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# Iptycene Quinones: Synthesis and Structure

Xiao-Zhang Zhu[†,‡] and Chuan-Feng Chen*[,†]

*Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate School, Chinese Academy of Sciences, Beijing 100080, China*

*cchen@iccas.ac.cn*

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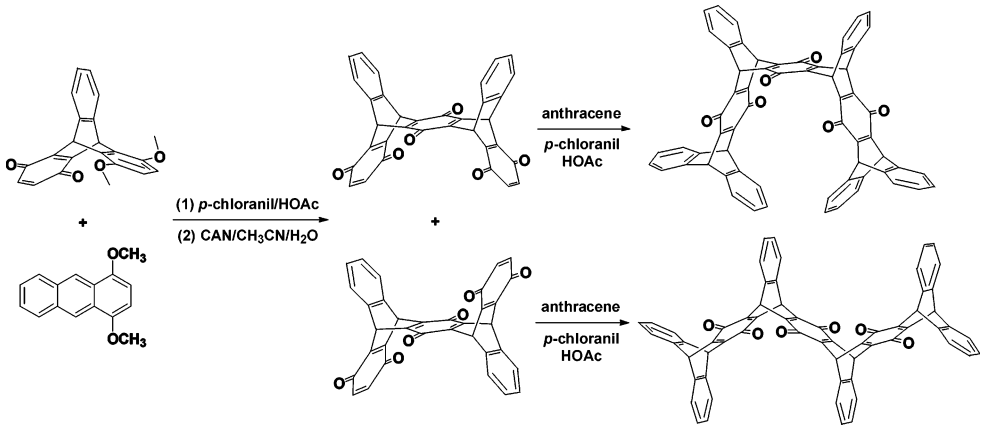


A practical and efficient method to synthesize iptycene quinones has been developed. As a result, a series of pentiptycene quinones **8**−**16** were conveniently synthesized by one-pot reaction of triptycene quinone **4** or **5** with anthracene **1** or its derivatives **2**−**3** in refluxing acetic acid in the presence of *p*-chloranil, followed by CAN oxidative demethylation. Similarly, a series of heptiptycene quinones **17**−**23** with U-shaped cavities were achieved with pentiptycene quinone **10** and triptycene diquinone **6** as precursors. Non-iptycene triquinones **24** with one tweezer-shaped cavity and **25** with two U-shaped cavities were synthesized by one-pot reactions of anthracene with pentiptycene triquinones **16a** and **16b**, respectively. Non-iptycene triquinone **26** with a dendritic structure was conveniently obtained by the reaction of anthracene with either pentiptycene diquinone **12** or triptycene triquinone **7**. The structures of regioisomers **16a** and **16b** were determined by the single-crystal structure analysis of **16b**. The structures of other regioisomers, including heptiptycene tetraquinones **19a/19b/19c** and heptiptycene triquinones **23a/23b**, were identified by comparative reactions.

## Introduction

Triptycene quinones[1] form an interesting class of compounds for their (1) rigid 3D structure of triptycene, (2) unique electrochemical[2] and photochemical[3] properties, (3) readily derivative ability, and (4) potential applications in material[4] and supramolecular chemistry.[5] Moreover, triptycene quinones exhibit interesting intramolecular charge-transfer characteristics.[6] Their derivatives have also found applications as acceptors, with

[†] Center for Molecular Science.
[‡] Graduate School.

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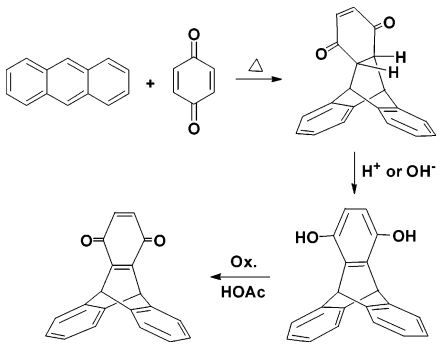
**SCHEME 1**




porphyrin and tetrathiafulvalene serving as donors, for the synthesis of electron-transfer model compounds to mimic the primary steps in photosynthesis[7] and molecular rectifiers.[8] Recently, there is increasing attention in the chemical and biological activities of triptycene quinones.[9] In particular, a number of triptycene quinones and their derivatives were found to show potent anticancer and antimalarial activities.[9a,10]

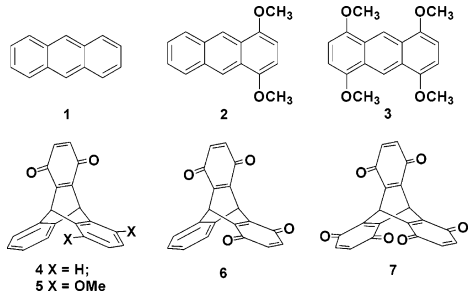
Iptycenes[11] are extended triptycenes. They have attracted considerable interest not only from their synthetic challenge but also for their attractive rigid frameworks, unique intramolecular cavities, and exceptional thermal stability. Iptycene quinones[9c,12] refer to derivatives of iptycene bearing at least one triptycene quinone unit. Pentiptycene monoquinones are a class of the most simple iptycene quinones. Their derivatives were found to be promising reagents for the preparation of fluorescent porous polymeric sensors for TNT,[13a] fluorescent chemosensors for $Cu^{2+}$,[13b] materials with monolayer assembly structures,[13c] electron-donor porphyrin quinone diads and triads,[7b,c] and building blocks for the construction of novel chain and channel networks.[13d] Compared with triptycene quinones and iptycenes, still less is known about iptycene quinones, especially complicated ones.

Typically, triptycene quinones are synthesized by the multistep method[1] as shown in Scheme 1. Recently, Senge and Kurreck[7b] reported a one-step synthesis of triptycene quinones by the reaction of anthracene and excess quinones in acetic acid. Although some simple pentiptycene quinones and their derivatives are known,[13] there is not a practical and efficient method for the synthesis of iptycene quinones until now. To a great extent, it restricts the development of iptycene quinone chemistry.

To develop novel receptors[14] based on iptycene quinones and their derivatives, iptycene quinones with unique molecular cavities are required. Initially, we followed the synthetic strategy of Senge and Kurreck to synthesize iptycene quinones but found that it had some problems. First, it consumed excess quinones so that it would be impractical when the quinones were not easily obtained. Second, complex results would be obtained if the excess iptycene multiquinones were used. Moreover, the oxidative capacity of the iptycene quinone is usually weaker than that of the simple quinone, which has a direct effect on the reactive result (low yield or only semiquinone product obtained). Considering that excess quinones only act as oxidants, we anticipated that *p*-chloranil, a commercially available stronger oxidant, could be utilized instead of the excess quinones in the one-pot method to synthesize iptycene quinones. In this paper, we report a practical and efficient method for the synthesis of iptycene quinones, including a series of pentiptycene quinones, heptiptycene quinones, and non-iptycene quinones. Moreover, the structures of regioisomers were determined by X-ray single-crystal structure analysis and comparative reactions.

## Results and Discussion

**Pentiptycene Quinones.** Triptycene monoquinones **4**[1a] and **5**[1b] were prepared by the reactions of anthracene **1** and 1,4-dimethoxyanthracene **2** with excess *p*-benzoquinone in a one-pot approach, respectively. Bisquinone **6**[1b] was obtained by the oxidation of **5** with cerium (IV) ammonium nitrate (CAN).[15] Triptycene triquinone **7**[1c] was synthesized by the reaction of 1,4,5,8-tetramethoxyanthracene **3** with excess *p*-benzoquinone in refluxing acetic acid, followed by demethylation with hydriodic acid and then oxidized by sodium bichromate in acetic acid.

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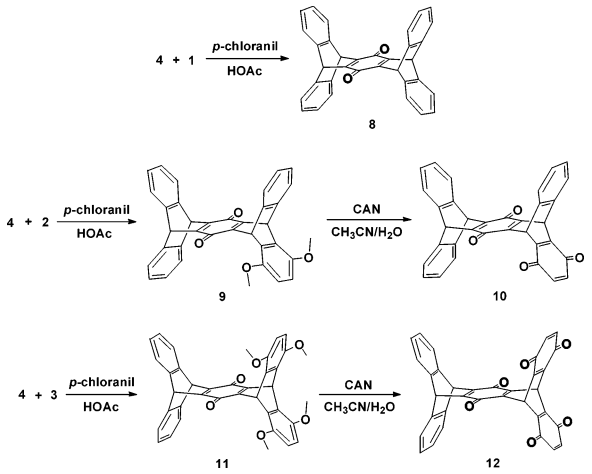
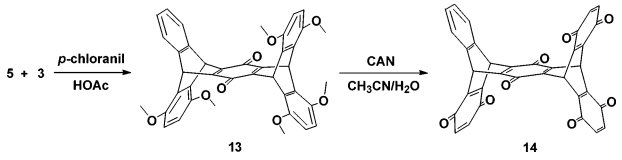
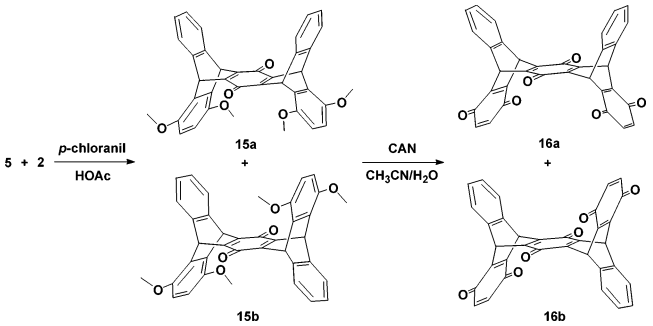
We first examined the reaction of 1 equiv of triptycene quinone **4** with anthracene in refluxing acetic acid in the presence of 1 equiv of *p*-chloranil and found that the pentiptycene monoquinone **8**[13a] could be directly obtained in 78% yield. Furthermore, the same reaction conditions were found to be suitable for the synthesis of other pentiptycene quinones with open cavities. Consequently, one-pot reaction of triptycene quinone **4** with 1,4-dimethoxyanthracene **2** gave dimethoxypentiptycene quinone **9** in 82% yield. Compound **9** was then demethylated by CAN oxidation to give pentiptycene diquinone **10**[9c] in a nearly quantitative yield. Similarly, the pentiptycene triquinone **12** was conveniently synthesized by the CAN oxidation of tetramethoxypentiptycene quinone **11**, which was obtained in 80% yield by the reaction of **4** with 1,4,5,8-tetramethoxyanthracene **3** in HOAc in the presence of *p*-chloranil. The $^1$H NMR spectrum of **12** showed two singlets for the bridgehead protons ($\delta$ 6.55, 5.81), a singlet for the CH═CH protons of the quinoid ring ($\delta$ 6.66), and two 4-proton multiplets for the aryl protons. Its $^{13}$C NMR spectrum showed two signals for the bridgehead carbons ($\delta$ 47.5, 38.7) and one signal for the carbonyl carbons ($\delta$ 180.9), which is consistent with its structure with $D_{2h}$ symmetry.




The reaction of dimethoxytriptycene quinone **5** with 1,4,5,8-tetramethoxyanthracene **3** in HOAc in the presence of *p*-chloranil gave pentiptycene quinone **13** in 63% yield. Further treatment of **13** with CAN in aqueous acetonitrile produced pentiptycene tetraquinone **14** in 82% yield. The $^1$H NMR spectrum of **14** showed two singlets for the bridgehead protons ($\delta$ 6.56, 6.17), three singlets for the CH═CH protons of the quinoid ring ($\delta$ 6.67, 6.65, 6.63), and two 2-proton multiplets for the aryl protons. In its $^{13}$C NMR spectrum, three peaks for the carbonyl carbons ($\delta$ 182.0, 180.8, 176.3) and two peaks for the bridgehead carbons ($\delta$ 42.3, 38.8) were observed.

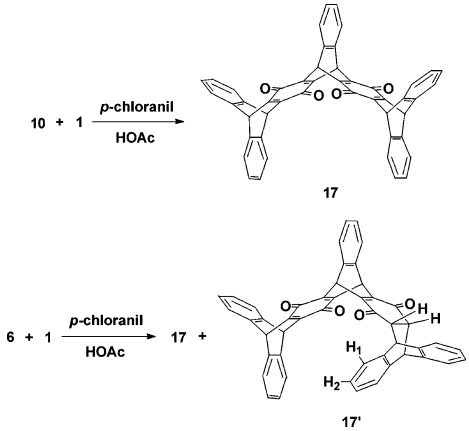



When the reaction of dimethoxytriptycene monoquinone **5** with dimethoxyanthracene **2** took place in refluxing acetic acid in the presence of *p*-chloranil, a mixture of two regioisomers **15a** and **15b** was obtained in 82% of total yield, which is obviously higher than the result with excess triptycene quinone as oxidant.[9c] The isomers **15a** and **15b** could hardly be separated by column chromatography; however, we found that their CAN oxidation products of pentiptycene triquinones **16a** and **16b** could be separated by column chromatography in 45% and 28% yields, respectively. The polarity of **16b** is smaller than that of **16a** when a mixture of dichloromethane/petroleum ether (3:1 v/v) was used as eluent. The isomers **16a** and **16b** showed almost the same $^1$H NMR spectrum (one singlet for the bridgehead protons, one singlet for the CH═CH protons of the quinoid ring, and two 2-proton multiplets for the aryl protons) and $^{13}$C NMR spectrum (two peaks for the carbonyl carbons, six peaks for the aromatic carbons, and one peak for the bridgehead carbons) and could not be distinguished by ordinary spectroscopic methods. Fortunately, we obtained the single crystals of the isomer **16b** from dichloromethane and *n*-hexane. The result of X-ray crystal structure analysis of **16b** showed that the two terminal quinoid rings are in the trans position (see Supporting Information). Interestingly, dichloromethane molecules were found to be incorporated in the crystal. Moreover, this combination strength between **16b** and dichloromethane was so strong that dichloromethane could not easily be removed even if the sample was heated more than one week under reduced pressure. Similar cases also occurred in the other iptycene multiquinones, but most of the precursor methoxy-substituted iptycene quinones did not show this phenomenon.



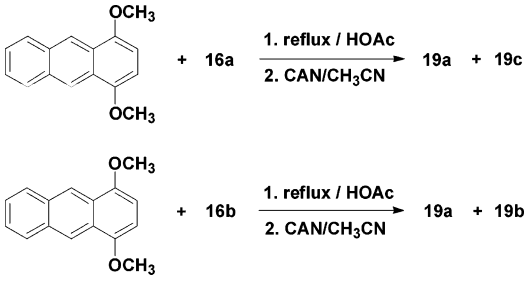

**Heptiptycene Quinones.** Heptiptycene diquinone **17** with a U-shaped cavity is composed of two equivalent pentiptycene diquinone **10** units. It was conveniently synthesized by a one-pot reaction of compound **10** with anthracene in refluxing acetic acid in the presence of *p*-chloranil. Under the same conditions, the reaction of triptycene diquinones **6** with 2 equiv of anthracenes produced heptiptycene diquinone **17** along with semiquinone **17′** obtained in considerable yield. In this case, the yield of compound **17** could be improved with the increase of the reaction time. The $^1$H NMR spectrum of **17** showed two singlets for the bridgehead protons ($\delta$ 6.09, 5.72) and two 10-proton multiplets for the aryl protons. Its $^{13}$C NMR spectrum showed two peaks for the bridgehead carbons ($\delta$ 47.3, 42.2) and one signal at $\delta$ 178.9 for the carbonyl carbons. Although there are two possible isomers, a single adduct of **17′** could be deduced from its $^1$H NMR spectrum in which only three singlets for the bridgehead protons ($\delta$ 5.81, 5.78, 4.55) and one singlet for the CH−CH protons of the semiquinoid ring

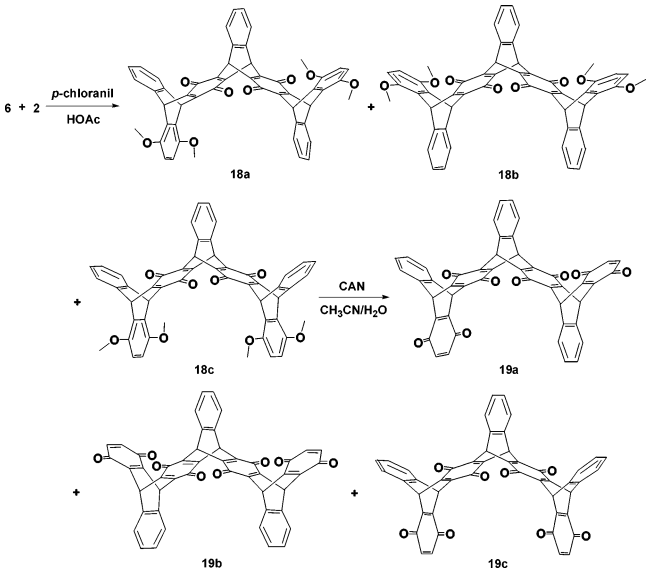
($\delta$ 3.06) besides aromatic proton signals were observed. The $^{13}$C NMR spectrum of **17′** showed one magnetically unique sp$^3$-hybridized carbon ($\delta$ 38.8) of the semiquinoid ring, three peaks for the bridgehead carbons ($\delta$ 51.1, 50.3, 42.3), and two peaks for the carbonyl carbons ($\delta$ 193.3, 178.5), which is also consistent with its structure. Furthermore, we found that the chemical shift of its aromatic proton H2 positioned remarkably upfield ($\delta$ 5.48), which suggested that **17′** is an endo-adduct.



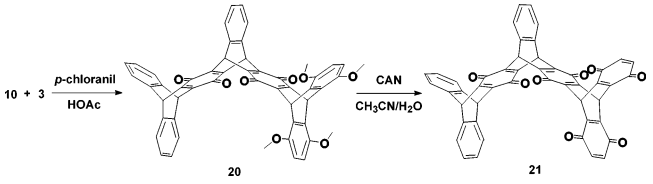

In the presence of *p*-chloranil, the reaction of triptycene diquinone **6** with 2 equiv of **2** in acetic acid gave a mixture of three adducts **18a**, **18b**, and **18c**, which could not be separated by the conventional column chromatography method. However, their CAN oxidative products **19a**, **19b**, and **19c** could be obtained by careful separation with column chromatography. The structure of heptiptycene tetraquinone **19a** was easily distinguished from the other two isomers by the NMR spectra. The $^1$H NMR spectrum of **19a** had three magnetically unique bridgehead protons ($\delta$ 6.04, 6.03, 6.01) and two unique vinyl protons of the quinoid rings ($\delta$ 6.50, 6.46). However, the isomers **19b** and **19c** showed very similar $^1$H NMR and $^{13}$C NMR spectra so that their structures could not be directly determined. To solve this problem, comparative reactions were carried out. Thus, by the reaction of 2 equiv of **16a** with 1,4-dimethoxyanthracene **2** in HOAc in the presence of *p*-chloranil and then CAN oxidation, two isomers of heptiptycene tetraquinones **19a** and **19c** were obtained. Similarly, the isomers of **19a** and **19b** were produced from **16b** with **2** (Scheme 2). The structures of the isomers **19b** and **19c** could be determined by TLC analysis compared with those for the products obtained from the reaction of **6** and **2** shown as above. The polarity order for the isomers in dichloromethane and petroleum ether (1:1 v/v) is as follows: **19a** < **19b** < **19c**.

**SCHEME 2**

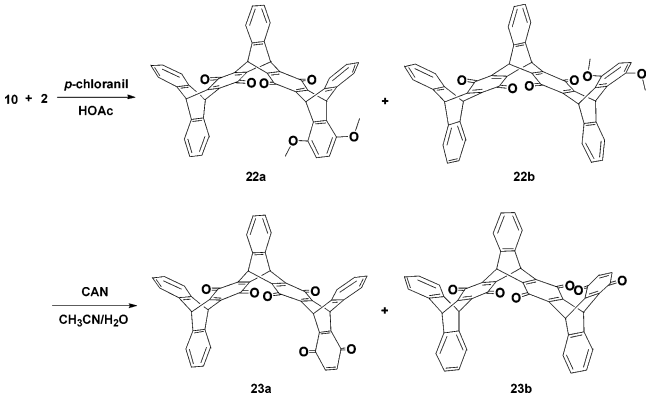


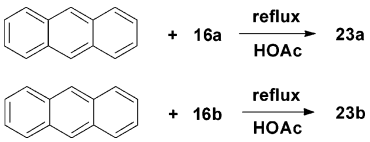

The reaction of pentiptycene quinone **10** with 1,4,5,8-tetramethoxyanthracene in acetic acid in the presence of *p*-chloranil gave the adduct **20** in 93% yield, which was further oxidized by CAN to yield heptiptycene tetraquinone **21** in 35% yield. **21** with U-shaped structure is composed of a pentiptycene diquinone unit and a pentiptycene tetraquinone unit. Its $^1$H NMR spectrum showed three singlets for the bridgehead protons ($\delta$ 6.51, 6.11, 5.74) and two singlets for the CH=CH protons of terminal quinoid rings ($\delta$ 6.62, 6.60). Its $^{13}$C NMR spectrum showed four signals for the carbonyl carbons (180.8, 180.7, 178.6, 176.4) and three signals for the bridgehead carbons (47.3, 42.3, 38.7) as required.




Similarly, the one-pot reaction of pentiptycene quinone **10** with 1,4-dimethoxyanthracene gave a mixture of two isomers **22a** and **22b**, which were then demethylated to the mixture of heptiptycene triquinone **23a** and **23b** in 80% yield. Similar to the case of **18**, **22a** and **22b** were hardly separated, but their oxidative products **23a** and **23b** could be obtained by the column chromatography method. The isomers **23a** and **23b** showed similar $^1$H

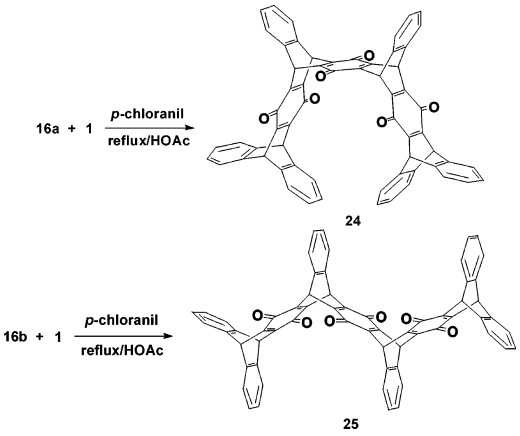


**SCHEME 3**

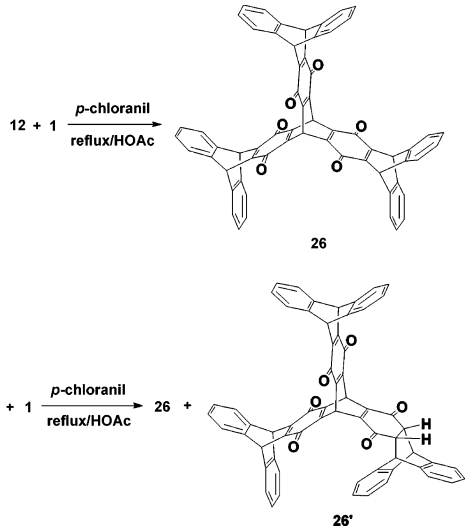



NMR and $^{13}C$ NMR spectra. Their structures were confirmed by comparative experiments with the products obtained by the reactions of 1 equiv of **1** with **16a** and **16b**, respectively (Scheme 3).

**Non-iptycene Quinones.** Non-iptycene triquinone **24** has a large tweezers-shaped molecular cavity. It was conveniently synthesized in 70% yield by the one-pot reaction of pentiptycene triquinone **16a** with anthracene in refluxing acetic acid in the presence of *p*-chloranil. At the same conditions, the reaction of **16b** with anthracene gave non-iptycene triquinone **25,** which is composed of two equivalent U-shaped cavities of heptiptycene triquinone. **24** and **25** are a couple of isomers. Although they all have 54 aromatic carbons and 8 aliphatic carbons, their $^{13}C$ NMR spectra showed only two signals for the bridgehead carbons and two signals for the carbonyl carbons; meanwhile, there were 12 signals in **24** and 10 signals in **25** for aromatic carbons. Their $^{1}H$ NMR spectra are also simple and showed only two singlets for the bridgehead protons and two 10-proton multiplets for the aryl protons. These results indicated that they have highly symmetric structures.




In the presence of *p*-chloranil, the reaction of pentiptycene triquinone **12** with 2 equiv of anthracene in refluxing acetic acid gave heptiptycene triquinone **26** in 17.2% yield. Under the same conditions, the one-pot reaction of triptycene triquinone **7** with excess anthracene produced a semiquinone derivative **26′** in addition to **26**. Heptiptycene triquinone **26** with a dendritic structure is composed of three equivalent U-shaped cavities. In its $^{1}H$ NMR spectrum, only two magnetically unique bridgehead protons ($\delta$ 6.36, 5.59) and two unique aryl protons were observed. Its $^{13}C$ NMR spectrum showed only two peaks for the bridgehead carbons ($\delta$ 46.3, 28.7) and one peak for the carbonyl carbons ($\delta$ 176.6), which is consistent with its $D_{3h}$ symmetry. Compared with the NMR spectrum of **26**, that of **26′** is much more complicated, which is also consistent with its structure.




## Conclusion

In this paper, we have described a practical and efficient method to synthesize iptycene quinones. As a result, a series of pentiptycene quinones, heptiptycene quinones, and non-iptycene triquinones were conveniently synthesized and characterized. The structures of the regioisomers were identified by X-ray single-crystal structure analysis and comparative reactions.

Molecular tweezers and cleft[14,16] are commonly used concepts for the host molecules that can form "sandwich" $\pi$-system hydrophobic complexes. Iptycene quinones have not only affluent electrochemical properties but also unique 3D cavities. Therefore, they could be considered as potential novel receptors for host−guest chemistry. Studies on the synthesis of more complex iptycene quinones (super-iptycene quinones) and the properties of iptycene quinones and their derivatives are now in progress in our laboratory.

## Experimental Section

**General Methods.** Melting points, taken on an electrothermal melting point apparatus, are uncorrected. IR spectra were recorded on a FT-IR spectrometer using KBr discs. $^{1}H$ and $^{13}C$ NMR spectra were obtained in $CDCl_3$ solution (except where mentioned otherwise). MALDI-TOF mass spectra were obtained by using 2-cyano-4′-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Analytical Laboratory of the Institute. Materials obtained commercially were used without further purification. 1,4-Dimethoxyanthracene **2**[9a] and 1,4,5,8-tetramethoxyanthracene **3**[17] were prepared according to the literature procedures.[18]

**9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dione (4).**[1a] A mixture of anthracene (0.8 g, 4.5 mmol) and *p*-quinone (2.7 g, 25 mmol) in acetic acid (40 mL) was refluxed for 3 h. The reaction mixture was then poured into water, and the precipitate was filtrated. The crude product was washed with hot water and purified by column chromatography to give 1.11 g (87%) of **4**.

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**9,10-Dihydro-5,8-dimethoxy-9,10-*o*-benzenoanthracene-1,4-dione (5).**[1b] A mixture of *p*-quinone (9.6 g, 88.9 mmol) and 1, 4-dimethoxyanthracene (4.23 g, 17.7 mmol) in acetic acid (120 mL) was refluxed for 5 h. The reaction mixture was then poured into water, and the precipitate was filtrated. The crude product was washed with hot water and purified by column chromatography to give 4.39 g (72%) of **5**.

**9,10-Dihydro-9,10-(*o*-benzeno)anthracene-1,4,5,8-tetraone (6).**[1b] A mixture of **5** (0.85 g, 2.47 mmol) and CAN (4.1 g, 7.48 mmol) in acetonitrile (120 mL) and water (25 mL) was stirred at room temperature for 2 h. The reaction mixture was extracted with dichloromethane. The organic layer was dried over anhydrous $Na_2SO_4$ and then concentrated under reduced pressure to give 0.75 g (98%) of **6**, which was used without further purification.

**Triptycene Triquinone (7).**[1c] A mixture of **3** (1.19 g, 4.0 mmol) and *p*-quinone (2.16 g, 20.0 mmol) in acetic acid (80 mL) was refluxed for 2 d. The resulting mixture was cooled, filtrated, and then washed with DMF and acetone to give an adduct, which was dissolved in HI acid (30 mL) and HOAc (100 mL) and then refluxed for 8 h. The reaction mixture was cooled, filtrated, and washed with acetone to give a solid, which was further oxidized with $Na_2Cr_2O_7{\cdot}2H_2O$ (0.98 g, 3.3 mmol) in HOAc (100 mL) for 2 h. The reaction mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous $Na_2SO_4$. Removal of the solvent gave 0.81 g (59% yield for three steps) of **7** as a yellow solid.

**5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzeno)pentacene-6,13-dione (8).**[13a] A mixture of **4** (0.28 g, 1 mmol), **1** (0.18 g, 1 mmol), and *p*-chloranil (0.25 g, 1 mmol) in HOAc (60 mL) was refluxed for 24 h. The resulting mixture was cooled to room temperature. The precipitate was filtered, washed with ether, and then dried in air to give 0.36 g (78%) of **8** as a yellow solid.

**1,4-Dimethoxyl-5,6,7,12,13,14-hexahydro-5,14:7,12-bis-(*o*-benzeno)pentacene-6,13-dione (9).** A mixture of **5** (0.69 g, 2 mmol), **1** (0.36 g, 2 mmol), and *p*-chloranil (0.49 g, 2 mmol) in HOAc (75 mL) was refluxed for 24 h. The resulting mixture was cooled to room temperature. The precipitate was filtered, washed with ether, and then dried under reduced pressure to give 0.85 g (82%) of **5** as a brick-red solid, which was further purified by column chromatography over silica gel with dichloromethane and petroleum ether (60−90 °C) (1:3, v/v) as the eluent: mp >320 °C; IR $\nu$ 1645 $cm^{-1}$; $^1H$ NMR $\delta$ 7.35−7.42 (m, 6H), 6.96−7.01 (m, 6H), 6.50 (s, 2H), 6.22 (s, 2H), 5.78 (s, 2H), 3.78 (s, 6H); $^{13}C$ NMR $\delta$ 180.0, 150.9, 150.8, 149.5, 144.2, 143.8, 143.7, 133.5, 125.4, 125.3, 125.2, 124.4, 124.1, 109.4, 56.4, 47.4, 41.4; MALDI-TOF MS *m/z* 520.9 ($M^+$). Anal. calcd for $C_{36}H_{24}O_4$: C, 83.06; H, 4.65. Found: C, 82.82; H, 4.70.

**1,4,5,6,7,12,13,14-Octahydro-5,14:7,12-bis(*o*-benzeno)-pentacene-1,4,6,13-tetraone (10).** To the solution of **9** (1.06 g, 2 mmol) in acetonitrile (200 mL) and water (20 mL) was added CAN (3 g, 5.5 mmol). After being stirred at room temperature for 5 h, the reaction mixture was poured into water, filtrated, washed with water, and then dried in air to give 0.98 g (99%) of **10** as a yellow solid. Further purification for elemental analysis was performed by column chromatography over silica gel with dichloromethane and petroleum ether (60−90 °C) (1:1, v/v) as eluent: mp >320 °C; IR $\nu$ 1660 $cm^{-1}$; $^1H$ NMR $\delta$ 7.37−7.44 (m, 6H), 6.98−7.04 (m, 6H), 6.60 (s, 2H), 6.14 (s, 2H), 5.79 (s, 2H); $^{13}C$ NMR $\delta$ 182.1, 178.6, 151.5, 151.1, 150.5, 143.2, 142.0, 135.2, 125.7, 125.4, 125.1, 124.2, 47.2, 42.0; MALDI-TOF MS *m/z* 492.4 ($[M + 2H]^+$). Anal. calcd for $C_{34}H_{18}O_4{\cdot}0.5CH_2Cl_2$: C, 77.75; H, 3.59. Found: C, 77.63; H, 3.72.

**1,1′,4,4′-Tetramethoxy-5,6,7,12,13,14-hexahydro-5,14:7,-12-bis(*o*-benzeno)pentacene-6,13-dione (11).** A mixture of **4** (0.24 g, 0.85 mmol), **3** (0.25 g, 0.84 mmol), and *p*-chloranil (0.23 g, 0.93 mmol) in HOAc (30 mL) was refluxed for 27 h. Workup as described for **9** yielded 0.39 g (80%) of **11** as a brick-red solid: mp >320 °C; IR $\nu$ 1646 $cm^{-1}$; $^1H$ NMR $\delta$ 7.35−7.38 (m, 4H), 6.96−6.99 (m, 4H), 6.62 (s, 2H), 6.49 (s, 4H), 5.77 (s, 2H), 3.79 (s, 12H); MALDI-TOF MS *m/z* 580.6 ($M^+$). Anal. calcd for $C_{38}H_{28}O_6{\cdot}0.5H_2O$: C, 77.41; H, 4.96. Found: C, 77.72; H, 5.07.

**1,1′,4,4′,5,6,7,12,13,14-Decahydro-5,14:7,12-bis(*o*-benzeno)pentacene-1′,4′,1,4,6,13-tetraone (12).** To the solution of **11** (0.18 g, 0.31 mmol) in acetonitrile (40 mL) and water (5 mL) was added CAN (1 g, 1.8 mmol). The reaction mixture was stirred at room temperature for 3.5 h. Workup as described for **10** gave 0.16 g (99%) of **12** as a yellow solid: mp >320 °C; IR $\nu$ 1656 $cm^{-1}$; $^1H$ NMR $\delta$ 7.40−7.43 (m, 4H), 7.02−7.04 (m, 4H), 6.66 (s, 4H), 6.55 (s, 2H), 5.81 (s, 2H); $^{13}C$ NMR $\delta$ 180.9, 152.0, 151.7, 143.4, 135.4, 125.7, 124.5, 47.5, 38.7; MALDI-TOF MS *m/z* 520.8 ($M^+$). Anal. calcd for $C_{34}H_{16}O_6{\cdot}H_2O$: C, 75.83; H, 3.37. Found: C, 75.94; H, 3.63.

**1,1′,4,4′,8,11-Hexamethoxy-5,6,7,12,13,14-hexahydro-5,-14:7,12-bis(*o*-benzeno)pentacene-6,13-dione (13).** A mixture of **3** (0.17 g, 0.5 mmol), **5** (0.15 g, 0.5 mmol), and *p*-chloranil (0.13 g, 0.5 mmol) in HOAc (30 mL) was refluxed for 40 h. Workup as described for **9** yielded 0.2 g (63%) of **13** as a brick-red solid: mp >320 °C; IR $\nu$ 1649 $cm^{-1}$; $^1H$ NMR $\delta$ 7.36−7.39 (m, 2H), 6.93−6.96 (m, 2H), 6.61 (s, 2H), 6.48 (s, 6H), 6.19 (s, 2H), 3.78 (s, 12H), 3.77 (s, 6H); MALDI-TOF MS *m/z* 640.6 ($M^+$). Anal. calcd for $C_{40}H_{32}O_8{\cdot}0.5H_2O$: C, 73.95; H, 5.12. Found: C, 74.10; H, 5.42.

**1,1′,4,4′,5,6,7,8,11,12,13,14-Dodecahydro-5,14:7,12-bis(*o*-benzeno)pentacene-1,1′,4,4′,8,11,6,13-octaone (14).** To the solution of **13** (0.13 g, 0.2 mmol) in acetonitrile (40 mL) and water (5 mL) was added CAN (1 g, 1.8 mmol). The reaction mixture was stirred at room temperature for 2 h. Workup as described for **10** gave 0.09 g (82%) of **14** as a yellow solid: mp >320 °C; IR $\nu$ 1660 $cm^{-1}$; $^1H$ NMR $\delta$ 7.44−7.48 (m, 2H), 7.04−7.09 (m, 2H), 6.67 (s, 2H), 6.65 (s, 2H), 6.63 (s, 2H), 6.56 (s, 2H), 6.17 (s, 2H); $^{13}C$ NMR $\delta$ 182.0, 180.8, 176.3, 152.0, 151.9, 151.4, 142.0, 135.4, 126.0, 125.5, 42.3, 38.8; MALDI-TOF MS *m/z* 550.5 ($M^+$). Anal. calcd for $C_{34}H_{14}O_8{\cdot}0.5H_2O$: C, 72.99; H, 2.70. Found: C, 72.84; H, 2.76.

**1,4,8,11-Tetramethoxy-5,6,7,12,13,14-hexahydro-*cis*/*trans*-5,14:7,12-bis(*o*-benzeno)pentacene-6,13 -dione (15a/15b).** A mixture of **5** (4.06 g, 11.8 mmol), **2** (3.1 g, 13.0 mmol), and *p*-chloranil (3.2 g, 13.0 mmol) in HOAc (300 mL) was refluxed for 28 h. Workup as described for **9** yielded 5.62 g (82%) of isomer **15a/15b** as a brick-red solid, which was used without further purification for the next step.

**1,4,5,6,7,8,11,12,13,14-Decahydro-*cis*/*trans*-5,14:7,12-bis(*o*-benzeno)pentacene-1,4,8,11,6,13-hexaone (16a/16b).** To the mixture of **15a/15b** (0.99 g, 1.71 mmol) in acetonitrile (100 mL) and water (20 mL) was added CAN (5.6 g, 10.2 mmol). The mixture was stirred at room temperature for 5 h. Workup as described for **10** with $CH_2Cl_2$ and petroleum ether (60−90 °C) (3:1, v/v) as eluent gave 0.25 g (28%) of **16a** and 0.4 g (45%) of **16b**. **16a**: a yellow solid, mp >320 °C; IR $\nu$ 1655 $cm^{-1}$; $^1H$ NMR $\delta$ 7.41−7.44 (m, 4H), 7.01−7.03 (m, 4H), 6.60 (s, 4H), 6.15 (s, 4H); $^{13}C$ NMR $\delta$ 182.2, 177.6, 151.6, 151.0, 142.0, 135.4, 126.0, 125.5, 42.3; MALDI-TOF MS *m/z* 520.7 ($M^+$). Anal. calcd for $C_{34}H_{16}O_6{\cdot}0.6\ CH_2Cl_2$: C, 72.72; H, 3.03. Found: C, 72.58; H, 3.15. **16b**: a yellow solid, mp >320 °C; IR $\nu$ 1659 $cm^{-1}$; $^1H$ NMR $\delta$ 7.42−7.46 (m, 4H), 7.02−7.06 (m, 4H), 6.59 (s, 4H), 6.15 (s, 4H); $^{13}C$ NMR $\delta$ 181.9, 177.4, 151.3, 150.7, 141.9, 135.2, 125.7, 125.2, 42.0; MALDI-TOF MS *m/z* 520.6 ($M^+$). Anal. calcd for $C_{34}H_{16}O_6{\cdot}1.2CH_2Cl_2$: C, 67.93; H, 2.98. Found: C, 67.64; H, 3.09.

**5,6,7,8,9,14,15,16,17,18-Decahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-6,8,15,17-tetraone (17) and 5a,5,6,7,8,-9,14,15,16,17,18,18a-Dodecahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-6,8,15,17-tetraone (17′).** Method 1: A mixture of **6** (80 mg, 0.25 mmol), **1** (90 mg, 0.5 mmol), and *p*-chloranil (120 mg, 0.5 mmol) in HOAc (15 mL) was refluxed for 24 h. The resulting mixture was filtrated and washed with ether. The crude product was then separated by column chromatography over silica gel with dichloromethane and petroleum ether (60−90 °C) (1:1, v/v) as the eluent to give 40 mg (24.1%) of **17** as a yellow solid and 90 mg (54.2%) of **17′** as

a yellow solid. When the reaction time was prolonged to 48 h, the yield of **17** was increased to 49.7%, whereas the yield of **17′** was decreased to 24.8%. **17**: mp >320 °C; IR $\nu$ 1654 $cm^{-1}$; $^1H$ NMR $\delta$ 7.29−7.37 (m, 10H), 6.89−6.98 (m, 10H), 6.09 (s, 2H), 5.72 (s, 4H); $^{13}C$ NMR $\delta$ 178.9, 151.2, 150.8, 143.5, 143.4, 142.1, 125.7, 125.6, 125.5, 125.4, 125.1, 124.3, 47.3, 42.2; HRMS calcd for $C_{48}H_{28}O_4$ $(M + 2H)^+$ 668.1982, found 668.1983. **17′**: mp >320 °C; IR $\nu$ 1666, 1652 $cm^{-1}$; $^1H$ NMR $\delta$ 7.55 (dd, $J$ = 3.43, 5.05 Hz, 2H), 7.38 (dd, $J$ = 3.45, 5.01 Hz, 2H), 7.30−7.34 (m, 4H), 7.13 (dd, $J$ = 3.34, 5.19 Hz, 2H), 7.07 (dd, $J$ = 3.33, 5.14 Hz, 2H), 6.99 (dd, $J$ = 3.36, 5.23 Hz, 2H), 6.94 (dd, $J$ = 3.36, 5.16 Hz, 2H), 6.73 (dd, $J$ = 3.48, 5.00 Hz, 2H), 5.81 (s, 2H), 5.78 (s, 2H), 5.48 (dd, $J$ = 3.40, 5.20 Hz, 2H), 4.55 (s, 2H), 3.06 (s, 2H); $^{13}C$ NMR $\delta$ 193.3, 178.5, 155.9, 151.0, 149.6, 143.8, 143.4, 141.5, 140.9, 139.0, 126.7, 126.4, 125.8, 125.8, 125.6, 125.1, 124.4, 124.3, 123.9, 123.9, 51.1, 50.3, 42.3, 38.8. HRMS calcd for $C_{48}H_{30}O_4$ $(M + 2H)^+$ 670.2138, found 670.2140. Method 2: A mixture of **10** (100 mg, 0.2 mmol), **1** (40 mg, 0.2 mmol), and *p*-chloranil (60 mg, 0.24 mmol) in HOAc (30 mL) was refluxed for 24 h. The resulting mixture was filtrated and washed with ether. A yield of 0.1 g (75.2%) of **17** was obtained.

**1,4,10,13-Tetramethoxy-5,6,7,8,9,14,15,16,17,18-decahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-6,8,15,17-tetraone (18a/18b/18c).** A mixture of **6** (0.32 g, 1 mmol), **2** (0.492 g, 2.1 mmol), and *p*-chloranil (0.51 g, 2.1 mmol) in HOAc (60 mL) was refluxed for 31 h. Workup as described for **9** yielded 0.4 g (51%) of a mixture of **18a/18b/18c** as a brick-red solid.

**1,4,5,6,7,8,9,10,13,14,15,16,17,18-Tetradecahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-1,4,6,8, 10,13,15,17-octaone (19a/19b/19c).** To the solution of **18a/18b/18c** (0.29 g, 0.37 mmol) in acetonitrile (60 mL) and water (10 mL) was added CAN (1.22 g, 2.2 mmol). The reaction mixture was stirred at room temperature for 5 h. Workup as described for **10** gave 0.23 g (85%) of a mixture of three isomers **19a/19b/19c** in about a 2:1:1 ratio, which can be carefully separated by column chromatography over silica gel with dichloromethane and petroleum ether (60−90 °C) (1:1, v/v) as eluent. **19a**: the first fraction, a yellow solid, mp >320 °C; IR $\nu$ 1660 $cm^{-1}$; $^1H$ NMR $\delta$ 7.29−7.33 (m, 6H), 6.89−6.95 (m, 6H), 6.50 (s, 2H), 6.46 (s, 2H), 6.04 (s, 2H), 6.03 (s, 2H), 6.01 (s, 2H); MALDI-TOF *m/z* 726.3 $(M^+)$. **19b**: the second fraction, a yellow solid, mp >320 °C; IR $\nu$ 1660 $cm^{-1}$; $^1H$ NMR $\delta$ 7.36−7.46 (m, 6H), 6.95−7.05 (m, 6H), 6.59 (s, 4H), 6.13 (s, 2H), 6.11 (s, 4H); $^{13}C$ NMR $\delta$ 182.0, 177.5, 151.5, 151.3, 150.8, 142.0, 141.9, 135.2, 125.7, 125.3, 42.1, 42.0; MALDI-TOF *m/z* 726.5 $(M^+)$. **19c**: the third fraction, a yellow solid, mp >320 °C; IR $\nu$ 1660 $cm^{-1}$; $^1H$ NMR $\delta$ 7.38−7.44 (m, 6H), 6.98−7.06 (m, 6H), 6.60 (s, 4H), 6.15 (s, 2H), 6.14 (s, 4H); $^{13}C$ NMR $\delta$ 182.0, 177.5, 151.6, 151.1, 151.0, 141.9, 141.8, 135.4, 126.0, 125.4, 42.3, 42.2; MALDI-TOF MS *m/z* 726.3 $(M^+)$.

**1,1′,4,4′-Tetramethoxy-5,6,7,8,9,14,15,16,17,18-decahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene -6,8,15,17-tetraone (20).** A mixture of **10** (0.26 g, 0.53 mmol), **3** (0.16 g, 0.54 mmol), and *p*-chloranil (0.14 g, 0.57 mmol) in HOAc (60 mL) was refluxed for 24 h. Workup as described for **10** yielded 0.39 g (93%) of **20** as a brick-red solid: mp >320 °C; IR $\nu$ 1653 $cm^{-1}$; $^1H$ NMR $\delta$ 7.31−7.36 (m, 6H), 6.93−6.98 (m, 6H), 6.58 (s, 2H), 6.47 (s, 2H), 6.44 (s, 2H), 6.10 (s, 2H), 5.73 (s, 2H), 3.76 (s, 6H), 3.75 (s, 6H); $^{13}C$ NMR $\delta$ 178.8, 153.0, 151.1, 150.9, 150.5, 149.6, 143.5, 143.4, 142.2, 133.9, 133.8, 125.6, 125.4, 125.3, 125.3, 125.0, 124.2, 109.7, 56.6, 47.3, 42.2, 35.6; MALDI-TOF MS *m/z* 786.4 $(M^+)$. Anal. calcd for $C_{52}H_{34}O_8$: C, 79.38; H, 4.36. Found: C, 78.97; H, 4.53.

**1,1′,4,4′,5,6,7,8,9,14,15,16,17,18-Tetradecahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-1,1′,4,4′, 6,8,15,17-octaone (21).** To a solution of **20** (80 mg, 0.1 mmol) in acetonitrile (20 mL) and water (2 mL) was added CAN (0.33 g, 0.6 mmol). The mixture was stirred at room temperature for 6 h, poured into water, and then extracted with dichloromethane. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated in vacuo to give a residue, which was separated by column chromatography over silica gel with $CH_2Cl_2$ and petroleum ether (60−90 °C) (3:1, v/v) as eluent to give 25 mg (35%) of **21** as a yellow solid: mp >320 °C; IR $\nu$ 1662 $cm^{-1}$; $^1H$ NMR $\delta$ 7.35−7.39 (m, 6H), 6.97−6.99 (m, 6H), 6.62 (s, 2H), 6.60 (s, 2H), 6.51 (s, 2H), 6.11 (s, 2H), 6.74 (s, 2H); $^{13}C$ NMR $\delta$ 180.8, 180.7, 178.6, 176.4, 152.0, 151.6, 151.4, 150.6, 143.6, 143.2, 141.8, 135.4, 126.0, 125.6, 125.5, 125.3, 124.4, 124.3, 47.3, 42.32, 38.7; MALDI-TOF MS *m/z* 726.7 $(M^+)$. Anal. calcd for $C_{48}H_{22}O_8 \cdot 2CH_2Cl_2$: C, 66.98; H, 2.92. Found: C, 67.25; H, 3.24.

**1,4-Dimethoxy-5,6,7,8,9,14,15,16,17,18-decahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-6,8,15,17-tetraone (22a/22b).** A mixture of **9** (0.26 g, 0.53 mmol), **2** (0.14, 0.59 mmol), and *p*-chloranil (0.14 g, 0.57 mmol) in HOAc (60 mL) was refluxed for 39 h. Workup as described for **9** yielded 0.32 g (85%) of the isomer **22a/22b** as a brick-red solid.

**1,4,5,6,7,8,9,14,15,16,17,18-Dodecahydro-5,18:7,16:9,14-tris(*o*-benzeno)heptacene-1,4,6,8,15,17-hexaone (23a/23b).** To a solution of **22a/22b** (0.21 g, 0.29 mmol) in acetonitrile (60 mL) and water (10 mL) was added CAN (0.5 g, 0.91 mmol). The reaction mixture was stirred at room temperature overnight and concentrated. The residue was then dissolved in acetonitrile (30 mL) and water (5 mL), and CAN was added (0.25 g, 0.46 mmol). The mixture was stirred at room temperature overnight, concentrated, and then extracted with $CH_2Cl_2$. The organic phase was dried over anhydrous $Na_2SO_4$, filtrated, and then concentrated to give 0.16 g (80%) of **23a/23b** at about a 1:1 ratio, which was separated by column chromatography over silica gel with $CH_2Cl_2$ and petroleum ether (60−90 °C) (1:1, v/v) as eluent to give **23a** and **23b**, respectively. **23a**: a yellow solid, mp >320 °C; IR $\nu$ 1656 $cm^{-1}$; $^1H$ NMR $\delta$ 7.34−7.43 (m, 8H), 6.98−7.03 (m, 8H), 6.56 (s, 2H), 6.12 (s, 4H), 5.76 (s, 2H); $^{13}C$ NMR $\delta$ 181.9, 178.5, 177.4, 151.4, 151.1, 151.0, 150.9, 150.7, 150.6, 143.4, 143.3, 143.1, 143.0, 141.7, 135.1, 125.7, 125.4, 125.3, 125.1, 125.0, 124.1, 47.3, 42.3, 42.2; MALDI-TOF MS *m/z* 696.5 $(M^+)$. Anal. calcd for $C_{48}H_{24}O_6 \cdot 0.9CH_2Cl_2$: C 75.97, H 3.36. Found: C 75.99, H 3.67. **23b**: a yellow solid, mp >320 °C; IR $\nu$ 1655 $cm^{-1}$; $^1H$ NMR $\delta$ 7.29−7.38 (m, 8H), 6.90−6.98 (m, 8H), 6.57 (s, 2H), 6.09 (s, 4H), 5.71 (s, 2H); $^{13}C$ NMR $\delta$ 182.0, 178.6, 177.5, 151.3, 151.1, 150.7, 150.4, 143.5, 143.3, 141.9, 141.8, 135.2, 125.6, 125.4, 125.3, 125.2, 125.0, 124.1, 47.2, 42.1, 42.0; MALDI-TOF MS *m/z* 696.7 $(M^+)$. Anal. calcd for $C_{48}H_{24}O_6 \cdot 1.5H_2O$: C 79.66, H 3.76. Found: C 79.77, H 3.97.

**Compound 24.** The mixture of **16a** (0.42 g, 0.81 mmol), **1** (0.32 g, 1.80 mmol), and *p*-chloranil (0.44 g, 1.8 mmol) in HOAc (60 mL) was refluxed for 40 h. The reaction mixture was cooled to room temperature, filtrated, and washed with ether. The crude product was purified by column chromatography over silica gel with dichloromethane and *n*-hexane (2:1, v/v) as eluent, and 0.61 g (86%) of **24** as a yellow solid was obtained: mp >320 °C; IR $\nu$ 1658 $cm^{-1}$; $^1H$ NMR $\delta$ 7.24−7.34 (m, 12H), 6.89−6.97 (m, 12H), 6.04 (s, 4H), 5.68 (s, 4H); $^{13}C$ NMR $\delta$ 178.6, 177.7, 151.7, 151.1, 150.7, 143.6, 143.4, 142.0, 125.8, 125.5, 125.4, 125.2, 124.3, 124.2, 47.3, 42.2; MALDI-TOF MS *m/z* 872.2 $(M^+)$. Anal. calcd for $C_{62}H_{32}O_6 \cdot 3H_2O$: C, 80.33; H, 4.13. Found: C, 80.70; H, 4.41.

**Compound 25.** The mixture of **16b** (0.13 g, 0.25 mmol), **1** (0.1 g, 0.56 mmol), and *p*-chloranil (0.14 g, 0.57 mmol) in HOAc (40 mL) was refluxed for 52 h. Then workup as described for **24** yielded 0.12 g (55%) of **25** as a yellow solid: mp >320 °C; IR $\nu$ 1656 $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 7.21−7.23 (m, 12H), 6.81−6.87 (m, 12H), 5.90 (s, 4H), 5.61 (s, 4H); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 179.1, 178.2, 151.8, 151.0, 144.1, 143.9, 142.4, 125.9, 125.8, 125.7, 125.3, 124.5, 47.7, 42.6; MALDI-TOF MS *m/z* 872.1 $(M^+)$. Anal. calcd for $C_{62}H_{32}O_6 \cdot C_6H_{14} \cdot H_2O$: C 83.59, H 4.95. Found: C, 83.95; H, 5.21.

**Compounds 26 and 26′.** Method 1: A mixture of **7** (90 mg, 0.26 mmol), **1** (0.14 g, 0.79 mmol), and *p*-chloranil (0.2 g, 0.81 mmol) in HOAc (40 mL) was refluxed for 24 h. The resulting mixture was filtrated and washed with ether. The crude product was then separated by column chromatography over silica gel with dichloromethane and *n*-hexane (2:1, v/v) as the

eluent to give 10 mg (4.5%) of **26** as a yellow solid and 65 mg (29.5%) of **26′** as a yellow solid. When the reaction time was extended to 4 d, another equivalent portion of *p*-chloranil was added and then refluxed for another 2 d, 9.2% of **26** and 40.8% of **26′** was obtained. **26**: mp >320 °C; IR $\nu$ 1655 $cm^{-1}$; $^1H$ NMR $\delta$ 7.17−7.21 (m, 12H), 6.79−6.82 (m, 12H), 6.36 (s, 2H), 5.59 (s, 6H); $^{13}C$ NMR $\delta$ 176.6, 150.5, 150.2, 124.4, 123.2, 46.3, 28.7; MALDI-TOF MS *m/z* 872.5 ($M^+$). Anal. calcd for $C_{62}H_{32}O_6 \cdot C_6H_{14} \cdot H_2O$: C 83.59, H 4.95. Found: C, 83.77; H, 5.00. **26′**: mp >320 °C; IR $\nu$ 1672 $cm^{-1}$, 1653 $cm^{-1}$; $^1H$ NMR $\delta$ 7.51−7.54 (m, 2H), 7.26−7.34 (m, 8H), 7.09−7.12 (m, 2H), 7.04−7.07 (m, 2H), 6.87−6.96 (m, 6H), 6.65−6.68 (m, 2H), 6.13 (s, 2H), 5.76 (s, 2H), 5.67 (s, 2H), 5.42−5.45 (m, 2H), 4.52 (s, 2H), 3.04 (s, 2H); $^{13}C$ NMR $\delta$ 192.1, 177.5, 177.2, 156.0, 151.5, 150.2, 150.0, 143.6, 143.4, 143.3, 143.2, 140.7, 139.8, 126.8, 126.4, 125.9, 125.6, 125.5, 124.4, 124.4, 124.3, 123.9, 51.2, 50.2, 47.38, 47.35, 38.7; MALDI-TOF MS *m/z* 874.1 ($M^+$). Anal. calcd for $C_{62}H_{34}O_6 \cdot H_2O$: C 83.39, H 4.06. Found: C, 83.25; H, 3.88. Method 2: A mixture of **12** (104 mg, 0.2 mmol), anthracene (72 mg, 0.40 mmol), and *p*-chloranil (0.11 g, 0.45 mmol) in HOAc (30 mL) was refluxed for 24 h. The resulting mixture was filtrated and washed with ether. The crude product was then separated by column chromatography over silica gel with dichloromethane and *n*-hexane (2:1, v/v) as the eluent to give 30 mg (17.2%) of **26** as a yellow solid.

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**Supporting Information Available:** X-ray crystallographic data and the refinement parameters for compound **16b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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