# Synthesis and Structures of 1,10-Phenanthroline-Based Extended Triptycene Derivatives

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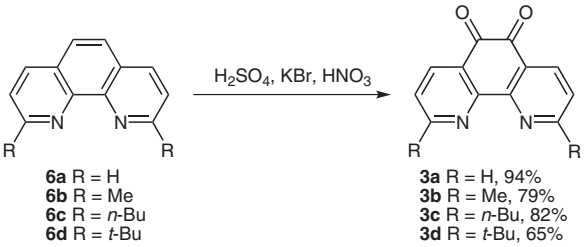
**Abstract:** A series of novel 1,10-phenanthroline-based extended triptycene derivatives were conveniently synthesized in good yields, and their structures were determined by $^1$H NMR, $^{13}$C NMR, MALDI-TOF MS spectra, and elemental analysis.

**Key words:** triptycene, 1,10-phenanthroline, synthesis

Triptycene[1] and its derivatives are a class of interesting compounds with unique three-dimensional rigid frameworks. They have been found wide potential applications in synthetic molecular machines,[2] materials science,[3] and supramolecular chemistry.[4] Triptycene skeleton could be extended by increasing the size of its arene blades, which provided chances for the synthesis of higher iptycenes.[5,6] Recently, King[7] reported a triphenylene-based triptycene, which was extended both parallel and perpendicular to its highest symmetry axis to result in large internal molecular free volumes (IMFV).[8] Although the triptycenes with large IMFV might play an important role in their practical applications, relevant examples are still rare.

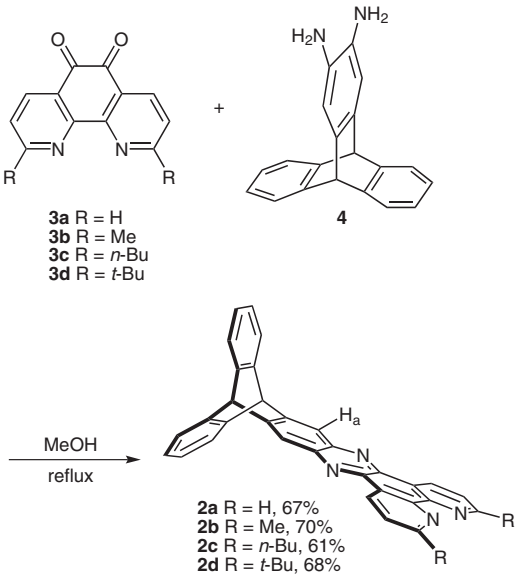
In recent years, we became interested in developing new supramolecular systems based on the triptycene-derived synthetic receptors.[9] Consequently, some of new triptycene derivatives with specific structures and properties are needed. As a part of our continuing work, we herein report the facile synthesis of a series of extended triptycene derivatives by the condensation of 1,10-phenanthroline-5,6-quinones with 2,3-diaminotriptycene or 2,3,6,7,14,15-hexaaminotriptycene. These extended triptycene derivatives containing phenanthroline moiety[10] show large IMFV, and can subsequently find wide potential applications in the development of new supramolecular systems and construction of functional materials.

According to a modified literature procedure,[11] we first prepared the 1,10-phenanthroline-5,6-quinone derivatives **3a–c** in good yields by the oxidation of phenanthroline derivatives **6a–c**[12] (Scheme 1). Similarly, we also obtained compound **3d** in 65% yield by the oxidation of **6d** at room temperature.[13] It was found that the temperature was important to the oxidation reaction. As a result, it was found that no product could be obtained when the reaction temperature of **6d** was above 60 °C.




**Scheme 1** Synthesis of 1,10-phenanthroline-5,6-quinones **3**

With the phenanthroline derivatives **3a–d** in hand, we then performed the condensation of **3a–d** and 2,3-diaminotriptycene **4**[14] in refluxed methanol. The reaction took place smoothly to give the extended triptycene derivatives **2a–d** in good yields (Scheme 2).[15] It was found that compounds **2a–d** have good solubility in chloroform and dichloromethane. In the $^1$H NMR spectra of **2a–d**, one singlet signal for the bridgehead proton and another singlet signal for the aromatic proton $H_a$ were observed. Meanwhile, their $^{13}$C NMR spectra all showed one signal for the bridgehead carbon and 12 signals for the aromatic carbons. These observations were consistent with their $C_2$




**Scheme 2** Synthesis of extended triptycene derivatives **2a–d**

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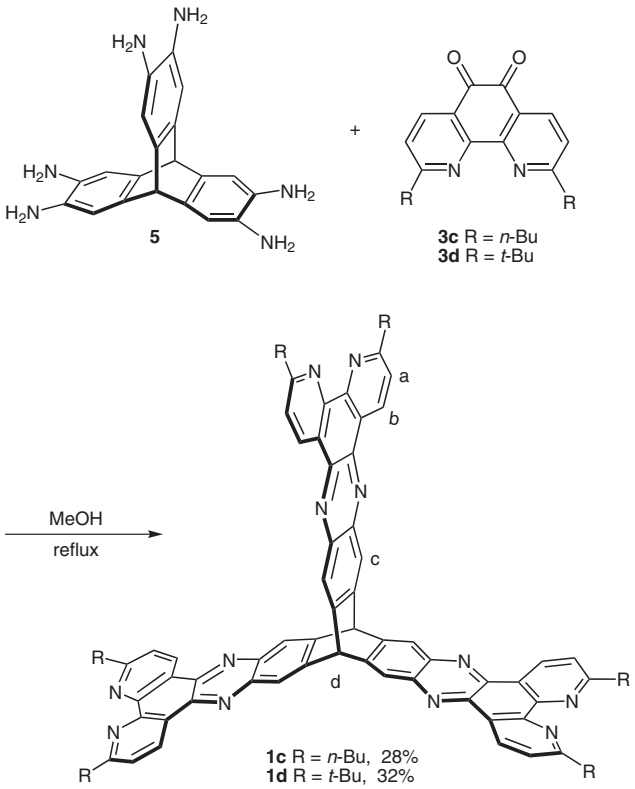
symmetry. Moreover, the structures of **2a–d** were also confirmed by their MALDI-TOF MS spectra and elemental analysis.

When compound **3a** or **3b** was reacted with 2,3,6,7,14,15-hexaaminotriptycene **5**,[14] we obtained yellow solids with low solubilities. MALDI-TOF MS spectra suggested the structures of targeted molecules **1a** and **1b**, but it was difficult to further confirm them by $^1$H NMR and $^{13}$C NMR spectra because of their poor solubilities. However, when **3c** was reacted with **5**, we found that the extended triptycene derivative **1c** could be synthesized in 28% yield (Scheme 3).[16] Similarly, **1d** was obtained in 32% yield from the reaction of **3d** with **5**. Compounds **3c** and **3d** were all purified by silica gel column chromatography, and confirmed by $^1$H NMR, $^{13}$C NMR, MALDI-TOF MS spectra, and elemental analysis. Moreover, it was found that both of **1c** and **1d** have good solubilities in common solvents including chloroform, THF, DMF, and dichloromethane.




**Scheme 3** Synthesis of extended triptycene derivatives **1c** and **1d**

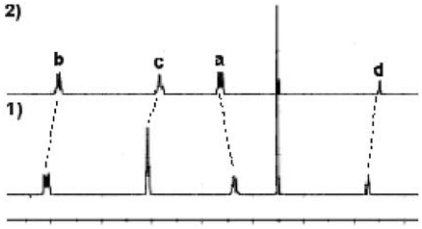



**Figure 1** Partial $^1$H NMR spectra (300Hz, $CDCl_3$) of (1) **1c** and (2) **1d**; resonance protons are labeled in Scheme 3

The partial $^1$H NMR spectra of both **1c** and **1d** were shown in Figure 1. One singlet ($H_d$) for the bridgehead proton and three signals ($H_b$–$H_d$) for the aromatic protons were found. Moreover, the $^{13}$C NMR spectra of both **1c** and **1d** only showed one signal for the bridgehead carbon and nine signals for the aromatic carbons. These results suggested they all have high $D_{3v}$ symmetry. Compared with **1c**, the signals of protons $H_b$–$H_d$ of **1d** shifted obviously upfield while $H_a$ shifted downfield, which was probably due to the stronger electron-donating ability of *tert*-butyl of **1d**. Moreover, we also calculated the structures of **1c** and **1d** by AM1 method, and the IMFV of **1c** and **1d** were found to be about 1150 Å$^3$, which is significantly larger than that reported by King.[7]

In summary, we have shown a facile approach to synthesize a series of 1,10-phenanthroline-based extended triptycene derivatives via the condensation of 2,3-diaminotriptycene or 2,3,6,7,14,15-hexaaminotriptycene with 1,10-phenanthroline-5,6-quinone derivatives. The useful 1,10-phenanthroline blocks were induced to triptycene skeleton to form new rigid scaffold geometry and generate large IMFV, which might be found potential applications in molecular assemblies and material chemistry.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(13) **Preparation and Spectroscopic Data of 3d**
An ice-cold mixture of concentrated $H_2SO_4$ (10 mL) and $HNO_3$ (5 mL) was added to **6d** (438 mg, 1.5 mmol) and of KBr (1 g, 8.4 mmol). The mixture was reacted at r.t. for 8 h. The yellow solution was poured to over 500 mL of ice, neutralized carefully with NaOH until neutral to slightly acidic pH, and extracted with $CHCl_3$ followed by drying with $Na_2SO_4$ and removal of solvent. The crude product was purified by silica gel column chromatography (eluant: PE–$CH_2Cl_2$ = 2:3) to afford **3d** in 65% yield as white solid; mp 144–146 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 1.52 (s, 18 H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 179.3, 177.1, 152.3, 137.1, 125.8, 121.0, 39.1, 29.8. MS (EI): *m/z* = 322 [M$^+$]. Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.34; H, 6.69; N, 8.57.

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(15) **Experimental Procedure and Characterizations for Representative Compound 2a**
To a solution of compound **4** (284 mg, 1 mmol) in MeOH (50 mL) was added **3a** (273 mg, 1.3 mmol). The solution was stirred under $N_2$ overnight to give a yellow solution. The solvent was removed by rotary evaporation, and the red-orange residue was purified by silica gel column chromatography (eluant: MeOH–$CH_2Cl_2$ = 1:100) to give the product **2a** in 67% yield as yellow solid; mp >300 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 9.45 (dd, *J* = 1.8, 6.3 Hz, 2 H), 9.17 (dd, *J* = 1.8, 2.7 Hz, 2 H), 8.19 (s, 2 H), 7.63–7.59 (m, 2 H), 7.55–7.51 (m, 4 H), 7.15–7.11 (m, 4 H), 5.74 (s, 2 H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 152.0, 147.7, 147.0, 143.6, 141.6, 140.0, 133.2, 127.3, 126.2, 124.2, 123.8, 122.8, 53.8. MS (MALDI-TOF): *m/z* = 459.2 [M + H]$^+$, 481.1 [M + Na]$^+$, 497.1 [M + K]$^+$. Anal. Calcd for $C_{32}H_{18}N_4$: C, 83.82; H, 3.96; N, 12.22. Found: C, 83.71; H, 4.13; N, 12.14.

(16) **Experimental Procedure and Characterizations for Representative Compound 1c**
To a solution of compound **5** (344 mg, 1 mmol) in MeOH (50 mL) was added **3c** (1.38 g, 4.3 mmol). The solution was stirred under $N_2$ overnight to give a yellow solution. The solvent was removed by rotary evaporation, and the red-orange residue was purified by silica gel column chromatography (eluant: MeOH–$CH_2Cl_2$ = 1:50) to give the product **1c** in 28% yield as yellow solid; mp >300 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 9.55 (d, *J* = 8.3 Hz, 6 H), 8.54 (s, 6 H), 7.69 (d, *J* = 8.3 Hz, 6 H), 6.36 (s, 2 H), 3.35–3.29 (m, 12 H), 1.90–1.89 (m, 12 H), 1.57–1.50 (m, 12 H), 1.02 (t, *J* = 7.3 Hz, 18 H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 165.9, 147.5, 143.5, 141.4, 140.8, 133.4, 124.9, 124.2, 123.0, 53.3, 39.0, 31.8, 22.9 14.1. MS (MALDI-TOF): *m/z* = 1203.6 [M + H]$^+$. Anal. Calcd for $C_{78}H_{74}N_{12}\cdot H_2O$: C, 78.23; H, 6.40; N, 14.04. Found: C, 78.34; H, 6.23; N, 13.91.