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Synthesis of novel twisted carbazole–quinoxaline derivatives with 1,3,5-benzene core: bipolar molecules as hosts for phosphorescent OLEDs

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ABSTRACT

A series of carbazole/quinoxaline hybrids have been synthesized by classic Ullmann and Pd/Cu-catalyzed Sonogashira coupling reaction. Their photophysical, thermal, and electrochemical properties were investigated. The introduction of electron rich carbazole and electron deficient quinoxaline on to the 1,3,5-benzene center leads to twisted structure with good glass forming property and imparts bipolar character. The triplet energies in the range of 2.34–2.53 eV indicate them as potential host materials in phosphorescent OLEDs.

Phosphorescent OLEDs (PHOLEDs) have gained much attention leading to a surge in design and synthesis of new materials as hosts, charge transporting materials, and emitters, presumably because of the possibility of 100% maximum internal quantum efficiency for phosphorescence based OLEDs.[1,2] PHOLEDs are able to harvest both singlet and triplet excitons for light emission, thus offer a tremendous possibility of highly efficient OLEDs.[2] Triplet emitters however owing to their relatively long emissive lifetimes, tend to be less efficient because of concentration quenching and triplet–triplet (T_1–T_1) annihilation during device operation.[3] An effective way to resolve this limitation is to dope the triplet emitters into organic host materials.[4] The host material in the emitting layer also serves as a recombination center for holes and electrons to generate the electronically excited states, followed by excitation energy transfer from the host to dopant.[5] Most of the existing triplet host materials are capable of preferentially transporting holes or electrons.[6] Due to the lack of bipolar character of the emitter, layer recombination occurs at the interface with the charge transport layer.[7] One approach to improve the performance of phosphorescent OLEDs is to use bipolar host materials.[8] Bipolar host materials contribute to the balanced transport of carriers and help to increase the probability of carrier recombination.[8] Recently there is a great deal of activity in developing new bipolar host materials.[4,8,9] In addition to the bipolar nature, the host materials should have amorphous nature for better device stability. Carbazole derivatives are widely used as host materials because of their high triplet energy and good hole-transporting properties.[6d,10] A few examples of generally used carbazole based hosts are 4,4′-*N,N*′-dicarbazole-biphenyl (**CBP**),[11] and 1,3-di(9*H*-carbazol-9-yl)benzene (**mCP**),[6b] but are prone to crystallization due to low glass transition temperatures (**CBP** = 62 °C, **mCP** = 60 °C), which is a major drawback for practical applications.

To our knowledge no study based on carbazole–quinoxaline hybrids as bipolar host material has been reported. In this context we designed bipolar, carbazole/quinoxaline coupled hybrids (Chart 1) having hole transporting (carbazole) and electron transporting (quinoxaline) properties.[12] The unique shape/geometry of these carbazole/quinoxaline hybrids further offers better thermal and film forming properties. The structural design introduced in these molecules (Chart 1) with triplet excited state can contribute toward PHOLEDs with good charge balance.

Synthesis of key intermediates (**8**, **9**, **11**, **13**) are shown in Scheme 1. Classic Ullmann coupling procedure was adopted in making **1**, **2**, & **3** (Scheme 1). The selectivity in making **1** was achieved by using >1.5 equiv of 1,3,5-tribromobenzene. 1,4-dibromobenzene was used in making **3**. *tert*-Butyl bromobenzene was reacted with TMS–acetylene under Sonogashira conditions to get compound **4** and this was converted readily into 4-*tert*-butylphenylacetylene

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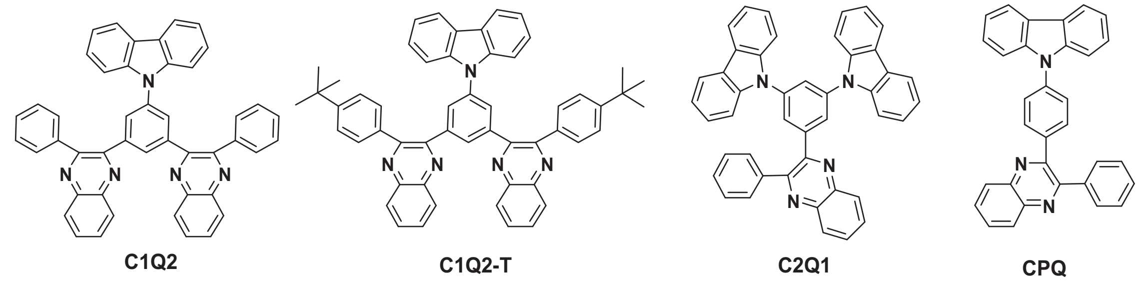
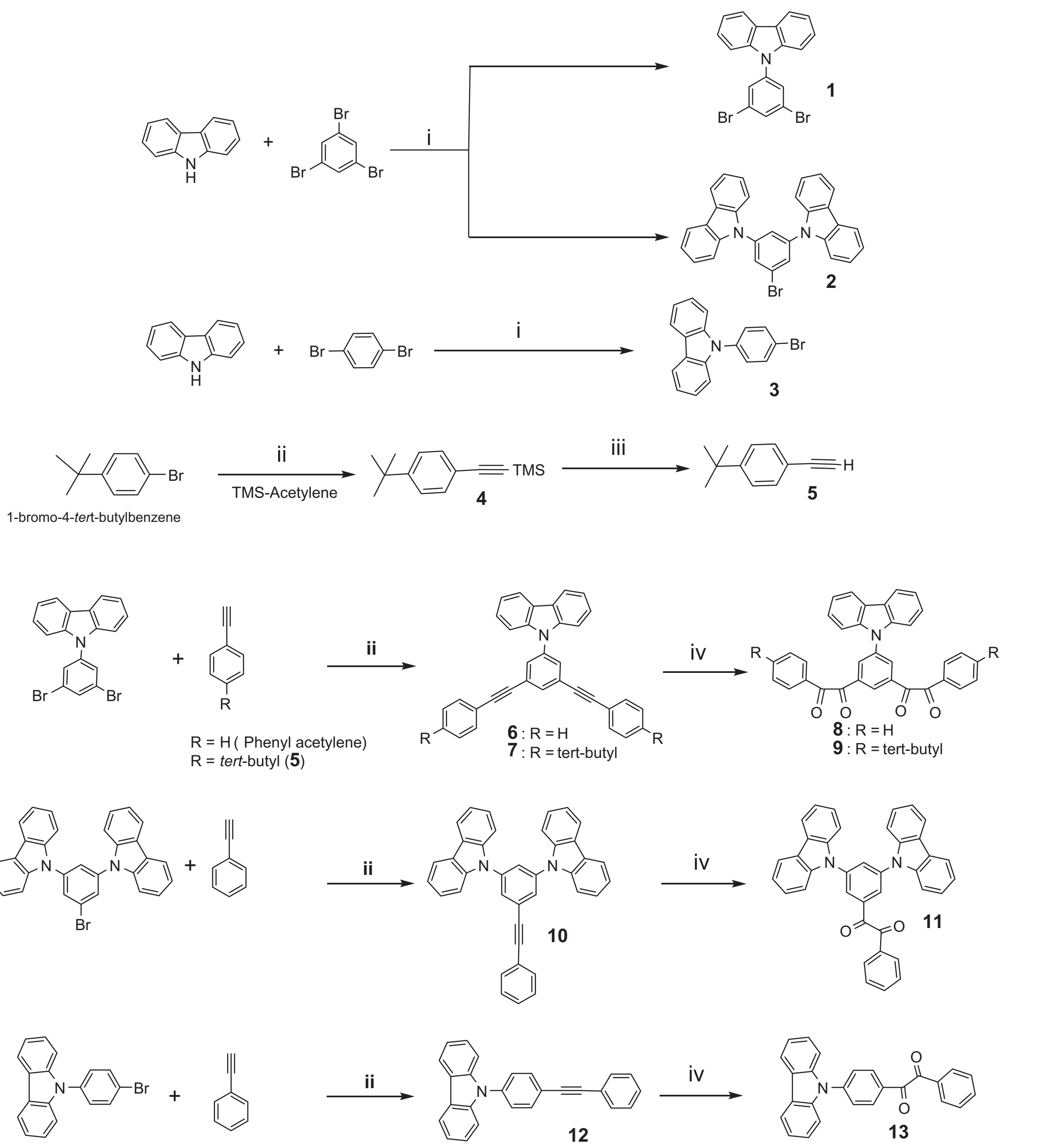


Chart 1. Structures of the benzene centered carbazole–quinoxaline hybrid compounds.



Scheme 1. Synthetic routes adopted in making key intermediates. Reagents and conditions: (i) CuI, K_2CO_3, 1,10-phenanthroline, DMF, reflux; (ii) $Pd(PPh_3)_2Cl_2$, CuI, TEA, Toluene, 80 °C; (iii) K_2CO_3, MeOH, CH_2Cl_2, rt; (iv) $KMnO_4$, $NaHCO_3$, $MgSO_4 \cdot 7H_2O$, Acetone, 4 h, rt .