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## Synthesis and Character of Low Substituted Dibenzo [*fg*, *op*] Naphthacenes\*

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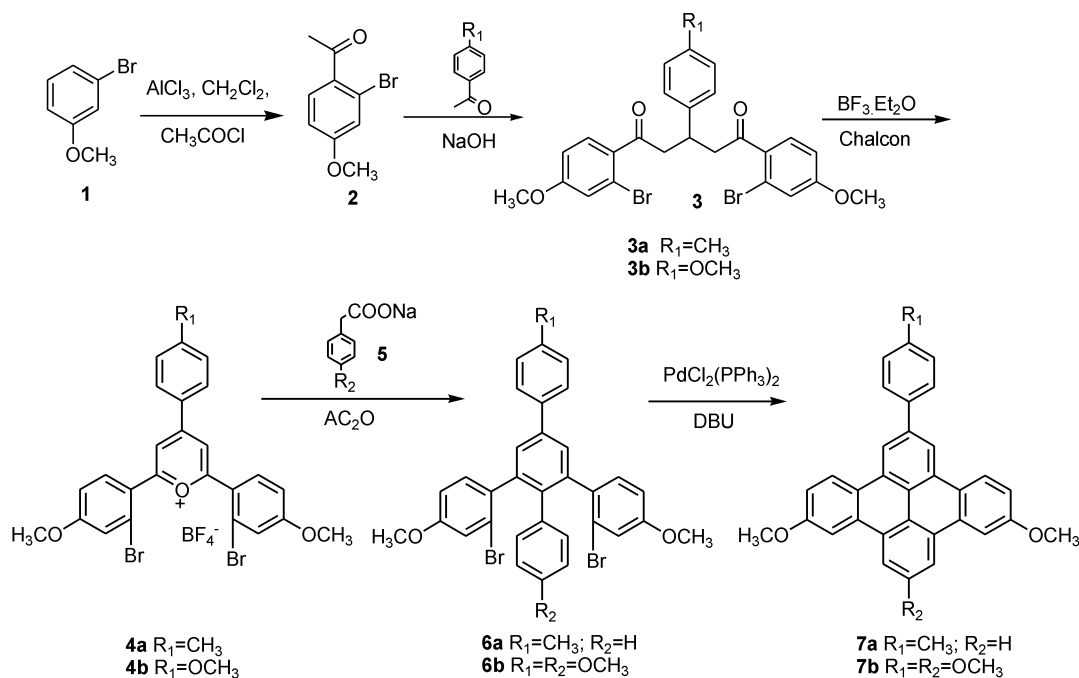
**Abstract:** Low substituted dibenzo [*fg*, *op*] naphthacenes were synthesized by using Friedel-Crafts acylation, tandem al-Michael solvent-free reaction and palladium catalyzed dehydrohalogenation cyclization as key steps. Their aggregation effect in solvent and emitting character are measured on the analysis of concentration dependent <sup>1</sup>H-NMR data and UV-vis, PL spectra respectively.

**Key words:** dibenzo [*fg*, *op*] naphthacene; synthesis; aggregation

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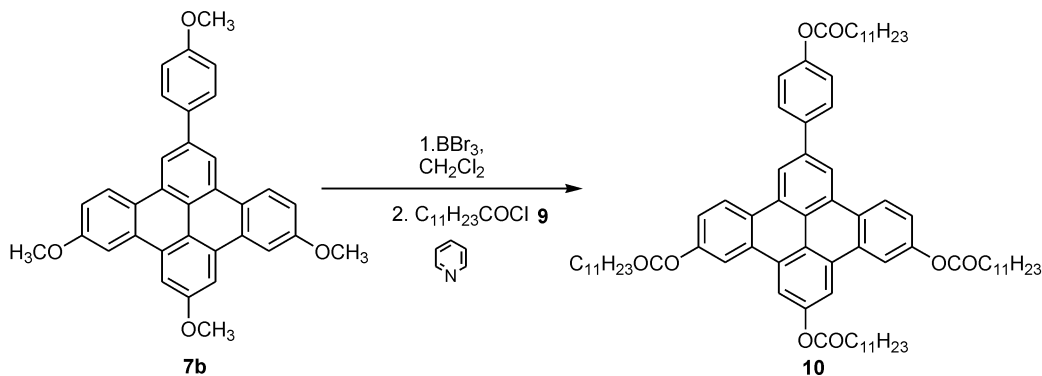
Recently it is of highly interesting to synthesis polycyclic aromatic hydrocarbons with solubilizing side chains because of their excellent electronic and optoelectronic properties<sup>[1]</sup>. Unfortunately till now only octaalkoxy-substituted DBN and hexaalkoxy-substituted DBN were synthesized under harsh conditions and or with poor yield<sup>[2]</sup>. Herein three new low substituted dibenzo [*fg*, *op*] naphthacenes were synthesized facially. Their aggregation effect in solution and emitting character are measured on the analysis of concentration dependent <sup>1</sup>H-NMR data and the UV-vis, PL spectra respectively. The synthesis of substituted DBN are shown in scheme 1:



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**Biography:** CHENG Xiaohong (1968- ), female, was born in Kunming City, Yunnan Province, Prof. Dr., PhD supervisor; research area are organic chemistry and supramolecular chemistry.



Scheme 1 Synthesis of Low Substituted DBN 7 and 10

## 1 Experimental

### 1.1 Apparatuses and Materials

All reactions were conducted under argon. Commercially available chemicals were used as received.  $^1\text{H-NMR}$  spectra: Bruker DRX-500 spectrometer. High resolution MS (HR-MS): Finnigan MAT 90 spectrometer, ionization potential 70 eV. Field-desorption (FD) mass spectra: VG ZAB 2-SE-SPD; Hewlett-Packard LD-TOF-system G2025A. Thin layer chromatography: silica gel 60 PF254 (Merck). Column chromatography: merck silica gel 60 (230~400 mesh).

### 1.2 Preparation

**2-Brom-3-methoxyacetophenone 2:** A mixture of 3-bromoanisole (0.2 mmol), anhydrous  $\text{AlCl}_3$  (0.24 mol) and 200 mL dry  $\text{CH}_2\text{Cl}_2$  was cooled below  $5^\circ\text{C}$  with ice-bath, acetyl chloride (0.2 mol) was added dropwise. The mixture was allowed to reach RT and stirred for 1 h. Then poured into ice-water containing 40 mL concentrated HCl and stirred to reach RT. The organic phase was separated, and the aqueous layer was washed with  $\text{CH}_2\text{Cl}_2$ . The combined organic phase was washed with  $\text{H}_2\text{O}$ , 10% aqueous NaOH,  $\text{H}_2\text{O}$  and brine, dried over  $\text{MgSO}_4$ , and then the solvent was removed in vacuo. The residue was purified by recrystallization from petroleum ether.

**1,5-bis-(2-brom-4-methoxy-phenyl)-3-(4-methoxy-phenyl)-pentane-1,5-dione 3:** With a pestle and mortar, NaOH pellets (0.21 mol) was crushed to powder, then 2 (0.21 mol) and corresponding aldehyd (0.1 mol) were added as liquid, the mixture was constant crushed together over a period of ca. 25 min. The high viscose yellow gel was dissolved in ether, the ether solution was washed with  $\text{H}_2\text{O}$ , brine, dried over  $\text{MgSO}_4$ , then the solvent was removed in vacuo. The residue was purified by column chromatography.

**4:** A mixture of 3 (12.8 mmol) and chalcone (12.8 mmol) was evacuated under Argon, then boron trifluoride etherate (25 mL) was added, the mixture was stirred at  $100^\circ\text{C}$  for 2 h, cooled, and diluted with  $\text{Et}_2\text{O}$  (20 mL), the solution was stand still for 12 h, the yellow solid was filtered and washed thoroughly with ether.

**6:** A mixture of 4 (11.5 mmol), corresponding sodium phenylacetate 5 (68.9 mmol) {prepared from corresponding phenylacetic acid and sodium methanolate in methanol (0.5 mmol/L)}, and acetic acid anhydride (40 mL) was stirred at  $150^\circ\text{C}$  for 2 h; cooled to RT, the acetic acid anhydride was distilled up with oil pump (high Vaco). The residue was solved in  $\text{Et}_2\text{O}$ , washed with 10% aqueous NaOH,  $\text{H}_2\text{O}$  and brine, dried over  $\text{MgSO}_4$ , then the solvent was removed in vacuo. The residue was purified by column chromatography.

**7:** Under Argon atmosphere, 1,8-Diazabicyclo[5.4.0]undec-7-en (0.7 mL) was added to a mixture of 6 (0.64 mmol) in dry N,N-dimethylacetamid (4 mL), then  $\text{Pd}(\text{OAc})_2$  (0.32 mmol) and  $\text{PPh}_3$  (0.48 mmol) was added, the mixture was stirred at  $160^\circ\text{C}$  for further 12 h, cooled to RT, purred into  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{H}_2\text{O}$ , and brine, dried over  $\text{MgSO}_4$ , then the solvent was removed in vacuo. The residue was purified by recrystallization from  $\text{CHCl}_3$ .

**8:** Under Argon atmosphere, 7b (0.82 mmol) was suspended in dry dichloromethane (15 mL), cooled to  $-78^\circ\text{C}$ ,  $\text{BBr}_3$  (1M in  $\text{CH}_2\text{Cl}_2$ , 9.84 mmol) was added in one portion. The mixture turned immediately blue, and was

stirred at RT overnight. The reaction was quenched by adding a drops of water. After 1 h stirring, water was added, the precipitated product was filtered and washed with water and PE and dried in vacuo at 30 °C for 4 h.

9: Under an Argon atmosphere, 8 (0.2 mmol) was solved in dry CH<sub>3</sub>CN (50 mL), then C<sub>11</sub>H<sub>23</sub>COCl 9 (0.9 mmol) and pyridine (1.6 mmol) were added, stirred at RT for 3 days, then poured into a mixture of ether and H<sub>2</sub>O. The organic layer was separated and washed with H<sub>2</sub>O and brine. After drying over MgSO<sub>4</sub> the solvent was removed in vacuo. The residue was purified by column chromatography.

**Table 1 Melting Points and HRMS (or MALDI-TOF) and Data of <sup>1</sup>H-NMR of Compound 2–10**

Comp.	m. p./ °C	HRMS (EI)	<sup>1</sup> H-NMR( <sup>a</sup> in CD <sub>2</sub> Cl <sub>2</sub> , <sup>b</sup> in CDCl <sub>3</sub> , <sup>c</sup> in DMSO-d <sub>6</sub> , <sup>d</sup> in MeOH-d <sub>3</sub> ), δ
2		Calc. for C <sub>9</sub> H <sub>9</sub> O <sub>2</sub> Br (M <sup>+</sup> ) 227.978 6; found: 227.979 6	<sup>a</sup> 7.59~ 7.57 (d, J = 8.9 Hz, 1H, ArH), 7.14~ 7.12 (d, J = 2.5 Hz, 1H, ArH), 6.88~ 6.44 (dd, J = 8.5 Hz, J = 2.1 Hz, 1H, ArH), 3.82 (s, 3H, OCH <sub>3</sub> ), 2.61 (s, 3H, CH <sub>3</sub> CO)
3a		Calcd for C <sub>26</sub> H <sub>24</sub> O <sub>4</sub> Br <sub>2</sub> (M <sup>+</sup> ) 560.002 1, found 560.000 5	<sup>b</sup> 7.35 (d, J = 8.7 Hz, 2H, Ar-H), 7.12 (d, J = 2.4 Hz, 2H, Ar-H), 7.07 (s, 4H, Ar-H), 6.86 (dd, J = 8.8 Hz, J = 2.5 Hz, 2H, Ar-H), 3.82 (m, 7H, CH, 2OCH <sub>3</sub> ), 3.34 (m, 4H, 2CH <sub>2</sub> CO), 2.28 (s, 3H, CH <sub>3</sub> )
3b		Calcd for C <sub>26</sub> H <sub>24</sub> O <sub>5</sub> Br <sub>2</sub> (M <sup>+</sup> ) 577.000 4, found 577.005 4	<sup>a</sup> 7.41~ 7.38 (d, J = 8.6 Hz, 2H, ArH), 7.17~ 7.16 (d, J = 2.5 Hz, 2H, ArH), 7.13 (s, 2H, ArH), 6.90~ 6.83 (m, 4H, ArH), 3.86 (m, 7H, 2 OCH <sub>3</sub> , CH), 3.78 (s, 3H, OCH <sub>3</sub> ), 3.41~ 3.45 (m, 4H, 2 CH <sub>2</sub> CO)
4a		Calcd for C <sub>26</sub> H <sub>21</sub> BBr <sub>2</sub> F <sub>4</sub> O <sub>3</sub> (M <sup>+</sup> ) 627.986 6, found 627.986 7	<sup>c</sup> 8.59 (s, 2H, Ar-H), 8.05 (d, J = 8.9 Hz, 4H, Ar-H), 7.55 (d, J = 8.2 Hz, 2H, Ar-H), 7.43 (dd, J = 2.4 Hz, 2H), 7.18 (dd, J = 8.5 Hz, J = 2.1 Hz, 2H, Ar-H), J = 2.1 Hz, 2H, Ar-H), 3.95 (s, 6H, 2OCH <sub>3</sub> ), 2.53 (s, 3H, CH <sub>3</sub> )
4b		Calcd for C <sub>26</sub> H <sub>24</sub> O <sub>5</sub> Br <sub>2</sub> (M <sup>+</sup> ) 643.981 5 found 643.981 5	<sup>c</sup> 8.93 (s, 2H, ArH), 8.56~ 8.53 (d, J = 9.1 Hz, 2H, ArH), 8.14~ 8.12 (d, J = 8.8 Hz, 2H, ArH), 7.58~ 7.57 (d, J = 2.5 Hz, 2H, ArH), 7.34~ 7.31 (d, J = 8.9 Hz, 4H, ArH), 3.99 (s, 3H, OCH <sub>3</sub> ), 3.94 (s, 6H, 2 OCH <sub>3</sub> )
6a	54~ 56	Calcd for C <sub>33</sub> H <sub>26</sub> O <sub>2</sub> Br <sub>2</sub> (M <sup>+</sup> ) 614.027 9, found 614.027 7	<sup>b</sup> 7.62 (s, 2H, ArH), 7.59~ 7.58 (d, J = 7.75 Hz, 2H, ArH), 7.40~ 7.36 (m, 4H, ArH), 7.27~ 7.26 (d, J = 4.85 Hz, 6H, ArH), 6.95~ 6.93 (m, 3H, ArH), 3.86 (s, 6H, 2 OCH <sub>3</sub> ), 2.41 (s, 3H, CH <sub>3</sub> )
6b	126~ 127	Calcd for C <sub>34</sub> H <sub>28</sub> Br <sub>2</sub> O <sub>2</sub> (M <sup>+</sup> ) 660.033 4, found 660.033 8.	<sup>a</sup> 7.61~ 7.57 (d, J = 8.2 Hz, 2H, ArH), 7.49~ 7.46 (d, J = 7.1 Hz, 2H, ArH), 7.07~ 6.43 (m, 5H, ArH), 6.95 (m, 3H, ArH), 6.78 (m, 4H, ArH), 3.79 (s, 3H, OCH <sub>3</sub> ), 3.70 (s, 6H, 2 OCH <sub>3</sub> ), 3.60 (s, 3H, OCH <sub>3</sub> )
7a	166~ 168	Calcd for C <sub>33</sub> H <sub>24</sub> O <sub>2</sub> (M <sup>+</sup> ) 453.181 0, found 453.190 1	<sup>b</sup> 8.68 (s, 1H, ArH), 8.68~ 8.66 (d, J = 9.0 Hz, 1H, ArH), 8.47~ 8.45 (d, J = 8.2 Hz, 1H, ArH), 8.0 (s, 1H, ArH), 7.80~ 7.79 (d, J = 7.85 Hz, 1H, ArH), 7.71~ 7.67 (m, 2H, ArH), 7.46~ 7.43 (m, 1H, ArH), 7.39~ 7.37 (m, 2H, ArH), 7.32~ 7.27 (m, 2H, ArH), 7.11~ 7.08 (m, 1H, ArH), 7.00~ 6.98 (d, J = 11.2 Hz, 1H, ArH), 4.05 (s, 3H, OCH <sub>3</sub> ), 3.88 (s, 3H, OCH <sub>3</sub> ), 2.43 (s, 3H, CH <sub>3</sub> )
7b	234~ 235	Caeld for C <sub>34</sub> H <sub>26</sub> O <sub>4</sub> (M <sup>+</sup> ) 499.186 5, found 499.190 3.	<sup>a</sup> 8.58 (s, 2H, ArH), 8.54~ 8.50 (d, J = 9.1 Hz, 2H, ArH), 7.96 (s, 2H, ArH), 7.81~ 7.77 (m, 4H, ArH), 7.21~ 7.17 (dd, J = 8.8 Hz, J = 2.4 Hz, 2H, ArH), 7.10~ 7.06 (d, J = 8.9 Hz, 2H, ArH), 4.01 (s, 3H, OCH <sub>3</sub> ), 3.95 (s, 6H, 2 OCH <sub>3</sub> ), 3.89 (s, 3H, OCH <sub>3</sub> )

## Continue

Comp.	m. p./ °C	HRMS( EI)	<sup>1</sup> H NMR( <sup>a</sup> in CD <sub>2</sub> Cl <sub>2</sub> , <sup>b</sup> in CDCl <sub>3</sub> , <sup>c</sup> in DMSO- d <sub>6</sub> , <sup>d</sup> in MeOH- d <sub>3</sub> ), δ
8			<sup>d</sup> 8.78 ( s, 2H, Ar- H), 8.73~ 8.69 ( d, J = 9.3 Hz, 2H, Ar- H), 8.18 ( s, 2H, Ar- H), 8.01~ 8.02 ( d, J = 2.4 Hz, 2H, Ar- H), 7.82~ 7.78 ( d, J = 8.8 Hz, 2H, Ar- H), 7.26~ 7.21 ( dd, J = 9.1, J = 2.4 Hz, 2H, Ar- H), 7.03~ 6.99 ( d, J = 9.1 Hz, 2H, Ar- H)
10	143~ 146	MS ( MALDI - TOF, Dihranol, Ag <sup>+</sup> ): 1170. 788 2 ( M <sup>+</sup> ), 1171. 791 6 ( M <sup>+1</sup> ) 1 172. 794 9 ( M <sup>+2</sup> ) 1 173. 798 1 ( M <sup>+3</sup> ) 1 174. 801 3 ( M <sup>+4</sup> )	<sup>b</sup> 8.85 ( s, 2H, Ar- H), 8.76~ 8.73 ( d, J = 9.1 Hz, 2H, Ar- H), 8.38 ( s, 2H, Ar- H), 8.29~ 8.27 ( d, J = 2.1 Hz, Ar- H), 7.91~ 7.88 ( m, 2H, Ar- H), 7.48~ 7.45 ( m, 2H, Ar- H), 7.33~ 7.31 ( dd, J = 8.9 Hz, J = 2.4 Hz, 2H, Ar- H), 7.26~ 7.25 ( d, J = 8.8 Hz, 2H, Ar- H), 2.79~ 2.62 ( m, 8H, 4 COCH <sub>2</sub> ), 1.95~ 1.81 ( m, 8H, 4 CH <sub>2</sub> ), 1.53~ 1.39 ( m, 48H, 24 CH <sub>2</sub> )

## 2 Results and Discussion

Starting from commercially available 3-bromoanisole 1 via Friedel-Crafts reaction gave out acetophenone 2 (80%), tandem Aldol-Michael solvent-free reaction between 2 and corresponding aldehyde, yield trialkyl-1, 3-diketone 3 (65%), which reacted with BF<sub>3</sub>·Et<sub>2</sub>O under the oxidation of chalcone, the obtained pyrylium salt 4 (90%) was then condensed with sodium phenyl acetate 5, finally alkyl (alkoxy) substituted DBN 7 was yielded in 60% yield by dehydrohalogenation cyclization of dibromoaromatic hydrocarbons 6 in the present of Pd(0), DBU and DMA at the temperature of 160 °C. Demethylation of 7b using BBr<sub>3</sub> at -78 °C yield phenol 8 (98%) that was transformed into ester 10 (46%) by esterified with acyl chloride 9 in the presence of pyridine.

7b was crystallized from CH<sub>2</sub>Cl<sub>2</sub> to afford slightly yellow crystals suitable for X-ray investigation (Fig. 1<sup>①</sup> [3]). The nearly perfectly planar polycyclic aromatics form infinite stacks which are arranged in a different motif as the other reported substituted DBN derivative<sup>[3]</sup>, and the most obvious difference lies in that the attached phenyl substituent in this structure is ordered.

The NMR signals of the DBN derivatives 7 and 10 are concentration dependent, an indication for the aggregation tendency through  $\pi$ - $\pi$  intermolecular interaction of these compounds. Under the assumption that the monomer-dimer equilibrium is the predominant process in solution, the aggregation constant for 7a, 7b and 10 in CH<sub>2</sub>Cl<sub>2</sub> were

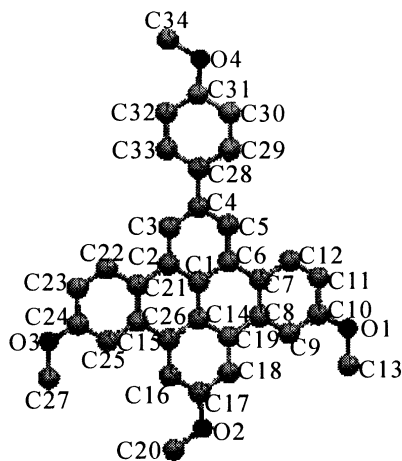


Fig. 1 Crystal Structure of 7b

① Crystal data for 6a: C<sub>34</sub>H<sub>26</sub>O<sub>4</sub>. Triclinic, space group P-1, Z = 2,  $\alpha = 73.450(11)$  Å,  $\beta = 89.614(9)$  Å,  $\gamma = 77.300(10)$  Å,  $V = 1508.5(3)$  Å<sup>3</sup>,  $D_c = 1.472$  g·cm<sup>-3</sup>,  $\mu = (\text{Mo K}\alpha) = 0.043$  4 mm<sup>-1</sup>; T = 150(2) K, Data collection: Stoe-IPDSII;  $\theta = 63.5^\circ$ ; 6644 reflections and 4241 with  $I > 2\sigma(I)$ ; 401 parameters (C, O anisotope, H isotrope), maximum residual electron density 0.681 e. Å<sup>-3</sup>; R1 = 0.088, wR2 = 0.19. The structure was solved and refined on F by using Full-matrix least-squares. Selected bond distances (Å): C(1) - C(2) 1.411(4), C(1) - C(6) 1.419(4), C(1) - C(14) 1.435(4), C(2) - C(3) 1.397(4), C(2) - C(21) 1.464(3), C(3) - C(4) 1.388(4), C(4) - C(5) 1.389(4), C(4) - C(28) 1.480(4), C(5) - C(6) 1.401(4), C(6) - C(7) 1.470(4), C(7) - C(8) 1.399(4), C(7) - C(12) 1.413(4), C(8) - C(9) 1.401(4), C(8) - C(19) 1.462(4), C(9) - C(10) 1.373(4), C(10) - C(11) 1.399(4), C(11) - C(12) 1.365(4), C(14) - C(15) 1.416(3), C(14) - C(19) 1.421(4), C(15) - C(16) 1.407(4), C(15) - C(26) 1.458(4), C(16) - C(17) 1.378(4), C(17) - C(18) 1.389(4), C(18) - C(19) 1.387(4), C(21) - C(26) 1.404(4), C(21) - C(22) 1.414(4), C(22) - C(23) 1.373(4), C(23) - C(24) 1.393(4), C(24) - C(25) 1.373(4), C(25) - C(26) 1.413(4), C(28) - C(33) 1.384(4), C(28) - C(29) 1.402(4), C(29) - C(30) 1.380(4), C(30) - C(31) 1.384(4), C(31) - C(32) 1.389(4), C(32) - C(33) 1.382(4).

determined to be 0.56, 0.442, 6.27 ( $M^{-1}$ ; M: mol/L) respectively<sup>[4]</sup>. The aggregation constant of 10 being larger than those of the other two is probably due to the much longer ester chains attached on the aromatic backbone.

The normalized UV-Vis absorption and PL spectra of compounds 7a, 7b and 10 in  $CDCl_3$  are shown in fig. 2. Comp. 7a shows no fine structure both in its UV-Vis absorption and PL spectra; 7b has fine structure only in its PL spectrum, while comp. 10 shows fine structure both in its UV-Vis absorption and PL spectra. This means the structure of 7a are more "soft" than the other two which leads to little different conformations between the ground and excited states, therefore only one peak was found in both its UV-Vis absorption and PL spectra. The PL spectrum of comp. 7b shows clearer vibrational structures as a consequence of the different molecular conformations between the ground and excited states. Therefore, the molecular geometry of comp. 7b in the excited state should be characterized by a more rigid planar conformation which could be proved by the non-rotated attached phenyl ring in its single crystal structure. Two distinct peaks are also found in the UV-Vis absorption spectrum of comp. 10 which is explained by its more crowded steric structure caused by the four long ester chains attached on the aromatic backbone.

The potential uses of these molecules could be an active material in OFLETs and blue emitter in OLEDs. Further work are going on.

Therefore low substituted dibenzo [*fg*, *op*] naphthalene were synthesised easily and their aggregation effect in solvent and emitting character are measured on the analysis of concentration dependent  $^1H$ -NMR data and UV-vis, PL spectra respectively.

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# 低取代二苯并并四苯的合成及性能研究

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**摘要:**以傅克酰基化反应、串联的 Aldol-Michael 反应及 Pd-催化的脱卤化氢环化反应为关键步骤, 合成了低取代的二苯并并四苯衍生物(DBN). 通过 $^1H$ -NMR 位移值随浓度改变而改变的方法测定了 DBN 在溶剂中的聚集效应, 通过紫外吸收及荧光发射光谱的测定分析了 DBN 的发光性能.

**关键词:** 二苯并并四苯; 合成; 聚集

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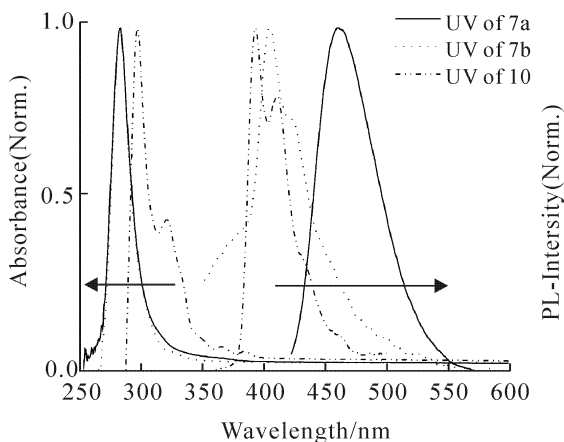


Fig. 2 UV and PL Spectra of 7 and 10 in  $CH_2Cl_2$  Solution and in Film State