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ARTICLE

Synthesis, structure and properties of polysubstituted benzo[g]chrysene by FeCl₃-promoted from diphenylacetylene and phenylacetaldehyde derivatives

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A newly and straightforward method has been developed to synthesize of the polysubstituted Benzo[g]chrysene (BgCh) according to controlling the exact stoichiometry of FeCl₃ from diphenylacetylene and phenylacetaldehyde derivatives under mild condition. The BgCh derivatives also can be functionalized by halogenation with Cl, Br and I on the new built aromatic ring. All compounds have been fully characterized as well as photophysical properties, and some of them demonstrated the extraordinary liquid crystallinity. The compounds 4e, 4h, 5e and 5h exhibited hexagonal columnar mesophases (Col_h). In particular, 5h showed rectangular columnar plastic phase (Col_r) under 35 °C on cooling. The fluorescence spectra of BgCh revealed a strong emission peak at 405 nm and a shoulder peak nearby 424 nm in DCM in the range of blue light.

Introduction

The polycyclic aromatic hydrocarbons (PAHs) have attracted considerable attentions on the synthesis, properties and application for several decades. They are regarded as the foundation and essential building blocks for the preparation of organic semiconductor materials applied extensively for organic photovoltaic (OPV),¹ organic light emitting diodes (OLED),² organic field effect transistors (OFETs),³ liquid crystal display (LCD)⁴ and so on.

The PAHs comprising less than five fused aromatic rings have acquired a great progress in the past, such as naphthalene,⁵ phenanthrene,⁶ anthracene / anthraquinone,⁷ pyrene,⁸ triphenylene,⁹ etc. However, PAH compounds composed of more fused aromatic rings have been paid rare attention owing to the complex manufacture and lower yields. In general, the extended aromatic cores are propitious to enhance the charge carrier mobility in organic material and dramatically improve their photophysical properties.¹⁰

Benzo[g]chrysene (BgCh) regard as a pentacyclic PAHs compound contains one fjord and two bay regions. Its potential application for biological and organic semiconductor materials. After the first successful synthesis of the BgCh reported in

1938,¹¹ a few approaches have been developed for various BgCh compounds from different starting materials including naphthalene, pyrene, chrysene, phenanthrene derivatives and so on. Zweig noted the BgCh could be prepared from 1-(2-biphenyl)-naphthalene with iodine under 254 mμ light for 15 hours in 1969.¹² Harvey also reported the BgCh could be synthesized from pyrene-4,5-dione by addition, reduction, cyclization and dehydration reaction in 1981.¹³ In 1985, the BgCh has been synthesized from the commercially available PAH chrysene by Boyd.¹⁴ The mono- and di-substituted BgCh derivative also have been prepared by Lehr and Laali from chrysene derivatives, respectively.¹⁵ Lehr has synthesized the BgCh from a complex substrate of 3, 4-dihydrotriphenylene-1(2H)-one in 1989.¹⁶ Harvey more recently reported a new method to synthesize 12-hydroxybenzo[g]chrysene from 9-bromophenanthrene over four steps.¹⁷ In 2005, this method also had been used for synthesizing a new PAHs dibenzo[c,p]chrysene from 6-bromochrysene by Sharma.¹⁸ Although the success of synthesis of the BgCh skeleton have been proved, it is more difficult to utilize the small naphthalene core as the beginning moiety to build up the whole five fused aromatic structure of the BgCh via overmuch synthetic steps or special reaction conditions. Although the chrysene or phenanthrene derivatives can be considered as more useful initial substrates, it is difficult to obtain these complex substrates from commercial source. Therefore, it is essential to exploit more efficient methods to synthesize a diverse range of BgCh derivatives with high yield from simple starting materials in a short synthetic route. In the meantime, polysubstituted BgCh derivatives could have more potential to exhibit multifunction properties in the application of organic materials.

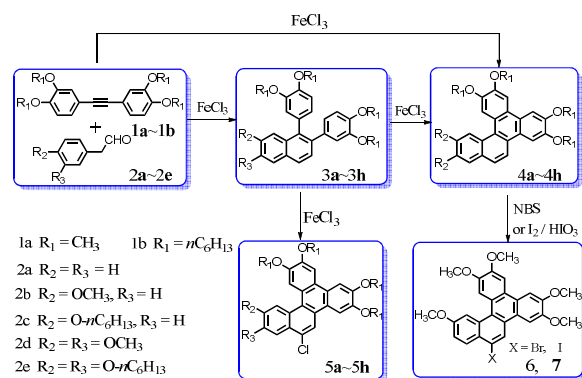
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Electronic Supplementary Information (ESI) available: Figure S1, S2 and S3; Table S1; Molecular geometry and energy of 4aa from computer calculation, The detail experiment section; Copies of ¹H NMR and ¹³C NMR spectra for all the products (PDF), and Crystallographic data of 5ab (CIF). See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of Benzo[*g*]chrysene (BgCh) 4a~4h, the chlorination products 5a~5h and the halogenated products 6 (bromine), 7 (iodine).

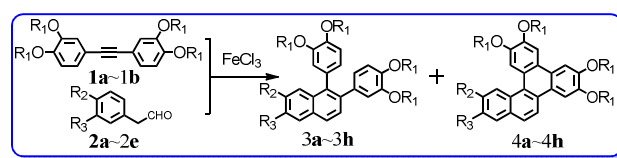
Herein, we describe a newly and straightforward method to synthesize the BgCh compounds in one pot from diphenylacetylene and phenylacetaldehyde derivatives promoted by iron(III) chloride (FeCl₃) as an oxidized agent (Scheme 1). The reactions occurred in dichloroethane (DCE) at room temperature under mild condition. The BgCh derivatives also can be functionalized by the chlorination in one pot as the stoichiometry of FeCl₃ is enough. In addition, the BgCh derivatives also can be halogenated by N-bromosuccinimide (NBS) or iodine (I₂) / iodic acid (HIO₃) in two steps. The introduction of halogen into a molecule can be an important part of synthetic sequence as a prelude to the formation of new multifunctional molecules via an organometallic method or a coupling reaction. In the end, we have studied their thermal and photophysical properties in preliminary.

Results and discussion

Synthesis and Characterization

The skeleton of BgCh can be divided into two different segments, naphthalene and phenanthrene. In the past decades, a lot of efficient methodologies have been explored for the synthesis of the polysubstituted naphthalene derivatives.¹⁹ It is noteworthy that it is very efficient approach to make the naphthalene structure via a tandem cycloaddition aromatization reaction by using internal alkyne and phenylacetaldehyde, in which the cheap reagent of FeCl₃ was established as Lewis acid to promote annulation reaction under mild condition.²⁰ In addition, FeCl₃ can always be used as a common oxidative reagent in the cyclodehydrogenation reaction at room temperature.²¹ Therefore, we believe that the feasibility of a tandem benzannulation and cyclodehydrogenation reaction can be demonstrated to achieve the BgCh skeleton by means of the FeCl₃-promoted one-pot reaction. In model experiments as shown in the entry 1~6 in table 1, we used 1,2-bis(3,4-dimethoxyphenyl)ethyne and phenylacetaldehyde as the initial compounds, FeCl₃ as an oxidative reagent in DCE at room temperature. We found that the stoichiometric ratio of FeCl₃ and 1,2-bis(3,4-dimethoxyphenyl)ethyne had a large impact on

Table 1. The synthesis of BgCh derivatives from diphenylacetylene and phenylacetaldehyde by FeCl₃-promoted^a.



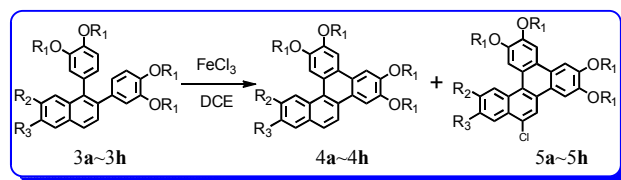
en	R ₁	R ₂	R ₃	FeCl ₃ (eq.)	main produ ct	yield (%) ^b
1	CH ₃	H	H	1.2	3a	68
2	CH ₃	H	H	1.5	3a	56
3	CH ₃	H	H	2	3a	41
4	CH ₃	H	H	3	4a	43
5	CH ₃	H	H	4	4a	49
6	CH ₃	H	H	5	4a	55
7	CH ₃	OCH ₃	H	1.2	3b	65
8	CH ₃	O- <i>n</i> C ₆ H ₁₃	H	1.2	3c	61
9	CH ₃	OCH ₃	OCH ₃	1.2	3d	62
10	<i>n</i> -C ₆ H ₁₃	H	H	1	3e	64
11	<i>n</i> -C ₆ H ₁₃	OCH ₃	H	1	3f	74
12	<i>n</i> -C ₆ H ₁₃	O- <i>n</i> C ₆ H ₁₃	H	0.8	3g	65
13	<i>n</i> -C ₆ H ₁₃	O- <i>n</i> C ₆ H ₁₃	O- <i>n</i> C ₆ H ₁₃	1	3h	58
14	CH ₃	OCH ₃	H	5	4b	41
15	CH ₃	O- <i>n</i> C ₆ H ₁₃	H	5	4c	43
16	CH ₃	OCH ₃	OCH ₃	4	4d	34
17	<i>n</i> -C ₆ H ₁₃	H	H	5	4e	24
18	<i>n</i> -C ₆ H ₁₃	OCH ₃	H	4	4f	20
19	<i>n</i> -C ₆ H ₁₃	O- <i>n</i> C ₆ H ₁₃	H	4	4g	14
20	<i>n</i> -C ₆ H ₁₃	O- <i>n</i> C ₆ H ₁₃	O- <i>n</i> C ₆ H ₁₃	4	4h	10

^a Reaction conditions: Aldehyde (1.2 equiv), alkyne (1.0 equiv), 1,2-DCE, rt.

^b Isolated by column chromatography on silica gel and recrystallization.

the yield of the desired product. when the stoichiometry ratio was applied less than 3 equivalents, the main product is 1,2-bis(3,4-dimethoxyphenyl)naphthalene 3a; otherwise, the main product was BgCh derivatives 4a. The best isolate yield of 4a was obtained in 55% with 5 equivalents FeCl₃. Having established a good scope with substrate in one pot, various of phenylacetaldehyde derivatives 2b~2d in entry 14~16 in table 1, namely 4-methoxybenzaldehyde, 4-(hexyloxy) benzaldehyde and 3,4-dimethoxybenzaldehyde has been used. At the same time, in order to investigate the applications of the BgCh derivatives in thin film materials, we also have synthesized the 1, 2-dibenzyl naphthalene derivatives 3b-3h and BgCh derivatives 4e~4h under this reaction condition in corresponding to entry 7~13 and 17~20 in table 1. In this synthesis route, the BgCh skeleton can be constructed by FeCl₃-promoted with diphenylacetylene and phenylacetaldehyde derivatives as starting substrates, but it is plagued by the low yields in one pot.

Table 2. The synthesis of BgCh derivatives from 1,2-dibenzyl naphthalene by FeCl₃-promoted^a.



Entr y	R ₁	R ₂	R ₃	FeCl ₃ (eq.)	Main products	yield (%) ^b
21	CH ₃	H	H	4	4a	71
22	CH ₃	OCH ₃	H	4.5	4b	81
23	CH ₃	<i>O-n</i> C ₆ H ₁₃	H	4	4c	78
24	CH ₃	OCH ₃	OCH ₃	4.3	4d	66
25	<i>n</i> -C ₆ H ₁₃	H	H	3	4e	68
26	<i>n</i> -C ₆ H ₁₃	OCH ₃	H	3.5	4f	71
27	<i>n</i> -C ₆ H ₁₃	<i>O-n</i> C ₆ H ₁₃	H	3	4g	78
28	<i>n</i> -C ₆ H ₁₃	<i>O-n</i> C ₆ H ₁₃	<i>O-n</i> C ₆ H ₁₃	3.5	4h	72
29	CH ₃	H	H	10	5a	72
30	CH ₃	OCH ₃	H	10	5b	81
31	CH ₃	<i>O-n</i> C ₆ H ₁₃	H	10	5c	68
32	CH ₃	OCH ₃	OCH ₃	7	5d	74
33	<i>n</i> -C ₆ H ₁₃	H	H	7	5e	77
34	<i>n</i> -C ₆ H ₁₃	OCH ₃	H	7	5f	76
35	<i>n</i> -C ₆ H ₁₃	<i>O-n</i> C ₆ H ₁₃	H	7	5g	74
36	<i>n</i> -C ₆ H ₁₃	<i>O-n</i> C ₆ H ₁₃	<i>O-n</i> C ₆ H ₁₃	7	5h	73

^a Reaction conditions: Aldehyde (1.2 equiv), alkyne (1.0 equiv), 1,2-DCE, rt.

^b Isolated by column chromatography on silica gel and recrystallization.

In the course of optimized the quantity of FeCl₃ for synthesis BgCh 4a~4h in the second synthesis route, a new byproduct has been found and the yield was increased by keep pace with the stoichiometry of FeCl₃ in entry 29~36 in table 2. For example, the 1,2-dibenzyl naphthalene 3b was treated with about 10 equivalents of FeCl₃ in the second synthesis route, the isolate yield of new product 5b is 81%. It's structure was fully characterized by using ¹H NMR, ¹³C NMR, Elementary analysis (EA) (as shown in ESI[†]) and Multi-stage mass spectrometry. The ¹H NMR spectra of 3b was compared with 4b and 5b in CDCl₃ in ESI figure S1. It is clearly shown that the product 5b was lost two protons compared with 4b.

The result of multi-stage mass spectra in positive-iron mode for 5b on an electrospray ionization linear ion trap mass spectrometer was shown in figure 1. The number of stages of mass analysis is represented as MS^{*n*} where *n* is the scan power. In order to obtain more structural information, the scan power was set from *n* = 1 to *n* = 7. The biggest molecule ion peak is about *m/z* 463.12 in mass detector and it has been selected as parent ion which also known as precursor ions. The fragment of product ions or secondary ion in MS² is about *m/z* 428.28 which was captured in ion trapping as the parent ions in collisions. The different value between MS and MS² is 34.84. In other words, the parent ion was lost a fragment which *m/z* value is 35. It is possible that the fragment is about a chloride ion. The third stage ion was acquired from the secondary ion in MS³. The different value between MS² with MS³ is 15.08, and it indicates that a CH₃⁺ fragment was lost from the MS² fragment. The different value in each stage from MS³ to MS⁷ is

about 15 and it is possible that four CH₃⁺ fragments were lost from the MS³ fragment.

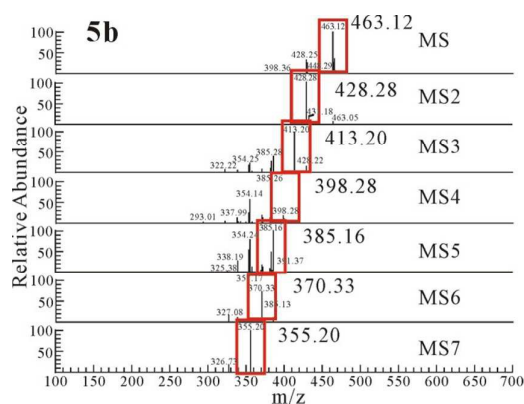


Figure 1. The result of multi-stage mass spectra for 5b in positive-iron mode.

The results of NMR and multi-stage mass spectra indicated that one of the protons in molecule 4b has been replaced by a chlorine ion and the position maybe is C10 in BgCh skeleton. Therefore, the molecular structure has been confirmed by single X-ray crystal diffraction further. The crystallography structure of 5b is depicted in figure 2, and as aforementioned analysis results, the hydrogen atom at C10 position has been substituted by a chlorine atom. The results also show that the aromatic core of BgCh is not a plane geometry. The dihedral angle between two parts of naphthalene and phenanthrene aromatic rings is about 17.89°.

The chlorination proceeded regioselectively to the C10-site of 4a~4h with Lewis acid FeCl₃ also has been confirmed by computer calculation. Figure 3 displays the molecular geometry and the HOMO energy distribution calculated for electron-deficient 4a at MP2/6-31G**//B3LYP/6-31G* level by Gaussian 09²². The NPA charge analysis shown that the C10

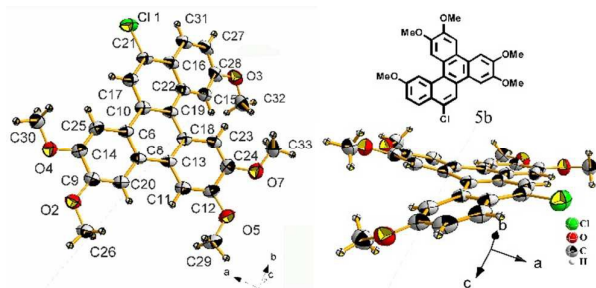


Figure 2. The crystal structure of 5b by X-ray (50% probability ellipsoids). Left is view down c-axis and right is side view down b-axis.

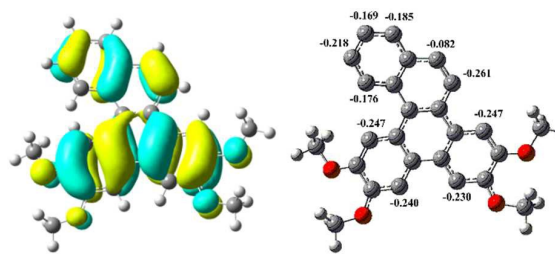


Figure 3. Energy-minimized structure (MP2/6-31G*/B3LYP/6-31G*) of electron-deficient compound 4a with a visualization of the HOMO energy distribution (left) and NPA charge distribution on sites available for chlorination (right).

atom only bears -0.082 e and it is very easy to chlorinate (electrophilic substitution reaction) compared with the other candidate carbon atoms. It is in agreement with the experimental observation.

Thermal and Liquid crystalline properties

Different molecular structures are required for different applications. The 4e~4h and 5e~5h maybe exhibit liquid crystalline properties as for the good proportion between the rigid core and the long soft chains. Their liquid crystalline properties have been detected by polarizing optical microscopy (POM), differential scanning calorimeter (DSC) and X-ray diffraction (XRD) with heating accessory.

Partial results of POM have been shown in figure 4. The texture of 4e, 4h, 5e and 5h is focal conic fan-shape (pseudofocal conic) which is the characteristic of hexagonal columnar mesophases (Col_h).²³ The mesophase temperature of 4e and 4h are much narrower than the compounds 5e and 5h, about 10~15 centigrade under POM. The picture A was the compound 5h at high temperature under the isotropization temperature, and the picture B was taken photo at nearby room temperature. The compounds 5f and 5g (figure 4C) revealed well-ordered spherulitic-like domains over the whole sample on cooling. Spherulite formation of discotics is relatively rare for low-molecular mass liquid crystals.²⁴ The rest compounds do not show any mesophases either on heating or cooling course.

The DSC traces of the BgCh derivatives with hexyloxy alkoxy chains are shown in figure 5 and ESI figure S2, and the heating / cooling rate is 10 °C /min under nitrogen atmosphere in commonly. The phase transition temperatures and enthalpy changes for studying compounds are summarized in ESI Table S1. The peak temperatures are given in °C

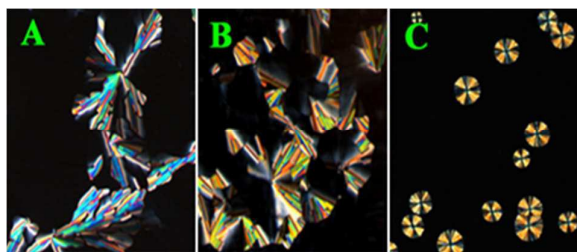


Figure 4. The Photographs observed by POM under crossed polarizers for 5g (C) and 5h (A at 90 °C and B at 25 °C) on cooling.

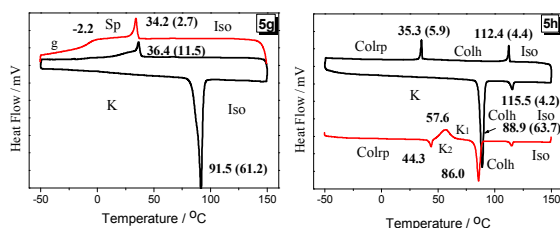


Figure 5. The DSC traces obtained for first heating and cooling cycles (dark trace), the rate of the red trace in 5g is 25 °C/min, and the red trace in 5h is the

second heating cycle at a rate of 10 °C/min. The numbers in parentheses are the enthalpy changes (ΔH) in kJ mol⁻¹.

As can be seen from the results, the formation of mesophases obviously was strongly dependent on the symmetry of π -electron atmosphere and the molecular structure. For example, the 5e~5h shows more complexes polymorphism than 4e~4h. That is because the induce effect of chloride atom made the π -electrons are evenly distributed over the entire molecule in relatively. Compound 5e exhibit monotropic mesomorphism from 48.9 to 21.0 °C on cooling and the 5h displays enantiotropic mesophases behavior. On cooling 5h shows isotropic-to-Col_h transition at 112.4 °C, and followed by Col_h to an unconfirmed columnar transition at 35.3 °C. The unconfirmed columnar phase keeps stable down to -50 °C, and the phase transition enthalpy is only 5.9 KJ / mol, so we cannot assign this phase change to the transition of liquid crystalline-to-crystal. After the first heating and cooling circle, the most complex polymorphism is found for 5h on the second heating DSC curve. It is important to note that there is only one phase transition peak at 35.8 and 49.3 °C for compounds 4e and 4h on cooling in corresponding, and the transition of isotropic-to-columnar phase is not apparent in DSC thermograms. Such behaviour also has been observed in other discotic molecules such as hexazatrinaphthylene,²⁵ tetrabenzocyclodecatetraene²⁶ and so on. As shown in figure 5, there is a broad and unsymmetrical transition peak on cooling curve as the rate is 10 °C /min for 5g. When the cooling rate is increased to 25 °C /min, the peak divided into two transition peaks, and they have been assigned to the transition of isotropic liquid phase to spherulite (Sp) and glass transition (Tg) in corresponding. The 5f also had shown a phase transition from isotropic liquid to Sp at 49.2 on cooling. Compound 4f and 4g containing four hexyloxy alkoxy and one methoxy chains at the rigid core periphery does not show any liquid crystalline behavior, melting-to-isotropic liquid at 83.3 and 80.4 °C respectively.

The liquid crystalline phase behavior of bulk compound 5h was researched by powder X-ray diffraction (XRD) with heating accessory in addition. In order to acquire a well flat film for test, the sample was laid onto the quartz glass pattern, and then it was heated to isotropic liquid temperature, cooled to room temperature. This procedure was repeated several times. In the end, the XRD patterns were recorded on heating and cooling cycles from 25 to 125 °C. The results supported the

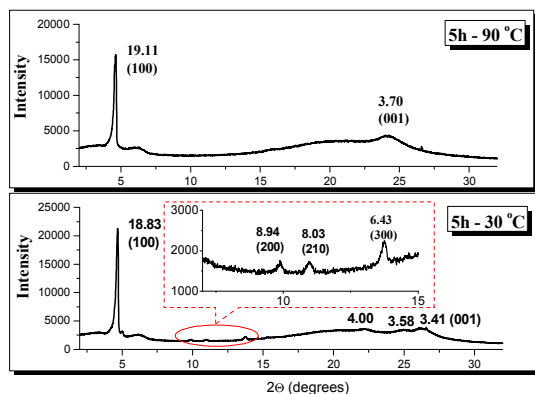


Figure 6. The X-ray diffraction (XRD) pattern of compound 5h at 30 and 90 centigrade.

DSC curve and they were shown in ESI figure S3 and figure 6. At the temperature of 30 °C on heating, there are a sharp peak and a small shoulder peak in small-angle regime, a set of weak peaks in middle-angle regime, an uneven broad diffuse halo and a second relatively narrow diffuse ring in the wide-angle regime. In the small-angle, the most intense peak is associated with the reflection (20), while the less intense peak should correspond to the reflection (11). The intensity of reflection (20) was increased as the temperature increased, and it indicated that the size of the unit cell slightly expanded. In the wide-angle region, the amorphous halos indicate that the sample lies to fluid-like nature. The broad diffuse halo corresponds to the disorder of the alkyl side chains, and the second relatively narrow diffuse ring around 3.4 Å ($2\theta = 26.2^\circ$) is related to layer distance between two disc-like molecule is 3.4 Å along the column axis. Beside the uneven halo with several weak peaks in wide-angle regime indicated that the molecular stack is ordered in relatively, and it tended to crystallization. Therefore, the phase of sample 5h is a rectangular columnar plastic phase (Col_h) at 30 °C.²⁷ As the temperature is over 40 °C, the XRD pattern is absolutely different from the sample at 30 °C, and it is clearly in crystal phase. The XRD pattern of 5h at 90 °C shows only one sharp reflection at small-angle region, an amorphous halo at 3.70 and a broad reflection in the wide angle region. These results suggested that the molecule beyond to the short-range order at high temperature as for the thermal activity. The center-to-center distance a between neighboring columns in Col_h is 2.23 nm, and the layer distance between two disc-like molecule is 3.70 Å.²⁸ Over the isotropic melt the hexagonal arrangement of the columns is lost and thus in the small-angle regime a diffuse ring is also observed. On cooling, the sample 5h was Col_h under isotropic temperature, and subsequently cooling to Col_p less than 35 °C.

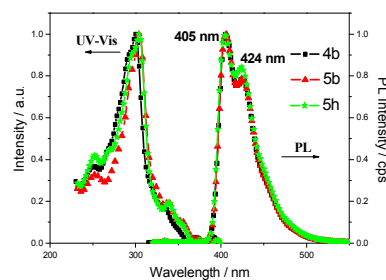


Figure 7. The UV-Vis absorption and fluorescence emission spectra of 4b, 5b and 5h in DCM, the concentration is 1×10^{-5} mol/L.

Photophysical properties

The UV-Vis absorption and emission spectra of the representative BgCh derivatives 4b, 5b and 5h in pure dichloromethane (DCM) were shown in figure 7, respectively. There is only one main absorption band was found in every new compound, and the wavelength of the strong absorption band was found around at 303 nm, indicating the strong $\pi-\pi^*$ transition of the electron delocalizing the whole conjugated backbone. The fluorescence spectra of these compounds exhibit a strong emission peak at ~ 405 nm and with a shoulder peak nearby 424 nm. No evidence confirm that the halogen atom, and the alkoxy chains have any influence on the maximum emission wavelength. Compare with the 2,3,6,7,10,11-hexakis(hexyloxy) triphenylene (HAT) (the maximum emission wavelength is about 384 nm),²⁹ BgCh derivatives illustrated their capacity of pure blue light emission, which made them feasible to be exploited as good candidates for designing new blue emission materials in OLED.

Conclusions

In summary, we have developed a newly method to construct the skeleton of BgCh with FeCl_3 as oxidizing agent in DCE at room temperature. According to optimized the amount of FeCl_3 and the BgCh 4a~4h have been obtained from diphenylacetylene and phenylacetaldehyde derivatives in one pot or the corresponding 1, 2-dibenzyl naphthalene derivatives 3a~3h in two steps at relatively higher yields. The proton at C10 in BgCh derivatives also can be substituted by chlorine in one pot from 3a~3h as the stoichiometry of FeCl_3 is enough. It also can be substituted by other halogen such as bromine and iodine. The mesophase and photophysical properties of them have been detected in preliminary. 4e, 4h, 5e and 5h shown Col_h under POM. In particular, the sample 5h was Col_h under isotropic temperature, and subsequently cooling to Col_p less than 35 °C on cooling. There is only one main absorption band in every new compound around 300 nm. The fluorescence spectra of these compounds exhibit a strong emission peak at 405 nm and a shoulder peak nearby 424 nm in visible light region. No evidence proved that the halogen atom, and the alkoxy chains have any influence on the maximum emission wavelength.

Experimental Section

General synthetic procedures and characterization data for 3a, 4a, 5a, 6 and 7 precursors are reported as an example. The others are same with the example compounds. Full data for all products are collected in the Supporting Information.

General synthesis procedure for 3a

1, 2-bis(3,4-dimethoxyphenyl)ethyne 1a (268 mg, 0.9 mmol) and 2-phenylacetaldehyde 2a (132 mg, 1.1 mmol), FeCl₃ (179 mg, 1.1 mmol) were dissolved in 10 mL DCE. The mixture was stirred at room temperature until the 1a disappeared by TLC detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization. Yield: 245 mg (68%) of light yellow powder. ¹H NMR (400MHz, CDCl₃): 7.91 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48 (td, *J* = 7.4 Hz, *J* = 0.8 Hz, 1H), 7.42 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 6.76- 6.87 (m, 4H), 6.72 (sd, *J* = 1.6 Hz, 1H), 6.64 (sd, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.68 (s, 3H), 3.61 (s, 3H). ¹³C NMR (100MHz, CDCl₃): 148.5, 147.9, 147.8, 147.4, 137.9, 137.1, 134.7, 132.8, 132.7, 131.7, 128.2, 127.8, 127.5, 126.7, 126.2, 125.5, 123.7, 122.1, 114.8, 113.6, 110.7, 110.5, 55.8, 55.7, 55.6. Mass (APCI, *m/z*), calcd for C₂₆H₂₄O₄: 400.17. Found: [M+H]⁺, 401.10. Anal. Calcd for C₂₆H₂₄O₄: C, 77.98; H, 6.04. Found: C, 77.86; H, 5.80.

General synthesis procedure for 4a

Method one: 1, 2-bis(3,4-dimethoxyphenyl)ethyne 1a (150 mg, 0.5 mmol), 2-phenylacetaldehyde 2a (72 mg, 0.6 mmol), FeCl₃ (406 mg, 2.5 mmol) were dissolved in 10 mL DCE. The mixture was stirred at room temperature until the 1a disappeared by TLC detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization. Yield: 110 mg (55%) of yellow powder.

Method two: 3a (120 mg, 0.3 mmol) was dissolved in 4 mL DCE, then FeCl₃ (195 mg, 1.2 mmol) was added and the mixture was stirred at room temperature until the derivatives of 3a was disappeared by TLC detected. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The product 4a was obtained from recrystallization. Yield: 84 mg (71%) of yellow powder. ¹H NMR (400MHz, CDCl₃): 8.98 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.41 (s, 1H), 8.00-8.02 (m, 2H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.88 (s, 1H), 7.86 (s, 1H), 7.56-7.63 (m, 2H), 4.17 (s, 3H), 4.16 (s, 3H), 4.15 (s, 3H), 4.06 (s, 3H). ¹³C NMR (100MHz, CDCl₃): 149.5, 149.1, 148.8, 147.9, 133.1, 130.2, 128.3, 127.6, 126.9, 126.6, 126.0, 125.7, 125.5, 125.2, 124.1, 123.6, 123.5, 120.8, 110.9, 104.9, 104.2, 103.8, 56.2, 56.1, 56.0. Mass (APCI, *m/z*), calcd for C₂₆H₂₂O₄: 398.15. Found: [M+H]⁺, 399.16. Anal. Calcd for C₂₆H₂₂O₄: C, 78.37; H, 5.57. Found: C, 78.52; H, 5.35.

General synthesis procedure for 5a

3a (100 mg, 0.25 mmol) was dissolved in 10 mL DCE, then FeCl₃ (406 mg, 2.5 mmol) was added and the mixture was stirred at room temperature until the 3a was disappeared by TLC detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization. Yield: 78

mg (72%) of yellow powder. ¹H NMR (400MHz, CDCl₃): 8.89 (d, *J* = 7.2 Hz, 1H), 8.46 (s, 1H), 8.43 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.22 (s, 1H), 7.78 (s, 2H), 7.77 (s, 1H), 7.59-7.67 (m, 2H), 4.13 (s, 3H), 4.12 (s, 3H), 4.11 (s, 3H), 4.00 (s, 3H). ¹³C NMR (100MHz, CDCl₃): 149.8, 149.2, 149.0, 148.0, 131.3, 130.1, 130.0, 127.9, 126.8, 126.3, 126.2, 125.3, 125.2, 124.8, 124.3, 122.9, 122.6, 121.1, 110.7, 104.5, 104.1, 103.7, 56.1, 56.0. Mass (APCI, *m/z*), calcd for C₂₆H₂₁ClO₄: 432.11. Found: [M+H]⁺, 433.19. Anal. Calcd for C₂₆H₂₁ClO₄: C, 72.14; H, 4.89. Found: C, 72.18; H, 4.85.

10-bromo-2,3,9,12,13-pentamethoxybenzo[g]chrysene 6

The 2,3,6,7,13-pentamethoxybenzo[g]chrysene 4b (214 mg, 0.5 mmol) and N-bromobutanamide (NBS) (107 mg, 0.6 mmol) were dissolved into 20 mL N, N-Dimethylformamide (DMF), and then the mixture was heated to 80 °C overnight. After cooling to room temperature, the mixture was poured into ice water and filter. The crude product was purified by column chromatography on a silica gel column, and a pure product was obtained by recrystallization (210 mg, 83%) as light yellow solid powder. ¹H NMR (CDCl₃, 400MHz): 8.58 (s, 1H), 8.34-8.37 (m, 3H), 7.87 (s, 1H), 7.85 (s, 1H), 7.83 (s, 1H), 7.32 (dd, *J* = 9.0 Hz, *J* = 2.4 Hz, 1H), 4.16-4.17 (m, 9H), 4.05 (s, 3H), 3.98 (s, 3H). ¹³C NMR (CDCl₃, 100MHz): 158.4, 149.9, 149.2, 148.9, 147.9, 132.6, 129.2, 128.0, 126.2, 125.3, 125.0, 124.3, 123.2, 122.7, 122.6, 121.2, 117.5, 110.0, 108.6, 104.7, 104.3, 103.8, 56.2, 56.1, 56.1, 56.0, 55.6. Mass (APCI, *m/z*), calcd for C₂₇H₂₃BrO₅: 506.07. Found: [M+H]⁺, 507.21. Anal. Calcd for C₂₇H₂₃BrO₅: C, 63.92; H, 4.57. Found: C, 63.58; H, 4.47.

10-iodo-2,3,6,7,13-pentamethoxybenzo[g]chrysene 7

2,3,6,7,13-pentamethoxybenzo[g]chrysene 4b (214 mg, 0.5 mmol) was dissolved into the mixture of glacial acid (15 mL), chloroform (5 mL), water (5 mL) and concentrated sulfuric acid (0.5 mL), then I₂ (51 mg, 0.2mmol) and HIO₃ (21 mg, 0.12 mmol) were added. The mixture was stirred for 24 h at 40 °C. After reaction, the mixture was washed with dilute solution of NaHSO₃ and water for three times. The organic layer was dried by MgSO₄, and the solvent was removed under vacuum. The residue was purified by column chromatography on a silica gel column, and a pure product was obtained by recrystallization (114 mg, 41%) as light yellow solid powder. ¹H NMR (CDCl₃, 400MHz): 8.86 (s, 1H), 8.35 (s, 1H), 8.31 (sd, *J* = 2 Hz, 1H), 8.21 (d, *J* = 5.2 Hz, 1H), 7.83-7.86 (m, 3H), 7.28 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 4.17-4.18 (m, 9H), 4.04 (s, 3H), 3.98 (s, 3H). ¹³C NMR (CDCl₃, 100MHz): 158.4, 149.8, 149.2, 148.9, 147.8, 134.2, 131.7, 130.4, 128.4, 125.8, 125.4, 124.2, 123.1, 123.0, 122.2, 117.8, 110.0, 108.5, 104.6, 104.2, 103.7, 97.7, 56.2, 56.1, 56.0, 55.6. Mass (APCI, *m/z*), calcd for C₂₇H₂₃I O₅: 554.06. Found: [M+H]⁺, 554.75. Anal. Calcd for C₂₇H₂₃I O₅: C, 58.50; H, 4.18. Found: C, 58.41; H, 4.01.

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Table of content

Benzo[*g*]chrysene (BgCh) is a new untapped virgin land in PAHs. A newly and straightforward method has been developed to synthesize of the polysubstituted BgCh according to controlling the exact stoichiometry of Lewis acid FeCl₃. Part of BgCh revealed hexagonal columnar mesophase and their maximum fluorescence emission wavelength is 405 nm in the range of blue light.

