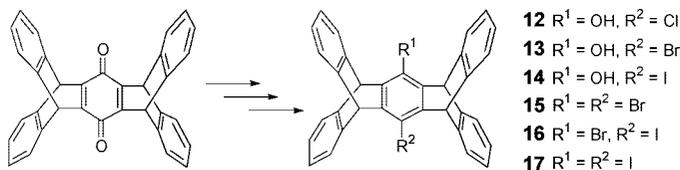


Synthesis of New Halogenated
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ABSTRACT



The synthesis of central-ring halogenated pentiptycene phenols **12–14** and dihalogenated pentiptycenes **15–17** is reported. Their utilities as building blocks for preparing new pentiptycene-derived π -conjugated systems through the Sonogashira, Heck, and Suzuki reactions are also demonstrated.

Pentiptycene (**1**) is a member of the iptycene family and possesses a rigid, aromatic, and H-shaped scaffold.¹ Such a structural feature has been applied to the formation of functional molecules such as fluorescent chemosensors,² molecular machines,³ and low dielectric constant materials,⁴ to the creation of intriguing supramolecular structures,⁵ and to the understanding of structure–property relationships.⁶ Interestingly, all of these applications are associated with

functionalization of the “sterically shielded” central phenylene ring. As such, the availability of the central-ring prefunctionalized pentiptycene building blocks is crucial in the development of new pentiptycene-based materials.

It has been shown that the readily prepared^{7,8} pentiptycene quinone **2** is an excellent precursor for a variety of central-ring functionalized pentiptycene building blocks.¹ Specifically, in addition to the symmetrically disubstituted pentiptycene hydroquinone (**3**) and pentiptycene diacetylene (**4**),⁷ a series of unsymmetrically substituted pentiptycenes such as compounds **5–11** have recently been derived from **2** (Scheme 1).⁹ However, previous attempts to prepare the halogenated pentiptycene phenols **12–14** and pentiptycene dihalides **15–17** were unsuccessful.^{9,10} We report herein the

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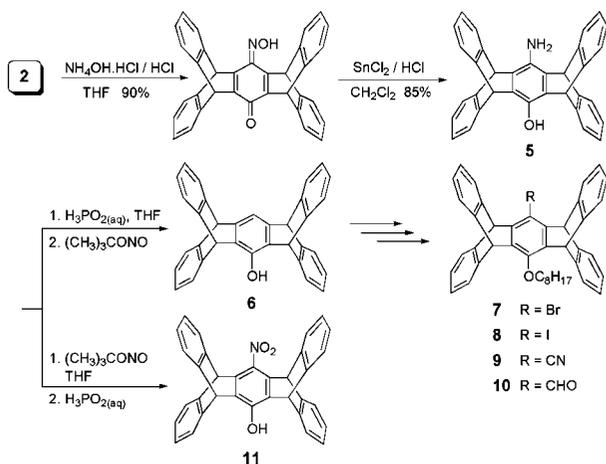
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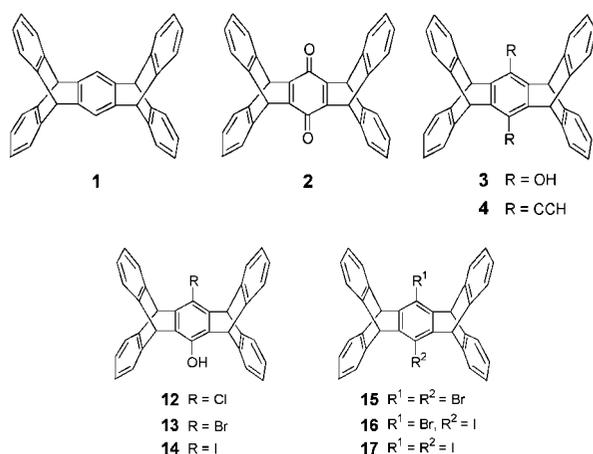
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Scheme 1

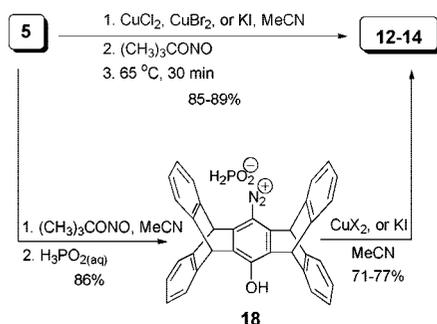


synthesis of these halogenated pentiptycene building blocks and their potential utility toward the development of new pentiptycene-incorporated π -conjugated systems.

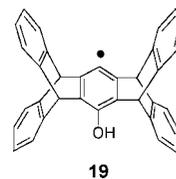


The halogenated pentiptycene phenols **12–14** can be prepared from the deaminative halogenation of **5** either in a one-pot reaction or by a two-step method through the diazonium salt **18** (Scheme 2). The one-pot reaction condition for the synthesis of **12** and **13** is based on the method of

Scheme 2



Doyle et al.,¹¹ where *tert*-butyl nitrite is the diazotizing agent, CuBr_2 or CuCl_2 is the source of halogens, acetonitrile (MeCN) is the solvent, and the reaction temperature is 65 °C. An extension of this method by replacing the cupric halides with KI affords the desired pentiptycene iodide **14**. It should be noted that the same reaction carried out in THF led to other undesired products, including compounds **2**, **3**, **6**, and **11**.⁹ Cadogan and Molina have suggested that THF can promote the decomposition of arenediazonium ions to form the corresponding aryl radicals.¹² Indeed, generation of the pentiptycene radical **19** followed by reactions with molecular oxygen, THF, and *tert*-butyl nitrite can nicely account for the products **3** (and the oxidized form **2**), **6**, and **11**, respectively.⁹ In other words, in THF the desired reactions between the diazonium ion and cupric halides or KI cannot compete with the THF-promoted pentiptycene radical formation and/or the subsequent reactions. The THF effect on promoting the decomposition of diazonium ions is further evidenced by the fact that the conversion **5** \rightarrow **11** shown in Scheme 1 is nearly terminated at the stage of the diazonium compound **18** when the solvent is replaced by MeCN (Scheme 2). As a result, the diazonium salt **18** can be isolated as a yellowish solid powder. Interestingly, the powder of **18** displays high thermal stability, as no noticeable decomposition was observed for **18** upon heating up to 300 °C (mp >300 °C) or keeping at 4 °C for as long as 60 days. We believe that, in addition to the hydroxyl substituent,¹³ both the steric and electronic factors of the pentiptycene scaffold play a role in its stability, namely, the steric shielding effect due to structural rigidity and bulkiness and the homoconjugative interactions¹⁴ among the peripheral and the central phenylene rings. The conversion of **18** \rightarrow **12–14** can be accomplished simply by stirring acetonitrile solutions of **18** and the corresponding halides (i.e., CuCl_2 , CuBr_2 , and KI) at room temperature for 24 h or at 65 °C for 30 min.



The synthesis of pentiptycene dihalides **15–17** is outlined in Scheme 3. The key step is the Pd-catalyzed reduction of the triflate group in **20** with triethylsilane, which generates the nitropentiptycene **21**. The reduction reaction is based on the method of Kotsuki et al.,¹⁵ but in our case it requires the more reactive Pd catalyst $\text{Pd}(\text{PPh}_3)_4$ to obtain a reasonable

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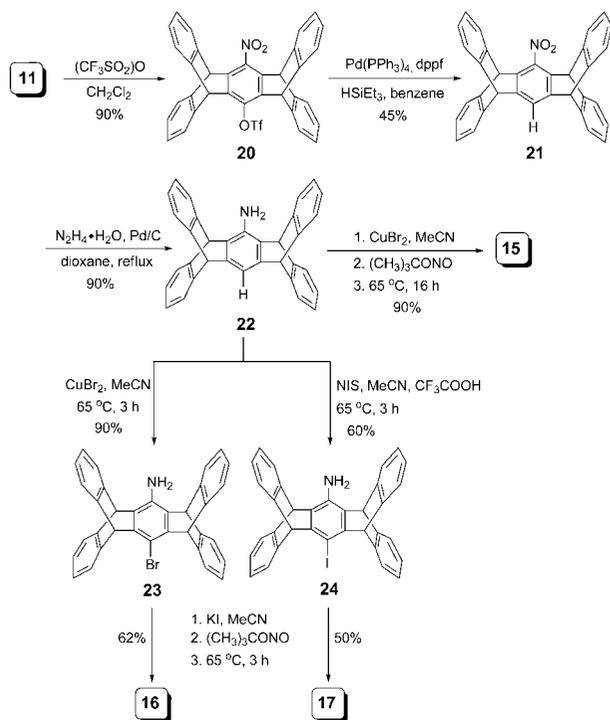
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Scheme 3



yield (45%). This reaction appears to be more efficient for aryl triflates containing electron-withdrawing substituents, because the corresponding triflate derived from **5** (i.e., an aryl triflate containing an electron-donating amino group) shows no such reactivity. The subsequent reduction of the nitro group provides the pentiptycene aniline **22**. Under the deaminative bromination conditions described for the reaction **5** \rightarrow **13**, aniline **22** can be readily converted to the desired pentiptycene dibromide **15**. The occurrence of oxidative bromination prior to deaminative bromination for anilines with $CuBr_2$ and *tert*-butyl nitrite in MeCN has previously been observed.¹⁶ With the knowledge of the reaction mechanism,¹⁶ the brominated aniline **23** can be obtained in the absence of *tert*-butyl nitrite, and the subsequent deaminative iodination affords the pentiptycene dihalide **16**. The aniline **23** can also be prepared by reacting **22** with *N*-bromosuccinimide (NBS) in DMF;¹⁷ however, the yield is much lower (40%). Nonetheless, this result inspired us to use *N*-iodosuccinimide (NIS) for the synthesis of **24** from **22**.¹⁸ It should be noted that the use of reagents I_2/Ag_2SO_4 ¹⁹ and benzyltriethylammonium dichloroiodate (ICl_2^-)²⁰ for the same purpose led to a mixture of unseparable compounds and unreacted starting material, respectively. The pentiptycene diiodide **17** can then be prepared through the

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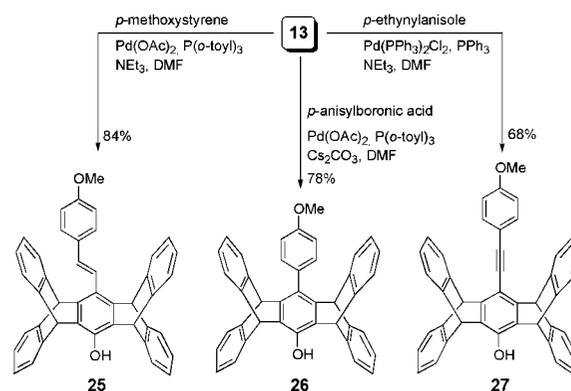
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deaminative iodination of **24** under the same condition for the conversion of **23** \rightarrow **16**.

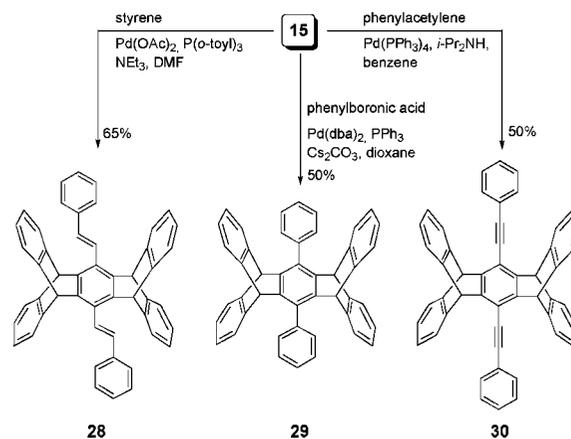
As represented by the building blocks **13** and **15** and the Heck, Suzuki, and Sonogashira reactions,²¹ a variety of pentiptycene-incorporated π -conjugated systems (**25**–**30**) can be constructed (Schemes 4 and 5). It should

Scheme 4



be noted that pentiptycene mono- or ditriflates display little or no such reactivity,^{1,2c} although many other aryl triflates have been shown to be alternative substrates for these Pd-

Scheme 5



catalyzed coupling reactions.²² In this context, the halogenated pentiptycenes are the critical building blocks toward new pentiptycene-derived π -conjugated systems. In particular, the pentiptycene dihalides **15**–**17** allow one to construct pentiptycene-incorporated π -conjugated polymers of a variety of backbones. Currently, the known pentiptycene-based conjugated polymers are limited to only the alternating arene-pentiptycene poly(*p*-phenyleneethynylene)s (PPEs), prepared from the Sonogashira coupling of the pentiptycene diacetylene **4** and dihalogenated arenes.^{2b,7}

In summary, the synthesis of several new pentiptycene halides and dihalides is reported, and their potential utilities

as building blocks for the construction of new π -conjugated systems are demonstrated. In addition to the halogenated pentiptycenes **12–17**, the central-ring functionalized pentiptycene intermediates **18** and **20–24** (Schemes 2 and 3) might also find particular utilities in constructing pentiptycene-based materials.

Acknowledgment. We thank the National Science Council of Taiwan, Academia Sinica, and National Taiwan University for financial support.

Supporting Information Available: Experimental procedures and characterization data for **12–18** and **20–30** and ^1H and ^{13}C NMR spectra for new compounds **12–18**, **20–28**, and **30**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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