis of the *c*-HBCs

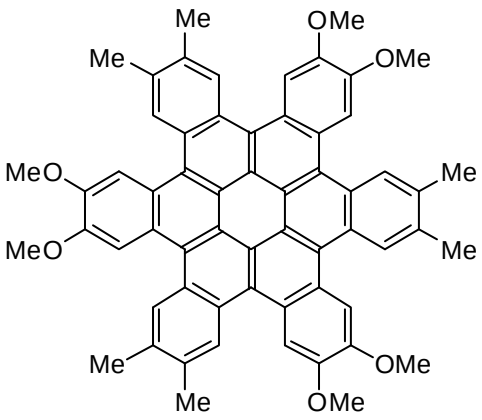



**Scheme S6:** The synthesis of *c*-HBCs




**3a**

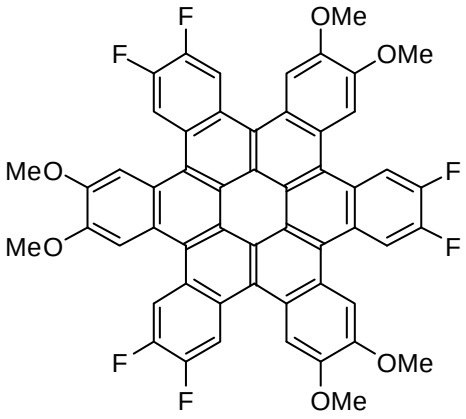
**General procedure for the synthesis of *c*-HBCs and *c*-TBTTCs was exemplified by the synthesis of *c*-HBC 3a.** To a solution of 3,4-dimethoxybenzaldehyde (274 mg, 1.65 mmol) and $Ac_2O$ (0.47 mL, 5 mmol) in 350 mL DCM was added a solution of $FeCl_3$ (16.2 mg, 0.1 mmol) in $CH_3NO_2$ (1 mL) while stirring at rt., followed by dropwise addition over 1 h of TBB **2a** (0.5 mmol, 264 mg) in DCM (50 mL). The resulting mixture was stirred at rt. overnight and then degassed with Ar for 15 min. A second portion of $FeCl_3$ (1.26 g, 7.2 mmol, 15.6 equiv) solution in $CH_3NO_2$ (20 mL) was added dropwise over 1 h under Ar atmosphere and stirred for 12 h. Then, cold $CH_3OH$ (100 mL) was added with stirring to quench the reaction and the mixture was poured into cold water (500 mL). The organic layer was separated, washed with water, dried by $Na_2SO_4$ and rotoevaporated in vacuo. The residue was purified by chromatography (silica gel, DCM:EA = 10:1, v/v) to give ***c*-HBC 3a** as a yellow solid. (432 mg, yield 90 %), Mp > 300 ºC. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.78 (s, 12H), 4.20 (s, 24H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.4, 125.0, 123.7, 120.4, 109.0, 56.1; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{60}H_{48}O_{12}$: 960.3 ($M^+$), found: 960.3.




**3b**

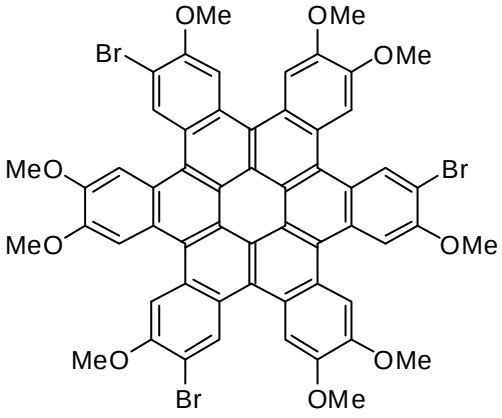
***c*-HBC 3b** was prepared from TBB **2a** (264 mg, 0.5 mmol) and 3,4-dimethylbenzaldehyde (222 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, DCM). Yellow solid (402

mg, 93 %); Mp > 300 ºC; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.06 (s, 6H), 8.53 (s, 6H), 4.15 (s, 12H), 2.72 (s, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 158.3, 158.0, 151.5, 134.3, 128.5, 126.3, 124.5, 109.0, 55.9, 20.5, 18.7; MS (MALDI-TOF) (CHCA): *m/z* calcd for $C_{60}H_{48}O_{12}$: 864.3 ($M^+$), found: 864.2.



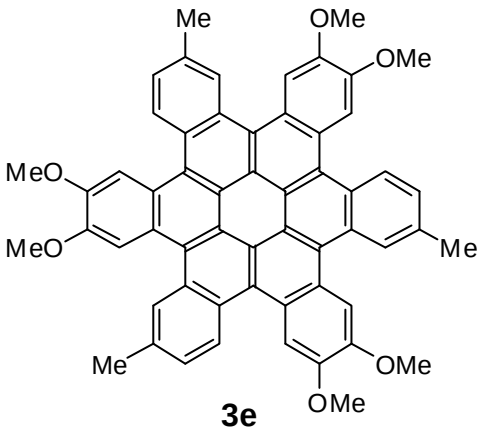
**3c**

***c*-HBC 3c** was prepared from TBB **2a** (264 mg, 0.5 mmol) and 3,4-difluorobenzaldehyde (234.5 mg, 1.65 mmol), and purified by washing with cold methanol. Yellow solid (422 mg, 95 %); Mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.11−9.05 (t, $J$ = 10.4 Hz, 6H), 8.56 (s, 6H), 4.22 (s, 12H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 149.25, 148.34, 127.11, 124.70, 124.98, 120.62, 115.74, 108.45, 50.21; MS(MALDI-TOF) (CHCA): *m/z* calcd for $C_{54}H_{30}F_6O_6$: 888.2 ($M^+$), found: 882.2.



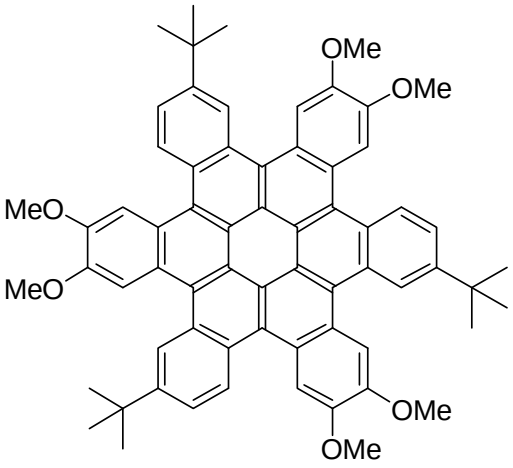
**3d**

***c*-HBC 3d** was prepared from TBB **2a** (264 mg, 0.5 mmol) and 3-bromo-4-methoxybenzaldehyde (355 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, DCM). Yellow solid (538 mg, 97 %); Mp > 300 ºC; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.57 (s, 3H), 8.77 (s, 3H), 8.72 (s, 3H), 8.60 (s, 3H), 4.24 (s, 9H), 4.22 (s, 9H), 4.20 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 158.0, 153.8, 149.0, 148.8, 135.1, 133.1, 132.8, 130.2, 125.0, 124.6, 116.2, 111.9, 109.4, 109.0, 108.5, 56.6, 56.1; MS (MALDI-TOF) (CHCA): *m/z* calcd for $C_{57}H_{39}Br_3O_6$: 1104.0 ($M^+$), found: 1104.2.



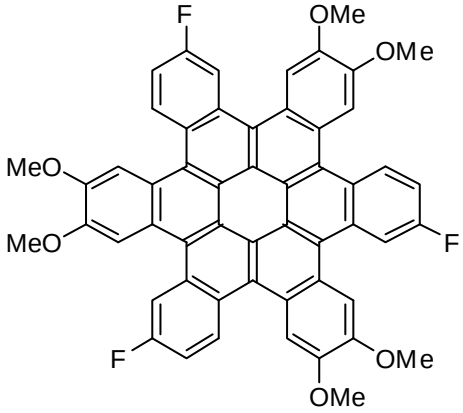
**3e**

***c*-HBC 3e** was prepared according to from TBB **2a** (264 mg, 0.5 mmol) and 4-methylbenzaldehyde (198 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, DCM). Yellow solid (379 mg, 92 %); Mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.21 (s, 3H), 9.18−9.16 (d, $J$ = 5.3 Hz, 3H), 8.75 (s, 3H), 8.70 (s, 3H), 7.64−7.61 (d, $J$ = 5.3 Hz, 3H), 4.19 (s, 18H), 2.73 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5, 135.8, 130.2, 128.2, 128.0, 127.6, 125.1, 125.0, 124.8, 121.0, 120.5, 109.4, 56.2, 56.1, 22.1; MS (MALDI-TOF)(CHCA): *m/z* calcd for $C_{57}H_{42}O_6$: 822.3 ($M^+$), found: 822.2.



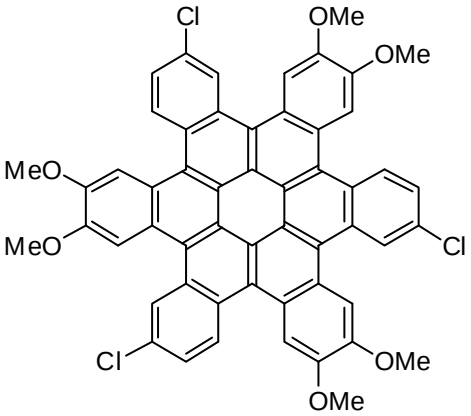

**3f**

***c*-HBC 3f** was prepared according to from TBB **2a** (0.5 mmol, 264 mg) and 4-*tert*-butylbenzaldehyde (268 mg 1.65 mmol) and purified by flash column chromatography (silica gel, DCM, v/v). Yellow solid (451 mg, 95 %); Mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.33 (s, 3H), 9.29−9.26 (d, $J$ = 6.3 Hz, 3H), 8.77 (s, 3H), 8.75 (s, 3H), 7.89−7.86 (d, $J$ = 6.3 Hz, 3H), 4.23 (s, 9H), 4.22 (s, 9H), 1.60 (s, 27H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.8, 148.5, 132.9, 128.0, 125.3, 125.0, 124.7, 124.6, 124.1, 109.5, 109.2, 95.0, 56.0, 35.4, 31.7; MS (MALDI-TOF) (CHCA): $m/z$ calcd for $C_{66}H_{60}O_6$: 948.4 ($M^+$), found: 948.3.



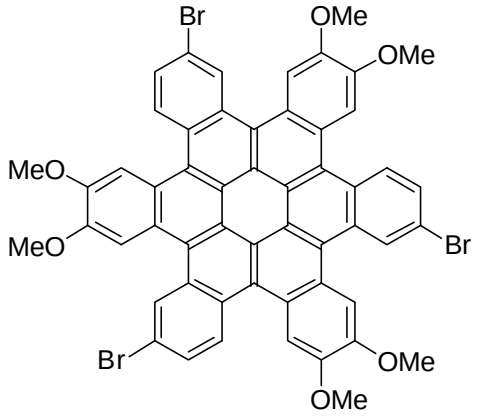

**3g**

***c*-HBC 3g** was prepared from TBB **2a** (264 mg, 0.5 mmol) and 4-fluorobenzaldehyde (205 mg, 1.65 mmol) and purified by washing with cold methanol. Yellow solid (392 mg, yield 94 %); Mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.27 (s, 3H), 8.97 (brs, 3H), 8.64 (s, 3H), 8.58 (s, 3H), 7.53 (brs, 3H), 4.23 (s, 9H), 4.18 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 161.82−160.19 (d, $J$= 244.8 Hz), 148.98, 148.84, 131.53, 131.48, 130.91, 130.86, 126.63, 125.20, 124.96, 124.75, 123.71, 121.21, 120.07, 114.96, 114.80, 112.82, 112.67, 109.18, 108.44, 56.16, 56.14; MS (MALDI-TOF)(CHCA): $m/z$ calcd for $C_{54}H_{33}F_3O_6$: 834.2 ($M^+$), found: 834.2.



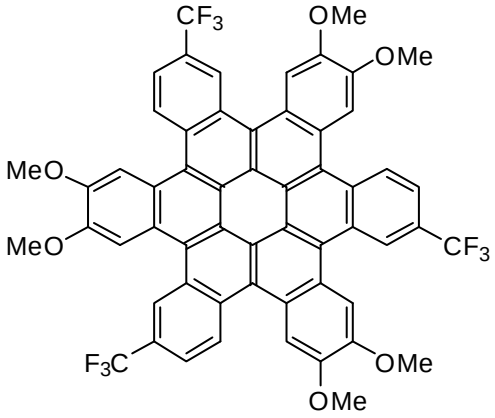

**3h**

***c*-HBC 3h** was prepared from TBB **2a** (0.5 mmol, 264 mg) and 4-chlorobenzaldehyde (231 mg 1.65 mmol) and purified by washing with cold methanol. Deep yellow solid (362 mg, yield 82 %); Mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.31 (s, 3H), 9.21−9.19 (d, $J$ = 8.0, 3H), 8.60 (s, 3H), 8.55 (s, 3H), 7.76−7.73 (d, $J$ = 8.0, 3H), 4.22 (s, 9H), 4.19 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 149.04, 148.89, 132.17, 130.89, 129.95, 128.04, 127.39, 126.40, 124.71, 123.59, 120.96, 120.39, 108.99, 108.69, 56.16; MS (MALDI-TOF) (CHCA): $m/z$ calcd for $C_{54}H_{33}Cl_3O_6$: 882.1($M^+$), found: 882.2.



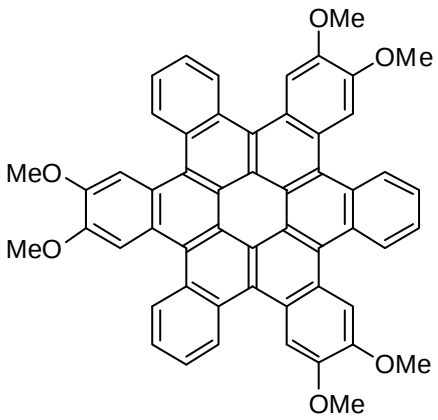

**3i**

***c*-HBC 3i** was prepared using TBB **2a** (264mg, 0.5 mmol) and 4-bromobenzaldehyde (305 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, chloroform). Yellow solid (437 mg, 86 % yield); Mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.43 (s, 3H), 9.09-9.06 (d, $J$ = 12 Hz, 3H), 8.45 (s, 3H), 8.41 (s, 3H), 7.85−7.82 (d, $J$ = 12 Hz, 3H), 4.20 (s, 9H), 4.16 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.0, 130.6, 130.1, 128.0, 124.4, 120.2, 112.6, 108.9, 108.6, 56.1; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{54}H_{33}Br_3O_6$: 1013.9 ($M^+$), found: 1013.6.



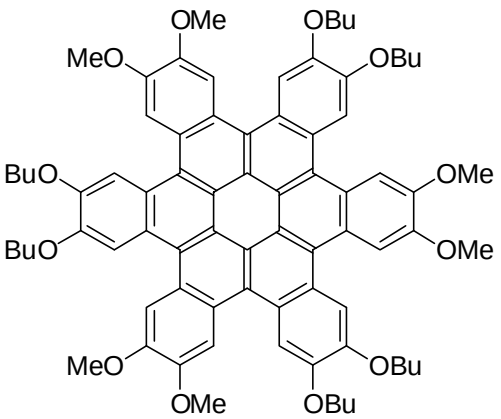

**3j**

***c*-HBC 3j** was prepared from TBB **2a** (0.5 mmol, 264 mg) and 4-(trifluoromethyl)benzaldehyde (287 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, chloroform). Yellow solid (192 mg, 39 % yield); Mp > 300 ºC; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.69 (s, 3H), 9.46−9.43 (d, $J$ = 9.0 Hz, 3H), 8.67 (s, 3H), 8.64 (s, 3H), 8.07−8.04 (d, $J$ = 9.0 Hz, 3H), 4.23 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.0, 149.1, 131.8, 129.3, 129.2, 129.0, 126.1, 126.0, 125.0, 124.85, 12.80, 124.5, 112.8, 109.1, 109.0, 56.3, 56.1; MS(MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{57}H_{33}F_9O_6$: 984.2 ($M^+$), found: 984.1.



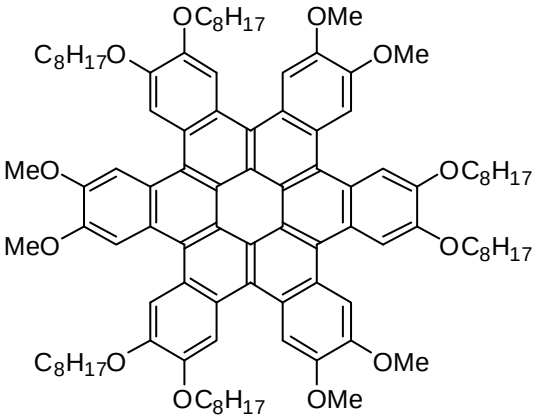

**3k**

***c*-HBC 3k** was prepared from TBB **2a** (0.5 mmol, 264 mg) and benzaldehyde (175 mg, 1.65 mmol) and washed by cold methanol. Yellow solid (344 mg, 88 % yield); Mp > 300 ºC; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.22 (s, 6H), 8.65 (s, 6H), 7.71 (s, 6H), 4.13 (s, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 151.6, 148.5, 129.9, 128.1, 126.0, 124.9, 124.6, 120.6, 109.2, 56.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{54}H_{36}O_6$: 780.2 ($M^+$), found: 780.1.



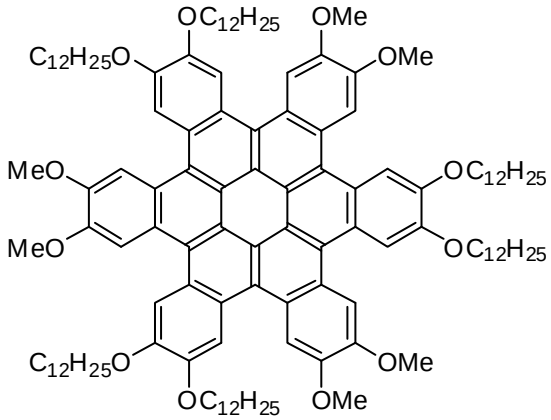

**3l**

***c*-HBC 3l** was prepared from TBB**2a** (0.5 mmol, 264 mg) and 3,4-dibutoxybenzaldehyde (412 mg, 1.65 mmol) and purified by flash column chromatography (silica, chloroform). Yellow solid (576 mg, 95 % yield); Mp > 300 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.78 (s, 12H), 4.40−4.25 (m, 12H), 4.20 (s, 18H), 2.04−1.99 (m, 12H), 1.68−1.60 (m, 12H), 1.10−1.05 (t, $J$ = 7.5 Hz, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.4, 148.2, 125.0, 123.6, 120.3, 110.7, 109.0, 69.1, 56.0, 31.5, 19.4, 13.9; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{78}H_{84}O_{12}$: 1212.6 ($M^+$), found: 1212.5.



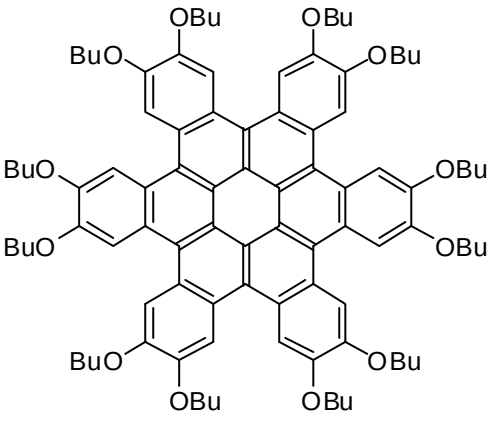

**3m**

***c*-HBC 3m** was prepared from TBB **2a** (106 mg, 0.2 mmol) and 3,4-bis(octyloxy)-benzaldehyde (260 mg, 0.36 mmol) and purified by flash column chromatography (silica gel, PE:DCM =1:1, v/v). Yellow solid (239 mg, 77 % yield); Mp 75–77 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.77 (s, 6H), 8.76 (s, 6H), 4.37−4.23 (m, 12H), 4.19 (s, 12H), 2.05−1.99 (m, 12H), 1.42−1.32 (m, 60H), 0.91−0.88 (m, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.4, 148.2, 125.0, 123.6, 120.3, 110.8, 109.1, 69.3, 56.0, 31.9, 29.7, 29.6, 29.4, 29.3 26.2, 22.6, 14.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{102}H_{132}O_{12}$: 1548.9 ($M^+$), found: 1548.9.



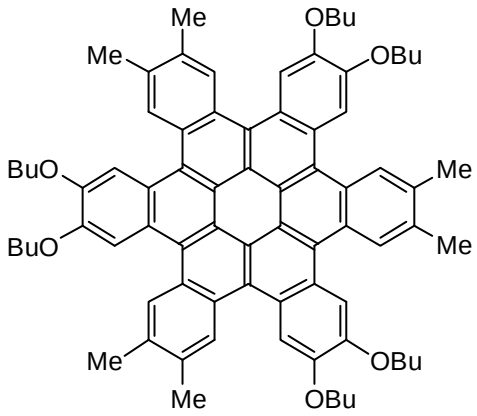

**3n**

***c*-HBC 3n** was prepared from TBB **2a** (0.2 mmol, 106 mg) and 3,4-bis(dodecyloxy) benzaldehyde (342 mg, 0.72 mmol) and purified by flash column chromatography (silica gel, PE:DCM = 1:1, v/v). Deep yellow oil (257 mg, 68 % yield); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.82 (s, 12H), 4.41−4.24 (m, 12H), 4.24 (s, 18H), 2.07−2.05 (m, 12H), 1.64−1.30 (m, 108H), 0.93−0.89 (m, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.4, 148.2, 125.0, 123.6, 120.3, 110.8, 109.1, 69.3, 56.0, 31.9, 29.7, 29.6, 29.4, 26.2, 22.6, 14.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{126}H_{180}O_{12}$:1885.3 ($M^+$), found: 1885.4.



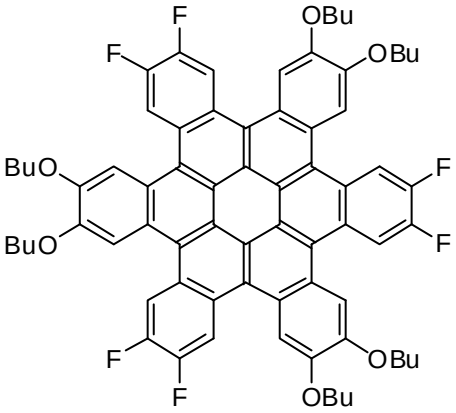

**3o**

***c*-HBC 3o** was prepared from TBB **2c** (0.25 mmol, 195 mg) and 3,4-dibutoxybenzaldehyde (225 mg, 0.9 mmol) and purified by flash column chromatography (silica gel, DCM). Yellow solid (345 mg, 94 % yield); Mp > 300 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.78 (s, 12H), 4.42−4.26 (m, 24H), 2.05−2.00 (m, 24H), 1.70−1.64 (m, 24H), 1.13−1.07 (t, $J$ = 9.0 Hz, 36H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.2, 125.0, 123.6, 120.3, 110.7, 68.9, 31.5, 19.4, 13.9; MS (MALDI-TOF)(CHCA): $m/z$ calcd for $C_{96}H_{120}O_{12}$: 1464.9 ($M^+$), found: 1464.7.



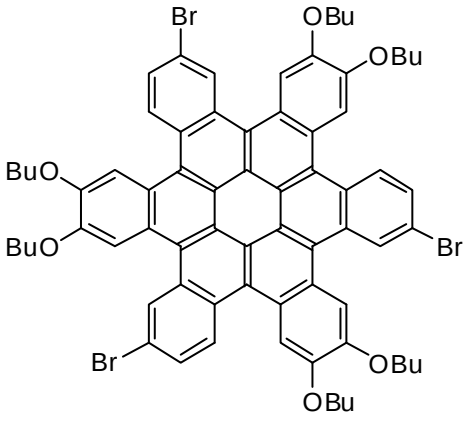

**3p**

***c*-HBC 3p** was prepared from TBB **2c** (0. 5 mmol, 391 mg) and 3,4-dimethylbenzaldehyde (222 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, PE:DCM = 1:3, v/v). Yellow solid (486 mg, 87 % yield), Mp > 300 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.06 (s, 6H); 8.60 (s, 6H), 4.40−4.24 (m, 12H), 2.71 (s, 18H), 2.07−2.02 (m, 12H), 1.70−1.65 (m, 12H), 1.13−1.07 (t, $J$ = 9.0 Hz, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.0, 134.4, 128.6, 128.2, 124.6, 120.3, 111.0, 68.8, 31.4, 20.6, 19.4, 13.9; MS (MALDI-TOF) (CHCA): $m/z$ calcd for $C_{72}H_{72}O_6$ ($M^+$): 1116.6, found: 1116.5.




**3q**

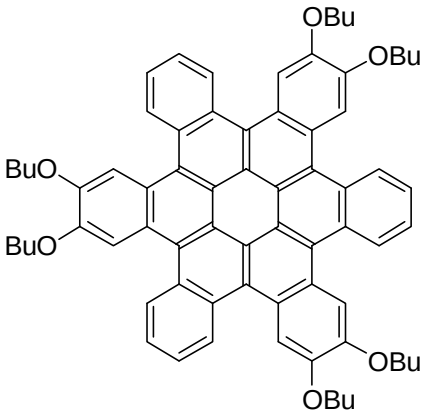
***c*-HBC 3q** was prepared from TBB **2c** (0.5 mmol, 391 mg) and 3,4-difluorobenzaldehyde (261 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, PE:DCM = 3:1, v/v); Yellow solid (524 mg, 92 % yield); Mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.01−8.95 (t, $J$ = 10.4 Hz, 6H); 8.48 (s, 6H), 4.43−4.24 (m, 12H), 2.06−2.01 (m, 12H), 1.70−1.66 (m, 12H), 1.12−1.08 (t, $J$ = 8.0 Hz, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.3, 127.0, 124.6, 123.7, 120.5, 115.8, 110.3, 69.1, 31.3, 19.4, 14.0; MS (MALDI-TOF) (CHCA): $m/z$ calcd for $C_{72}H_{66}F_6O_6$: 1140.5 ($M^+$), found: 1140.7.




**3r**

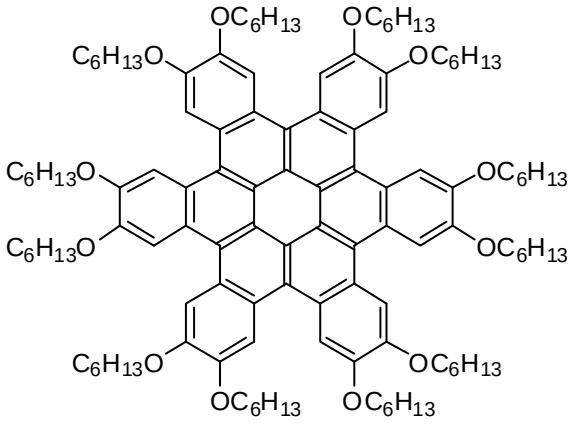
***c*-HBC 3r** was prepared from TBB **2c** (0.25 mmol, 196 mg) and 4-bromobenzaldehyde (166 mg, 0.9 mmol) and purified by column chromatography (silica gel, chloroform). Yellow solid (286 mg, 90 % yield); Mp > 300 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.42 (s, 3H), 9.09−9.06 (d, $J$ = 9.0 Hz, 3H), 8.51 (s, 3H), 8.46 (s, 3H), 7.85−7.82 (d, $J$ =

9.0 Hz, 3H), 4.47−4.22 (m, 12H), 2.09−1.97 (m, 12H), 1.72−1.61 (m, 12H), 1.13−1.06 (m, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 149.0, 148.8, 130.9, 130.6, 130.2, 128.5, 128.0, 124.4, 123.1, 120.6, 120.0, 110.8, 110.3, 69.0, 31.3, 19.4, 14.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{72}H_{69}Br_3O_6$: 1267.3 (M + 1), found: 1267.2.



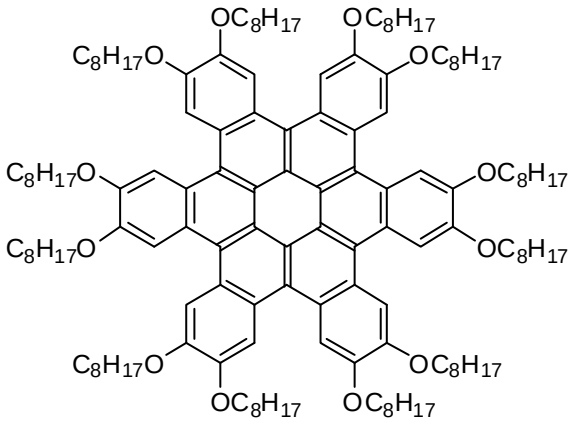

**3s**

***c*-HBC 3s** was prepared from TBB **2b** (0.5 mmol, 391 mg) and benzaldehyde (175 mg, 1.65 mmol) and purified by flash column chromatography (silica gel, PE:DCM = 3:1, v/v). Yellow solid (418 mg, 81 % yield); Mp > 300 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 9.25−9.22 (d, 6H), 8.67 (s, 6H), 7.74−7.72 (d, 6H), 4.41−4.19 (m, 12H), 2.02−1.96 (m, 12H), 1.07 (t, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.7, 130.0, 128.3, 125.9, 125.1, 124.7, 120.7, 111.3, 69.0, 31.4, 19.4, 14.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{72}H_{72}O_6$ ($M^+$): 1032.5, found: 1032.5.




**3t**

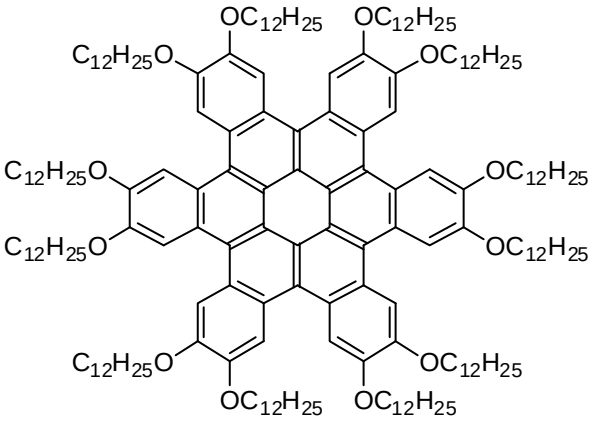
***c*-HBC 3t** was prepared from TBB **2c** (0.25 mmol, 237 mg) and 3,4-bis(hexyloxy)benzaldehyde (275 mg, 0.825 mmol) and purified by flash column chromatography (silica gel, PE:DCM = 1:1, v/v). Yellow solid (409 mg, 91 % yield); Mp > 300 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.76 (s, 12H), 4.40−4.22 (m, 24H), 2.04−1.99 (m, 24H), 1.61−1.42 (m, 72H), 0.98−0.95 (t, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.2, 125.0, 123.6, 120.3, 110.7, 69.3, 31.7, 29.5, 25.9, 22.7, 14.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{120}H_{168}O_{12}$: 1801.3 ($M^+$), found: 1801.4.




**3u**

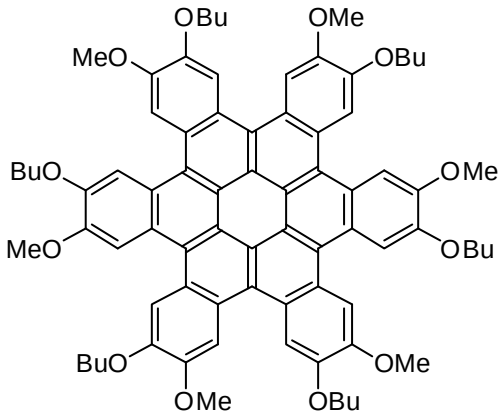
***c*-HBC 3u** was prepared from TBB **2d** (0.1 mmol, 279 mg), 3,4-bis(octyloxy)benzaldehyde (130 mg, 0.36 mmol) and purified by flash column chromatography (silica gel, DCM). Brown solid (146 mg, 68 % yield); Mp 67–70 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.74 (s, 12H), 4.37−4.22 (m, 24H), 2.04−1.99 (m, 24H), 1.59−1.33 (m, 120H),

0.92−0.89 (m, 36H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 147.9, 124.7, 123.4, 120.3, 110.2, 69.0, 31.8, 29.5, 29.3, 26.2, 22.7, 14.1; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{144}H_{216}O_{12}$: 2137.6 ($M^+$), found: 2137.6.



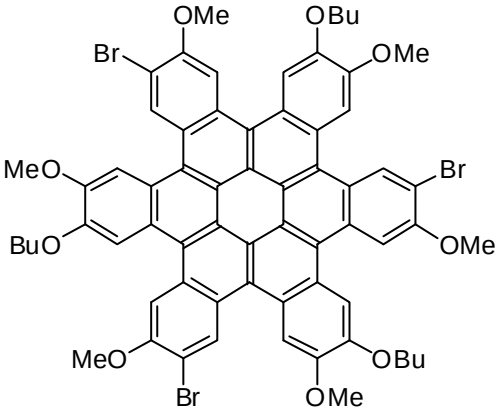

**3v**

*c*-HBC **3v** was prepared from TBB **2e** (0.1 mmol, 145 mg) and 3,4-bis- (dodecyloxy)benzaldehyde (170 mg, 0.36 mmol) and purified by flash column chromatography (silica gel, DCM) to give a brown oil (181 mg), then recrystallized in DCM/MeOH. Brown solid (143 mg, 51 % yield); Mp 62–65 ºC; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.74 (s, 12H), 4.38−4.20 (m, 24H), 2.03-1.99 (m, 24H), 1.59−1.28 (m, 216H), 0.90−0.87 (t, 36H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.1, 125.0, 123.6, 120.3, 110.6, 69.3, 31.7, 29.4, 25.9, 22.7, 14.0; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{192}H_{312}O_{12}$: 2810.3 ($M^+$), found: 2810.1.




**3w**

*c*-HBC **3w** was prepared from TBB **2b** (261 mg, 0.25 mmol), 4-butoxy-3-methoxybenzaldehyde (187 mg, 0.9 mmol) and purified by flash column chromatography (silica gel, DCM). Yellow solid (261 mg, 86 % yield); Mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.77 (s, 6H), 8.75 (s, 6H), 4.42−4.24 (m, 12H), 4.17 (s, 18H), 2.05−2.01 (m, 12H), 1.65−1.60 (m, 12H), 1.08−1.04 (t, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 148.5, 147.9, 125.0, 124.9, 123.6, 120.3, 110.1, 109.2, 68.9, 56.1, 31.4, 19.4, 13.9; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{78}H_{84}O_2$: 1212.6 ($M^+$), found: 1212.6.

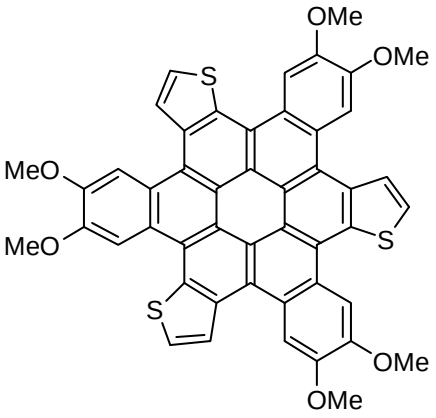



**3x**

*c*-HBC **3x** was prepared from TBB **2b** (0.25 mmol, 261 mg) and 3-bromo-4-methoxybenzaldehyde (194 mg, 0.9 mmol) and purified by washing with cold methanol. Yellow solid (251 mg, 81 % yield); Mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.57−9.52 (m, 3H), 8.77−8.72 (m, 6H), 8.61−8.59 (m, 3H), 4.51−4.17 (m, 24H), 2.10−2.01 (m, 6H), 1.69−1.60 (m, 6H), 1.13−1.04 (m, 9H); MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{66}H_{57}Br_3O_9$: 1230.2 ($M^+$), found: 1230.1.

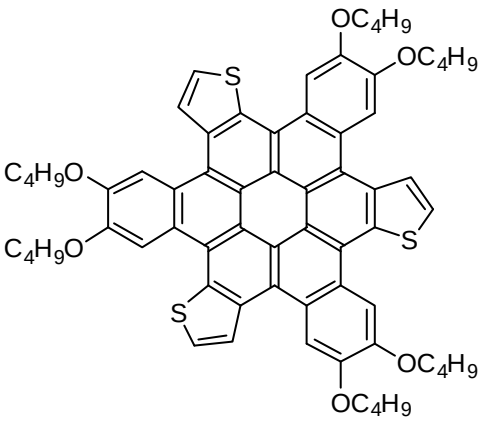
## 3.3 The synthesis of the TBTTCs

### 3.3.1 The synthesis of the TBTTCs using 3-thienaldehyde



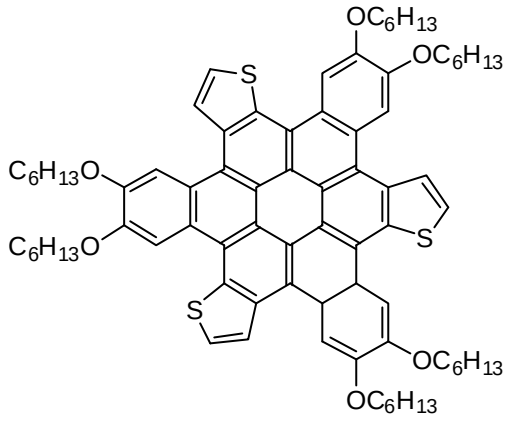

**4a**

TBTTC **4a** was synthesized from 3-thienaldehyde (0.9 mmol) and TBB **2a** (0.20 mmol) according the similar method of **4b**, A second portion of $FeCl_3$ (1.26 g, 7.2 mmol, in 20 mL $CH_3NO_2$) solution was added dropwise over 1 h under Ar atmosphere and stirred for 4 h at rt. The crude product was purified by column chromatography (silica gel, chloroform:EA = 5:1, v/v). Yellowish brown powder (51 mg, 32 % yield); Mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.25 (s, 3H), 8.77−8.76 (d, $J$ = 4.4 Hz, 3H), 8.74 (s, 3H), 7.88-7.86 (d, $J$ = 4.4 Hz, 3H), 4.34 (s, 9H), 4.27 (s, 9H); MS (MALDI-TOF) (CHCA): $m/z$ calcd for $C_{48}H_{30}O_6S_3$: 798.1 ($M^+$), found: 798.3.




**4b**

TBTTC **4b** was synthesized from 3-thienaldehyde (0.9 mmol) and TBB **2c** (0.20 mmol) and purified by column chromatography (silica gel, PE:DCM = 1:1, v/v). Yellowish brown powder (99 mg, 49 % yield); mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.12(s, 3H), 8.67−8.66 (d, $J$ = 5.6 Hz, 3H), 8.62 (s, 3H), 7.77−7.76(d, $J$ = 5.6 Hz, 3H), 4.49−4.46 (t, $J$ = 6.6 Hz, 6H), 4.39−4.36 (t, $J$ = 6.6 Hz, 6H), 2.12−2.04 (m, 12H), 1.76−1.67 (m, 12H), 1.16−1.10 (m, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.4, 148.7, 135.3, 134.0, 126.8, 125.0, 124.1, 123.7, 122.2, 121.0, 111.5, 108.3, 69.2, 69.1, 315, 31.4, 19.5, 19.4, 14.0; MS (MALDI-TOF) (CHCA): $m/z$ calcd for $C_{66}H_{66}O_6S_3$: 1050.4 ($M^+$), found: 1050.6.

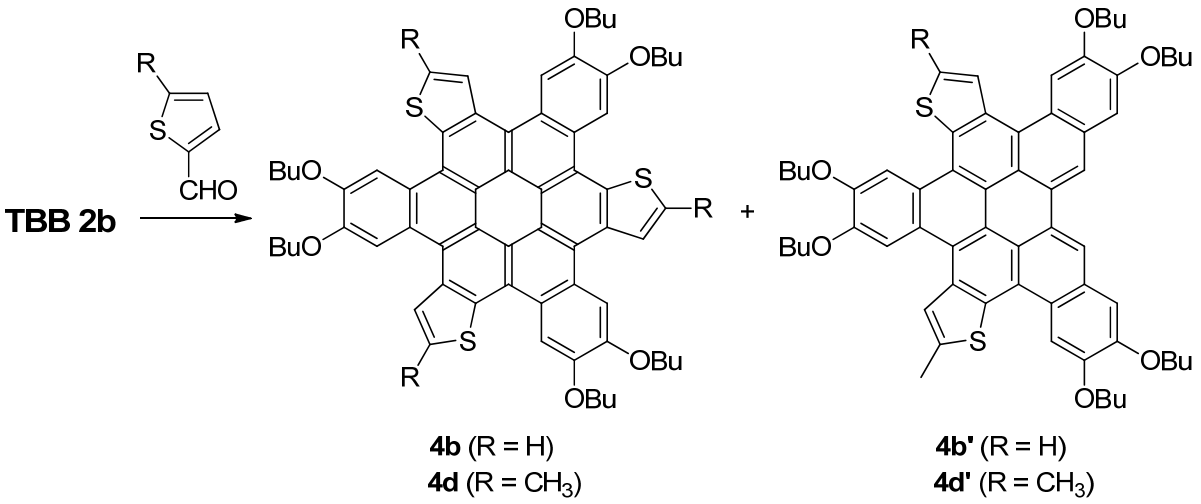



**4c**

TBTTC **4c** was synthesized according to TBTTC **4b** from 3-thienaldehyde (0.9 mmol) and TBB **2c** (0.20 mmol) and purified by column chromatography (silica gel, PE:DCM = 5:1, v/v). Yellowish brown powder (115 mg, 47 %

yield); mp > 300 ºC; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.18 (s, 3H), 8.72−8.70 (d, $J$ = 5.6 Hz, 3H), 8.68 (s, 3H), 7.83−7.81 (d, $J$ = 5.6 Hz, 3H), 4.49−4.46 (t, $J$ = 6.6 Hz, 6H), 4.40−4.36 (t, $J$ = 6.6 Hz, 6H), 2.13−1.45 (m, 48H), 1.01−0.97 (m, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 149.3, 148.6, 135.1, 133.8, 126.7, 124.8, 124.0, 123.6, 122.4, 121.9, 120.8, 111.5, 108.3, 69.5, 69.4, 31.8, 29.5, 29.4, 26.0, 25.9, 22.7, 14.1; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{78}H_{90}O_6S_3$: 1218.6 ($M^+$), found: 1218.8.

### 3.3.2 Attempted access to TBTTC 4b and trimethyl-TBTTC 4d using 2-thienaldehyde and 5-methyl-2-thienaldehyde




**Scheme S7:** The attempt synthesis of TBTTC 4b and trimethyl-TBTTC 4d using 2-thienaldehyde and 5-methyl-2-thienaldehyde

**TBTTC 4b.** The reaction of 2-thienaldehyde and TBB **2b** under the identical conditions afforded a mixture of TBTTC **4b** and a byproduct **4b'** with two thieno-units. After conventional workup, the mixture was purified by column chromatography (silica gel, PE:DCM = 1:5, v/v) and recrystallized from DCM/EtOH to give a yellowish brown solid. MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{66}H_{66}O_6S_3$ (**4b**) 1050.4($M^+$) and for $C_{62}H_{66}O_6S_2$ (**4b'**): 970.4 ($M^+_{\mathbf{4b}}$ – thiopheno unit + 2H), found: 1050.6, 970.6.

**Trimethyl-TBTTC 4d.** The reaction of 5-methyl-2-thienaldehyde and TBB **2b** under the identical conditions afforded a mixture of TBTTC **4d** and a byproduct **4d'** with two thieno-units. After conventional workup, the mixture was purified by column chromatography (silica gel, PE:DCM = 1:5, v/v) and recrystallized from DCM/EtOH to give a brown solid. MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{69}H_{72}O_6S_3$ (**4d**) 1092.4 ($M^+$) and for $C_{64}H_{70}O_6S_2$ (**4d'**): 998.5 ($M^+_{\mathbf{4d}}$ – methylthiopheno unit + 2H), found: 1092.5, 998.4.

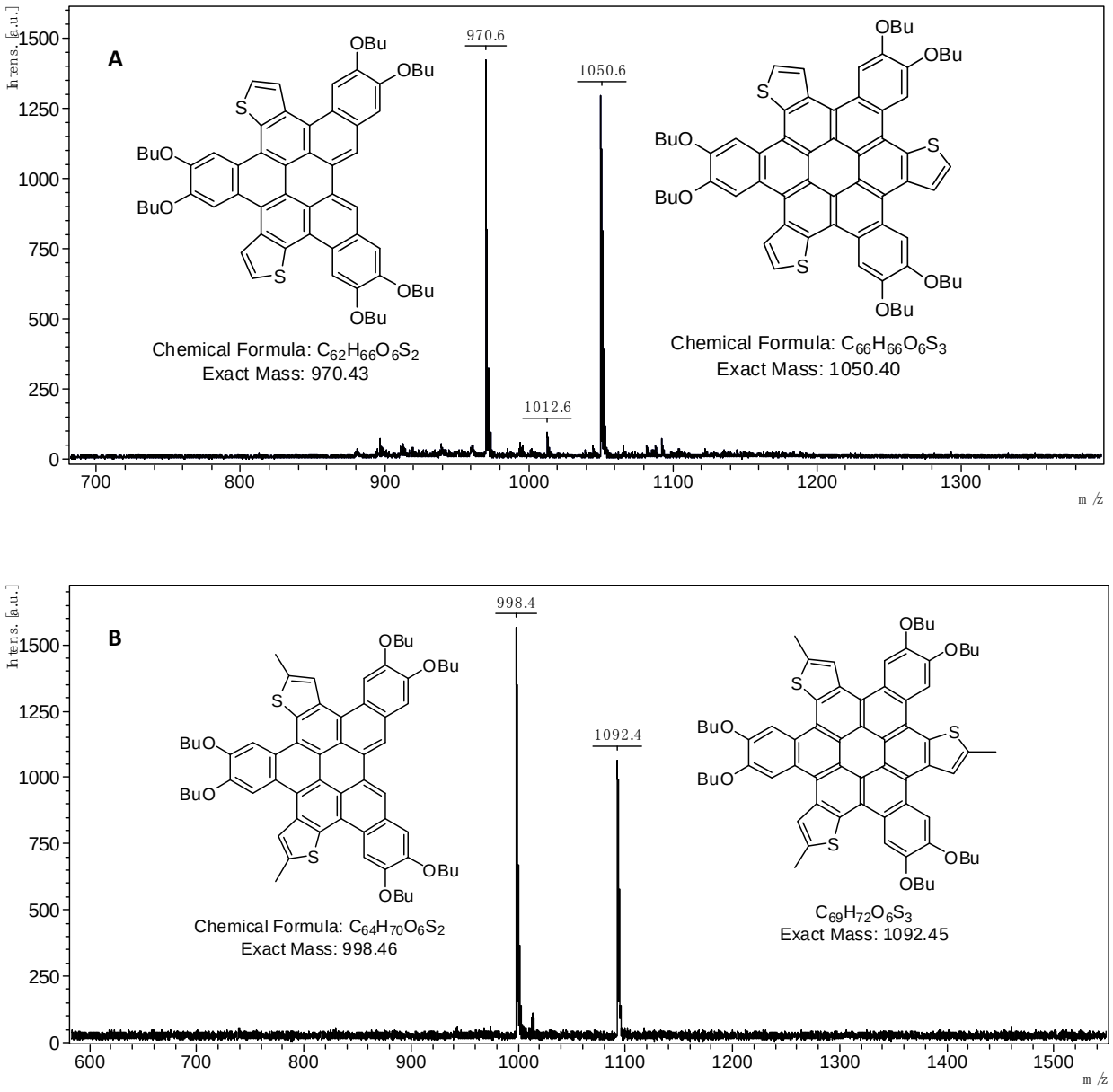



**Figure S1** The MS spectra of the unisolatable mixture from TBB **2c** and 2-thienaldehyde (A) or 5-methyl-2-thienaldehyde (B).

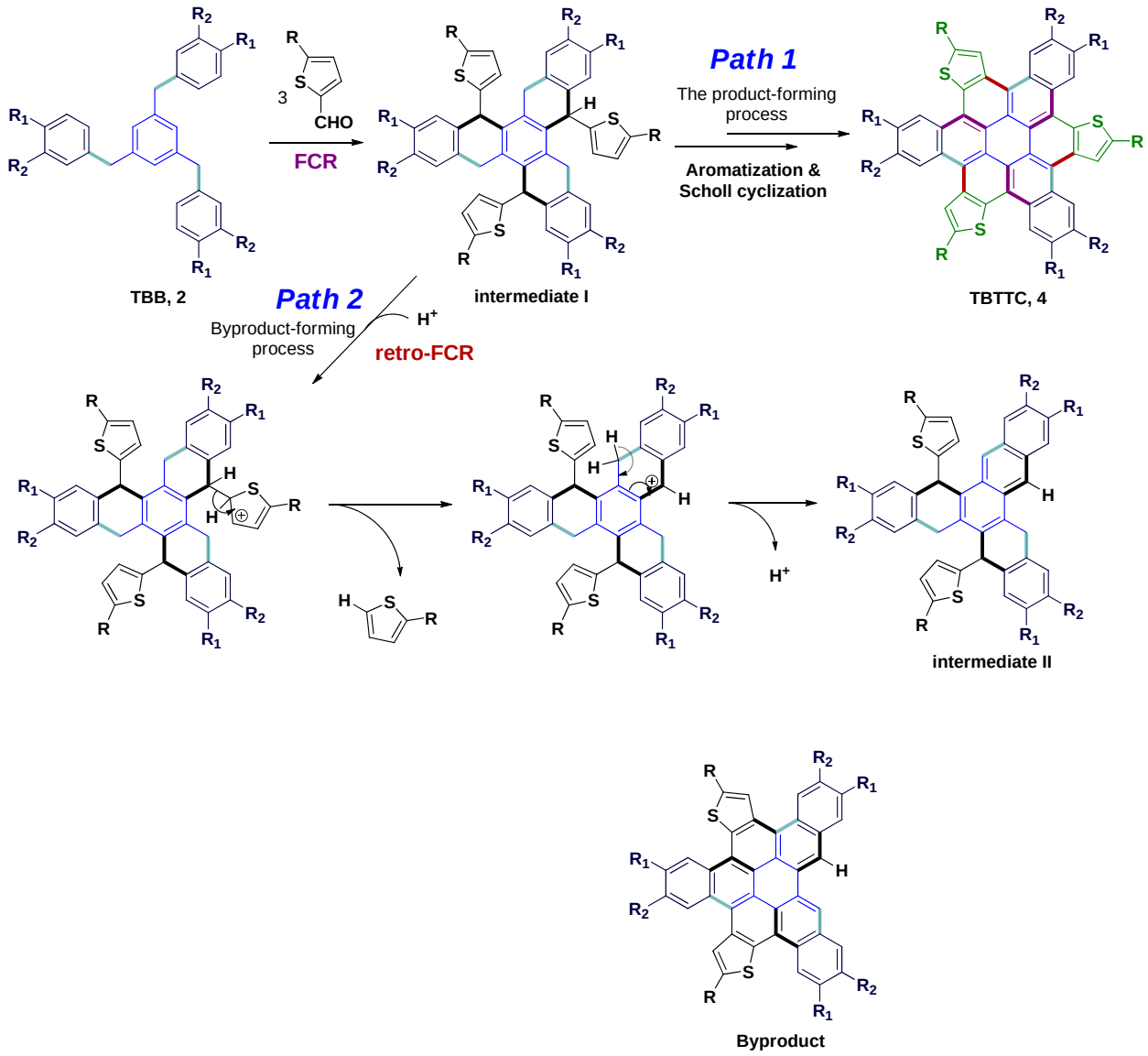
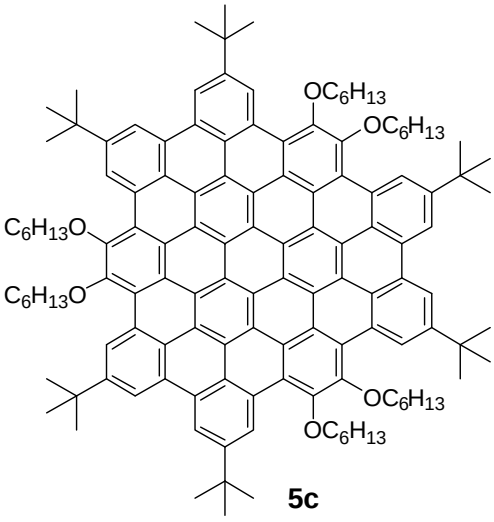


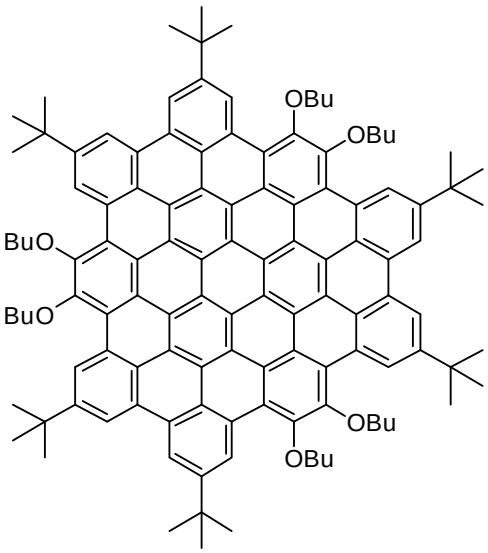

**Figure S2** A possible mechanistic pathway for the formation of the byproduct.

## 3.4 The synthesis of the HBCCs



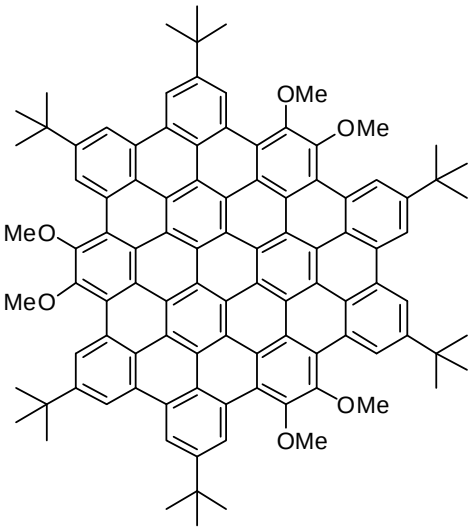

To a solution of 3,6-di-*tert*-butyl-9-phenanthraldehyde (114.5 mg, 0.36 mmol) and $Ac_2O$ (0.24 mL, 2.5 mmol) in 350 mL DCM was added a solution of $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol %) in $CH_3NO_2$ (1 mL) while stirring at rt, followed by dropwise addition of a solution of TBB **2c** (0.1 mmol, 94.8 mg) in 50 mL DCM. The resulting mixture was allowed to stir for 48 h at rt. Then it was degassed with Ar for 10 min and then added dropwise a second portion of $FeCl_3$ (1.92 g, 12 mmol) solution in 20 mL $CH_3NO_2$ over 1 h under Ar atmosphere. After

being stirred at 0 °C for an additional 4 h, the mixture was added 100 mL $CH_3OH$ with stirring and then poured into cold water. The biphasic mixture was separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with water, dried by $Na_2SO_4$, filtered, and rotoevaporated in vacuo. The residue was purified by chromatography (silica gel, PE:DCM = 10:1) to give **5c** as a brick red solid. (97 mg, 53 % yield), mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.77 (s, 6H), 9.70 (s, 6H), 4.48-4.45 (t, $J$ = 4.5 Hz, 12H), 2.40−1.98 (m, 12H), 1.94 (s, 54H), 1.60−1.37 (m, 36H), 0.95−0.91 (t, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 151.0, 149.1, 130.1, 129.3, 124.6, 124.2, 123.4, 123.0, 120.8, 120.3, 119.4, 74.7, 36.2, 32.4, 31.9, 25.8, 22.7, 14.0; MS (MALDI-TOF) (CHCA): *m/z* calcd for $C_{132}H_{144}O_6$: 1825.1 ($M^+$), found: 1825.3.




**5b**

**HBCC 5b** was synthezied following the same procedure from 3,6-di-*tert*-butylphenanthrene-9-carbaldehyde (114 mg, 0.36 mmol) and TBB **2b** (0.1 mmol, 78 mg) and purified by column chromatography (silica gel, PE:DCM = 10:1, v/v). Brick red solid (78 mg, 47 % yield); mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.79 (s, 6H), 9.72 (s, 6H), 4.51−4.48 (t, $J$ = 4.5 Hz, 12H), 2.38−2.31 (m, 12H), 1.98 (s, 54H), 1.65−1.60 (m, 12H), 1.08−1.05 (t, $J$ = 7.4 Hz, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 151.0, 149.1, 130.1, 129.3, 124.6, 124.2, 123.4, 123.0, 120.82, 120.80, 120.3, 119.4, 74.7, 36.2, 33.0, 32.4, 29.7, 19.4, 14.2; MS (MALDI-TOF) (CHCA): *m/z* alcd for $C_{120}H_{120}O_6$: 1656.9 ($M^+$), found: 1656.8.




**5a**

**HBCC 5a** was synthezied following the same procedure from 3,6-di-*tert*-butylphenanthrene-9- carbaldehyde (114 mg, 0.36 mmol) and TBB **2a** (53 mg, 0.1 mmol). except a second step ferric chloride (1.94 g, 12.0 mmol) in 20 mL nitromethane was added dropwise over 1 h at room temperature, then stirred additon 4 h at room temperature, the crude product was purified by column chromatography (silica gel, PE:DCM = 2:1, v/v) to give a brick red solid, 51 mg, yield 36 %, mp > 300 ºC; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.85 (s, 6H), 9.74 (s, 6H), 4.48 (s, 18H), 2.00 (s, 54H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 151.4, 149.3, 130.1, 128.9, 124.6, 124.1, 123.5, 122.6, 120.9, 120.4, 119.2,

61.3, 36.1, 32.3; MS (MALDI-TOF) (CHCA): *m*/*z* calcd for $C_{102}H_{84}O_6$: 1404.6 ($M^+$), found: 1404.8.

# 4 X-ray crystallographic analysis

## 4.1 X-ray crystallographic analysis of *c*-HBC 3a (CCDC 984246)

X-ray quality crystals of ***c***-HBCs **3a** were obtained by slow evaporation of the solution of the compound in 1,2,4-trichlorobenzene (DCB) at room temperature for *ca.* 2 months.

A suitable orange crystal was selected and collected on a single crystal diffractometer (GEMINIE). The crystal was kept at room teperature during data collection. The structure was solved with the Olex2 program using Charge Flipping and refined with the Olex2 using Gauss-Newton minimisation.

### 4.1.1 Crystal data and structure refinement for *c*-HBC 3a

**Table S1** Crystal data and structure refinement for ***c***-HBC **3a**

| | |
|---|---|
| Empirical formula | $C_{39}H_{28.5}Cl_{4.5}O_6$ |
| Formula weight | 752.69 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.6060(3) |
| b/Å | 17.7693(4) |
| c/Å | 18.5377(5) |
| α/° | 90 |
| β/° | 91.524(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 3492.40(16) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.4314 |
| m/mm$^{-1}$ | 3.829 |
| F(000) | 1558.8 |
| Crystal size/mm$^3$ | 0.32 × 0.3 × 0.27 |
| 2Θ range for data collection | 6.9 to 132.06° |
| Index ranges | $-12 \le h \le 12$, $-18 \le k \le 21$, $-22 \le l \le 17$ |
| Reflections collected | 12715 |
| Independent reflections | 6074[R(int) = 0.0179] |
| Data/restraints/parameters | 6074/0/450 |
| Goodness-of-fit on $F^2$ | 1.052 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0859, $wR_2$ = N/A |
| Final R indexes [all data] | $R_1$ = 0.1022, $wR_2$ = 0.2642 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.21/-0.86 |

### 4.1.2 Selected Geometries for *c*-HBC 3a

The coronene core in the *c*-HBCs:

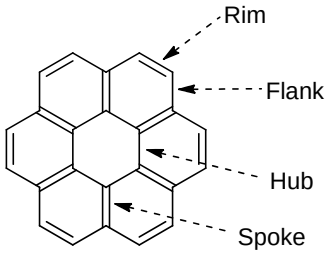



**Figure S3** The instruction of coronene core

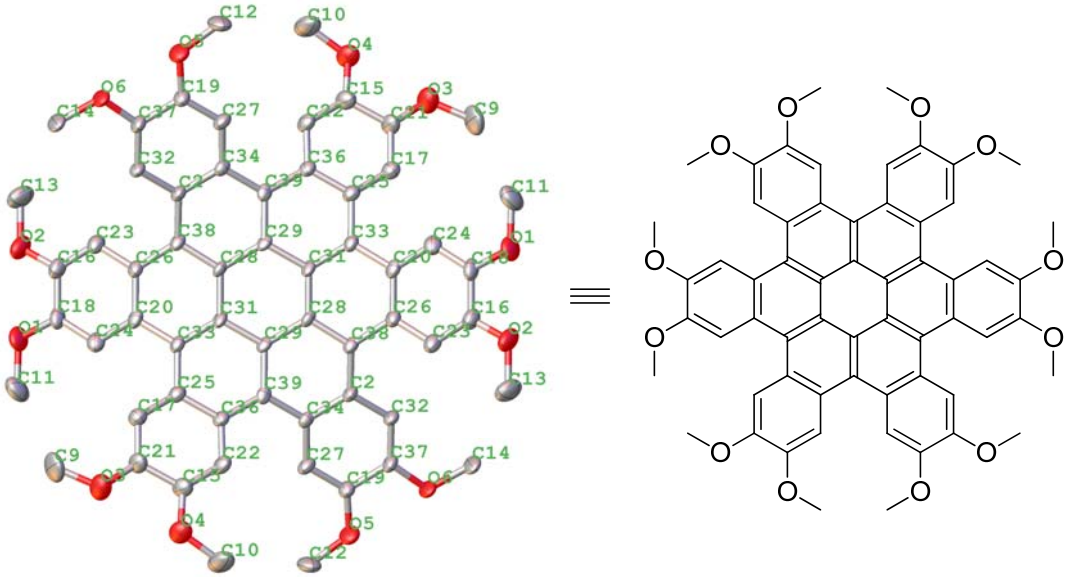


**Figure S4** The X-ray single crystal structure of *c*-HBC **3a**

**Table S2** Selected bond lengths of the coronene core in *c*-HBC **3a** (Å)

| Hub bonds | | Spoke bonds | | Flank bonds | | Rim bonds | |
|---|---|---|---|---|---|---|---|
| Bond | Bond length | Bond | Bond length | Bond | Bond length | Bond | Bond length |
| C(31)-C(28) | 1.435(5) | C(38)-C(28) | 1.400(4) | C(33)-C(25) | 1.445(5) | C(2)-C(34) | 1.409(5) |
| C(31)-C(29) | 1.437(4) | C(33)-C(31) | 1.402(5) | C(39)-C(36) | 1.443(5) | C(36)-C(25) | 1.414(5) |
| C(28)-C(29) | 1.442(5) | C(39)-C(29) | 1.399(5) | C(39)-C(34) | 1.447(4) | C(20)-C(26) | 1.413(5) |
| | | | | C(38)-C(2) | 1.444(4) | | |
| | | | | C(38)-C(26) | 1.448(5) | | |
| | | | | C(33)-C(20) | 1.449(5) | | |
| Average | 1.438 | Average | 1.400 | Average | 1.446 | Average | 1.415 |

**Table S3** Bond lengths of the benzo units in *c*-HBC **3a** (Å)

| Bond | Bond length | Bond | Bond length | Bond | Bond length |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| C(17)-C(25) | 1.425(5) | C(17)-C(21) | 1.363(5) | C(21)-C(15) | 1.418(5) |
| C(36)-C(22) | 1.416(5) | C(22)-C(15) | 1.367(5) | C(37)-C(19) | 1.418(5) |
| C(34)-C(27) | 1.416(5) | C(27)-C(19) | 1.366(5) | C(18)-C(16) | 1.418(6) |
| C(32)-C(2) | 1.427(4) | C(37)-C(32) | 1.359(5) | | |
| C(26)-C(23) | 1.425(5) | C(23)-C(16) | 1.374(5) | | |
| C(24)-C(20) | 1.417(5) | C(24)-C(18) | 1.371(5) | | |
| Average | 1.423 | Average | 1.366 | Average | 1.418 |

**Table S4** Splay angles in the molecule of *c*-HBC **3a**

| Splay angle | Splay angle/° |
|---|---|
| C(17)-C(25)-C(20)-C(24) | 40.699 |
| C(23)-C(26)-C(2)-C(32) | 42.363 |
| C(27)-C(34)-C(36)-C(22) | 41.607 |
| Average | 41.556 |

**Table S5** Fold angles in the benzofused rings in *c*-HBC **3a**

| Best plane-1 | Best plane-1 | Fold angle/° |
|---|---|---|
| C(39)-C(36)-C(25)-C(33) | C(39)-C(29)-C(31)-C(33) | 17.951 |
| C(38)-C(2)-C(34)-C(39) | C(38)-C(28)-C(29)-C(39) | 17.827 |
| C(33)-C(20)-C(26)-C(38) | C(33) -C(31)-C(28)-C(38) | 18.027 |
| Average | | 17.935 |

**Table S6** Torsion angles of methoxy groups with benzo units in ***c***-HBC **3a**

| | Torsion angle/° | | Torsion angle/° |
|---|---|---|---|
| C(11)-O(1)-C(18)-C(16) | 3.888 | C(10)-O(4)-C(15)-C(21) | 9.889 |
| C(13)-O(2)-C(16)-C(18) | 4.483 | C(12)-O(5)-C(19)-C(37) | 9.212 |
| C(9)-O(3)-C(21)-C(15) | 5.633 | C(14)-O(6)-C(37)-C(19) | 0.935 |
| Average torsion angle = 6.272°. Max. torsion angle = 5.633°, min. torsion angle = 0.935°. | | | |

### 4.1.3 Crystal packing of *c*-HBC 3a

The dodecamethoxy ***c***-HBC **3a** was crystallized with three DCB molecules **(Figure S5)**. In crystals, the three solvent molecules are sandwiched into two neighboring layers and associated with each other by intermolecular π–π stacking interactions with a centriod-centriod distance of 3.727 Å. They are arranged almost perpendicularly to the central ring planes of two *c*-HBC **3a** layers. Two outer TCB molecules are antiparallel arranged to each other and interrelated around an inversion center. The axes along the 1,4-dichloro groups are essentially vertical the crystallographic *a*-axis; while the in-between TCB molecule, which looks as if a 1,2,4,5-tetrachlorobenzene molecule, is packed in a staggered stacking arrangement with respect of the two side TCB molecules by

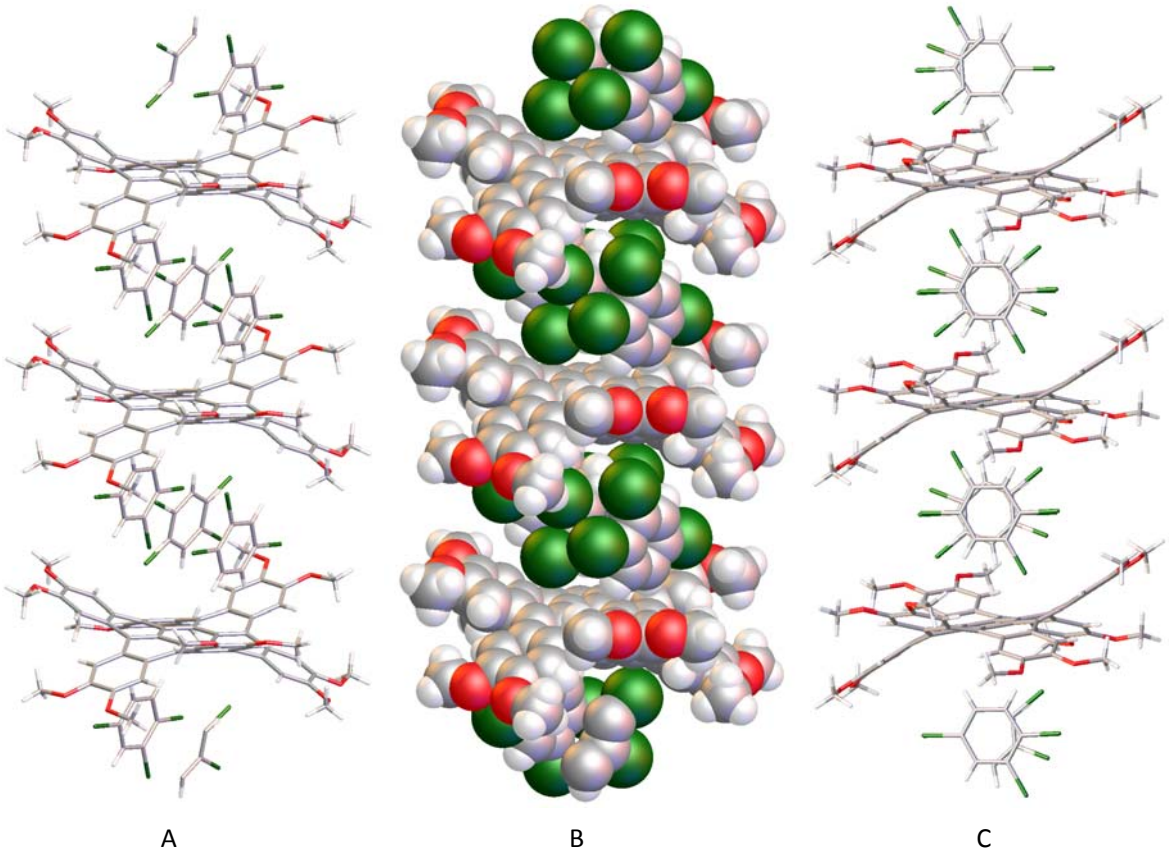



**Figure S5** The columnar packing of *c*-HBC **3a** along *a*-axis (A and B: cooperative interaction between TCB and the *c*-HBC; C: viewed from the co-axial direaction of three TCB molecules)

approximately 24 °. The plane of in-between TCB molecule is approximately parallel to those of the outer TCB molecule. Most notably, all these TCB molecules interact with neighboring *c*-HBC **3a** layers through cooperative T-shaped CH-π and Cl-π interactions. In addition, the chlorine atoms may interact with the close hydrogen atoms of some methoxy groups or benzo rings to a certain extent. In other words, three π-stacked TCB molecules cooperatively mediate the neighboring *c*-HBC molecules via CH-π, Cl-π, and Cl-H interactions, thus forming a unique columnar arrangement by alternating *c*-HBC and TCB molecules. The columnar packing is parallel to the crystallographic *a*-axis with the central ring planes of *c*-HBC **3a** layers roughly perpendicular.

**Table S7** Stacking interactions of TCB with *c*-HBC **3a**

| Entry | H atom | Ring | $D_{ATP}$* | $d_{\pi CH}$ | $\theta$/° |
|---|---|---|---|---|---|
| **1** | H(4) | C(28)-C(38)-C(2)-C(34)-C(39)-C(29) | 2.771 | 2.827 | 78.60 |
| **2** | H(30) | C(28)-C(38)-C(2)-C(34)-C(39)-C(29) | 2.773 | 3.016 | 66.85 |
| **3** | H(8) | C(29)-C(31)-C(33)-C(39)-C(36)-C(25) | 2.804 | 2.837 | 81.30 |
| **4** | Cl(4) | C(29)-C(31)-C(33)-C(39)-C(36)-C(25) | 3.331 | 3.415 | 77.28 |
| **5** | Cl(2) | C(27)-C(34)-C(2)-C(32)-C(37)-C(19) | 3.493 | 3.508 | 84.70 |

*$D_{ATP}$ = Distance of the atom to plane

Interestingly, our dodecamethoxy *c*-HBC **3a** displays much different packing behaviors from the bare *c*-HBC reported by Nuckolls et al.[16] wherein two TCB molecules are sandwiched between two *c*-HBC layers and parallel to the central benzene planes, indicating that the high and symmetric substitution of drastically change the supermolecular property of *c*-HBC core. It should be pointed out that the in-between TCB molecule is not a real 1,2,4,5-tetrachlorobenzene. The resean may be that this TCB molecule is encapsulated in the symmetric hole formed by two TBC cores and two c-HBC molecules with the formation of four types of conformations, cooresponding to the four possibilities for removal of any one chlorine atom from 1,2,4,5-tetrachlorobenzene or of setting three chlorine atoms at 1,2,4,5-positions of a benzene ring. Because that the four possibilities are equal, the probability that chlorine atom appears at each of the 1,2,4,5-positions is 3/4, while that of hydrogen is 1/4 probably because the DCB were simply flipped over in the lattice and present in equal abundance. In fact, the empirical formula $C_{39}H_{28.5}Cl_{4.5}O_6$ reveals that *c*-HBC **3a** is solvated with three DCB molecules in solid state.

## 4.2 X-ray crystallographic analysis of *c*-HBC 3t (CCDC 984247)

The single crystals of *c*-HBC **3t** was growed from the co-solvent ($CH_2Cl_2$:EtOH = 1:1, v/v) at room temperature.

A suitable orange crystal was selected and collected on a single crystal diffractometer (GEMINIE). The crystal was kept at room teperature during data collection. The structure was solved with the Olex2 program using Charge Flipping and refined with the Olex2 using Gauss-Newton minimisation.

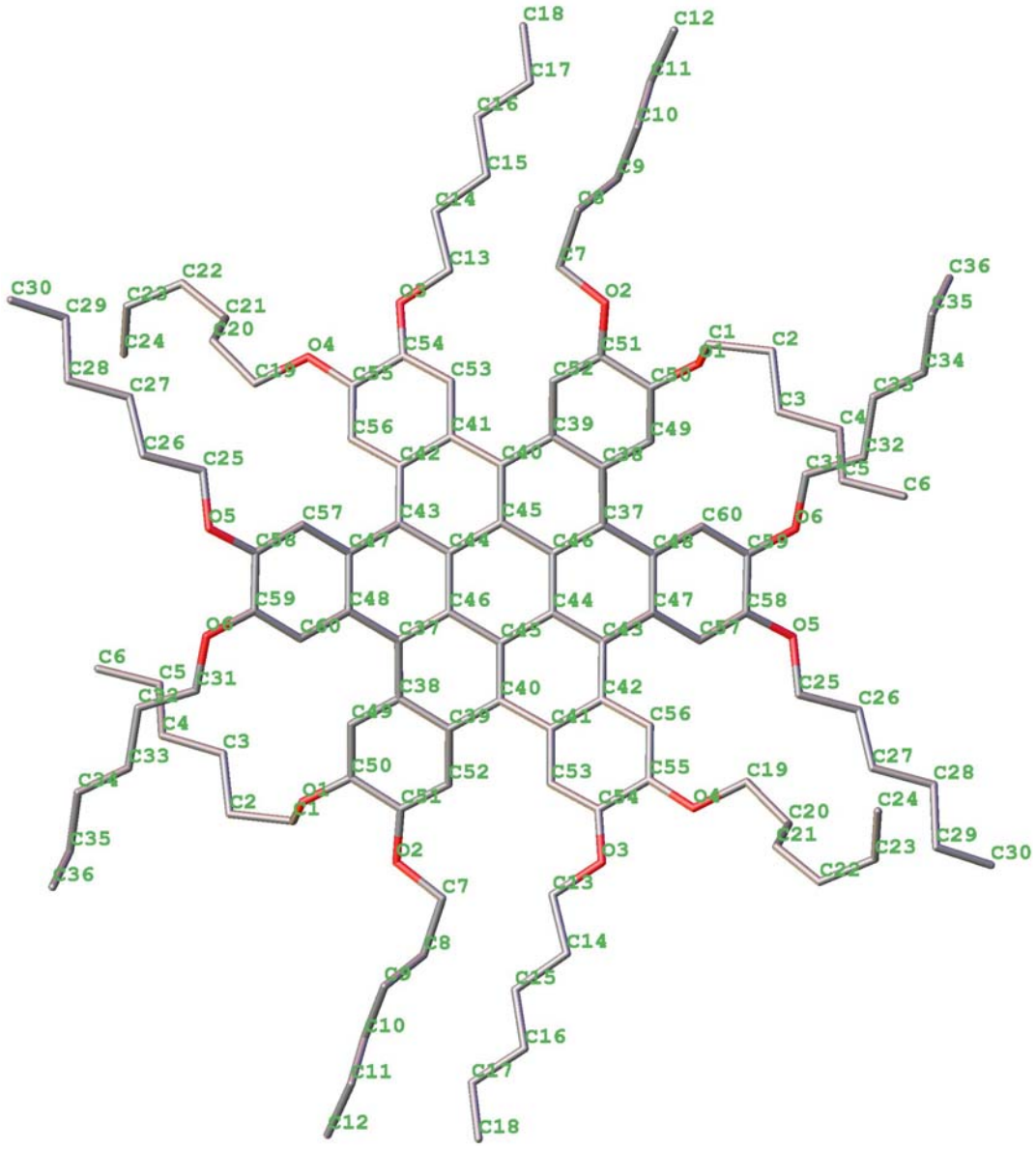
### 4.2.1 Crystal data and structure refinement for *c*-HBC 3t

**Table S8** Crystal data and structure refinement for ***c***-HBC **3t**

| | |
|---|---|
| Empirical formula | $C_{128}H_{224}O_{32}$ |
| Formula weight | 2275.07 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.5229(7) |
| b/Å | 14.2127(8) |
| c/Å | 17.6666(12) |
| α/° | 88.113(5) |
| β/° | 73.225(6) |
| γ/° | 66.912(5) |
| Volume/Å$^3$ | 2757.9(3) |
| Z | 1 |
| $\rho_{calc}$mg/mm$^3$ | 1.370 |

| | |
|---|---|
| m/mm$^{-1}$ | 0.775 |
| F(000) | 1248.0 |
| Crystal size/mm$^3$ | 0.37 × 0.28 × 0.36 |
| 2Θ range for data collection | 6.78 to 132.08° |
| Index ranges | -10 ≤ h ≤ 14, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20 |
| Reflections collected | 17313 |
| Independent reflections | 9613[R(int) = 0.0220] |
| Data/restraints/parameters | 9613/0/853 |
| Goodness-of-fit on $F^2$ | 1.027 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0751, $wR_2$ = 0.2298 |
| Final R indexes [all data] | $R_1$ = 0.0958, $wR_2$ = 0.2653 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.36/-0.28 |

### 4.2.2 Molecular structure and selected geometries for *c*-HBC 3t



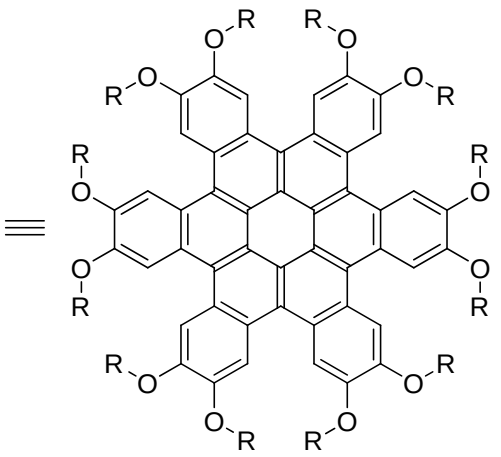



**Figure S6** The X-ray single crystal structure of *c*-HBC **3t**

**Table S9** Bond lengths of the coronene core in *c*-HBC **3t** (Å)

| Hub bonds | | Spoke bonds | | Flank bonds | | Rim bonds | |
|---|---|---|---|---|---|---|---|
| Bond | Bond length | Bond | Bond length | Bond | Bond length | Bond | Bond length |
| C(44)-C(45) | 1.446(3) | C(40)-C(45) | 1.396(3) | C(40)-C(41) | 1.445(3) | C(38)-C(39) | 1.409(3) |
| C(45)-C(46) | 1.440(3) | C(43)-C(44) | 1.389(3) | C(42)-C(43) | 1.448(3) | C(41)-C(42) | 1.418(3) |
| C(44)-C(46) | 1.439(3) | C(37)-C(46) | 1.399(3) | C(43)-C(47) | 1.454(3) | C(47)-C(48) | 1.408(3) |
| | | | | C(37)-C(48) | 1.445(3) | | |
| | | | | C(37)-C(38) | 1.449(3) | | |
| | | | | C(39)-C(40) | 1.461(3) | | |
| Average | 1.442 | Average | 1.395 | Average | 1.450 | Average | 1.412 |

**Table S10** Bond lengths of the benzo units in *c*-HBC **3t** (Å)

| Bond | Bond length | Bond | Bond length | Bond | Bond length |
|---|---|---|---|---|---|
| C(39)-C(52) | 1.413(3) | C(57)-C(58) | 1.363(4) | C(50)-C(51) | 1.412(4) |
| C(41)-C(53) | 1.422(3) | C(59)-C(60) | 1.355(4) | C(58)-C(59) | 1.411(4) |
| C(42)-C(56) | 1.411(3) | C(49)-C(50) | 1.354(3) | C(54)-C(55) | 1.418(3) |
| C(47)-C(57) | 1.411(4) | C(51)-C(52) | 1.375(3) | | |
| C(48)-C(60) | 1.424(3) | C(53)-C(54) | 1.365(3) | | |
| C(38)-C(49) | 1.419(3) | C(55)-C(56) | 1.362(3) | | |
| Average | 1.415 | Average | 1.362 | Average | 1.421 |

**Table S11** Splay angles in the molecule of *c*-HBC **3t**

| | Splay Angle/° |
|---|---|
| C(57)-C(47)-C(42)-C(56) | 41.106 |
| C(53)-C(41)-C(39)-C(52) | 38.648 |
| C(49)-C(38)-C(48)-C(60) | 40.608 |
| Average | 41.121 |

**Table S12** Torsion angles of hexoxy groups with respect to benzo-units in ***c***-HBC **3t**

| | Torsion angle/° | | Torsion angle/° |
|---|---|---|---|
| C(1)-O(1)-C(50)-C(51) | 65.808 | C(19)-O(4)-C(55)-C(54) | 2.289 |
| C(7)-O(2)-C(51)-C(50) | 6.516 | C(25)-O(5)-C(58)-C(59) | 12.016 |
| C(13)-O(3)-C(54)-C(55) | 3.894 | C(31)-O(6)-C(59)-C(58) | 18.420 |

**Table S13** Fold angles of *c*-HBC **3t**

| Best plane-1 | Best plane-2 | Fold angle/° |
|---|---|---|
| C(43)-C(40)-C(45)-C(44) | C(43)-C(41)-C(42)-C(44) | 18.361 |
| C(37)-C(45)-C(46)-C(40) | C(37)-C(38)-C(39)-C(40) | 17.891 |
| C(37)-C(44)-C(46)-C(43) | C(37)-C(38)-C(47)-C(43) | 17.964 |
| Average | | 18.072 |

## 4.3 X-ray crystallographic analysis of TBTTC 4b (CCDC 984248)

Single crystals of TBTTC **4b** ($C_{66}H_{66}O_6S_3$) were obtained by slow evaporation of the solution of **4b** in a mixed solvent ($CH_2Cl_2$:$CHCl_3$:EtOH = 1:1:2, v/v/v) at room temperature for 2 weeks.

A suitable crystal was selected and collected on an X-ray single crystal diffractometer (SuperNova) and the crystal was kept at 105(7) K during data collection. The structure was solved with the Olex2. Structure solution program using Charge Flipping and refined with the Olex2 using Gauss-Newton minimisation.

### 4.3.1 Crystal data and structure refinement for TBTTC 4b

**Table S14** Crystal data and structure refinement for TBTTC **4b**

| | |
|---|---|
| Empirical formula | $C_{66}H_{66}O_6S_3$ |
| Formula weight | 1051.37 |
| Temperature/K | 105(7) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.1545(19) |
| b/Å | 13.507(2) |
| c/Å | 19.3873(17) |
| α/° | 98.703(11) |
| β/° | 95.789(10) |
| γ/° | 108.038(15) |
| Volume/Å$^3$ | 2954.4(8) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.182 |
| m/mm$^{-1}$ | 0.175 |
| F(000) | 1116.0 |

| | |
|---|---|
| Crystal size/mm$^3$ | 0.3 × 0.26 × 0.25 |
| 2Θ range for data collection | 6 to 52.04° |
| Index ranges | -15 ≤ h ≤ 14, -16 ≤ k ≤ 16, -22 ≤ l ≤ 23 |
| Reflections collected | 21794 |
| Independent reflections | 11472[R(int) = 0.0387] |
| Data/restraints/parameters | 11472/126/740 |
| Goodness-of-fit on $F^2$ | 0.946 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0734, $wR_2$ = 0.1964 |
| Final R indexes [all data] | $R_1$ = 0.1000, $wR_2$ = 0.2162 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.50/-0.57 |

### 4.3.2 Molecular structure and selected geometrical data of TBTTC 4b

### 4.3.2 Molecular structure of TBTTC 4b

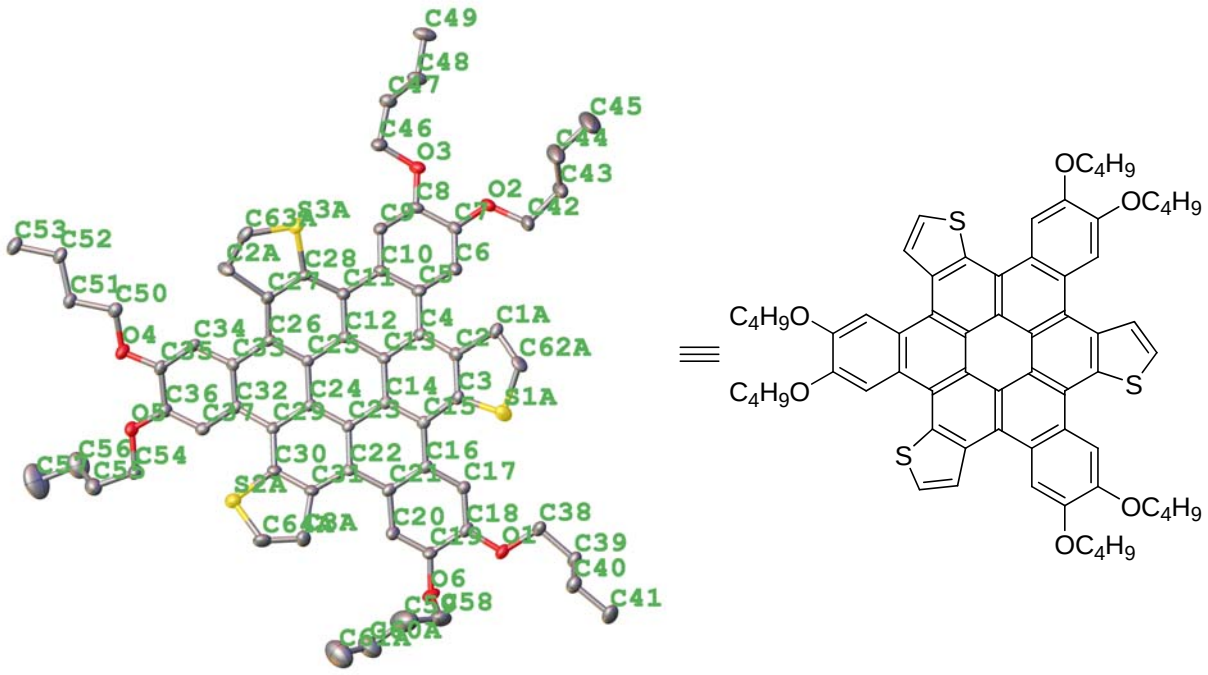



**Figure S7** The X-ray single crystal structure of TBTTC **4b** (Hydrogen bonds are symbolized by dashed lines)

**Table S15.** Bond lengthes of the coronene core in TBTTC **4b** (Å)

| Bonds in the hub | | Spoke bonds | | Flank bonds | | Rim bonds | |
|---|---|---|---|---|---|---|---|
| Bond | Length | Bond | Length | Bond | Length | Bond | Length |
| C(12)-C(25) | 1.442(4) | C(11)-C(12) | 1.402(4) | C(10)-C(11) | 1.447(4) | C(2)-C(3) | 1.396(4) |
| C(24)-C(25) | 1.439(4) | C(4)-C(13) | 1.396(4) | C(11)-C(28) | 1.421(4) | C(30)-C(31) | 1.402(4) |
| C(23)-C(24) | 1.444(4) | C(14)-C(15) | 1.409(4) | C(5)-C(6) | 1.415(4) | C(27)-C(28) | 1.399(4) |
| C(14)-C(23) | 1.442(4) | C(22)-C(23) | 1.419(4) | C(2)-C(4) | 1.437(4) | C(16)-C(21) | 1.402(4) |
| C(13)-C(14) | 1.454(4) | C(24)-C(29) | 1.418(4) | C(3)-C(15) | 1.437(4) | C(32)-C(33) | 1.413(4) |
| C(12)-C(13) | 1.436(4) | C(25)-C(26) | 1.423(4) | C(15)-C(16) | 1.453(4) | C(5)-C(10) | 1.399(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | C(21)-C(22) | 1.447(4) | | |
| | | | | C(22)-C(31) | 1.429(4) | | |
| | | | | C(29)-C(30) | 1.419(4) | | |
| | | | | C(29)-C(32) | 1.446(4) | | |
| | | | | C(26)-C(33) | 1.443(4) | | |
| | | | | C(26)-C(27) | 1.434(4) | | |
| Average | 1.443 | Average | 1.411 | Average | 1.436 | Average | 1.402 |

**Table S16** Bond lengthes of thieno- and benzo-units in TBTTC **4b**

| Bond | Length/Å | Bond | Length/Å | Bond | Length/Å |
|---|---|---|---|---|---|
| In the thieno-units | | | | | |
| S(1B)-C(2) | 1.663(3) | S(1B)-C(62B) | 1.707(18) | | |
| S(2B)-C(31) | 1.676(3) | S(2B)-C(64B) | 1.717(10) | | |
| S(3B)-C(63B) | 1.701(17) | S(3B)-C(27) | 1.682(3) | | |
| Average | 1.680 | Average | 1.702 | | |
| C(1B)-C(3) | 1.713(3) | C(62B)-C(1B) | 1.323 | | |
| C(2B)-C(28) | 1.698(3) | C(63B)-C(2B) | 1.343 | | |
| C(3B)-C(30) | 1.697(3) | C(64B)-C(3B) | 1.301 | | |
| Average: | 1.703 | Average | 1.322 | | |
| In the benzo-units | | | | | |
| C(16)-C(21) | 1.412 (4) | C(16)-C(17) | 1.407(4) | C(17)-C(18) | 1.377(4) |
| C(32)-C(33) | 1.413(4) | C(20)-C(21) | 1.418(4) | C(19)-C(20) | 1.369(4) |
| C(32)-C(33) | 1.399(4) | C(32)-C(37) | 1.411(4) | C(35)-C(36) | 1.428(4) |
| Average | 1.412 | C(33)-C(34) | 1.427(4) | C(36)-C(37) | 1.374(4) |
| C(18)-C(19) | 1.408(5) | C(9)-C(10) | 1.431(4) | C(8)-C(9) | 1.370(4) |
| C(35)-C(36) | 1.428(4) | C(5)-C(6) | 1.415(4) | C(6)-C(7) | 1.381(4) |
| C(7)-C(8) | 1.419(5) | Average | 1.418 | Average | 1.383 |
| Average | 1.418 | | | | |

C(3B)= S(2A); C(3B)=C(2B); C(1B)= S(1A)

**Table S17** The splay angles at the bay regions in TBTTC **4b**

| All-carbon bays | Torsion angle/° | Sulfur-containing bays | Torsion angle/° |
|---|---|---|---|
| C(1B)-C(28)-C(11)-C(9) | 23.155 | S(1B)-C(2)-C(5)-C(6) | 34.279 |
| C(2B)-C(28)-C(10)-C(9) | 31.496 | S(2B)-C(31)-C(21)-C(20) | 24.647 |
| C(3B)-C(30)-C(32)-C(37) | 32.776 | S(3B)-C(27)-C(34)-C(33) | 21.419 |
| Average | 26.782 | Average | 29.142 |

**Table S18** Dihedronal angles of the rings between central and extior rings in TBTTC **4b**

| Entry | | Best plane-1 | Best plane-2 | Fold angle/° |
|---|---|---|---|---|
| Thieno-fused rings | 1 | C(15)-C(2)-C(3)-C(4) | C(15) -C(14)-C(13)-C(4) | 12.957 |
| | 2 | C(11)-C(12)-C(25)-C(26) | C(11)-C(28)-C(27)-C(26) | 13.250 |
| | 3 | C(29)-C(24)-C(23)-C(22) | C(29)-C(30)-C(31)-C(22) | 11.439 |
| Benzo-fused rings | 4 | C(26)-C(25)-C(24)-C(29) | C(26)-C(33)-C(32)-C(29) | 13.509 |

| | | | | |
|---|---|---|---|---|
| | 5 | C(22)-C(23)-C(14)-C(15) | C(22)-C(21)-C(16)-C(15) | 13.572 |
| | 6 | C(4)-C(5)-C(10)-C(11) | C(4)-C(13)-C(12)-C(11) | 15.570 |

**Table S19** The torsion angles of butoxy groups with the benzo units in TBTTC **4b**

| Selected angle | Torsion angle/° | Selected angle | Torsion angle/° |
|---|---|---|---|
| C(38)-O(1)-C(18)-C(19) | 8.548 | C(50)-O(4)-C(35)-C(36) | 8.061 |
| C(42)-O(2)-C(7)-C(8) | 9.130 | C(54)-O(5)-C(36)-C(35) | 1.291 |
| C(46)-O(3)-C(8)-C(7) | 9.501 | C(58)-O(6)-C(19)-C(18) | 75.716 |

### 4.3.2 Packing diagram of TBTTC 4b

TBTTC **4b** is a twisted, chiral core molecule. $^1$H NMR spectrum shows two well-resolved doublets assignable to two vicinal protons of the thieno unit, indicating its three-fold symmetry in solution. In the solid state, however, the $C_3$ symmetry is destroyed. In fact, no structural data in the equivalent part in the molecule is identical. Three intramolecular H-bonds are observed in the molecule with the H–S distances of 2.305 Å, 2.325 Å, and 2.438 Å.

In crystals, two opposite enantimers of this chiral core compounds form a racemic dimer (Figure **S9**). Between two enantiomeric molecules, the center-center distance is 3.710 Å; the cofacial separation is 3.439 Å. Two molecules are slipped along a tetraceno[2,3-b]thiophene motif by 1.390 Å, close to a half width of benzene ring. Two enantiomers form a shape-complementarity via π-stacking interactions in a centrosymmetric head-to-tail arrangement.

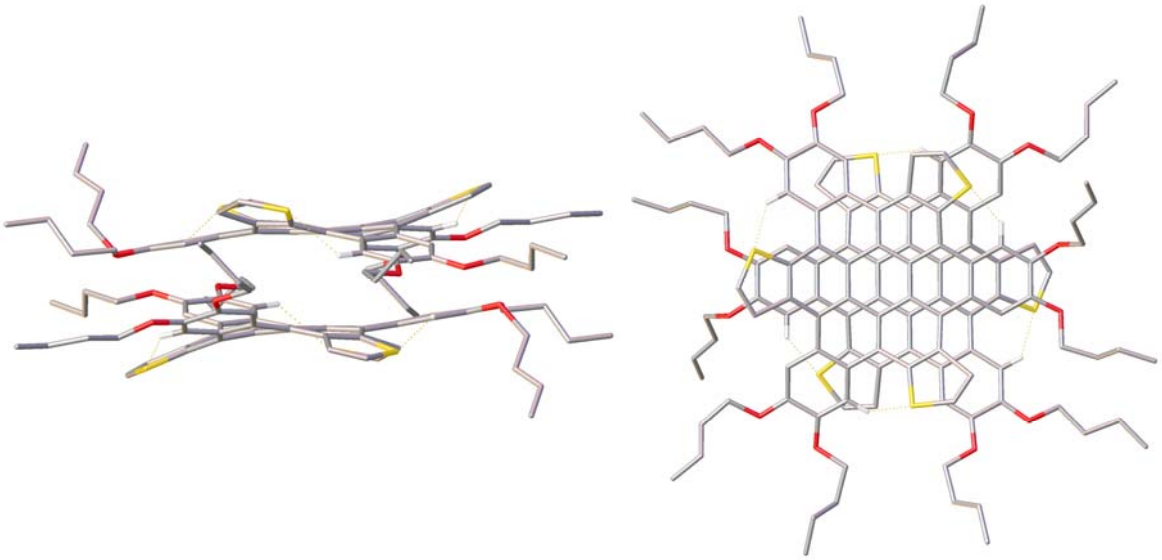


**Figure S8** The racemic dimer of two opposite enantiomers of TBTTC **4b** (left: side view; right: view of two neighboring molecules projected onto the planes)

## 4.4 X-ray crystallographic analysis of HBCC 5c (CCDC 984249)

The single crystals of HBCC **5c** were growed from a mixed solvent ($CHCl_3$:EtOH = 1:1, v/v) at room temperature.

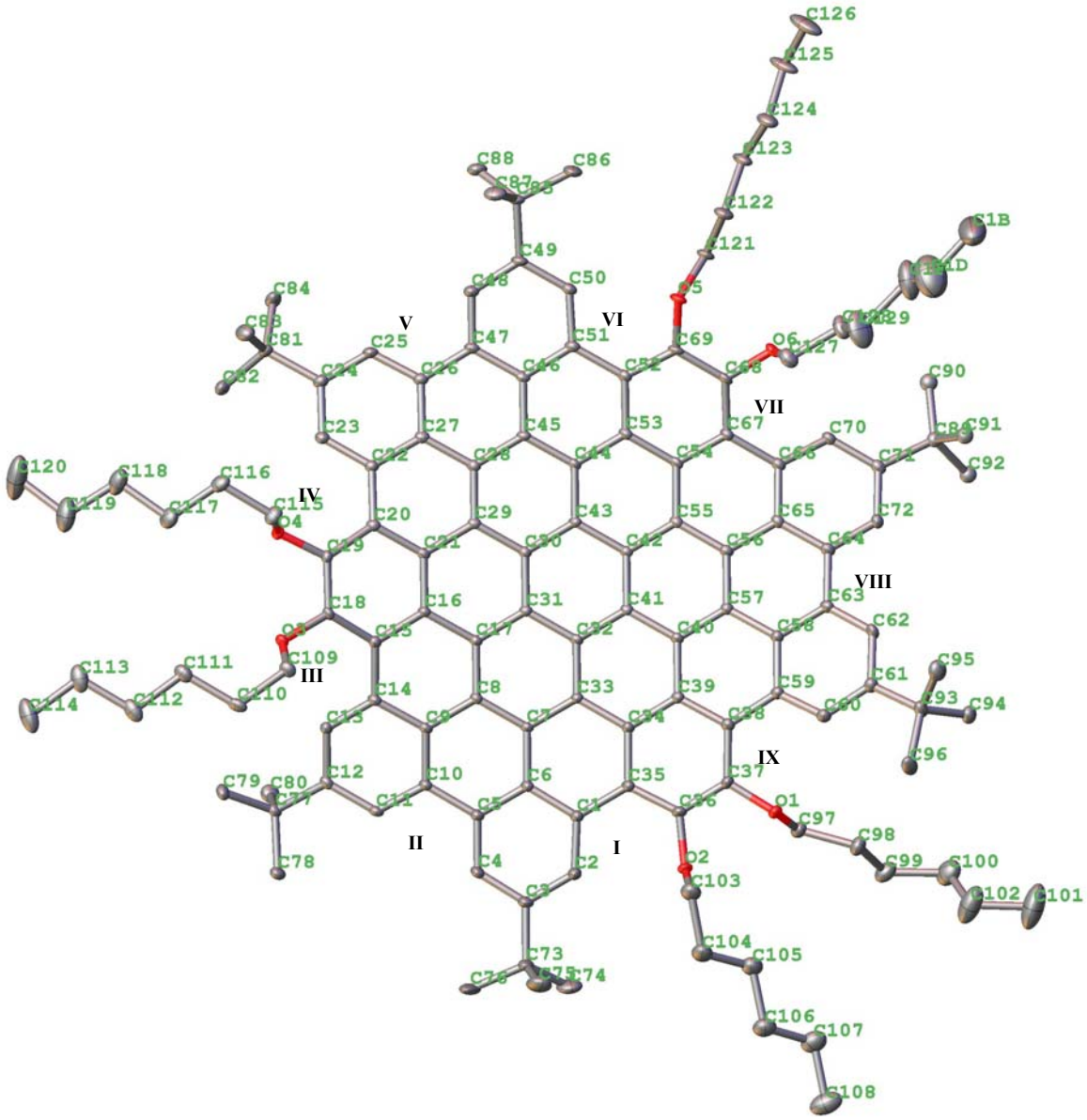
A suitable crystal was selected and collected on a single crystal diffractometer (SuperNova). The crystal was kept at 100(10) K during data collection. The structure was solved with the Olex2 program using charge flipping and refined with the Olex2 using Gauss-Newton minimization.[17]

### 4.4.1 Crystal data and structure refinement for HBCC 5c

**Table S20** Crystal data and structure refinement for HBCC **5c**

| Empirical formula | $C_{134}H_{146}Cl_6O_6$ |
|---|---|
| Formula weight | 2065.21 |
| Temperature/K | 100.00(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 14.3699(2) |
| b/Å | 18.8611(4) |
| c/Å | 20.7510(4) |
| α/° | 91.3836(17) |
| β/° | 93.8054(15) |
| γ/° | 100.7521(16) |
| Volume/Å$^3$ | 5509.42(19) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.245 |
| m/mm$^{-1}$ | 1.866 |
| F(000) | 2200.0 |
| Crystal size/mm$^3$ | 0.34 × 0.3 × 0.23 |
| 2Θ range for data collection | 6.52 to 145.24° |
| Index ranges | $-12 \le h \le 17$, $-23 \le k \le 23$, $-25 \le l \le 25$ |
| μ(CuKα) | 1.866 mm$^{-1}$ |
| Reflections collected | 70899 |
| Independent reflections | 21767[R(int) = 0.0344] |
| Data/restraints/parameters | 21767/65/1347 |
| Goodness-of-fit on $F^2$ | 1.169 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0964, $wR_2$ = 0.2761 |
| Final R indexes [all data] | $R_1$ = 0.1115, $wR_2$ = 0.2967 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.74/-1.56 |

**4.4.2 Molecular structure and selected geometries of for HBCC 5c**



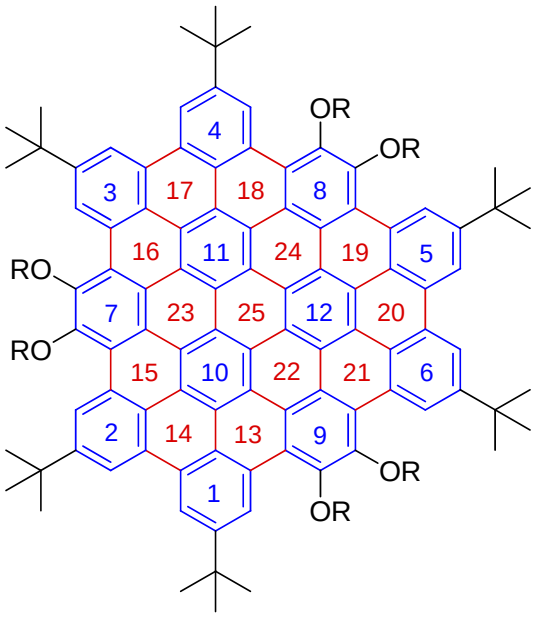



**Figure S9** The X-ray single crystal structure of HBCC **5c** (R = *n*-$C_6H_{13}$)

The all-benzenoid nature of this aromatic core is observed from the difference between inter- and intra-benzenoid C−C bonds (1.435–1.469 and 1.380–1.425 Å, respectively).

**Table S21** The bond lengths of inter- and intra-benzenoid C−C bonds

| Intra-benzenoid C−C bonds (average 1.409 Å) | | | | | | Inter-benzenoid C−C bonds (average 1.448 Å) | | |
|---|---|---|---|---|---|---|---|---|
| Ring | Bond | Length/Å | Ring | Bond | Length/Å | Ring | Bond | Length/Å |
| 1 | C(1)-C(2) | 1.405(4) | 7 | C(20)-C(21) | 1.411(4) | 13 | C(1)-C(35) | 1.469(4) |
| 1 | C(2)-C(3) | 1.394(4) | **7** | C(21)-C(16) | 1.425(4) | 13, 14 | C(6)-C(7) | 1.439(4) |
| 1 | C(3)-C(4) | 1.381(4) | 7 | C(16)-C(15) | 1.414(4) | 13, 22 | C(33)-C(34) | 1.445(4) |
| 1 | C(4)-C(5) | 1.396(4) | 7 | C(15)-C(18) | 1.408(4) | 14 | C(5)-C(10) | 1.455(4) |
| 1 | C(5)-C(6) | 1.425(4) | 7 | C(18)-C(19) | 1.387(4) | 14, 15 | C(8)-C(9) | 1.443(4) |
| 1 | C(6)-C(1) | 1.420(4) | 7 | C(19)-C(20) | 1.422(4) | 15 | C(15)-C(14) | 1.459(4) |
| 2 | C(9)-C(10) | 1.412(4) | 8 | C(68)-C(69) | 1.387(4) | 15, 23 | C(16)-C(17) | 1.441(4) |
| 2 | C(10)-C(11) | 1.406(4) | 8 | C(68)-C(52) | 1.422(4) | 16 | C(20)-C(22) | 1.463(4) |
| 2 | C(11)-C(12) | 1.387(4) | 8 | C(52)-C(53) | 1.421(4) | 16, 17 | C(27)-C(28) | 1.438(4) |
| 2 | C(12)-C(13) | 1.392(4) | 8 | C(53)-C(54) | 1.422(4) | 16, 23 | C(21)-C(29) | 1.444(4) |
| 2 | C(13)-C(14) | 1.404(4) | 8 | C(54)-C(67) | 1.419(4) | 17 | C(26)-C(47) | 1.467(4) |
| 2 | C(14)-C(9) | 1.416(4) | 8 | C(67)-C(68) | 1.419(4) | 17, 18 | C(45)-C(46) | 1.442(4) |
| 3 | C(25)-C(26) | 1.401(4) | 9 | C(38)-C(37) | 1.408(4) | 18 | C(51)-C(52) | 1.460(4) |
| 3 | C(26)-C(27) | 1.416(4) | 9 | C(37)-C(36) | 1.389(4) | 18, 24 | C(44)-C(53) | 1.451(4) |
| 3 | C(27)-C(22) | 1.420(4) | 9 | C(36)-C(35) | 1.409(4) | 19 | C(66)-C(67) | 1.454(4) |
| 3 | C(22)-C(23) | 1.403(4) | 9 | C(35)-C(34) | 1.429(4) | 19, 20 | C(56)-C(65) | 1.442(4) |
| 3 | C(23)-C(24) | 1.394(4) | 9 | C(34)-C(39) | 1.429(4) | 19, 24 | C(55)-C(54) | 1.442(4) |
| 3 | C(24)-C(25) | 1.397(4) | 9 | C(39)-C(38) | 1.419(4) | 20 | C(63)-C(64) | 1.459(4) |
| 4 | C(46)-C(47) | 1.421(4) | 10 | C(32)-C(33) | 1.423(4) | 20, 21 | C(57)-C(58) | 1.435(4) |
| 4 | C(47)-C(48) | 1.395(4) | 10 | C(33)-C(7) | 1.418(4) | 21 | C(38)-C(59) | 1.463(4) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 4 | C(48)-C(49) | 1.399(4) | 10 | C(7)-C(8) | 1.413(4) | 21, 22 | C(40)-C(39) | 1.446(4) |
| 4 | C(49)-C(50) | 1.380(4) | 10 | C(8)-C(17) | 1.412(4) | 22, 25 | C(41)-C(32) | 1.435(4) |
| 4 | C(50)-C(51) | 1.413(4) | 10 | C(17)-C(31) | 1.417(4) | 23, 25 | C(30)-C(31) | 1.435(4) |
| 4 | C(51)-C(46) | 1.419(4) | 10 | C(31)-C(32) | 1.416(4) | 24, 25 | C(42)-C(43) | 1.435(4) |
| 5 | C(70)-C(71) | 1.386(4) | 11 | C(44)-C(45) | 1.414(4) | | | |
| 5 | C(71)-C(72) | 1.389(4) | 11 | C(45)-C(28) | 1.423(4) | | | |
| 5 | C(72)-C(64) | 1.398(4) | 11 | C(28)-C(29) | 1.412(4) | | | |
| 5 | C(64)-C(65) | 1.412(4) | 11 | C(29)-C(30) | 1.415(4) | | | |
| 5 | C(65)-C(66) | 1.412(4) | 11 | C(30)-C(43) | 1.424(4) | | | |
| 5 | C(66)-C(70) | 1.417(4) | 11 | C(43)-C(44) | 1.423(4) | | | |
| 6 | C(63)-C(62) | 1.390(4) | 12 | C(55)-C(56) | 1.411(4) | | | |
| 6 | C(62)-C(61) | 1.394(4) | 12 | C(56)-C(57) | 1.421(4) | | | |
| 6 | C(61)-C(60) | 1.388(4) | 12 | C(57)-C(40) | 1.415(4) | | | |
| 6 | C(60)-C(59) | 1.409(4) | 12 | C(40)-C(41) | 1.417(4) | | | |
| 6 | C(59)-C(58) | 1.412(4) | 12 | C(41)-C(42) | 1.422(4) | | | |
| 6 | C(58)-C(63) | 1.423(4) | 12 | C(42)-C(55) | 1.421(4) | | | |

**Table S22** Torsion angles in the bay regions for HBCC **5c***

| No | Atom-atom, atom-atom | Torsion angle/° | No | Atom-atom, atom-atom | Torsion angle/° |
|---|---|---|---|---|---|
| I | C(2)-C(1)-C(35)-C(36) | 3.435 | VI | C(50)-C(51)-C(52)-C(69) | 6.810 |
| II | C(4)-C(5)-C(10)-C(11) | 8.660 | VII | C(68)-C(67)-C(66)-C(70) | 24.085 |
| III | C(13)-C(14)-C(15)-C(18) | 22.882 | VIII | C(72)-C(64)-C(63)-C(62) | 17.995 |
| IV | C(19)-C(20)-C(22)-C(23) | 17.748 | IX | C(60)-C(59)-C(38)-C(37) | 17.851 |
| V | C(25)-C(26)-C(47)-C(48) | 10.575 | | | |

* Only one twist angle at bay region is less than 5 °.

**Table S23** Torsion angles of hexoxy with the attached benzene ring in HBCC **5c**

| | Torsion angle/° | | Torsion angle/° |
|---|---|---|---|
| C(97)-O(1)-C(37)-C(36) | 82.019 | C(115)-O(4)-C(19)-C(18) | 82.226 |
| C(103)-O(2)-C(36)-C(37) | 78.346 | C(121)-O(5)-C(69)-C(68) | 67.970 |
| C(109)-O(3)-C(18)-C(19) | 69.581 | C(127)-O(6)-C(68)-C(69) | 87.020 |

**Table S24** Intermolecular CH···π interactions between two dimers of HBCC **5c**

| H(C) atom | Ring faced by H atom | CH···π plane distance/Å | $d_{cH}$ | θ/° | Project |
|---|---|---|---|---|---|
| H(C109) | C(29)-C(21)-C(16)-C(17)-C(31)-C(30) | 2.930 | 2.933 | 87.59 | 0.123 |
| H(C110) | C(28)-C-C(29)-(45)-C(44)-C(43)-(30) | 2.676 | 2.680 | 86.86 | 0.147 |
| H(C111) | C(30)-C(31)-C(32)-C(41)-C(42)-C(43) | 2.820 | 2.835 | 84.18 | 0.287 |
| H(C112) | C(42)-C(43)-C(44)-C(53)-C(54)-C(55) | 2.770 | 2.776 | 86.15 | 0.186 |
| H(C113) | C(40)-C(41)-C(42)-C(55)-C(56)-C(57) | 2.706 | 2.750 | 79.71 | 0.491 |
| H(C114) | C(54)-C(55)-C(56)-C(65)-C(66)-C(67) | 2.790 | 2.806 | 83.98 | 0.294 |
| H(C115) | C(01)-C(06)-C(07)-C(33)-C(34)-C(35) | 2.671 | 2.696 | 82.22 | 0.365 |
| H(C116) | C(01)-C(06)-C(07)-C(33)-C(34)-C(35) | 2.671 | 2.696 | 82.22 | 0.365 |

| | | | | | |
|---|---|---|---|---|---|
| H(C117) | C(32)-C(33)-C(34)-C(39)-C(40)-C(41) | 2.942 | 2.984 | 80.29 | 0.503 |
| H(C118) | C(34)-C(35)-C(36)-C(37)-C(38)-C(39) | 2.838 | 2.852 | 84.23 | 0.287 |
| H(C119) | C(38)-C(39)-C(40)-C(57)-C(58)-C(59) | 2.987 | 3.119 | 73.70 | 0.896 |
| Average | | 2.800 | 2.829 | | |

### 4.4.3 Crystal packing of HBCC 5c

**Figure S10** illustrates the π-π dimer and the C–H···π dimer of HBCC **5c**. The π-π dimer is stabilized by the shape complementary π–π stacking interactions between two opposite conformers, which associate the molecules into centrosymmetrically related pairs (racemates). Between two π-π dimers, two neighboring molecules are held together by a series of 22 coorperative intermolecular C–H···π interactions between the hydrogens of the aliphatic long chains and the benzene rings of the large π-system, forming a C–H···π dimer around an inversion center. Two terminal methyl groups, which are denoted in green cycles in Figure **S11**, do not participate the intermolecular C–H···π interactions since they are positioned out off the rims of the π-systems. Notice the bent conformation of the hexoxy groups which follow the surface topography of the adjacent aromatic core, keeping the distance of 2.671–2.987 Å between an aliphatic H atom and the π-plane of the nearest ring that the H atom is facing. All these C–H···π distances are within the common used cutoff distance (3.05 Å)[18] for C–H···π interactions.

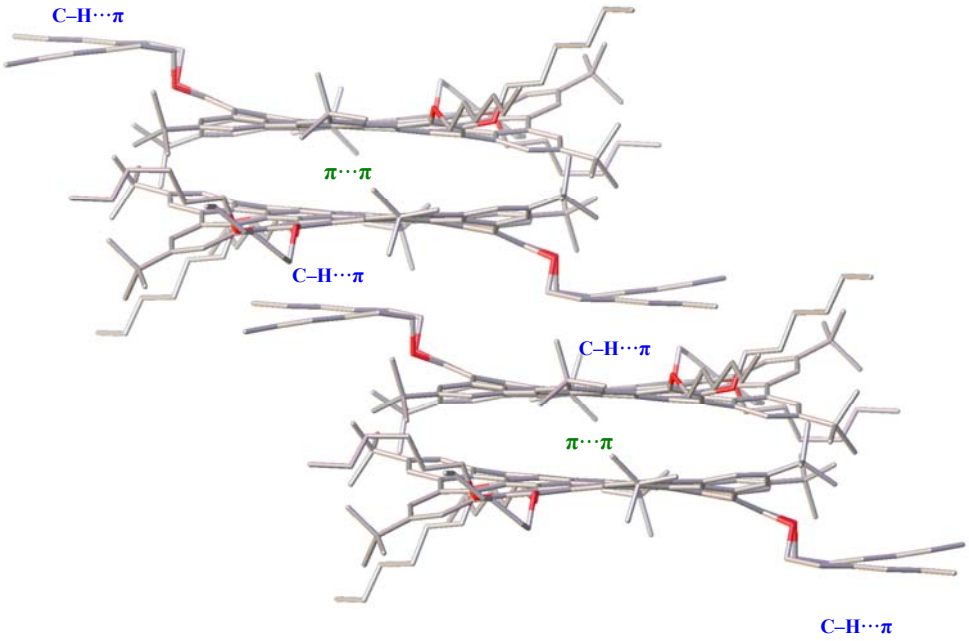



**Figure S10** The π-π dimer and the C–H···π dimer of HBCC **5c**

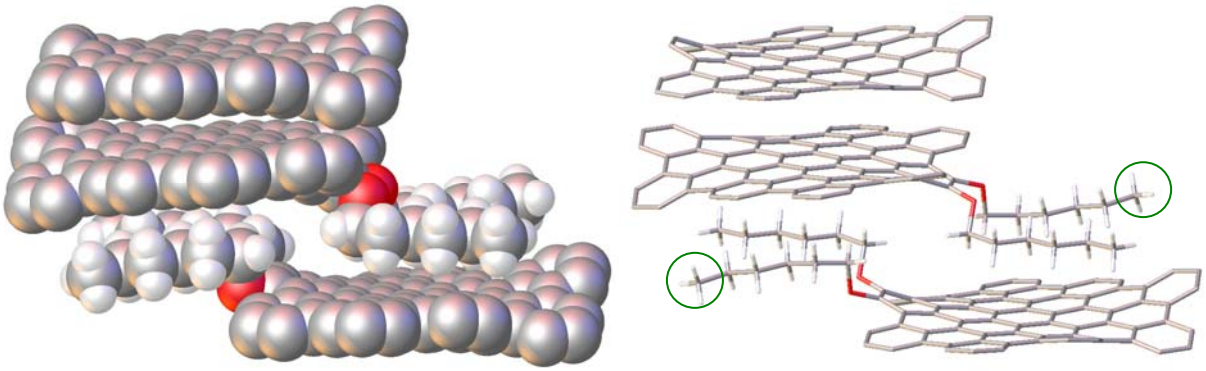


**Figure S11** The shape complementary π-π dimer and the C–H···π dimer of HBCC **5c** (left: filling mode; right: tube mode) (Hydrogens and other substituents on the aromatic cores are omitted for clarity)

# 5 Photophysical properties and thermal stability

## 5.1 UV-Vis spectra of the representative *c*-HBCs and TBTTCs

**Table 25** UV-Vis spectra of some ***c***-HBCs and TBTCCs (in $CH_2Cl_2$, $4.0 \times 10^{-6}$ mol·L$^{-1}$)

| Product | $R^1/R^2$ | $R^3/R^4$ or R | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$cm$^{-1}$ | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$cm$^{-1}$ |
|---|---|---|---|---|---|---|
| **HBC 3a** | $OCH_3/OCH_3$ | $OCH_3/OCH_3$ | 277 | 135000 | 389 | 231000 |
| **HBC 3b** | $OCH_3/OCH_3$ | $CH_3/CH_3$ | 276 | 95000 | 386 | 152000 |
| **HBC 3e** | $OCH_3/OCH_3$ | $CH_3$/H | 275 | 95000 | 386 | 159000 |
| **HBC 3h** | $OCH_3/OCH_3$ | Cl/H | 277 | 62000 | 390 | 103000 |
| **HBC 3i** | $OCH_3/OCH_3$ | Br/H | 279 | 48000 | 391 | 81000 |
| **HBC 3k** | $OCH_3/OCH_3$ | H/H | 275 | 111000 | 385 | 186000 |
| **HBC 3l** | $OCH_3/OCH_3$ | $OC_4H_9/OC_4H_9$ | 278 | 129000 | 390 | 207000 |
| **HBC 3m** | $OCH_3/OCH_3$ | $OC_8H_{17}/OC_8H_{17}$ | 278 | 107000 | 391 | 195000 |
| **HBC 3n** | $OCH_3/OCH_3$ | $OC_{12}H_{25}/OC_{12}H_{25}$ | 279 | 757000 | 391 | 149000 |
| **HBC 3o** | $OC_4H_9/OC_4H_9$ | $OC_4H_9/OC_4H_9$ | 279 | 124000 | 392 | 215000 |
| **HBC 3p** | $OC_4H_9/OC_4H_9$ | $CH_3/CH_3$ | 278 | 145000 | 388 | 242000 |
| **HBC 3r** | $OC_4H_9/OC_4H_9$ | Br/H | 279 | 67000 | 394 | 81000 |
| **HBC 3t** | $OC_6H_{13}/OC_6H_{13}$ | $OC_6H_{13}/OC_6H_{13}$ | 279 | 106000 | 392 | 183000 |
| **HBC 3v** | $OC_{12}H_{25}/OC_{12}H_{25}$ | $OC_{12}H_{25}/OC_{12}H_{25}$ | 280 | 63000 | 391 | 125000 |
| **HBC 3w** | $OC_4H_9/OCH_3$ | $OC_4H_9/OCH_3$ | 278 | 119000 | 391 | 183000 |
| **TBTTC 4b** | $OC_4H_9/OC_4H_9$ | H | 271 | 75000 | 382 | 113000 |
| **TBTTC 4c** | $OC_6H_{13}/OC_6H_{13}$ | H | 271 | 88000 | 383 | 112000 |

**Table S26** UV-Vis spectra of the HBCCs (in $CH_2Cl_2$, $2.0 \times 10^{-6}$ mol·L$^{-1}$)

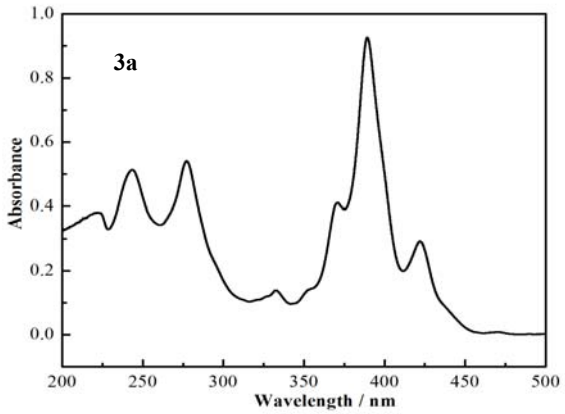
| Product | $R^1/R^2$ | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$cm$^{-1}$ | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$cm$^{-1}$ | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$cm$^{-1}$ | $\lambda_{max}$/nm | $\varepsilon$/M$^{-1}$cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **HBCC 5a** | $OCH_3/OCH_3$ | 249 | 265000 | 303 | 130000 | 450 | 174000 | 486 | 189000 |
| **HBCC 5b** | $OC_4H_9/OC_4H_9$ | 250 | 151000 | 303 | 106000 | 450 | 340000 | 486 | 192000 |

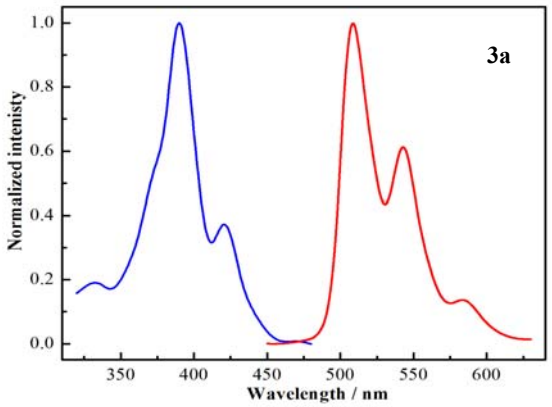
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **HBCC 5c** | $OC_6H_{13}/OC_6H_{13}$ | 249 | 216000 | 303 | 115000 | 450 | 321000 | 487 | 177000 |

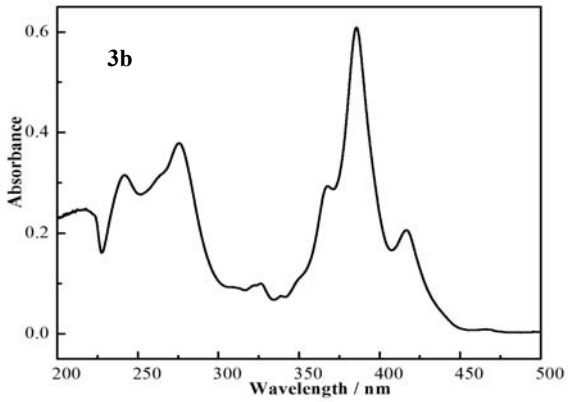
## 5.2 The emission and excitation spectra of the products

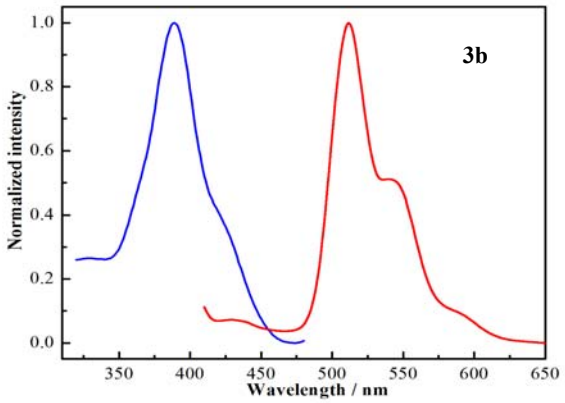
**Table S27** The emission and excitation spectra of the products **3a-h** ($CH_2Cl_2$, $4 \times 10^{-7}$ mol·L$^{-1}$)

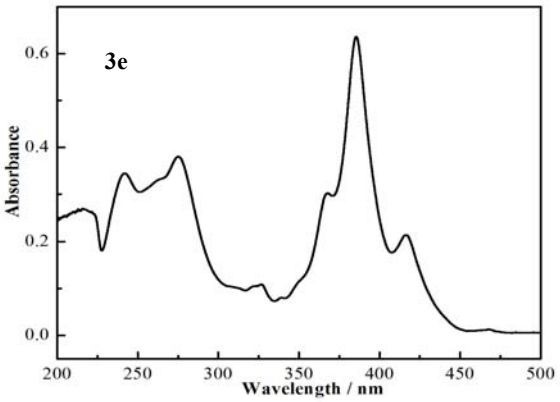
| Product | $\lambda_{ex}$/ nm | $\lambda_{em}$/ nm | Stocks shift | Product | $\lambda_{ex}$/ nm | $\lambda_{em}$/ nm | Stocks shift |
|---|---|---|---|---|---|---|---|
| **3a** | 390 | 508 | 108 | **3o** | 388 | 506 | 118 |
| **3b** | 387 | 507 | 120 | **3r** | 392 | 511 | 119 |
| **3e** | 385 | 504 | 119 | **3t** | 394 | 510 | 106 |
| **3h** | 388 | 508 | 120 | **3v** | 393 | 511 | 108 |
| **3i** | 391 | 510 | 119 | **3w** | 390 | 507 | 117 |
| **3k** | 384 | 503 | 119 | **4b** | 377 | 492 | 115 |
| **3l** | 391 | 510 | 119 | **4c** | 378 | 492 | 114 |
| **3m** | 391 | 510 | 109 | **5a** | 451 | 585 | 154 |
| **3n** | 392 | 510 | 108 | **5b** | 451 | 584 | 153 |
| **3o** | 393 | 510 | 117 | **5c** | 451 | 583 | 152 |

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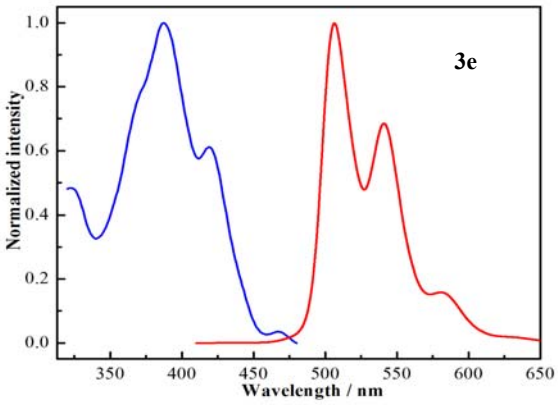
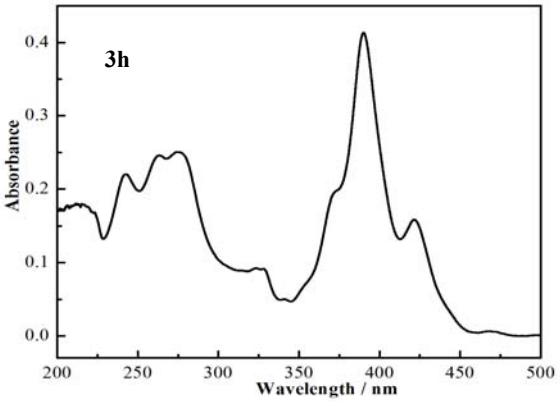
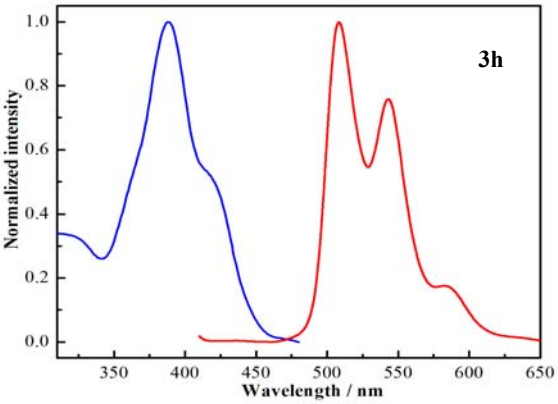
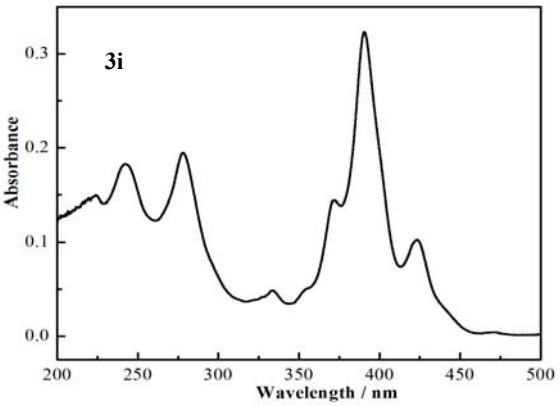
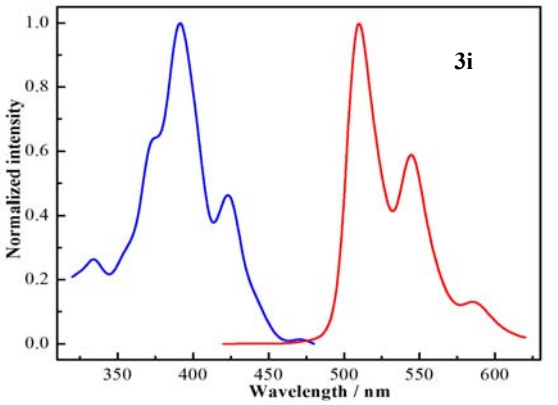
Absorbance
Wavelength / nm

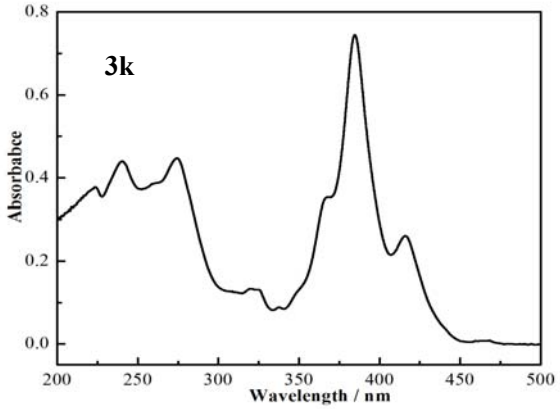

3e
Normalized intensity
Wavelength / nm

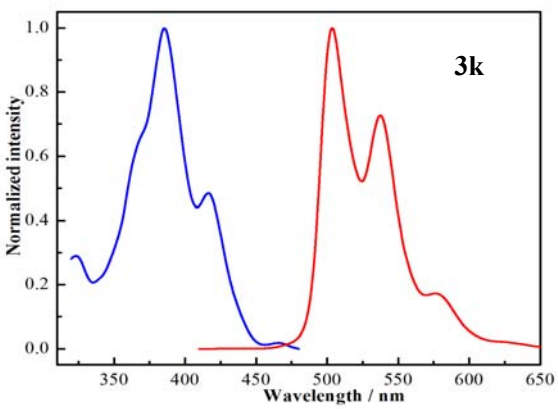

3h
Absorbance
Wavelength / nm

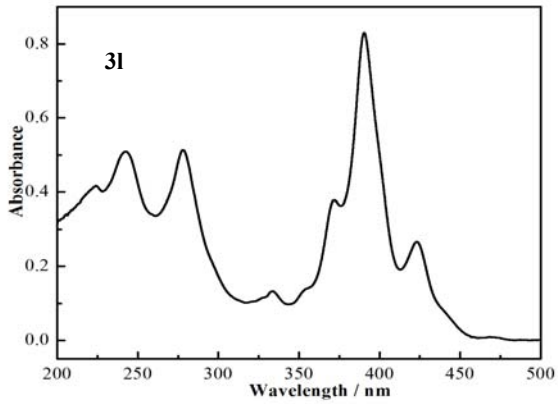

3h
Normalized intensity
Wavelength / nm

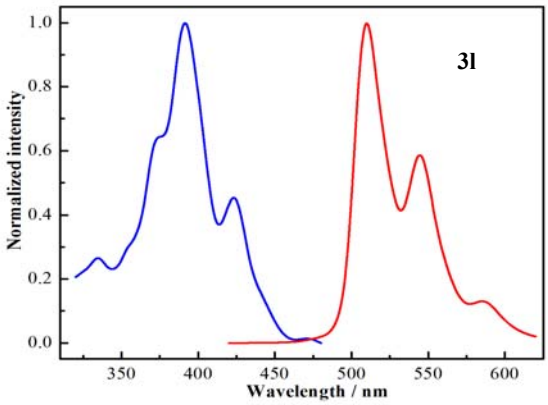

3i
Absorbance
Wavelength / nm

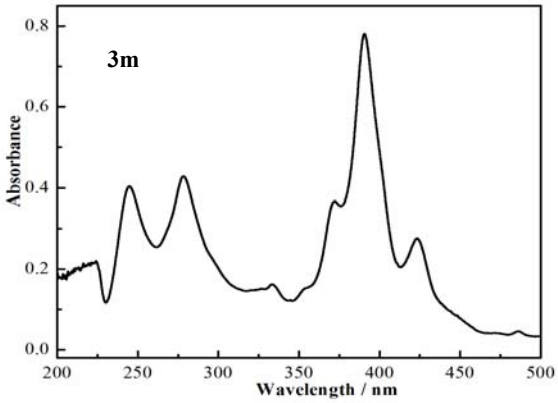

3i
Normalized intensity
Wavelength / nm

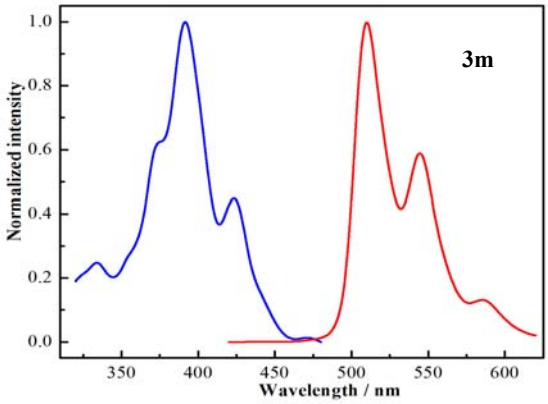

3k
Absorbabce
Wavelength / nm

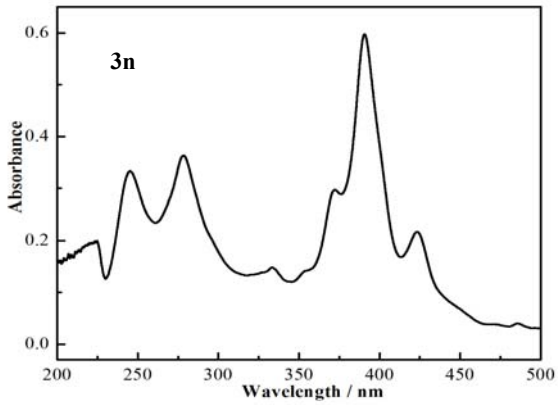

3k
Normalized intensity
Wavelength / nm

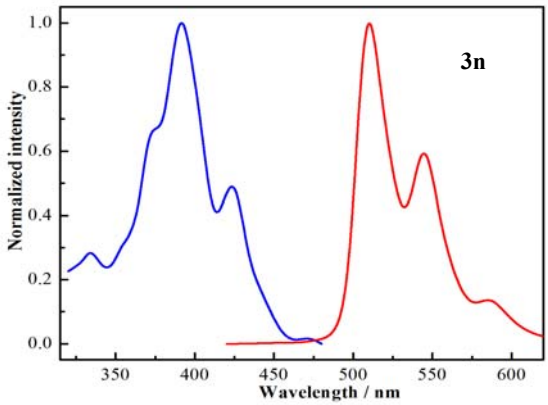

3l
Absorbance
Wavelength / nm

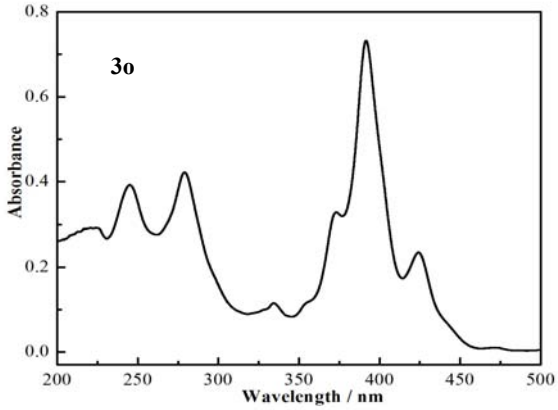

3l
Normalized intensity
Wavelength / nm

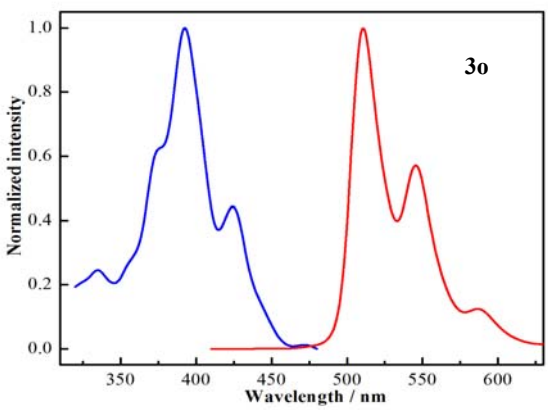

3m
Absorbance
Wavelength / nm

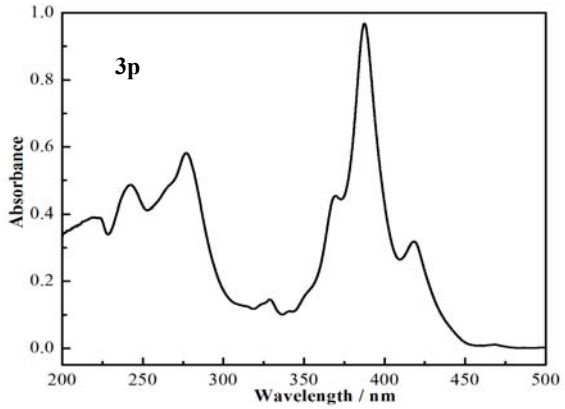

3m
Normalized intensity
Wavelength / nm

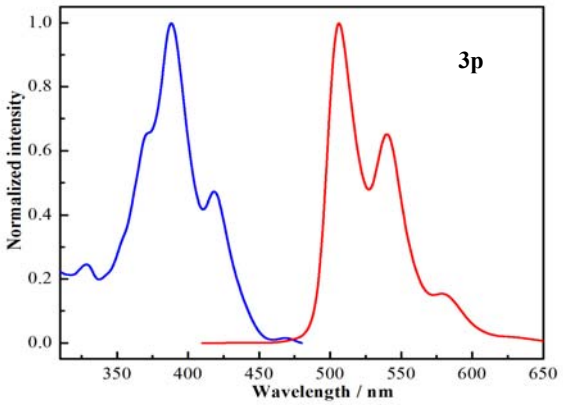

3n
Absorbance
Wavelength / nm

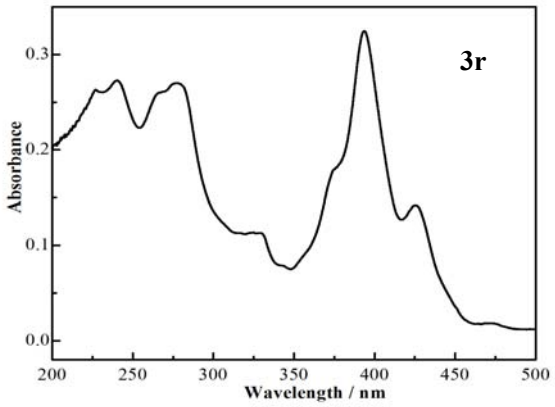

3n
Normalized intensity
Wavelength / nm

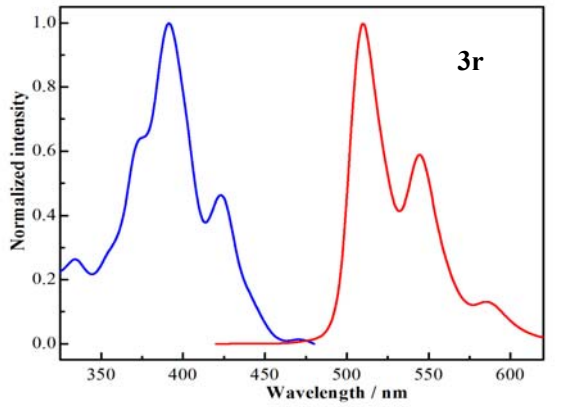

3o
Absorbance
Wavelength / nm

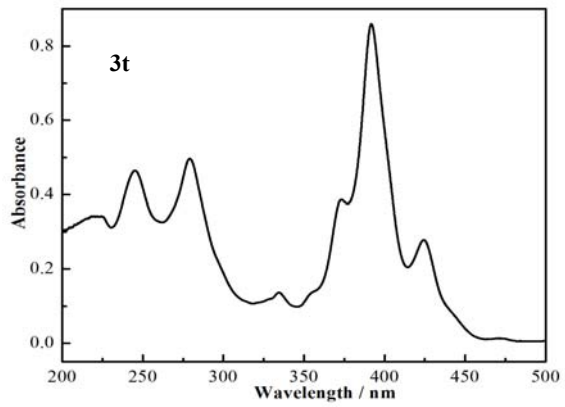

3o
Normalized intensity
Wavelength / nm

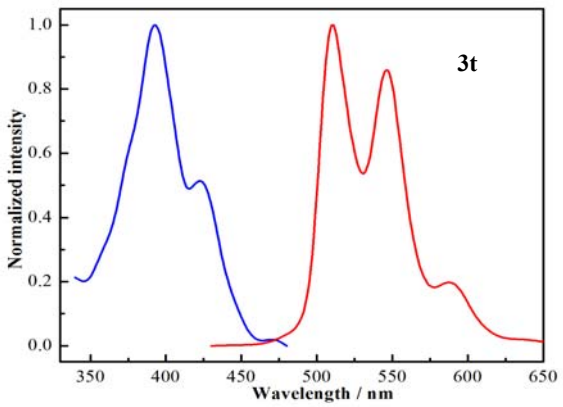

3p
Absorbance
Wavelength / nm

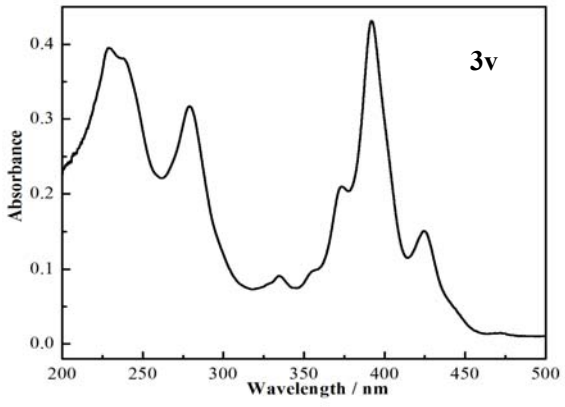

3p
Normalized intensity
Wavelength / nm

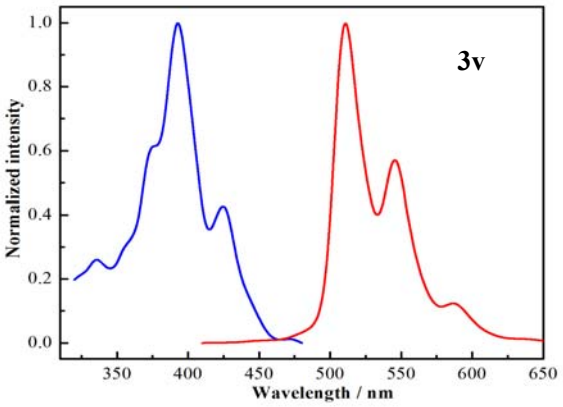

3r
Absorbance
Wavelength / nm

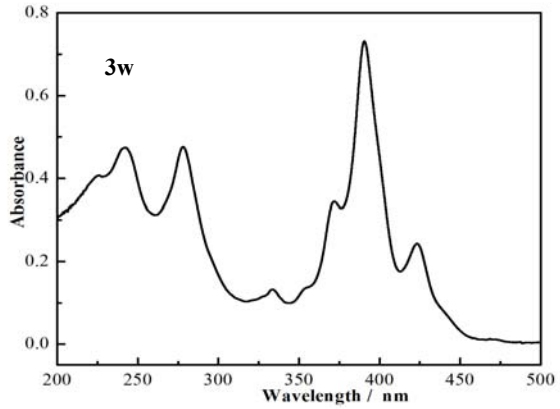

3r
Normalized intensity
Wavelength / nm

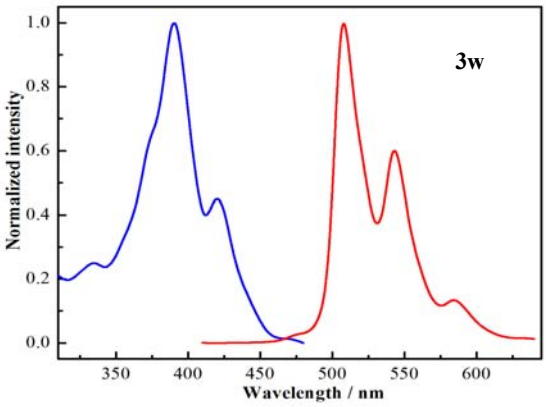

3t
Absorbance
Wavelength / nm

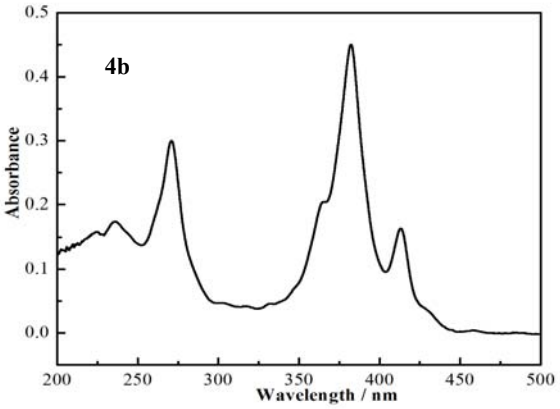

3t
Normalized intensity
Wavelength / nm

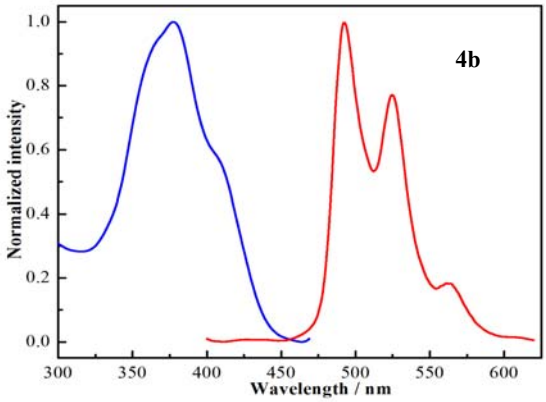

3v
Absorbance
Wavelength / nm

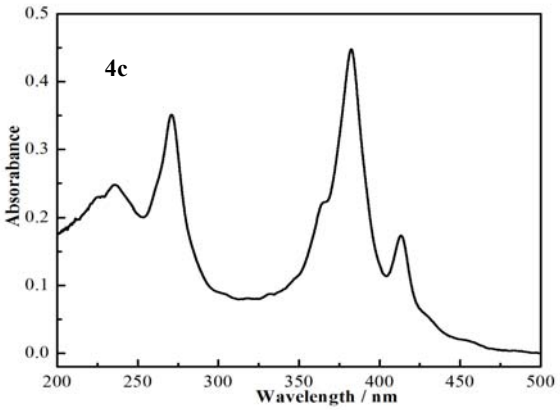

3v
Normalized intensity
Wavelength / nm

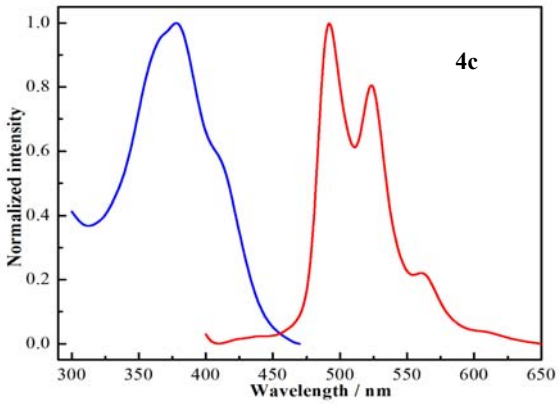

3w
Absorbance
Wavelength / nm

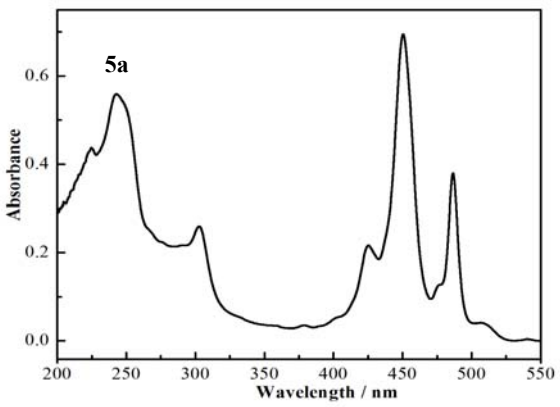

3w
Normalized intensity
Wavelength / nm

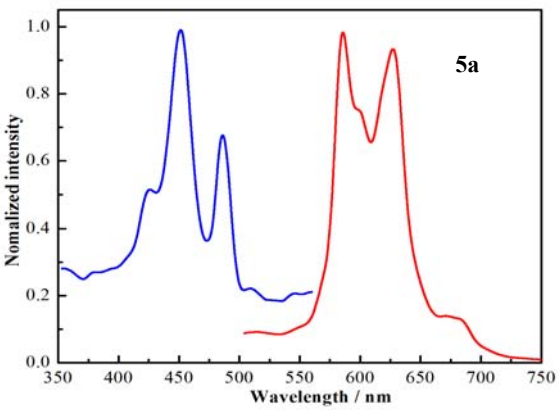

4b
Absorbance
Wavelength / nm


4b
Normalized intensity
Wavelength / nm


4c
Absorabance
Wavelength / nm


4c
Normalized intensity
Wavelength / nm


5a
Absorbance
Wavelength / nm


5a
Nomalized intensity
Wavelength / nm

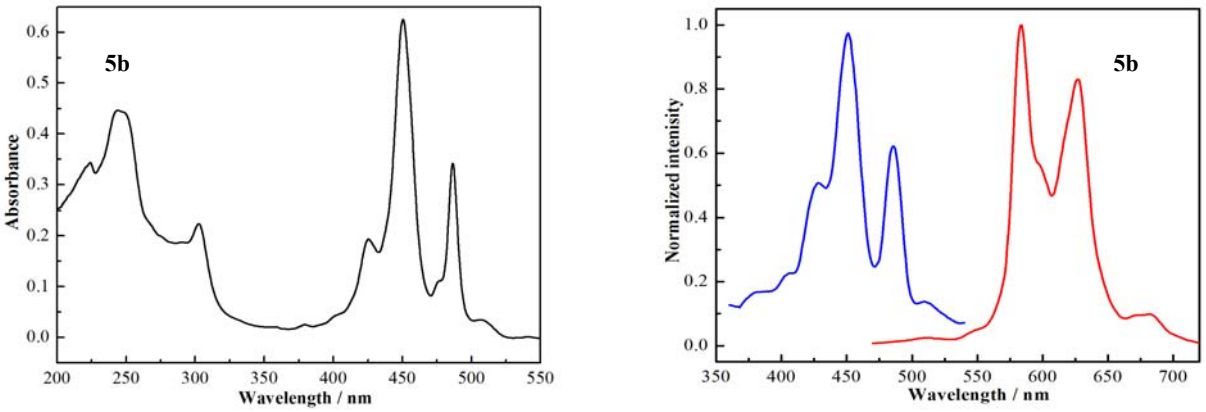



**Figure S12** The cross UV-visible spectra (left: black) of and the fluorescence spectrum (right: $E_x$ blue, $E_m$ red) of the selected HBCs, TBTTCs, and HBCCs

## 5.3 The fluorescence quantum yield of 5c

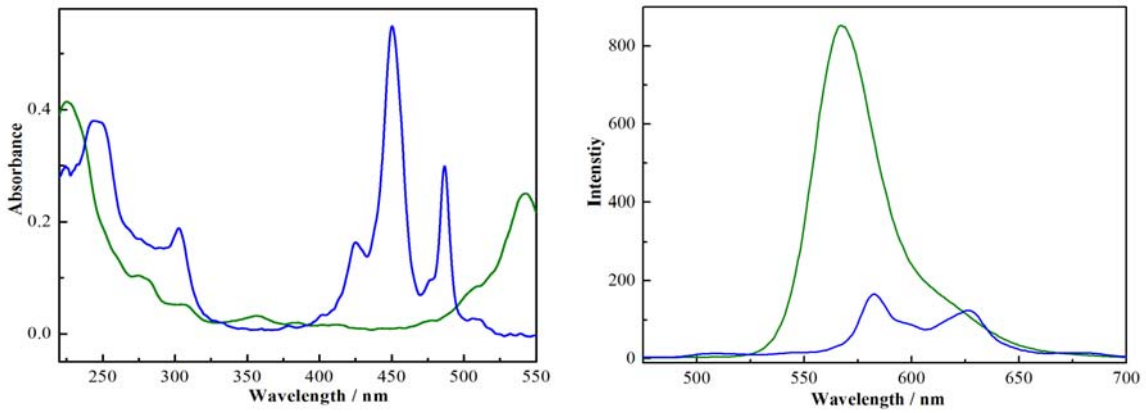
The fluorescence quantum yield [19-21] of **5c** was calculated according to the following equation

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

Where $\Phi$ is the fluorescence quantum yield, $\Phi_R$ is the fluorescence quantum yield, $A$ is the absorbance of the unknown fluorescent substance, $A_R$ is the absorbance of the standard fluorescent substance, $I_R$ refers to corrected emission intensity of the standard fluorescent substance. $I$ refers to corrected emission intensity of the unknown fluorescent substance. $\eta$ is the refractive index of the solvent of unknown fluorescent substance, $\eta_R$ is the refractive index of the solvent of the standard fluorescent substance, R refers to the reference standard of known quantum yield**.** Rhodamine B in 2 μM ethanol absolute (literature quantum yield 0.89) was chose as a standard. **5c** 1.8 μM DCM (The fluorescence emission spectrum was employed the same absorbance wavelength method, which is exciting at (391.2 nm), excitation slide 10 nm, emission slide 10 nm, PMT voltage medium, scanning speed: slow , room temperature.

**Table S28** The fluorescence quantum yield of **5c**

| Entry | Integrated wavelength range (nm) | $A$ | $\eta$ or $\eta_R$ | $\Phi$ |
|---|---|---|---|---|
| Rhodamine B | 475～700 | 39056 | 1.362（EtOH） | 0.89 (the standard) |
| **5c** | 475～700 | 10097 | 1.424（DCM） | 0.24 |



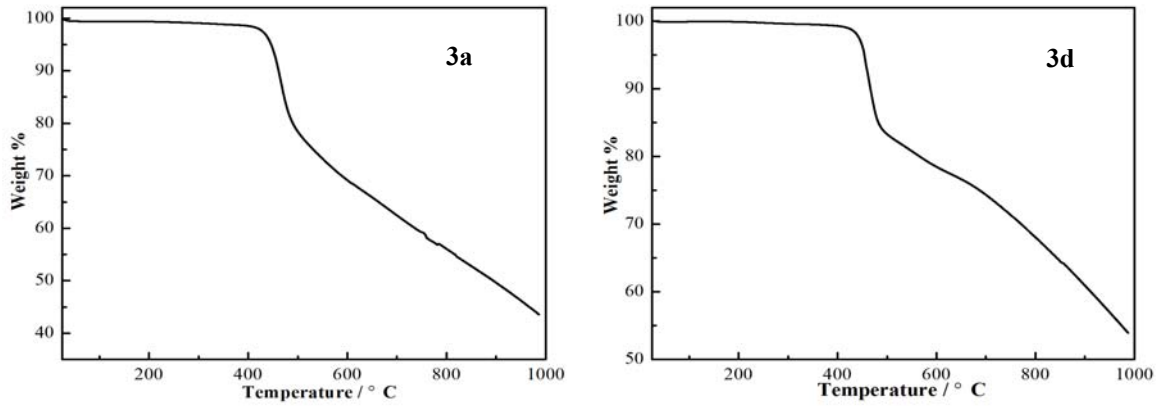

**A:** The cross UV-visible spectra of Rhodamine (green) and **5c** (blue), **B:** The emission spectrum of Rhodamine B (green) and **5c** (blue)

**Figure S13** The cross UV-visible spectra (A) of and the emission spectrum (B) of Rhodamine (green) and **5c** (blue)

## 5.4 Thermal stability of representive compounds

**Table S29** The thermal decomposition temperature ($T_d$) of representive compounds.

| Product | **3a** | **3d** | **3h** | **3j** | **3k** | **3t** | **4b** | **5c** |
|---|---|---|---|---|---|---|---|---|
| $T_d$ (℃) | 466 | 456 | 424 | 451 | 353 | 434 | 436 | 464 |



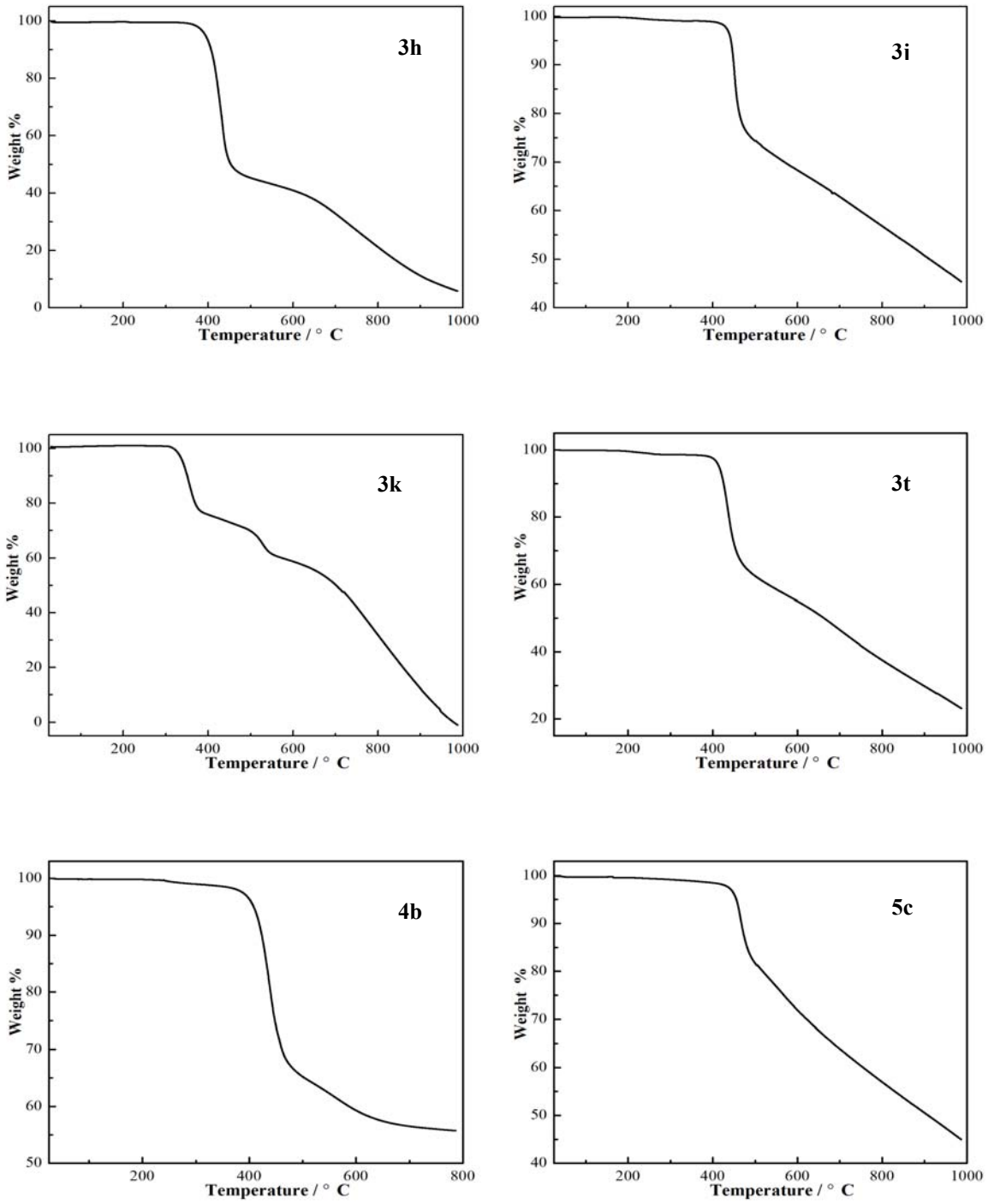



**Figure S14** The TG profile of representive compounds

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