

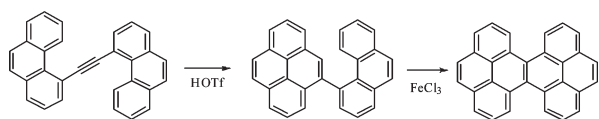
**A Convenient Synthesis of Tetrabenzo[*de,hi,mn,qr*]naphthacene from Readily Available 1,2-Di(phenanthren-4-yl)ethyne**

Anupam Mukherjee, Kamalkishore Pati, and Rai-Shung Liu\*

Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan, ROC

rslu@mx.nthu.edu.tw

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We report here a convenient synthesis of tetrabenzo[*de,hi,mn,qr*]naphthacenes from 1,2-di(phenanthren-4-yl)ethynes through initial Brønsted acid-catalyzed hydroarylation, followed by  $\text{FeCl}_3$ -oxidative coupling reactions. This new method is applicable to tetrabenzo[*de,hi,mn,qr*]naphthacenes bearing various alkyl substituents.

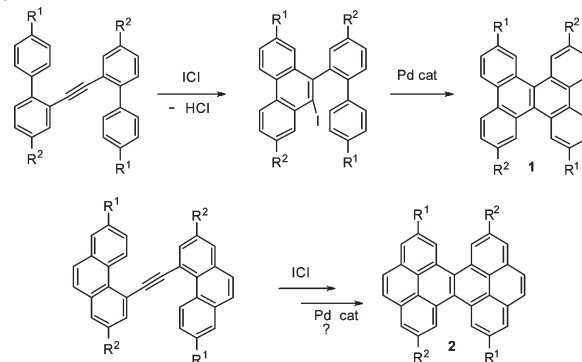
Discotic molecules of benzenoid polycyclic aromatic compounds (BPAH's) such as triphenylenes, dibenzopyrenes, and hexabenzocorenes represent organic materials of important classes.<sup>1</sup> Substantial progress has been achieved in preparing discotic molecules of new BPAHs, including their functionalization to alter their photophysical properties.<sup>2</sup> We reported derivatives of dibenzochrysenes **1** prepared from bis(biaryl)acetylenes via sequential ICl cyclization and Mizoroki–Heck coupling reaction, as depicted in Scheme 1.<sup>2b,3</sup> This new method provides diverse dibenzochrysenes bearing both electron-rich and -deficient substituents, which alter their electronic structures significantly. Similar to dibenzochrysenes, the synthesis of tetrabenzo[*de,*

*hi,mn,qr*]naphthacenes is troubled with low yields and long synthetic procedures of starting substrates, even though several methods<sup>4</sup> are reported for its unsubstituted form **1** ( $\text{R}^1 = \text{R}^2 = \text{H}$ ). The planarity twist of tetrabenzo[*de,hi,mn,qr*]naphthacene **2** ( $\text{R}^1 = \text{R}^2 = \text{H}$ ) is close to that of dibenzochrysenes **1** ( $34^\circ$  versus  $35^\circ$ );<sup>5,6</sup> a smaller energy gap and a strong intermolecular  $\pi$ – $\pi$  interaction are thus anticipated for such derivatives.<sup>6</sup> These features make it more attractive than dibenzochrysenes **1** in material applications.

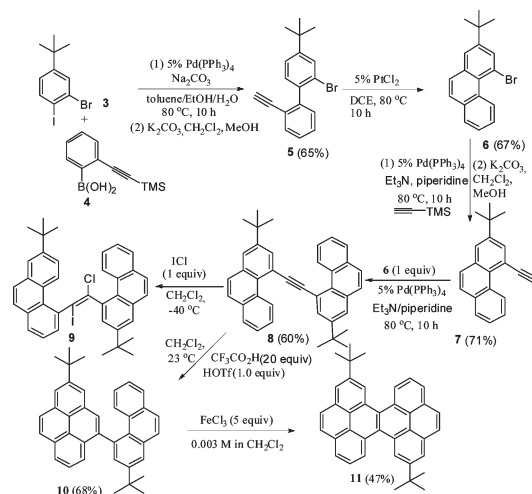
Scheme 2 shows the synthesis of required substrate **8** used in our protocol; this species was readily prepared from 2-bromo-4-*tert*-butyl-1-iodobenzene **3**<sup>7</sup> through Suzuki coupling with 2-(2'-silylethynyl)phenylboric acid **4** and  $\text{K}_2\text{CO}_3$ -desilylation sequence, giving coupling product **5** in 61% yield.

A  $\text{PtCl}_2$ -catalyzed<sup>8</sup> aromatization provided 4-bromophenanthrene **6** in 67% yield, which was converted to 4-ethynylphenanthrene **7** in 71% yield, through Sonogashira

**SCHEME 1**



**SCHEME 2**



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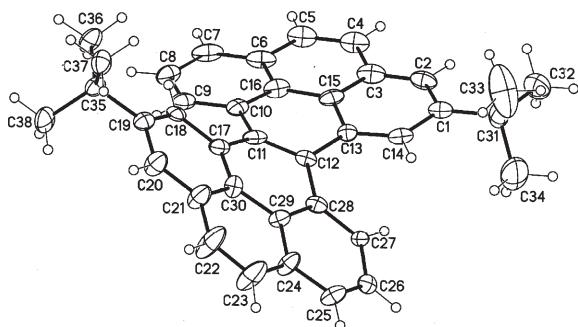


FIGURE 1. X-ray crystal structure of compound **11**.

coupling reaction. A second Sonogashira coupling afforded targeted 1,2-di(phenanthren-4-yl)ethyne **8** in 60% yield. To our disappointment, a ICl-mediated benzannulation<sup>2c,3</sup> of compound **8** gave undesired 1,2-addition product **9** (62%) that was characterized by NMR and X-ray diffraction study.<sup>9</sup> Gratifyingly, we found that a mixture of triflic acid (1 equiv)/CF<sub>3</sub>CO<sub>2</sub>H (20 equiv)<sup>10</sup> in CH<sub>2</sub>Cl<sub>2</sub> (23 °C, 30 min) implemented the aromatization to give 4-(phenanthren-4-yl)pyrene **10** in 68% yield. A final oxidative coupling of this bisaryl species with FeCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (23 °C)<sup>11</sup> gave desired tetrabenzodehi, mn, qr naphthacene **11** in 47% yield. The molecular structure of compound **11** (Figure 1) reveals a twist between the two phenanthrenyl planes of ca. 35°, which is the same as that of dibenzochrysenes **1**.<sup>9</sup> The central benzene is highly distorted with two long C(10)–C(11) = 1.451(9) Å and C(12)–C(13) = 1.466(9) Å lengths, which are significantly longer than the remaining four carbon–carbon distances (1.391(9)–1.422(9) Å) within the same benzene ring.

Substituted tetrabenzodehi, mn, qr naphthacene derivatives remain unknown;<sup>4</sup> we investigate the scope of the methods that are proved to be applicable to preparation of dialkyl-d and tetraalkyl-substituted analogues **12b–f**.

Although such a two-step reaction sequence gave an overall 11.5% yield for unsubstituted parent compound **14a**, we found that overall yields of final products increased when the R<sup>1</sup>-position has large substituents on starting substrates (Table 1). For starting substrates **12a–c**, the cyclization efficiency follows the trend R<sup>1</sup> = *n*-Bu > Me > H, according to their respective overall yields (entries 1–3). An identical pattern was observed for tetraalkyl-substituted products **14d–f**. We envisage that large substituents tend to avoid intermolecular π–π interaction, thus avoiding undesired oligomerization during the Brønsted acid-catalyzed aromatization<sup>10</sup> and FeCl<sub>3</sub>-oxidative coupling reactions.<sup>11</sup> This hypothesis was confirmed by a control experiment in entry 6 for which we obtained a low yield (36%) of desired tetra(*tert*-butyl)-substituted compound **14f** when the FeCl<sub>3</sub> oxidation was run at a high concentration of substrate ([**13f**] = 0.01 M).

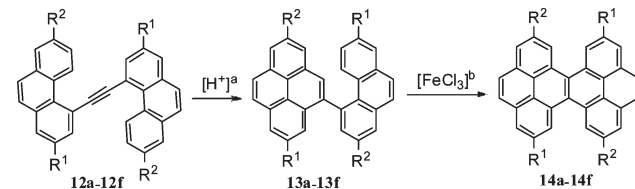
We obtained 4-(phenanthren-4-yl)pyrenes **13h–j** (Scheme 3) bearing 2,2'-alkoxy, 2,2'-diacetyl, and 1,3'-difluoro substituents,

(9) X-ray crystallographic data of compounds **9** and **11** are provided in the Supporting Information.

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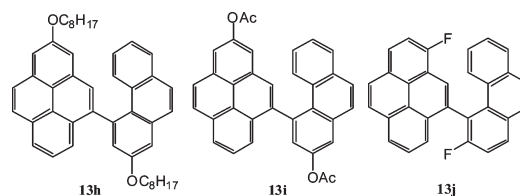
TABLE 1. Synthesis of Substituted Tetrabenzodehi, mn, qr naphthacenes



entry	<b>12</b>	<b>13</b> <sup>c</sup>	<b>14</b> <sup>c</sup>
1	R <sup>1</sup> = R <sup>2</sup> = H ( <b>12a</b> )	<b>13a</b> (41%)	<b>14a</b> (28%)
3	R <sup>1</sup> = <i>n</i> Bu, R <sup>2</sup> = H ( <b>12c</b> )	<b>13c</b> (55%)	<b>14c</b> (42%)
2	R <sup>1</sup> = Me, R <sup>2</sup> = H ( <b>12b</b> )	<b>13b</b> (53%)	<b>14b</b> (40%)
4	R <sup>1</sup> = R <sup>2</sup> = Me ( <b>12d</b> )	<b>13d</b> (64%)	<b>14d</b> (41%)
5	R <sup>1</sup> = <i>t</i> Bu, R <sup>2</sup> = Me ( <b>12e</b> )	<b>13e</b> (65%)	<b>14e</b> (57%)
6	R <sup>1</sup> = R <sup>2</sup> = <i>t</i> Bu ( <b>12f</b> )	<b>13f</b> (70%)	<b>14f</b> (69%, 36% <sup>d</sup> )

<sup>a</sup>[**12**] = 5 × 10<sup>−2</sup> HOTf (1 equiv), CH<sub>2</sub>Cl<sub>2</sub>, 30 min. <sup>b</sup>[**13**] = 0.003 M in CH<sub>2</sub>Cl<sub>2</sub>, FeCl<sub>3</sub> (5 equiv) in MeNO<sub>2</sub>, argon. <sup>c</sup>Yields are reported after separation from silica column. <sup>d</sup>The reaction was run at [**13f**] = 0.01 M.

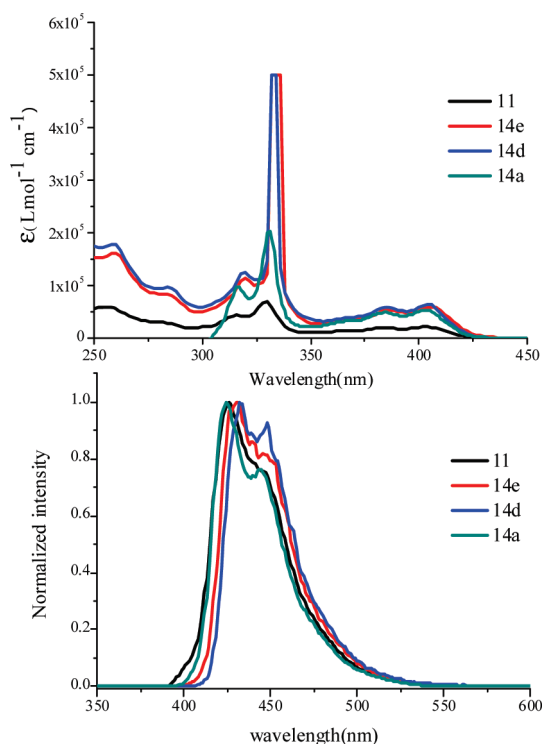
SCHEME 3



but their FeCl<sub>3</sub>-oxidative coupling gave a messy mixture of products. Attempts to use I<sub>2</sub>/hv<sup>12</sup> to promote this coupling reaction were also ineffective for these three substrates.

We examined the photophysical properties of these tetrabenzodehi, mn, qr naphthacenes. The dialkyl- and tetraalkyl-substituted derivatives **14b**, **11**, and **14d–e** bear close resemblance to parent species **14a** in their absorption and emission spectra with little difference. The quantum yields of the emissions are 0.27, 0.28, 0.24, and 0.26 for species **11**, **14a**, **14d**, and **14e**, respectively. As shown in Figure 2, the UV spectra have onsets at 422–429 cm<sup>−1</sup> whereas the emission maxima appear in the 422–430 cm<sup>−1</sup> region; these wavelengths are ca. 20–25 cm<sup>−1</sup> red-shifted from those of dibenzochrysenes **1**<sup>2c</sup> (R<sup>1</sup> = R<sup>2</sup> = H, Scheme 1). The energy gaps of these tetrabenzodehi, mn, qr naphthacenes are within 2.89–2.94 eV, significantly smaller than that (3.16 eV) of dibenzochrysenes **1**.<sup>2c</sup> We estimated their HOMO energy levels from their oxidation potentials (*E*<sub>1/2</sub><sup>ox</sup>) that gave a narrow range of values (5.34–5.40 eV) ca. 0.21–0.25 eV higher than that (5.65 eV) of dibenzochrysenes **1**. In contrast, the 2.40–2.48 eV range of LUMO orbitals of the same species is nearly the same as that (2.49 eV) of dibenzochrysenes. Upon comparison of their photophysical properties with that of dibenzochrysenes, these photophysical data clearly indicate a significantly improved π-conjugation within tetrabenzodehi, mn, qr naphthacene frameworks.

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**FIGURE 2.** UV and PL spectra of tetrabenzo[*de,hi,mn,qr*]naphthacenes **11**, **14a**, **14d**, and **14e** in  $\text{CH}_2\text{Cl}_2$ .

In summary, we have developed a convenient new synthesis of tetrabenzo[*de,hi,mn,qr*]naphthacenes using readily available 1,2-di(phenanthren-4-yl)ethynes through Brønsted acid-mediated aromatization and  $\text{FeCl}_3$  oxidative coupling. Large substituents are more suitable for this approach because of a decrease in undesired oligomerization. On the basis of their photophysical properties, tetrabenzo[*de,hi,mn,qr*]naphthacenes show an extensive  $\pi$ -conjugation, resulting in a raise of the HOMO energy levels and a decrease of the HOMO–LUMO energy gaps, compared to those of unsubstituted dibenzochrysene **1**.

## Experimental Section

**Synthesis of (2-Bromo-4-*tert*-butyl-2'-ethynylbiphenyl) (5).** To a solution of  $\text{Na}_2\text{CO}_3$  (5.95 g, 56.64 mmol) in toluene (45 mL), ethanol (15 mL), and water (15 mL) was added 2-bromo-4-*tert*-butyl-1-iodobenzene (3.19 g, 9.44 mmol) at room temperature, and the solution was degassed with nitrogen. To this mixture was added 2-[(trimethylsilyl)ethynyl]phenylboronic acid (2.26 g, 10.4 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.73 g, 5 mol %), and the resulting mixture was heated to 80 °C for 10 h. After completion of the reaction, the solution was cooled to room temperature and washed with water, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate, washed with brine solution, dried over  $\text{MgSO}_4$ , and concentrated. The residues were eluted through a silica column to give the desired [(2'-bromo-4'-*tert*-butylbiphenyl-2-yl)ethynyl]trimethylsilane (0.54 g, 1.4 mmol) in 61% yield. To a solution of this silyl species (0.54 g, 1.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) and MeOH (10 mL) was added  $\text{K}_2\text{CO}_3$  (0.29 g, 3.89 mmol), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was filtered through a Celite bed and purified on a silica column to afford compound **5** (0.56 g, 1.79 mmol) in 69% yield.

**Synthesis of 4-Bromo-2-*tert*-butylphenanthrene (6).** To a dichloroethane (10 mL) solution of 2-bromo-4-*tert*-butyl-2'-ethynylbiphenyl

(0.56 g, 1.79 mmol) was added  $\text{PtCl}_2$  (0.023 mg, 0.089 mmol) in argon, and the mixture was heated at 80 °C for 10 h. To this solution was added water, and the organic layer was extracted with diethyl ether. The extract was dried over  $\text{MgSO}_4$  and eluted through a silica column to give 4-bromo-2-*tert*-butylphenanthrene (**6**) as a colorless oil (0.373 g, 1.19 mmol, 67%).

**Synthesis of (2-*tert*-Butyl-4-ethynylphenanthrene) (7).** To a solution of  $\text{CuI}$  (0.006 g, 10 mol %) in  $\text{Et}_3\text{N}$  (6 mL) and piperidine (2 mL) was added 4-bromo-2-*tert*-butylphenanthrene (0.10 g, 0.32 mmol) and the mixture was degassed with nitrogen for 15 min at 23 °C. To this resulting solution was added  $\text{Pd}(\text{PPh}_3)_4$  (0.025 g, 5 mol %), and the mixture was stirred for 15 min before being treated with ethynyltrimethylsilane (0.053 mL, 0.38 mmol) dropwise. The solution was heated at 80 °C for 10 h, and then filtered through a Celite bed, concentrated, and eluted through a silica column to give the crude coupling silyl product (0.058 g, 0.21 mmol) in 66% yield. To a  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  solution (1/1, 20 mL) of this silyl species (0.058 g, 0.21 mmol) was added  $\text{K}_2\text{CO}_3$  (0.043 g, 0.317 mmol), and the mixture was stirred at 23 °C for 2.5 h. The solution was filtered through a Celite bed and purified through a silica column to obtain the desired 2-*tert*-butyl-4-ethynylphenanthrene (**7**) (0.040 g, 0.158 mmol) in 76% yield.

**Synthesis of 1,2-Bis(7-*tert*-butylphenanthren-4-yl)ethyne (8).** To a  $\text{Et}_3\text{N}$  (6 mL) and piperidine (3 mL) solution of  $\text{CuI}$  (0.0087 g, 10 mol %) was added compound **6** (0.144 g, 0.4614 mmol), and the mixture was degassed with nitrogen for 15 min at 23 °C. To this resulting solution was added  $\text{Pd}(\text{PPh}_3)_4$  (0.036 g, 5 mol %), and the mixture was stirred for 15 min before addition of compound **7** (0.143 g, 0.554 mmol). The solution was heated at 80 °C for 10 h, filtered through a Celite bed, concentrated, and eluted through a silica column to give 1,2-bis(7-*tert*-butylphenanthren-4-yl)ethyne (**8**) (0.14 g, 0.28 mmol) in 60% yield.

**Synthesis of [5,5'-(1-Chloro-2-iodoethene-1,2-diyl)bis(2-*tert*-butylphenanthrene)] (9).** To a  $\text{CH}_2\text{Cl}_2$  solution (30 mL) of compound **8** (150 mg, 0.31 mmol) was added  $\text{ICl}$  (1.0 M in  $\text{CH}_2\text{Cl}_2$ , 0.30 mL) at –78 °C, and the mixture was stirred at –40 °C for 0.5 h before being quenched with sodium thiosulfate solution. The organic layer was extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$ , and purified by column chromatography to give compound **9** as white solid (123 mg, 0.19 mmol) in 62% yield.

**Synthesis of [(2-*tert*-Butyl-5-(2-*tert*-butylphenanthren-4-yl)pyrene] (10).** To a  $\text{CH}_2\text{Cl}_2$  solution (140 mL) of compound **8** (0.50 g, 1.02 mmol) was added  $\text{CF}_3\text{CO}_2\text{H}$  (7.6 mL, 101 mmol) at 0 °C, and the mixture was stirred for 10 min at 23 °C, giving a dark violet solution. To this solution was added  $\text{CF}_3\text{SO}_3\text{H}$  (0.152 mg, 1.02 mmol) dropwise; the resulting black colored solution was stirred at 23 °C for 30 min before it was washed with water and  $\text{NaHCO}_3$  solution. The organic layer was separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$ , and purified by a silica column to give compound **9** (0.34 g, 0.69 mmol) in 68% yield.

**Synthesis of (2,10-di-*tert*-butyltetrabenzo[*de,hi,mn,qr*]tetracene) (11).** Compound **10** (0.10 g, 0.204 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (70 mL), and the solution was bubbled with argon for 20 min. To this solution was added dry  $\text{CH}_3\text{NO}_2$  (0.20 mL, 5.0 M, 1.01 mmol) and  $\text{FeCl}_3$  dropwise at 23 °C; the reaction was quenched by adding methanol (50 mL) after 30 min. The solvent was removed under reduced pressure and purified by a silica column (46 mg, 47%). Compound **11** was obtained as a pale green crystalline solid after recrystallization from  $\text{CH}_2\text{Cl}_2$ –MeOH (1:2).

**Spectral data for 2,10-Di-*tert*-Butyltetrabenzo[*de,hi,mn,qr*]tetracene (11).** Pale green solid; IR (neat,  $\text{cm}^{-1}$ ) 3054 (m), 2918 (m), 1730 (w), 1365 (s), 1539 (s), 1130 (m), 862 (s), 769 (vs), 871 (s), 691 (vs), 545 (m);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.31

(d,  $J=1.7$  Hz, 1 H), 9.16 (dd,  $J=5.0$  Hz, 7.9 Hz, 1H), 8.26 (d,  $J=1.7$  Hz, 1 H), 8.21 (d,  $J=7.4$  Hz, 1 H), 8.12 (d,  $J=4.2$  Hz, 2 H), 8.02 (t,  $J=7.8$  Hz, 1 H), 1.61 (s, 9 H);  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 138.2, 131.2, 131.1, 128.9, 128.9, 128.7, 127.6, 127.1, 125.6, 125.2 (2 $\times$ CH), 123.9, 123.0, 122.1, 35.4, 31.8 (3  $\times$   $\text{CH}_3$ ); HRMS calcd for  $\text{C}_{38}\text{H}_{32}$  488.2504, found 488.2498.

**Acknowledgment.** We thank National Science Council, Taiwan, for financial support of this work.

**Supporting Information Available:** Spectral data and NMR spectra of new compounds and X-ray crystallographic data of compounds **9** and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.