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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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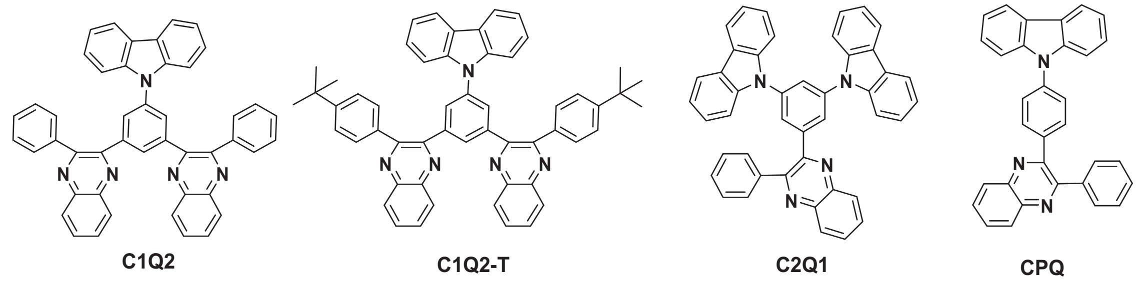
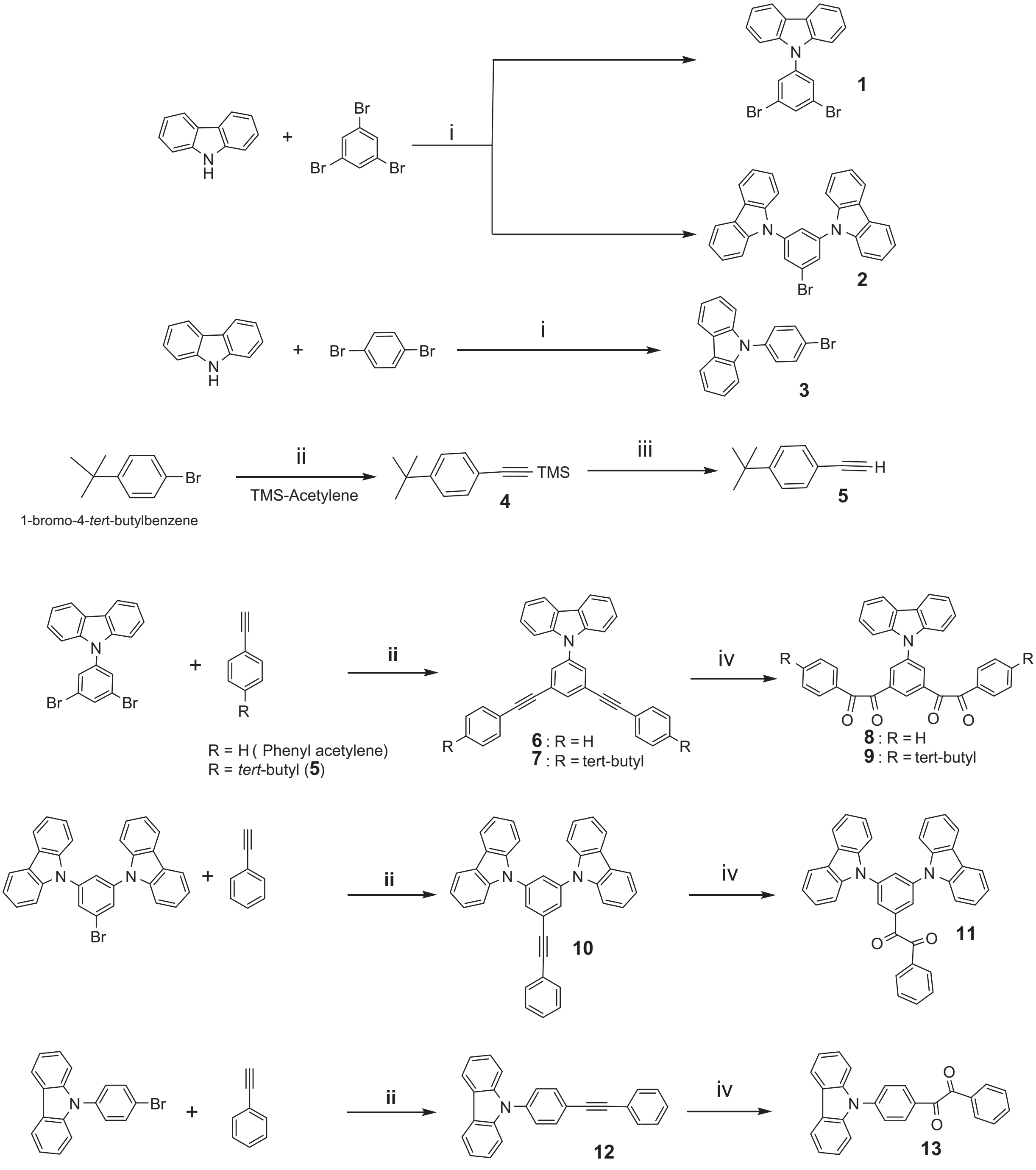
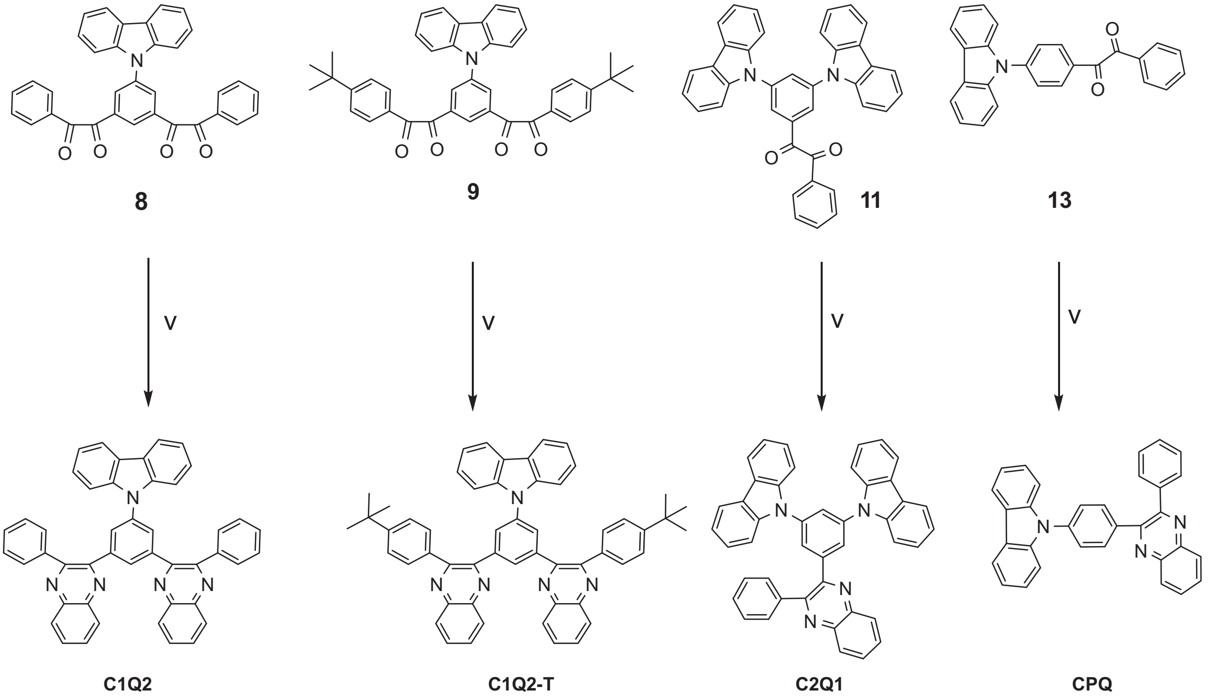


Chart 1. Structures of the benzene centered carbazole–quinoxaline hybrid compounds.



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 .



Scheme 2. Synthesis of **C1Q2, C1Q2-T, C2Q1** and **CPQ** using key intermediates. Reagents and conditions: 1,2-phenylenediamine, $CHCl_3$, PTSA, reflux.

5.[13] Sonogashira coupling condition developed in making compounds **6**, **7**, **10,** and **12** (Scheme 1). Compounds **6**, **7**, **10,** and **12** were subjected to triple bond oxidation leading to diketones (**11** and **13**) and tetraketones (**8** and **9**) as the main intermediates for the final compounds.[14] Scheme 2 illustrates the synthesis of final carbazole/quinoxaline coupled hybrid compounds. The diketones **11** and **13** and teraketones **8** and **9** were cyclocondensed with *o*-phenylenediamine to get final carbazole–quinoxaline bipolar benzene centered hybrid compounds. The compounds are characterized by spectroscopic analysis and additionally X-ray crystal structures for **C1Q2** and **C1Q2-T** are also solved to understand the molecular interactions in the solid state (Fig. 1).

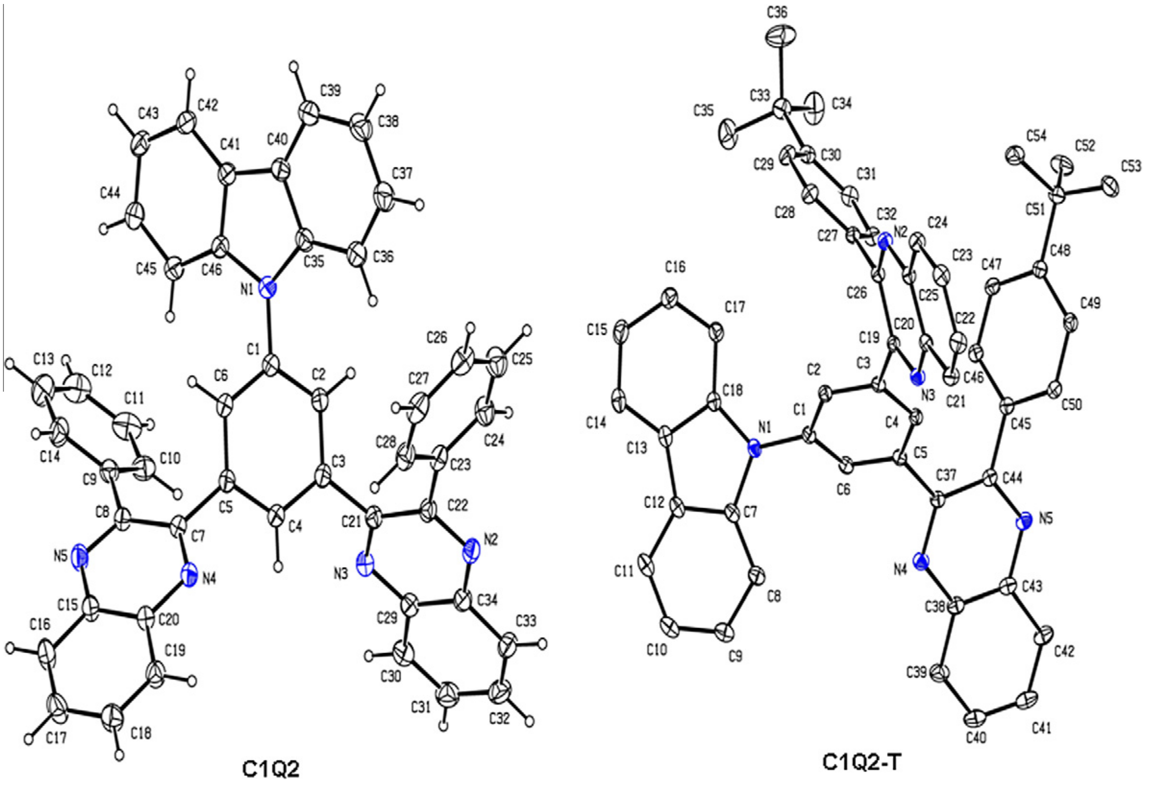


Figure 1. ORTEP diagrams of **C1Q2** and **C1Q2-T**.

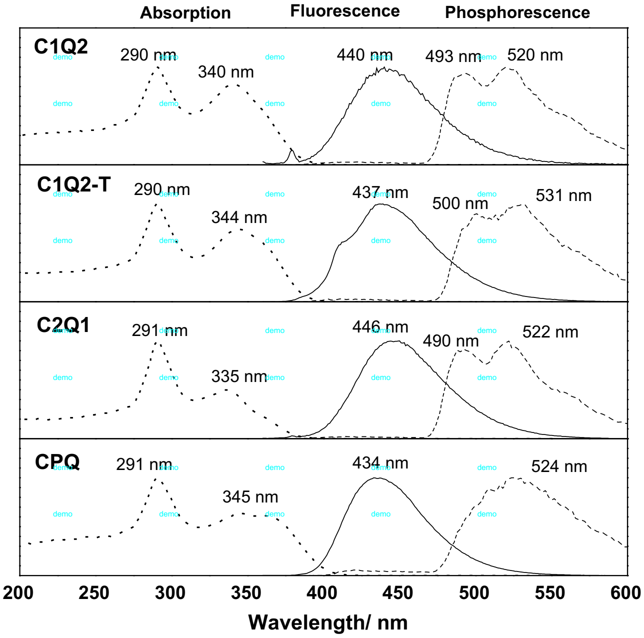


Figure 2. UV–vis absorption, fluorescence and phosphorescence of **C1Q2, C1Q2-T, C2Q1** and **CPQ**. 10^{-5} M toluene solutions at rt for fluorescence; 10^{-5} M Ethyl acetate solutions at 77 K for phosphorescence.

Absorption, fluorescence and phosphorescence spectra were recorded for all the compounds and are shown in Figure 2 and summarized in Table 1. Similar UV–Vis absorption spectra were obtained for these compounds with two main absorption peaks, a carbazole centered n–π* transitions at ~290 nm and less intense absorption bands in the region ~335–345 nm could be assigned to π–π* transitions from electron rich carbazole to electron accepting quinoxaline moiety.[15,9f] All the compounds emit in blue region with the emission peaks in the range of 434–440 nm in toluene and 427–450 nm in the solid state. The similarity of emission in solution and solid suggests weak interactions in the solid state. **C1Q2** and **C1Q2-T** have optical bandgap values of 3.33 and 3.35 eV, respectively (Table 1). **CPQ** has the lowest bandgap of 3.24 eV, which is attributed to better π-conjugation of the *para*-linked over the *meta* substituted derivatives. The influence of solvent polarity on absorption wavelengths was negligible (no red shifts), but prominent bathochromic shifts were observed for the emission bands for all the compounds. Figure 3 shows the effect of solvent on fluorescence. The influence of solvents polarity, more on emission than on absorption band, indicates a small dipole moment of the ground state relative to the dipole of excited state.[16] This suggests intramolecular charge transfer occurring from the less polar ground state to the more polar excited state. The incredibly large stokes shift of >100 nm in polar solvents like acetonitrile and DMF clearly shows the stabilization of the intramolecular CT excited state. The relative fluorescence quantum yields (Φ_f) of these compounds were measured in dilute toluene solution using 9,10-diphenylanthracene (Φ_f ~0.9) as standard.[17a] The low quantum yields of fluorescence for these derivatives are also explained by this characteristic ICT state.[16]

The basic requirement for any material to be applicable as an efficient host material, the triplet energy (E_T) of host should be higher than that of guest to prevent reverse energy transfer from the guest back to host and confine triplet excitons on guest molecules.[18] Phosphorescent spectrum is red shifted by 60 nm compared to the fluorescence spectrum. The triplet energy (E_T), determined from the highest-energy vibronic sub-band of the phosphorescence spectra[17b] at 77 K in ethyl acetate matrix, follow the order of **C2Q1** (2.53 eV) > **C1Q2** (2.51 eV) > **C1Q2-T** (2.48 eV) > **CPQ** (2.34 eV). The experimentally observed E_T and DFT B3LYP calculated adiabatic singlet–triplet gaps are in good agreement (Table 1).[19] The E_T values of these compound are lower than the independent carbazole (E_T = 3.02 eV).[20] The E_T values of **C2Q1** and **C1Q2** are close to generally used host material **CBP** (2.56 eV),[10a] implying that they may act as appropriate host materials for green emitter iridium(III) *fac*-tris(2-phenylpyridine) [Ir(ppy)$_3$, E_T = 2.42 eV] and the red-emitter bis(2,4-diphenylquinolyl-*N*,C2) iridium (acetylacetonate) [(ppq)$_2$Ir(acac), E_T = 2.01 eV].[18b]

The thermal stabilities of the new compounds were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1 and Fig. 4). Their decomposition temperatures (5% weight loss) range from 420 to 470 °C. A key physical parameter which indicates the stability of the amorphous state of a given material is the glass transition temperature (T_g). 1,4-Substituted, **CPQ** derivative has the lowest glass transition (T_g = 81 °C), whereas the 1,3,5- trisubstituted, meta linked derivatives **C1Q2**, **C1Q2-T**, **C2Q1** exhibit high T_g values of 138, 132, and 134 °C ,respectively, and are much higher than the most commonly used host materials namely (**CBP**, 62 °C) and (***m*CP**, 60 °C)[10b] indicating that these are preferred.

The electrochemical behavior of the four new derivatives **C1Q2**, **C1Q2-T**, **C2Q1**, and **CPQ** is probed by cyclic voltammetry (CV) with standard calomel electrode as reference in CH$_2$Cl$_2$ solvent. All of them showed reversible/quasireversible oxidations and reversible reductions. An additional peak observed for the oxidation scan of **C1Q2**, **C1Q2-T,** and **CPQ** at ~1.1 V is attributed to electropolymer-

Table 1
Photophysical, thermal and electrochemical data of **C1Q2**, **C1Q2**-T, **C2Q1** and **CPQ**

Compds.	Photo physical					Thermal	Electrochemical				
	λ_{abs}[a] (nm)	λ_{em}[a,b] (nm)	Φ_f [c]	$E_g^{opt\,d}$ (eV)	E_T[e] (eV)	T_d/T_g (°C)	$E_{\frac{1}{2}}^{oxd}$ (V)	$E_{\frac{1}{2}}^{red}$ (V)	HOMO[f,g] (eV)	LUMO[g,h] (eV)	HLG[i]
C1Q2	340, 290	440(446)	0.27	3.33		425/138	1.37	−1.62	−5.77 (−5.62)	−2.78 (−2.46)	2.99 (3.16)
C1Q2-T	344, 290	437(451)	0.35	3.35	2.48 (2.47)	470/132	1.43	−1.68	−5.83 (−5.62)	−2.72 (−2.39)	3.11 (3.24)
C2Q1	335, 291	446(443)	0.19	3.42	2.53 (2.49)	420/134	1.08, 1.39	−1.57	−5.48 (−5.75)	−2.83 (−2.53)	2.65 (3.22)
CPQ	345, 291	434(427)	0.32	3.24	2.34 (2.42)	395/81	1.37	−1.64	−5.77 (−5.69)	−2.76 (−2.42)	3.01 (3.27)

[a] Recorded in 10^{-5} M Solutions of toluene at rt.
[b] Values in parentheses correspond to fluorescence in solid state.
[c] Quantum yield (Φ_f) measured in dilute toluene relative to that of 9,10-diphenyl anthracene(0.9 in cyclohexane). Excitation wavelength = 340 nm.
[d] Optical band gap estimated from the absorption threshold.
[e] Triplet energy obtained from the highest energy transition of the phosphorescence spectrum. Spectra recorded in ethyl acetate at 77 K. The values in parentheses are theoretically estimated using B3LYP/6-31g(d,p).
[f] Obtained by adding 4.4 to the $E_{1/2}$ oxidation potentials.
[g] The B3LYP/6-311+G(d,p)//6-31G(d,p) obtained values are given in parenthesis.
[h] Obtained by adding 4.4 to the $E_{1/2}$ reduction potentials.
[i] HOMO-LUMO gap (HLG), theoretical obtained values are in parentheses.

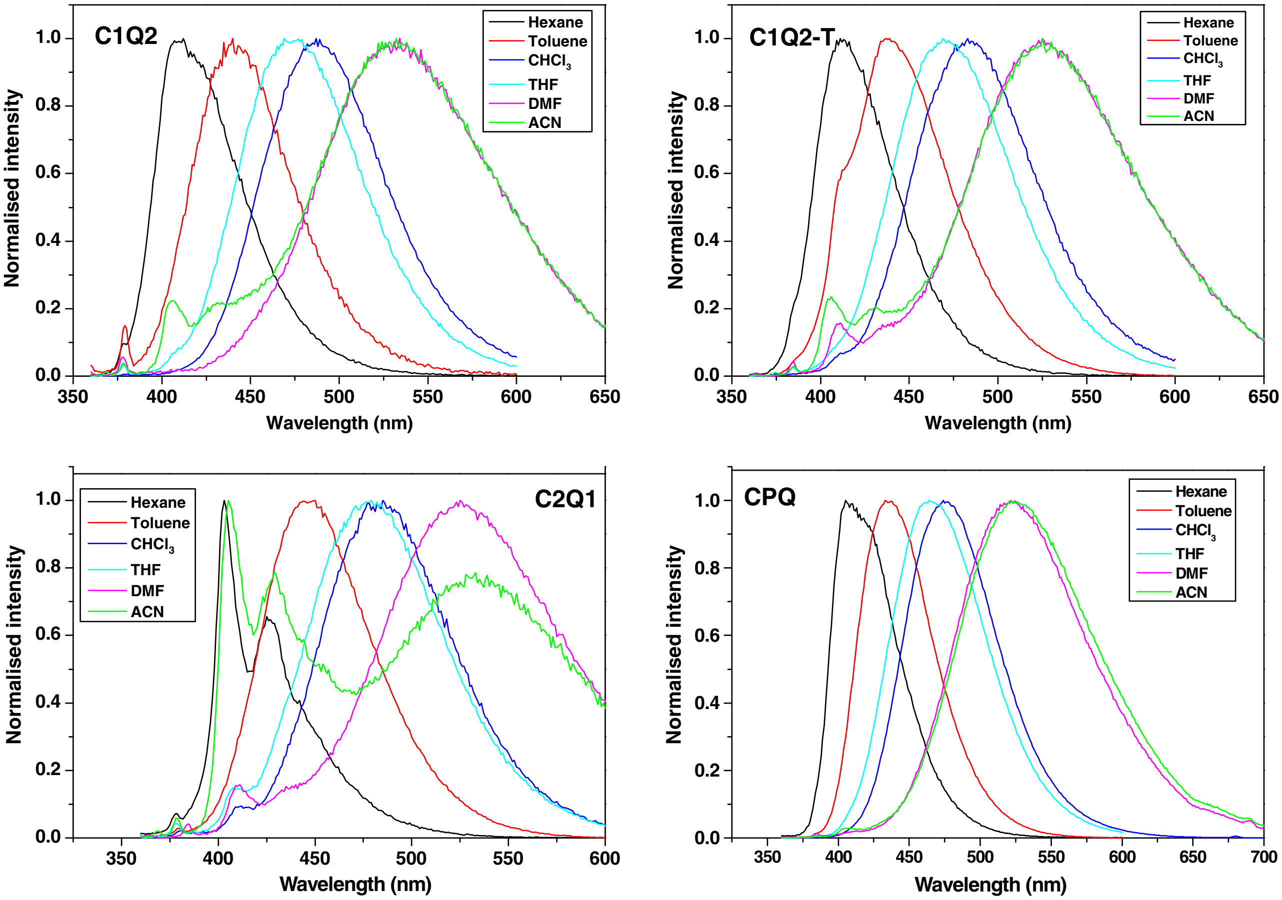


Figure 3. Solvent polarity effect on the fluorescence of **C1Q2**, **C1Q2**-T, **C2Q1** and **CPQ** at 10^{-5} M solutions.

ization at the 3rd and 6th positions of carbazole.[9f] The formation of stable radical cation and radical anion suggests bipolar nature of all the synthesized molecules. Table 1 summarizes the HOMO and LUMO levels determined from the $E_{1/2}$ oxidation and reduction potential values.[21] The HOMO levels varied from −5.48 to −5.83 eV and the LUMO values were in the range −2.72 to −2.83 eV for the four derivatives. **C1Q2**, **C1Q2-T**, and **CPQ** have similar HOMO energy levels (~5.8 eV), while **C2Q1** has higher value at −5.48 eV. The HOMO and LUMO levels determined at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p) level are also shown in the same table. A good correlation with the experimental data is seen. The distribution of HOMO and LUMO electron densities obtained by DFT calculations is shown in Supplementary data. From the density distribution it is clear that for all the molecules HOMO is mainly located on the carbazole group while LUMO on qunioxaline groups. It is interesting to note that for **C2Q1** the distribution of HOMO is only on one carbazole group. **C2Q1** undergoes two quasireversible oxidations ($E_{1/2}$ = 1.08 and 1.39 V) which could be understood in terms of the electron density distribution of HOMO-1 (Supplementary data).

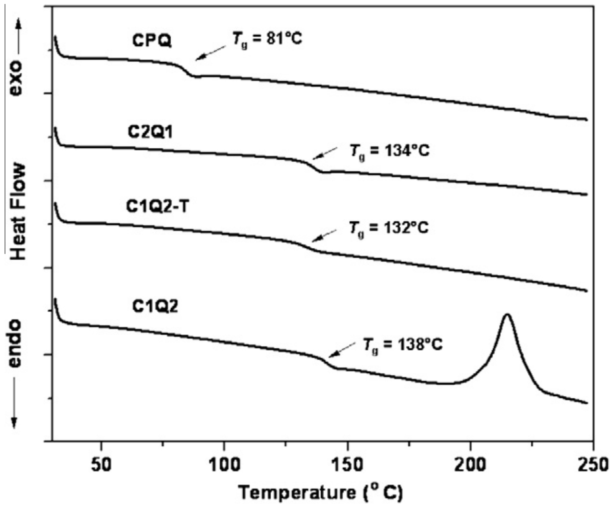


Figure 4. DSC thermograms for **C1Q2**, **C1Q2**-T, **C2Q1** and **CPQ**, measured at 10 °C/min under N_2 atm.

In conclusion, we have described a facile and efficient method for the synthesis of benzene centered novel carbazole–quinoxaline hybrid derivatives. The new compounds exhibit excellent thermal and morphological stabilities owing to the twisted geometry of the molecules. The optical studies reveal the interaction of the donor carbazole with the electron deficient quinoxaline in the molecule. The bipolar nature of these compounds along with high thermal stability (T_g ~138 °C) and favourable electrochemical properties makes them promising for their potential use as host materials in red and green phosphorescent based OLEDs.

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Supplementary data

Supplementary data (The synthesis, ^{1}H and ^{13}C NMR spectra, molecular orbital pictures, crystal data and cyclic voltammograms (CV) of compounds **C1Q2**, **C1Q2-T**, **C2Q1**, **CPQ**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.10.074.

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