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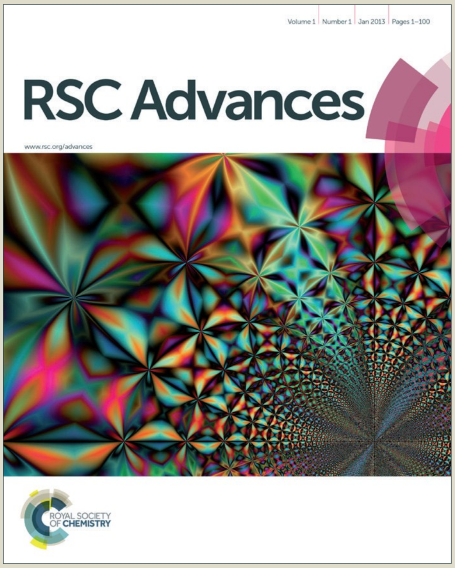

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Synthesis and characterization of pyrimidine-containing hexaarylbenzene derivatives

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Three pyrimidine-containing claw-shaped unusual hexaarylbenzene derivatives have been successfully synthesized by cobalt-catalyzed cyclotrimerization of corresponding 3,3’-diaryldiphenylacetylenes. Cyclotrimerization of symmetric tolan derivative **6** gave symmetric product **1**, while unsymmetric tolan derivative **15** afforded two geometric isomers, C_3-symmetric **2** and unsymmetric analogue **3**, which have been successfully separated by preparative thin-layer chromatography in 1:2 ratios. The coordination of **1** with Ag^+, Cu^{2+} and Zn^{2+} was studied by UV-vis, fluorescence spectra and TEM.

Introduction

Hexaarylbenzene derivatives (HABs) have attracted considerable attention due to their potential application in broad fields such as graphitic materials,[1] self-assembly,[2] energy storage,[3] aromatic hydrocarbons,[4] energy transfer,[5] charge delocalization,[6] and organic zeolites.[7] So far, a variety of HABs with different functional groups have been synthesized,[8] and their electrochemical and optical properties have been intensively characterized.[9] Most of reported HABs were focused on introducing the functional groups into *para*-position of peripheral phenyls to form star-shaped geometry, however, the molecules substituted in *meta*-position of peripheral phenyls were still limited despite the fact that these unusual HABs might show different optical, electronic, self-aggregation and coordination properties.

On the other hand, introduction of azaheteroaryl groups such as pyridyl, pyrimidinyl and imidazolyl *etc*. into HABs skeleton opened the possibility to coordinate with various metal ions, which hardly realized by full phenyl groups substituted HABs. As a heteroaryl moiety, pyrimidinyl modified HABs was least exploited although pyrimidine has high electron affinity and good coplanarity acting as an appropriate building block in construction of semiconductors,[10] liquid crystalline materials,[11] electroluminescent diodes,[12] and fluorescent molecules.[13] Moreover, pyrimidine can participate in hydrogen bonding formation and also can coordinate with various metal ions.[14] Draper and co-workers have reported the synthesis of *N*-heterosuperbenzene by cyclodehydrogenation of pyrimidinyl-contained hexaarylbenzene,[15] and its transition metal complexes have shown interesting optical, electrochemical and structural properties.[16] However, up to now, the synthesis and characterization of pyrimidine-contained hexaarylbenzenes has rarely been reported. In this work, we designed and synthesized three kinds of claw-shaped unusual hexaarylbenzenes, where the pyrimidyl groups *meta*-substituted at peripheral phenyls, and investigated their coordinating ability with metal ions (Chart 1).

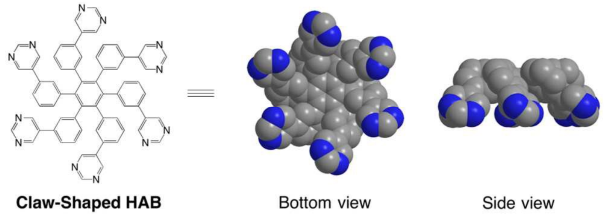
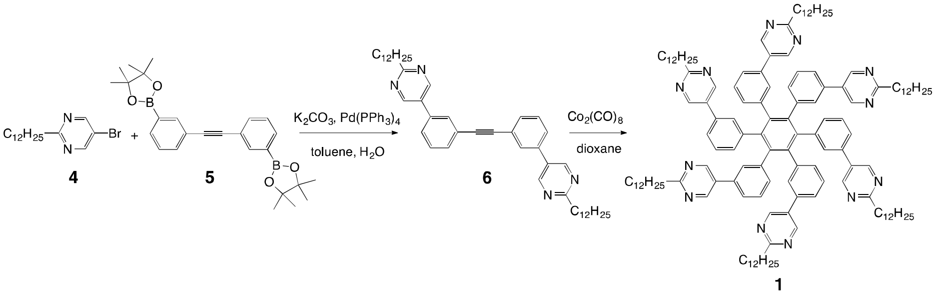


Chart 1. Molecular structure and space-filling modes of claw-shaped *meta*-substituted hexaarylbenzene.

Results and discussion

The symmetric 3,3'-disubstituted tolan derivative **6** was obtained in 75% yield by Suzuki coupling reaction (Scheme 1). Highly symmetric hexaarylbenzene **1** with six pyrimidine groups was synthesized by cobalt-catalyzed cyclotrimerization of the corresponding tolan precursor **6** in 90% yield (Scheme 1). Although other metal-complexes have also been known to catalyze this type of reaction, the cobalt complex is the most effective.[17]



Scheme 1. Synthesis of HAB derivative **1**.

As shown in Fig. 1a, the ^{1}H NMR spectrum of **1** exhibited two types of aromatic signals at downfield. Signals around at δ = 8.40-8.29 ppm integrating for 12 hydrogen atoms were assignable to the hydrogen atoms of the pyrimidine rings. Another one from 7.25 to 6.93 ppm was characterized to the aromatic protons of the phenyls. The multiplet rather than singlet of proton signals of pyrimidyl in compound **1** at room temperature revealed that six pyrimidyl rings were not magnetic equivalence. In general, six phenyl groups of HABs were arranged around a central benzene ring in a propeller-like fashion, and the dihedral angle between the phenyl substituent and the central benzene ring was approximate 60^o which reduced direct orbital overlap (*ortho-ortho* interactions) and conjugational effects.[18] In the present work, the pyrimidine pendants located at *meta*-position of peripheral phenyl rings, the terminal pyrimidine rings and peripheral phenyl rings were nonplanar due to the *ortho-ortho* interactions, which might cause the molecule adopting claw-shaped configuration rather than two-dimentional star-shaped geometry (Chart 1). Molecules with this configuration further self-aggregated by strongly π-π interactions between deficient electron pyrimidyl and phenyl ring of the neighboring molecule to form oligomers**,** which resulted in multiplet signals in ^{1}H NMR spectra. When temperature was increased to 50 °C, the proton signals of pyrimidyl tended to decreased to two peaks and shifted to downfield (Fig. 1b), which implied the dissociation of oligomers accelerated at higher temperature. Moreover, the molecular structure of **1** was also characterized by MALDI-TOF mass spectrometry, the desired molecular ion-peak and isotopic distributions was observed (Fig. 2).

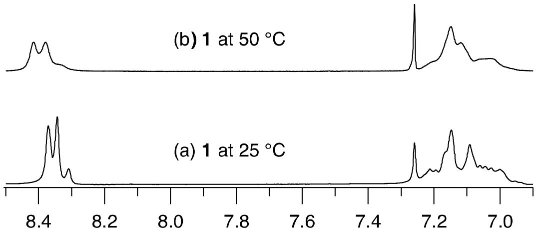


Fig. 1. Partial ^{1}H NMR spectra of **1** in aromatic region (400 MHz, $CDCl_3$).

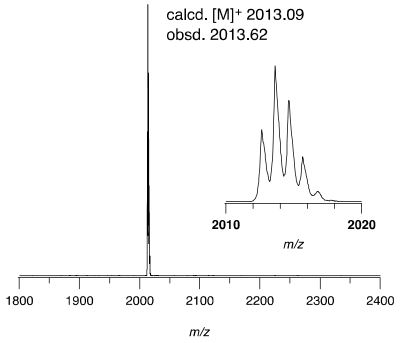


Fig. 2. MALDI-TOF mass spectrum of **1**.

For comparison, compounds **2** and **3** were synthesized over seven steps (Scheme 2). Firstly, compound **8** was synthesized from **7** according to a literature procedure,[19] then **8** was converted to **9** by Suzuki coupling reaction. The TMS group of **9** was easily replaced by iodine using ICl as an iodination reagent. Next, compound **12**, which obtained by reaction of **11** with 3-bromoiodobenzene, reacted with trimethylsilylacetylene (TMSA) yielded **13**. Deprotection of **13** with tetrabutylammonium fluoride (TBAF) gave **14** in quantitative yields. The resulted terminal acetylene derivative **14** was then coupled with **10** *via* Sonogashira cross coupling to afford **15**. Finally, the C_3-symmetric **2** and unsymmetric analogue **3** were synthesized by cyclotrimerization of unsymmetric tolan derivative **15**.

In principle, cobalt-catalyzed cyclotrimerization of tolan derivatives following the metallacyclopentadiene intermediates mechanism,[18,20] the alkynyl π-complex (a) was firstly formed from two equivalents of alkyne with cobalt, and then two metallacycles (b) and four alkynyl π-complexes (c) were produced as intermediates, and then seven membered metallacycloheptatrienes (d) were formed, the resulting isomers were produced by reductive elimination reaction (Fig. 3). Therefore, two geometric isomers **2** and **3** were formed by cyclotrimerization of unsymmetric **15** (Scheme 2). The separation of isomers was very difficult by column chromatography. However, after many trials, we successfully separated the isomers by preparative thin layer chromatography with mixture of ethyl acetate/ dichloromethane/ petroleum ether (1:10:10) as eluent in 27% of **2** and 56% of **3** in yield, respectively (Fig. S20, $R_{f,\mathbf{2}} = 0.90$ and $R_{f,\mathbf{3}} = 0.65$; see supporting information. The polarity of C_3-symmetric **2** was smaller than that of unsymmetric analogue **3**). The ratio of **2** to **3** was not in agreement with that of statistical results because the steric and electronic factors might play important role in deciding the regiochemical outcome of the reaction.[21] By means of MALDI-TOF mass spectrometry measurement, molecular ion-peaks appeared at 2007.92 and 2007.83 for **2** and **3** respectively (Fig. S17 and Fig. S19, see supporting information), which were identical to their theoretical molecular weight.

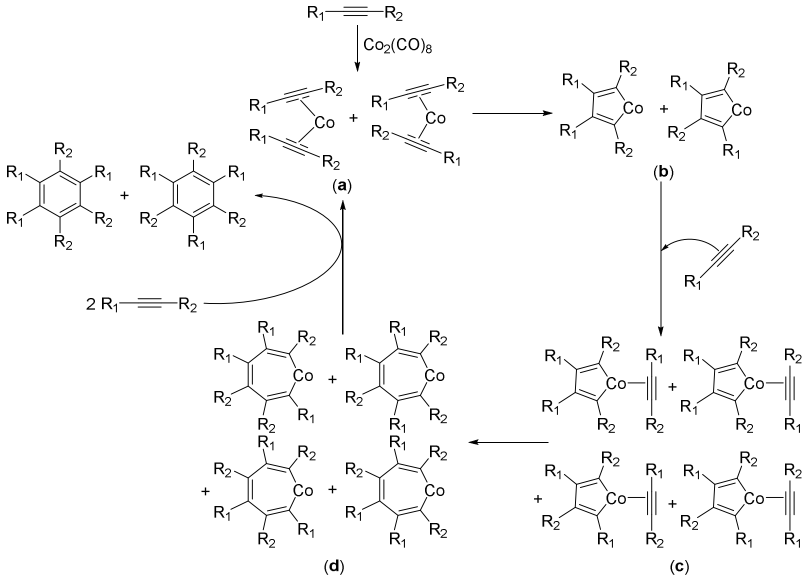
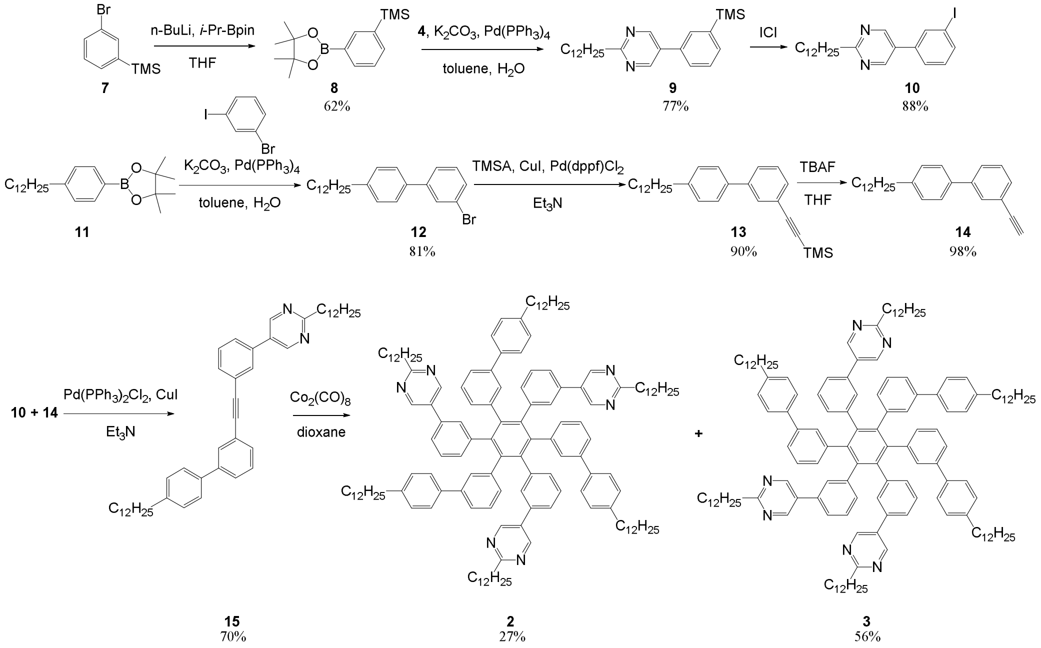


Fig. 3. Catalytic cycle for the cyclotrimerization of unsymmetric alkyne.



Scheme 2. The synthetic route to HAB derivatives **2** and **3**.

The pyrimidine-containing hexaarylbenzene derivatives **2** and **3** did not exhibit the aggregation phenomena although their structures were similar to **1**. In the ^{1}H NMR spectrum of **1**, two types of aromatic signals for C_3-symmetric **2** or unsymmetric analogue **3** at downfield was observed (Fig. 4). Multiplet signals around δ = 7.19-6.87 ppm for both **2** and **3** were assigned to protons of phenyls, however, different peak patterns were clarified that peak split for unsymmetric **3** was more complicate, which proved that two isomers were completely separated. Interestingly, proton signal of the pyrimidine in **2** or **3** appeared only as singlet at δ = 8.39 ppm in ^{1}H NMR spectra at room temperature (Fig. 4), which was quite different from that of **1**. As mentioned above, the self-aggregated **1** possessing six deficient electron pyrimidyl rings exhibited the multiplet signals in ^{1}H NMR spectrum (Fig. 1). Nevertheless, only three pyrimidyl rings for both **2** and **3** were insufficient to induce the self-aggregation between molecules. Therefore, they existed as monomer rather than oligomer in solution, if any, that dynamically, which caused singlet signal of pyrimidyl rings of C_3-symmetric **2**. As to unsymmetric **3**, singlet signal might be owed to that chemical shift values of three pyrimidyl were very closed and overlapped together. In fact, no change of their peak patterns and chemical shifts were observed in ^{1}H NMR spectra even at high temperature. These results indicated that the number of pyrimidyl groups in HABs play an important role for self-aggregation.

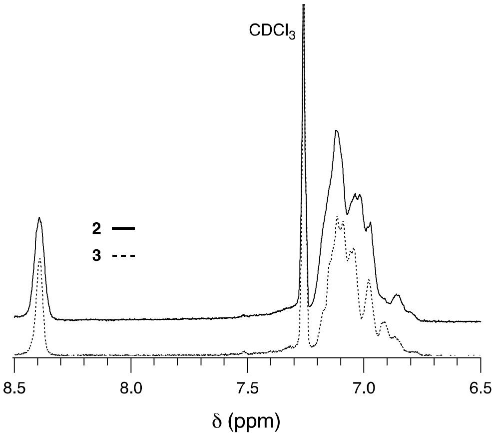


Fig. 4. Partial ^{1}H NMR spectra of **2** and **3** in aromatic region (400 MHz, CDCl$_3$).

Pyridine or pyrimidine-containing compounds were widely used as ligands in coordination chemistry for generating supramolecular objects with various morphologies, such as rotor, sandwich, nanoball and MOFs.[22] Newly synthesized claw-shaped hexaarylbenzenes with pyrimidine units, which were expected to coordinate with metal ions under an appropriate condition to form amusing nanostructure. Therefore, the coordination with metal ions was investigated using **1** as a platform. Fig. 5 shows the absorption and fluorescence spectral changes of **1** as a function of Ag^+, Cu^{2+} and Zn^{2+} in CH_2Cl_2 solution at room temperature. The UV-vis spectrum of **1** showed the maximum band at 255 nm, which was attributed to overlapping π-π* excitations.[23] Upon addition of $AgCF_3SO_3$ into the solution of **1**, the absorption band at 255 nm decreased remarkably, and concomitantly a new band at 237 nm appeared (Fig. 5a). Complexation also took place immediately when Cu^{2+} or Zn^{2+} was added into the system. As shown in Fig. 5a, the 255 nm absorption band decreased following the formation of new band centered at 242 nm. However, the interesting issue is the entirely different fluorescence spectra changes after addition of Ag^+, Cu^{2+} and Zn^{2+} (Fig. 5b). Free **1** exhibited a structureless fluorescence emission at 382 nm (λ_{ex} = 255 nm), upon addition of Ag^+, the λ_{max}em undergone a blue shift to

337 nm. Although no significant difference in absorption spectroscopy after addition of Cu^{2+} and Zn^{2+}, obvious changes were observed in fluorescence spectroscopy. When Cu^{2+} was added to the solution of **1**, the emission intensity quenched, while the emission intensity greatly increased along with red-shift by 110 nm when Zn^{2+} was introduced (Fig. 5b). Further mechanism research, particularly to prove the origin of the changes, are in progress.

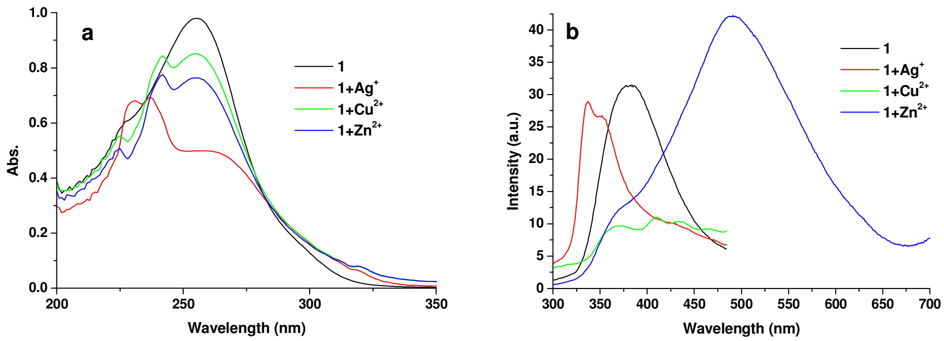


Fig. 5. UV-vis and fluorescence spectra (excitation at 255 nm) of **1**, **1** + Ag^{+}, **1** + Cu^{2+} and **1** + Zn^{2+} in dichloromethane (1 × 10^{-5} mol/L) at room temperature.

To enable direct visualization of the solid state morphologies resulting from molecular interactions between metal ions and **1**, transmission electronic microscopy (TEM) was employed. As indicated by Fig. 6a, molecules of metal-free **1** self-aggregated into sphere nanostructures with different sizes. Highly monodispersed silver nanoparticles were coated on the sphere nanostructures of **1** when Ag^{+} was added (Fig. 6b), the nanospheres with silver nanoparticles had more uniform sizes than that of metal-free **1**, this results implied that the self-aggregated oligomers of **1** were dissociated due to the coordination between **1** and Ag^{+}. In contrast, upon addition of Cu^{2+}, nanospheres changed into nanofibers (Fig. 6c). With the introduction of Zn^{2+}, nanostructures with belt-like morphology were formed (Fig. 6d). The different morphologies obtained for the self-aggregation of the molecule **1** with metal ions reflected the differences of coordination modes. Though the reasons for this unusual morphology changes were not perfectly understood, it could be assumed that the metal ions played an important role. These self-aggregations are currently being further investigated to explain the role of the metal ions in the self-aggregations process and to elucidate the exact mode of self-aggregation.

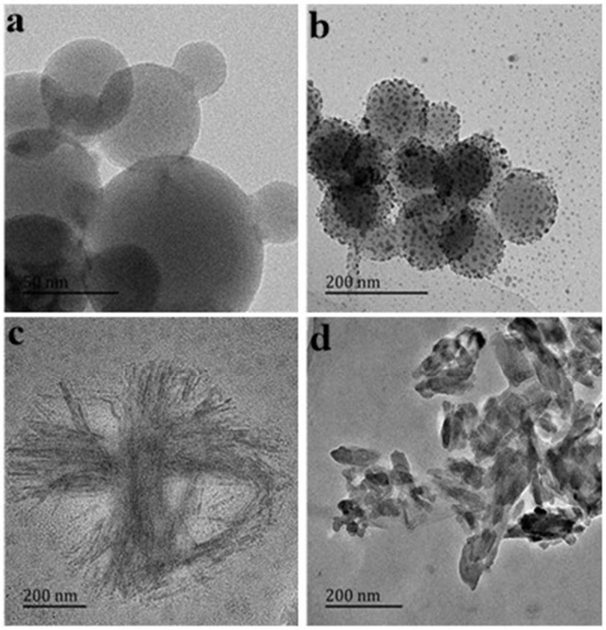


Fig. 6. TEM images of (a) **1**, (b) **1** + Ag^+, (c) **1** + Cu^{2+} and (d) **1** + Zn^{2+}.

Conclusions

In conclusion, we designed and synthesized three pyrimidine-containing claw-shaped unusual hexaarylbenzene derivatives (HABs) by cobalt-catalyzed cyclotrimerization of corresponding tolan derivatives. Moreover, the well-defined morphological transformation of **1** was successfully realized by addition of different metal ions. Furthermore, efforts are now in progress to investigate the full scope of the transformation to obtain a detailed mechanism and to apply this method to other coordination systems.

Experimental Section

General Information: Unless otherwise stated, all reactions were carried out under an atmosphere of argon. Commercially available chemicals were used as received. 5-Bromo-2-dodecylpyrimidine (**4**)[24] and 3,3'-diboronatetolane (**5**)[25] were prepared as reported in the literature. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Model Avance DMX 400 (400 MHz) at ambient temperature. Chemical shifts in NMR were reported in ppm (δ), relative to the internal standard of tetramethylsilane (TMS). Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF mass) was recorded on 4800 Module Diagnostics from ABSCIEX. Electronic absorption spectra were recorded on a PERSEE model TU-1901 spectrophotometer using a quartz cell of 1 cm path length. Fluorescence spectra were recorded on a HORIBA model Fluoromax-4 spectrophotometer. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass.

Synthesis of 6

Under an argon atmosphere, to a 100 mL flask were added **4** (689 mg, 2.11 mmol), **5** (230 mg, 0.53 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), 2 M K_2CO_3 aqueous solution (6 mL, 7.95 mmol) and toluene (15 mL), respectively. The mixture was stirred at 90 °C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by column chromatography (SiO_2, EA/CH_2Cl_2 = 1:40) to allow isolation of **6** as a white solid in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.91 (s, 4H), 7.76 (s, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.58-7.49 (m, 4H), 3.03 (t, *J* = 7.6 Hz, 4H), 1.95-1.80 (m, 4H), 1.26-1.24 (m, 36H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm): 170.59, 154.93, 134.88, 131.81, 130.51, 129.94, 129.52, 126.95, 124.18, 89.59, 39.11, 31.92, 30.90, 29.66, 29.64, 29.54, 29.46, 29.42, 29.35, 28.78, 22.68, 14.10. MALDI-TOF mass: calcd. for $C_{46}H_{62}N_4$ $[M]^+$: m/z = 671.01, found: 671.53.

General procedure of cyclotrimerization

A suspension of tolan derivatives (1 eq.) in dioxane was degassed several times with argon, then $Co_2(CO)_8$ (0.15 eq.) was added. The resulting mixture was refluxed for 12 hours until starting materials disappeared, as detected by TLC. While cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 (3× 20 mL). The organic extracts was washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure.

Synthesis of 1

$Co_2(CO)_8$ (15.5 mg, 0.045 mmol) was added to a suspension of **6** (200 mg, 0.30 mmol) in dioxane (30 mL). The resulting mixture was refluxed for 12 hours and treated as described in the general procedure. Purification by column chromatography on silica gel with acetone-CH_2Cl_2 (1:5) gave 180 mg (90%) **1** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34 (t, *J* = 12.3 Hz, 12H), 7.25-6.93 (m, 24H), 2.92 (t, *J* = 7.7 Hz, 12H), 1.89-1.67 (m, 12H), 1.41-1.20 (m, 108H), 0.86 (t, *J* = 6.7 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.32, 154.71, 154.67, 141.05, 140.32, 133.88, 133.71, 131.73, 130.68, 130.11, 128.42, 124.76, 39.19, 31.91, 30.91, 29.67, 29.65, 29.62, 29.56, 29.53, 29.50, 29.47, 29.45, 29.35, 28.89, 28.81, 22.68, 14.11. MALDI-TOF mass: calcd. for $C_{138}H_{186}N_{12}$ $[M]^+$: m/z = 2013.09, found: 2013.62.

Synthesis of 9

The mixture of **4** (200 mg, 0.578 mmol), **8** (145 mg, 0.53 mmol), $Pd(PPh_3)_4$ (50 mg, 0.0525 mmol), 2 M K_2CO_3 aqueous solution (2.62 mL, 5.3 mmol) and toluene (15 mL) was degassed by three “freeze-pump-thaw” cycles, and the resulting mixture was heated at 90 °C under an argon atmosphere for 12 h. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by column chromatography (SiO_2, CH_2Cl_2/PE = 1:2) to allow isolation of **9** as a white solid in 77% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.86 (s, 2H), 7.66 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 1H), 7.56–7.46 (m, 2H), 3.01 (t, *J* = 7.7 Hz, 2H), 1.90-1.82 (m, 2H), 1.48-1.18 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.22, 155.06, 142.10, 133.97, 133.57, 131.72, 131.57, 128.62, 127.30, 39.21, 31.92, 29.67, 29.64, 29.55, 29.48, 29.44, 29.35, 28.80, 22.68, 14.10. MALDI-TOF mass: calcd. for $C_{25}H_{40}N_2Si$ $[M]^+$: m/z = 396.68, found: 397.23.

Synthesis of 10

A solution of ICl (1.2 mL, 1.0 M in CH_2Cl_2, 1.2 mmol) was added dropwise to a solution of **9** (160 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The solution was stirred overnight at room temperature under darkness, saturated sodium thiosulfate was added until the reaction mixture turned to colorless, the organic layer separated, the aqueous layer extracted with CH_2Cl_2, and the combined organic layer dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (SiO_2, EA/PE = 1/10) to give **10** as a white solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.83 (s, 2H), 7.91 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 3.03 (t, *J* = 7.9 Hz, 2H), 1.91-1.81 (m, 2H), 1.38-1.20 (m, 18 H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.91, 154.90, 137.59, 136.81, 135.75, 130.90, 129.82, 126.10, 95.11, 39.22, 31.92, 29.66, 29.63, 29.54, 29.45, 29.41, 29.35, 28.76, 22.68, 14.10. MALDI-TOF mass: calcd. for $C_{22}H_{31}N_2I$ $[M]^+$: m/z = 450.40, found: 447.28.

Synthesis of 11

The mixture of 1-bromo-4-dodecylbenzene (2.00 g, 6.20 mmol), bis(pinacolato)diboron (3.5 g, 12.4 mmol), $PdCl_2$(dppf) (220 mg, 0.30 mmol), KOAc (1.75 g, 17.9 mmol) and DMF (50 mL) was degassed by three “freeze-pump-thaw” cycles, and the resulting mixture was heated at 90 °C under an argon atmosphere for 12 h. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by column chromatography (SiO_2, PE/CH_2Cl_2 = 10:1) to give **11** as colorless oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.67-1.57 (m, 2H), 1.36 (s, 12H), 1.29-1.25 (m, 18H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 146.42, 134.80, 127.89, 83.59, 36.20, 31.93, 31.35, 29.67, 29.66, 29.59, 29.51, 29.36, 29.32, 25.03, 24.86, 22.69, 14.12. MALDI-TOF mass: calcd. for $C_{24}H_{41}BO_2$ $[M]^+$: m/z = 372.39, found: 374.25.

Synthesis of 12

A mixture of **11** (1 g, 2.69 mmol), 1-bromo-3-iodobenzene (1.14 g, 4.03 mmol.),

$Pd(PPh_3)_4$ (150 mg, 0.14 mmol), 2 M K_2CO_3 aqueous solution (13.5 mL, 27 mmol) and THF (40 mL) was degassed by three "freeze-pump-thaw" cycles, and the resulting mixture was heated at 50 °C under an argon atmosphere for 12 h. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by column chromatography (SiO_2, PE) to give **12** as colorless liquid in 81% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (s, 1H), 7.55-7.44 (m, 4H), 7.32-7.27 (m, 3H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.70-1.62 (m, 2H), 1.36-1.24 (m, 18H), 0.91 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 143.37, 142.85, 137.02, 130.19, 130.04, 129.86, 128.96, 126.94, 125.56, 122.87, 35.64, 31.96, 31.47, 29.71, 29.70, 29.68, 29.63, 29.55, 29.39, 29.37, 22.72, 14.14. MALDI-TOF mass: calcd. for $C_{24}H_{33}Br$ $[M]^+$: m/z = 401.42, found: 400.33.

Synthesis of 15

The mixture of **12** (900 mg, 2.25 mmol), TMSA (460 mg, 4.5 mmol), $Pd(PPh_3)_2Cl_2$ (63 mg, 5% mmol), CuI (21 mg, 5% mmol) and Et_3N (40 mL) was degassed by three "freeze-pump-thaw" cycles, and the resulting mixture was heated at 80 °C under an argon atmosphere for 12 h. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by column chromatography (SiO_2, PE) to give **13** as colorless liquid.

The solution of tetrabutylammonium fluoride (TBAF) (940 mg, 2.25 mmol) in THF (2 mL) was added into a solution of **13** (400 mg) in THF (10 mL). The resulting mixture was stirred under an argon atmosphere for 5 min and poured into saturated ammonium chloride solution. The mixture was extracted twice with ethyl acetate. The combined extracts were washed with water and dried over $MgSO_4$. After the solvent was removed, 312 mg product was obtained, which was used in the next step without further purification.

The mixture of **10** (312 mg, 0.693 mmol), **14** (242 mg, 0.693 mmol),

$Pd(PPh_3)_2Cl_2$ (25 mg, 0.037 mmol), CuI (7 mg, 0.039 mmol) and Et_3N (40 mL) was degassed by three "freeze-pump-thaw" cycles, and the resulting mixture was heated at 70 °C under an argon atmosphere for 12 h. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford the crude product, which was purified by column chromatography (SiO_2, EA/PE = 1/8) to give **15** as champagne solid in 70% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.90 (s, 2H), 7.77 (d, *J* = 14.6 Hz, 2H), 7.63-7.40 (m, 9H), 7.28 (s, 1H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.92-1.85 (m, 2H), 1.70-1.60 (m, 2H), 1.48-1.22 (m, 36H), 0.88 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.64, 154.95, 142.61, 141.48, 137.52, 134.88, 131.72, 130.52, 130.23, 130.11, 129.89, 129.42, 128.91, 128.81, 127.26, 126.92, 126.63, 124.59, 123.23, 90.54, 88.57, 39.21, 35.63, 31.92, 31.46, 29.67, 29.64, 29.60, 29.55, 29.52, 29.47, 29.44, 29.36, 28.79, 22.69, 14.10. MALDI-TOF mass: calcd. for $C_{48}H_{64}N_2$ $[M]^+$: m/z = 669.04, found: 669.62.

Synthesis of 2 and 3

$Co_2(CO)_8$ (15.5 mg, 0.045 mmol) was added to a suspension of **15** (300 mg, 0.30 mmol) in dioxane (30 mL). The resulting mixture was refluxed for 12 hours and treated as described in the general procedure. The mixture could hardly be separated by column chromatography because of their similar polarities. The ratio of EA/DCM/PE = 1:10:10 was adapted to separate the isomers in thin-layer chromatography. Two isomers **2** and **3** could be separated by repeatedly preparative TLC in this solvent system to get the final product **2** in 27% yields as white solid and **3** in 56% yields as a white solid.

Compound **2**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (s, 6H), 7.21-6.82 (m, 36H), 2.98-2.88 (m, 6H), 2.60-2.50 (m, 6H), 1.86-1.72 (m, 6H), 1.62-1.52 (m, 6H), 1.36-1.24 (m, 108H), 0.86 (t, *J* = 6.2 Hz, 18H). MALDI-TOF mass: calcd. for $C_{144}H_{192}N_6$ $[M]^+$: m/z = 2007.11, found: 2007.92.

Compound **3**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39 (s, 6H), 7.19-6.87 (m, 36H), 2.98-2.92 (m, 6H), 2.58-2.50 (m, 6H), 1.85-1.75 (m, 6H), 1.62-1.52 (m, 6H), 1.32-1.18 (m, 108H), 0.86 (t, J = 6.3 Hz, 18H). MALDI-TOF mass: calcd. for $C_{144}H_{192}N_6$ $[M]^+$: m/z = 2007.11, found: 2007.83.

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