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Tuning the Optoelectronic Properties of 4,4′-*N*,*N*′-Dicarbazole-biphenyl through Heteroatom Linkage: New Host Materials for Phosphorescent Organic Light-Emitting Diodes

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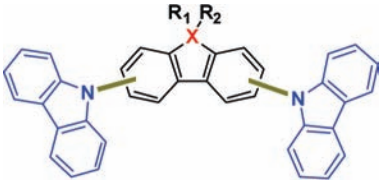
ABSTRACT



Five carbazole end-capped heterofluorenes (CzHFs) designed by structurally mimicking 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) via connecting the biphenyl core of CBP with the linking atom of C, P, N, O, and S, respectively, were synthesized successfully, and their optoelectronic properties were investigated. The theoretical calculations and experimental results demonstrate that CzHFs are potential green, red, and even blue hosts for phosphorescent light-emitting diodes (PHOLEDs) with more desirable localization and energy levels of HOMO and LUMO and also higher triplet energy than CBP.

PHOLEDs have attracted much attention, mainly because it is possible to increase the internal quantum efficiency of the devices up to 100% as a result of their harvesting of both single and triplet excitons.[1] However, a high-performance host material is essential for the fabrication of such kind of devices to prevent the undesired concentration self-quenching or T_1-T_1 annihilation. Also, the development of the suitable host materials especially for blue emitters has turned out to be a rather challenging task. There are some physical requirements[1] for the host materials: (1) a triplet energy (E_T) higher than the triplet emitter to prevent reverse energy transfer from the guest back to the host, (2) good and balanced charge transporting properties with appropriate highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) energy levels, and (3) decent thermal and morphological stabilities to increase the device's lifetime.

Carbazole derivatives have been widely used as host materials in PHOLEDs because of their sufficiently large triplet energy (up to 3.05 eV) and good hole-transporting ability.[2] CBP is a convenient host for green and red emitters because of its high triplet energy (2.56 eV); however, for the general blue triplet guests (2.7 eV), CBP is not applicable because of inefficient energy transfer from the host to the guest.[2]

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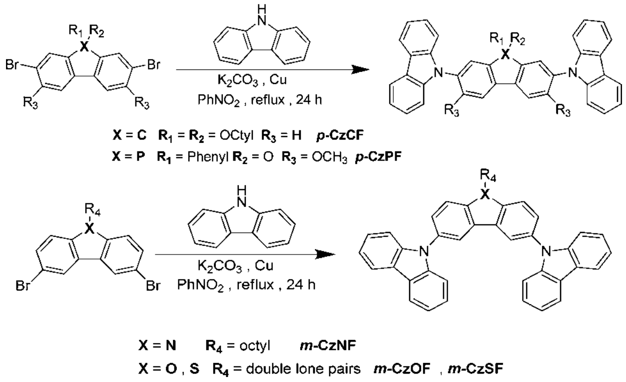
Table 1. Absorption and Emission Peaks (in nm) in THF and Thin Solid Film and DFT Calculations of the Absorption Peaks (in nm), Dipole Moment (μ), Torsion Angle (σ), and Singlet Band Gap ($^{cal}E_g$, eV) of CzHFs

	THF		thin film			calculated			
compound	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	$^{op}E_g{}^a$	λ_{abs}	μ	σ	$^{cal}E_g$
CBP[2d]	292, 318	369	332	378		303, 348	0.0003	53.8	4.08
p-CzCF	291, 339	362 (377)	293, 342	367, 406	3.37	308, 361	0.0972	55.4	3.95
p-CzPF	289, 339	427	289, 338	364, 469	2.96	305, 397	2.8079	60.7	3.64
m-CzNF	262, 289, 339	386, 406	291, 319, 345	(365, 384) 414, 437	3.34	300, 352	4.8042	61.0	3.97
m-CzOF	280, 325, 336	378	284, 332	375, 410, 435	3.41	297, 361	1.6235	59.0	3.92
m-CzSF	289, 326, 338	378	293, 330	361, 391 (412, 434)	3.39	305, 368	1.6481	57.6	3.93

[a] Optical band gaps obtained from the absorption edge on spin-coated films ($E_g = hc/\lambda_{onset}$).

One strategy to design new functional materials is to mimic the structure of the famous and well-studied compounds, although their synthesis may be a great challenge. Structurally, CBP can be considered as a carbazole end-capped biphenyl. Then, what will the material be if the diphenyl of CBP were connected by other bridging atoms? The nonplanar biphenyl core becomes a planar heterofluorene, and a new series of compounds (CzHFs) can be produced. Heterofluorenes[3] such as nitrogafluorene (carbazole, NF),[4] sulfafluorene (SF),[5] silafluorene (SiF),[6] germafluorene (GeF),[7] and phosphafluorene (PF)[8] have received interest due to their particular electronic and optical properties. The marriage of carbazole with heterofluorene in a way as that in CBP may produce interesting materials, especially of high-performance host materials for blue emitters.

Scheme 1. Synthesis of the CzHFs



In this paper, we successfully synthesized a series of carbazole end-capped fluorene (CzCF),[9] phosphafluorene (CzPF), nitrogafluorene (CzNF),[10] oxygafluorene (CzOF), and sulfafluorene (CzSF) by connecting the biphenyl core of CBP with the linking atom of C, P, N, O, and S, respectively. The optoelectronic properties of the CzHFs have been measured and discussed by a combined research of experimental and theoretical study. This study suggests that CzHFs are good host materials with more desirable localization and energy level of HOMO and LUMO and also higher triplet energy than CBP, and *p*-CzPF is also an excellent blue light emitting materials.

The heteroatom linkage of the biphenyl of CBP was realized in two steps with high yields. The first step is to prepare the dibromoheterofluorenes.[8] The second step is to attach the 9-position of the carbazole moiety to the terminal ends of the heterofluorene cores using an optimized Ullmann C−N cross-coupling reaction between the carbazole and dibromoheterofluorene as shown in Scheme 1. The optimized Ullmann reaction[11] proceeded in refluxing nitrobenzene in the presence of copper bronze as catalyst and K_2CO_3 as base and produced the desired compounds in high yields. The target compounds of CzHFs were fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis. The detailed synthetic procedures and structural characterizations are presented in Supporting Information. CzHFs show good solubility in common solvents and good thermal stabilities (see Table S1 in Supporting Information) revealed by differential scanning calorimetry (DSC).

The optical properties of CzHFs in dilute THF and in solid film were investigated and are summarized in Table 1. Both in solution and in solid film, two absorption bands can be observed (see Figure 1). The first absorption band around 290 nm that is also observed in CBP can be assigned to the carbazole-centered n-π* transition,[12] and the other long wavelength absorption around 320−340 nm is attributed to the π−π* transition of the entire conjugated backbone. This two absorption bands are quite different for *p*- and *m*-CzHFs, in that they show the strongest absorption at the second and

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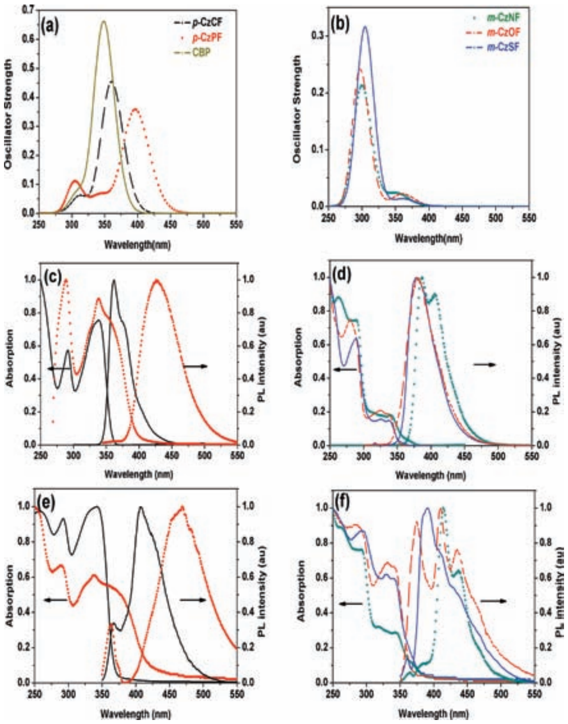

Figure 1. Calculated absorption spectra in vacuum (a, b) and normalized absorption and photoluminescent spectra in dilute THF (c, d) and in thin solid film (e, f) of CzHFs

the first bands, respectively. This difference is due to the different substitution pattern of the carbazole, which can be verified by DFT calculations. Theoretical transition configuration analysis reveals that the first absorption corresponding to a $S_0 \rightarrow S_2$ electronic transition is mainly related to HOMO → LUMO_{+1} and HOMO → LUMO_{+2}, whereas the second band of $S_0 \rightarrow S_1$ transition is mainly contributed by HOMO → LUMO. As a result of different frontier orbital electron distribution overlap between the initial and the final states, the different oscillator strength that stands for different absorption intensity results. The theoretical prediction is quite consistent with the actual spectra of the CzHFs. In comparison with the absorption in THF solution, CzHFs exhibit little spectral shift (within 5 nm) in solid films, suggesting that in the solid state the molecular interaction of CzHF is weak as a result of its nonplanar molecular geometry (see the torsion angle in Table 1). The optical energy band gaps (${}^{op}E_g$) of the CzHFs determined from the onset of the UV−vis spectra in solid film are are very similar (3.34−3.41 eV), and *m*-CzOF has the highest one, except for *p*-CzPF, which has a very low ${}^{op}E_g$ (2.96 eV) due to its para-linkage effects of carbazole and the oxidized phosphorus atom linkage.

For the photoluminescene (PL) of CzHFs, identical emission spectra can be obtained whether excited at the $\pi-\pi^*$ transition ($S_0 \rightarrow S_1$) or at the $n-\pi^*$ transition ($S_0 \rightarrow S_2$) absorption band, indicating the efficient energy transfer from the peripheral carbazole dendrons to the heterofluorene core. In THF solution, *p*-CzPF has the longest emission peak at 427 nm, which is significantly longer than that of other CzHFs (362−386 nm). Most CzHFs have only one emission peak, but *p*-CzCF and *m*-CzNF have two. However, in the thin solid film, more PL peaks appear and the spectra become quite complicated. The emission in the thin film was generally red-shifted as a result of the stronger intermolecular interactions in the solid state, but blue-shifted emission peaks still can be founded. The short wavelength emission of the *p*-CzCF, *m*-CzNF, *m*-CzSF, and *m*-CzOF in the film can be attributed to the emission of the single molecule as with the similar emission behaviors in the dilute THF solutions. However, in the *p*-CzPF film, an even bluer emission than that in dilute THF solution was observed. Among all of the CzHFs, *p*-CzPF has the highest PL quantum efficiency ($\Phi = 1.14$, in cyclohexane), suggesting its great potential as a highly efficient blue (469 nm) light-emitting material.

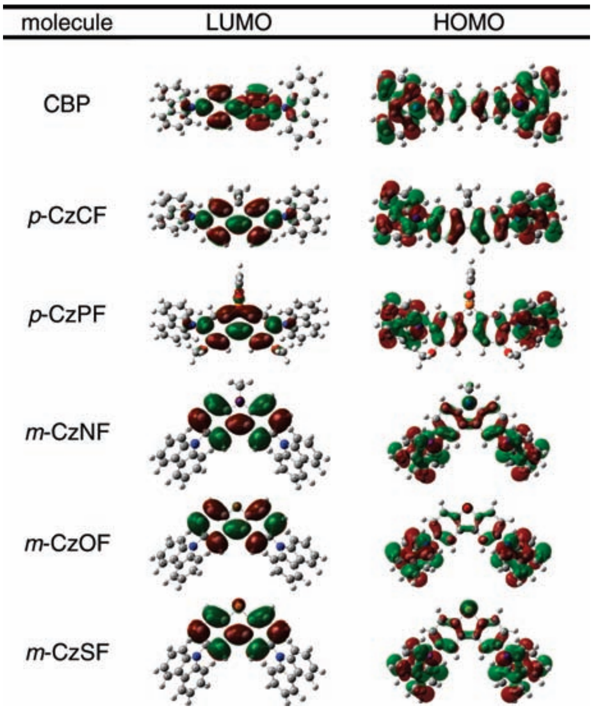

Figure 2. Computed isodensity surface of the HOMO and LUMO obitals of CzHFs

From the HOMO and LUMO orbitals shown in Figure 2, CzHFs have quite similar frontier orbital electron density distributions. The HOMOs are mainly determined by carbazole, although heterofluorenes also have their influence, whereas the LUMOs are predominately localized on and are primarily determined by the central heterofluorenes. A clear difference between *p*- and *m*-CzHFs can be observed; LUMOs of *p*-type CzHFs have also contributions from the N atoms in the carbazole substituent, since the nitrogen would provide its lone pair to form an extended conjugation, suggesting the better conjugation of *p*-CzHFs compared with that of the *m*-CzHFs, which explains the facts found in the optical and electrochemical measurements. The separately determined HOMO and LUMO by carbazole and heterofluorene result in the separated electron density distribution between the HOMO and LUMO of CzHFs. This separation is preferable for efficient hole- and electron-transporting properties and the prevention of reverse energy transfer,[13] enabling CzHFs the excellent potential host materials.

Table 2. Experimental and Theoretical HOMO, LUMO, Singlet Band Gap (${}^{exp}E_g$,), and Triplet State Energy (${}^{exp}E_T$ and ${}^{cal}E_T$) of CzHFs (in eV)

	from CV			B3LYP/6-31G*			
compound	HOMO	LUMO	${}^{exp}E_g$	HOMO	LUMO	${}^{cal}E_T$	${}^{exp}E_T$
CBP[14]	−5.70	−2.00	3.70	−5.31	−1.23	2.72	2.56
p-CzCF	−5.42	−2.20	3.22	−5.24	−1.29	2.69	2.61
p-CzPF	−5.44	−2.58	2.86	−5.39	−1.75	2.48	2.30
m-CzNF	−5.34	−2.22	3.12	−5.17	−1.20	2.97	2.86
m-CzOF	−5.40	−2.26	3.14	−5.37	−1.45	3.08	2.98
m-CzSF	−5.42	−2.26	3.16	−5.36	−1.43	3.05	2.87

The electrochemical behaviors of CzHFs were investigated by cyclic voltammetry (CV) as shown in Figures S18 and S19 in Supporting Information. Except for *p*-CzCF, which is chemically reversible as reported in the literature, the other CzHFs show quasi-reversible or irreversible redox behaviors, and their irreversibility becomes more apparent when the CV scans are performed in solution as illustrated in Figure S20 in Supporting Information. The irreversible redox behaviors of CzHFs (except for *p*-CzCF) are due to the active 3- and 6-positions of carbazole that can undergo dimerization reactions during the CV scan as proposed by Ma et al., when they were investigating the carbazole-containing host materials.[2c] The first oxidation process of CzHFs around +0.8 V can be assigned to the simultaneous multielectron oxidation process of the peripheral carbazole units resulting the formation of radical cations, and the second oxidation process around +1.0 V corresponds to the removal of electrons from the interior heterofluorene core generating radical dications.[11] From the onset potential of electrochemical reduction and oxidation, HOMO and LUMO were calculated and are listed in Table 2. Because after the first CV scan irreversible cross-linking through the 3- and 6-positions of carbazole occurs and the material works at that state, the HOMOs were calculated from the second CV scan. The highest HOMO is found for *m*-CzNF (−5.34 eV), and the other CzHFs have very close HOMOs (−5.40 to −5.44 eV), which are much higher than CBP (−5.7 eV). The lowest LUMO is found for *p*-CzPF (−2.58 eV), and the other CzHFs all have LUMOs (−2.20 to −2.26 eV) lower than that of CBP (−2.0 eV). As for the electrochemical singlet band gaps (${}^{exp}E_g$), *p*-CzPF has the lowest one (2.86 eV)m and the other CzHFs have ${}^{exp}E_g$'s very close (3.12−3.22 eV) but lower than that of CBP (3.7 eV). The CV measured frontier obitals are well predicted by the DFT calculations with good coordination as listed in Table 2. The higher HOMO and lower LUMO of CzHFs compared with that of CBP suggest that CzHFs have better hole and electron injection and transfer abilities than CBP that are beneficial for the device performance improvement.

Phosphorescent spectra of CzHFs were detected at 77K with 5 ms delay as shown in Figure S21 in Supporting Information, and the triplet state energy (${}^{exp}E_T$) was read by taking the highest energy peak of phosphorescence as the transition energy of $T_1 \rightarrow S_0$. The CzHFs show higher ${}^{exp}E_T$'s (2.61−2.98 eV) compared with that of CBP (2.56 eV) except *p*-CzPF (2.30 eV), indicating that these compounds are suitable host materials for green, red, and even blue triplet emitters. From Table 2, the *m*-CzHFs have ${}^{exp}E_T$'s much higher than those of the *p*-CzHFs, and with the triplet energy higher than 2.8 eV, they can host blue emitters. A small systemic error of about 0.1 eV between DFT calculation and experimental measurement on evaluating triplet state energy was observed with good coordination. It is interesting that CzHFs have E_T's higher than those of CBP, although their E_g's are lower, probably due to the great modification abilities of the heteroatom linkage. The higher HOMOs, lower LUMOs, but still higher ${}^{exp}E_T$'s compard with those of CBP make CzHFs attractive host materials for triplet emitters.

In summary, by mimicking the molecular structure of CBP, we have successfully synthesized a new series of host materials of CzHFs using Ullmann C−N coupling reaction, and their optoelectronic properties were systematically studied. The combined theoretical and experimental results demonstrate that CzHFs are a kind of promising green, red, and even blue host material for PHOLEDs with their more desirable localization and energy level of HOMOs and LUMOs and also higher triplet energies compared with those of CBP. Also, *p*-CzPF is also an excellent blue light-emitting material with strong fluorescent emission.

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Supporting Information Available: Experimental procedures and spectra for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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