Perspective on Host Materials for Thermally Activated Delayed Fluorescence Organic Light Emitting Diodes

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Organic light emitting diode (OLED) is a new yet promising technology that is anticipated to replace the liquid crystal display technology in the very near future. The development of both the emitter and host materials for OLEDs is indispensable to realize high device efficiency and optimal performance. Though the presently commercialized OLED panels mostly utilize phosphorescence emitters, the all-organic thermally activated delayed fluorescence (TADF) emitting materials have some obvious advantages. Considerable progress has been made in search of better performing TADF OLEDs in the past few years. Although major research attention has been drawn toward reporting new TADF emitters, the hosts are equally important in TADF OLEDs, as the doped films of the emitters mostly yield better results than the nondoped films. There are already some good reviews on the TADF emitters in literature. In this review article, the literature data specifically aimed at hosting TADF dopants are carefully selected and comprehensively summarized and categorized into several sub-groups based on their structural features to draw the attention of the organic electronics research community toward developing new host materials for TADF OLEDs.

1. Introduction

The introduction of the organic light emitting diode (OLED) technology as a replacement for the conventional backlit flat panel liquid crystal displays (LCDs) is an obvious advancement in the display industry. As the individual pixel of the OLEDs is source of light which could be turned ON and OFF, the subsequent displays have many striking advantages over conventional LCDs such as: a) considerably thinner, b) can achieve higher contrast ratio (black is perfectly black), c) faster response time, d) wide viewing angle, e) could be fabricated on a flexible substrate, etc.[1,2] In the semiconducting inorganic light emitting diodes, charge carriers are introduced in the respective bands through doping and these carriers move around the crystal lattice under an electric bias.[3] However, carriers are injected at the two opposite electrodes in case of organic LEDs where a multilayer device structure facilitates charge injection and transportation, carrier recombination, and to say, the overall device performance. There has been a revolution of the device architecture since the first practical OLED built by Tang and Van Slyke at Eastman Kodak.[4]

In an OLED, the external quantum efficiency (EQE, η_int) is defined as a product of internal quantum efficiency (IQE, η_int) and light out-coupling efficiency (η_out). The η_int is directly proportional to the photoluminescence quantum yield (PLQY, Φ_pl) of the emission layer. For the practical application of a device, it should obtain high brightness at a low driving voltage which demands high Φ_pl. The fundamental difference between photoluminescence and electroluminescence lies in the formation of the excited state. In the former process, the electronic excited state is directly formed by absorption of photons of appropriate frequency which induces electronic transition between the frontier molecular orbitals (FMOs) maintaining the law of conservation of angular momentum. However, in the phenomenon of electroluminescence, the excited state is generated through carrier injection at the valence and conduction bands of the emitter. At this stage, a bound state (exciton) is formed by Coulombic attraction between the charge carriers (electron and hole), which is slightly lower in energy than the total energy of the injected carriers. The exciton thus formed could follow any of the several photophysical deactivation processes as indicated by a simplified Perrin–Jablonski diagram in Figure 1.

As the injected carriers are spin-half particles, their recombination to form the excited states of proper multiplicity would be governed by the spin statistics. Likely, there is 25% chance the recombination sees singlet excited state and 75% of the excitons are expected to be triplet.[5] Apart from taking care of the issues such as, a) optimally aligned layer topology to reduce charge injection barrier and improve carrier mobility, b) maintaining appropriate recombination zone, c) confinement of the excitons within the emission layer, d) thermal and morphological stability of the organic materials, etc., which directly impact device performance and stability, enormous research attention has also been drawn to extract most of the photons out of the electrogenerated excitons. The two foremost emission channels that the corresponding excitons follow are fluorescence by the
singlets and phosphorescence by the triplets. The former being a spin allowed process occurs at a faster time-frame and consequently has a shorter decay time, usually a few tens of nanoseconds. However, as phosphorescence involves transitions between two states of different spin multiplicity, it follows a slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up). Needless to say that due to elongated slow kinetics and thus the triplet excitons have longer lifetime between two states of different spin multiplicity, it follows a consequently has a shorter decay time, usually a few tens of nanoseconds. However, as phosphorescence involves transitions between two states of different spin multiplicity, it follows a slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up). Needless to say that due to elongated slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up). Needless to say that due to elongated slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up). Needless to say that due to elongated slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up). Needless to say that due to elongated slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up).

As the conventional fluorescent OLEDs rely solely on the singlet excitons (25% probability), most of the electrical power is wasted for producing dark triplet excited states (75% probability). Therefore, the \( \eta_{\text{int}} \) of the first generation fluorescent OLED devices is limited to only about 5–7.5% assuming 100% \( \Phi_{\text{pl}} \) and 20–30% \( \eta_{\text{out}} \) which is a serious limitation for industrial applications. The discovery of the phosphorescence OLEDs (PhOLEDs) is surely a breakthrough in this regard because of the capability of the phosphors to implement all the electronegated excitons by the respective singlets and phosphorescence by the triplets. The former being a spin allowed process occurs at a faster time-frame and consequently has a shorter decay time, usually a few tens of nanoseconds. However, as phosphorescence involves transitions between two states of different spin multiplicity, it follows a slow kinetics and thus the triplet excitons have longer lifetime (microseconds or up). Needless to say that due to elongated lifetime, the triplets are prone to many detrimental processes.

Figure 1. A simplified Perrin–Jablonski diagram showing the various excited state processes. Only the unimolecular processes are shown. The rate constants are as follows: \( k_f \) (fluorescence), \( k_{nr} \) (nonradiative processes), \( k_{pl} \) (delayed fluorescence), \( k_p \) (phosphorescence), \( k_{ISC} \) (intersystem crossing), \( k_{RISC} \) (reverse intersystem crossing).

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Though majority of the commercial OLEDs utilize organometallic phosphors of heavy transition metals (e.g., cyclometallated iridium complexes), they have some serious drawbacks such as a) toxicity of these metals, b) their rarity, c) fabrication cost, d) device stability of the blue devices, etc. Another triplet harnessing process is triplet–triplet annihilation (TTA, also known as P-type delayed fluorescence). Interestingly, TTA could be observed in pure organic fluorescent probes. The rate constant of emission for TTA is not that of fluorescence but depends on the rate of formation of triplet excitons. Though some reports demonstrated higher OLED efficiency than that of the fluorescent devices using TTA in pure organic chromophores, the \( \eta_{\text{int}} \) was still limited to 62.5% as compared to 100% for the PhOLEDs. If the 0–0 singlet–triplet energy separation (hereafter \( \Delta E_{\text{ST}} \)) of an organic chromophore falls in the order of available thermal energy in surroundings (≈25.6 meV at 298 K), then the triplet excitons could undergo reverse intersystem crossing (RISC).
to the corresponding singlets followed by emission of delayed fluorescence. This is known as thermally activated delayed fluorescence (TADF) which was first observed from a deoxygenated solution of eosin in glycerol and ethanol at room temperature.[11] Though the emission spectrum of the prompt fluorescence and TADF have similar wavelength characteristics, the lifetime of TADF is comparable to that of triplets. The rate constant for emission is temperature dependent and can be expressed by an Arrhenius type equation as $k_{\text{TADF}} = A \exp\left(-\frac{\Delta E_{\text{ST}}}{RT}\right)$, where $A$ is the frequency factor and $R$ is the gas constant. It can show the ratio of quantum yields of TADF ($\Phi_{\text{TADF}}$) and phosphorescence ($\Phi_p$).

$$\Phi_{\text{TADF}} = \Phi_f \frac{A}{k_p} \exp\left(-\frac{\Delta E_{\text{ST}}}{RT}\right)$$

where $\Phi_f$ and $k_p$ are fluorescence quantum yield and phosphorescence rate constant, respectively.[5] This indicates that the ratio is independent of triplet formation yield and any triplet quenching process.

It appears that TADF is the most promising exciton harvesting mechanism for OLEDs, as both the singlets and triplets could be utilized for producing light from pure organic chromophores. Adachi and co-workers demonstrated this strategy utilizing a Sn–porphyrin complex.[12] Though the devices lacked any practical usefulness, but this enticing pioneering work opened a new direction for OLED technology. The research group has demonstrated several examples with improved functional properties, e.g., charge transfer (1CT, 3CT), charge transfer (1CT, 3CT), etc., are affected differently through dipole-dipole interactions. Consequently, alike the solution state, a polar host stabilizes the 1CT state more than it does so on the 3LE state which is less polar than the 1CT state. The $\Delta E_{\text{ST}}$ value is then influenced by the host. However, contrary to the liquid state which has greater entropy than the solid state, the molecular kinetics are very limited in the later phase. The mode of solute–solute interaction is slightly different in the solid state in the macroscopic sense. The restricted molecular motion in the solid state causes extremely slow solvation (typically in picosecond timescale in nonviscous solutions), which could give rise to strong and permanent local electric field around the emitter molecules. Penfold and co-workers have demonstrated the effect of solid state solvation and its effect on TADF emitters based on simulation studies in a recent article.[17] The role of the host matrix to fine-tune the $\Delta E_{\text{ST}}$ value has been nicely demonstrated by Monkman and co-workers in a recent report. Based on the blue emitter, 2,7-bis(9,9-dimethyl-acridin-10-yl)-9,9-dimethylthioxanthenene-S,S-dioxide (DDMA-TXO2), which has strong TADF character, and some polar (e.g., bis[2-(diphenylphosphino)phenyl] ether oxides (DPEPO)) and nonpolar hosts, the article demonstrates how the host polarity affects the RISC efficiency and consequently the TADF.[18a] A polar host matrix such as DPEPO minimizes the RISC activation energy and enhances the TADF efficiency, which is immediately realized by improved overall device performance. Interestingly, the DPEPO hosted device with DDMA-TXO2 as an emitter exhibits a low turn-on voltage of about 3 V, $\eta_{\text{max}}$ of 22.4% at 127.4 cd m$^{-2}$ together with high brightness level and low efficiency roll-off.[18b] In a very recent article, Han et al. demonstrated how the host excited state dipole moment affected quenching of excitons of blue TADF dopants through host–dopant dipole–dipole interactions by synthesizing hosts with donor–π–acceptor architecture.[18b] According to the authors, a strong excited state dipole field of the host worsens the quenching scenario and in order to suppress that, hosts with reduced excited state dipole moment could be beneficial.
It is commonly observed that the TADF emission which usually occurs in microsecond or longer time scale shows a spectral shift with time in polar hosts. Careful analysis of the time-resolved spectra of the delayed luminescence reveals that the delayed emission is initially shifted to lower energy followed by a blue-shift at longer delay time. The actual reason behind this intriguing observation which happens to realize only in the solid state but not in solution is yet to be fully understood but two alternative explanations persist in literature. One explanation aims at the conformational heterogeneity of the highly twisted TADF molecules in the solid matrix. As rotation is severely hindered in the solid state, a distribution of molecular conformation with slightly different torsion angle between the D–A constituents exists. The charge transfer interaction between the D and A fragments and consequently polarity of the excited state and the emission wavelength of the TADF molecules which usually consist of sterically hindered D/A arrangement is highly dependent of the said dihedral angle. This complexity usually does not arise in the nonviscous solution medium where rapid molecular motions such as tumbling, rotation, etc., drive the excited states to quickly attain the most relaxed geometry. Another theory explains this observation considering the microenvironment around the excited chromophore.

As can be understood from the above discussion, the host matrix is as important as the TADF emitter in a TADF-OLED. The host–guest system in general owes enhanced device efficiency compared to the nondoped systems due to the dilute nature of the former system which retards the before mentioned detrimental effects. Therefore, development of efficient hosts for TADF emitters and their detail physicochemical characterization are important for optimal device performance. As phosphorescence and TADF both involve the triplet excitons in their emission channel, both the PhOLEDs and TADF-OLEDs require dispersion of the emitters in hosts with higher triplet energy than the emitters. As the excited state energy levels of such hosts are considerably greater than that of the emitters, the backward (dopant to host) energy transfer and thus the unwanted quenching of the emitter exciton are suppressed. Also, in this way the host confines the excitons within the emitting layers and prevents any leakage. Another benefit is that the host transfers its excitation energy to the emitter molecules, which improves the exciton formation scenario within the emission layer. This becomes more effective if the emitter frontier molecular orbitals fall within the FMO energy window of the host. Another important feature the hosts should have is substantial overlap of their emission spectra with the absorption spectra of the dopant so as to turn on the energy transfer mechanism. Compared to unipolar hosts, the bipolar materials are known to perform better due to balanced charge transport property of the latter. Adachi and co-workers demonstrated suppression of efficiency roll-off in a TADF OLED by controlling molecular orientation of a CBP host matrix. Based on some simulation and photophysical studies, the authors concluded that the efficiency roll-off was influenced neither by the optical characteristic of the devices nor by the photophysical properties of the TADF emitter, but it was the hole mobility in the emission layer which was responsible for this phenomenon. During the device fabrication at high temperature, the host molecules oriented themselves randomly which lowered the hole mobility and shifted the recombination zone away from the interface of emission and electron-transporting layers. This random orientation of the host molecules was thought influence suppression of the efficiency roll-off. Wang and co-workers in a recent report demonstrated restoration of the singlet–triplet gap of a TADF emitter by the host–guest intermolecular interactions. In another report, Naito and coworkers demonstrated controlling of the singlet–triplet gap of a TADF emitter 4,5-di(9H-carbazol-9-yl) phthalonitrile (2CzPN) by variation of the concentration of a polar inert molecule camphoric anhydride in a host matrix of mCP. The finding was straightforward, addition of the secondary polar molecule increased the polarity of the microenvironment around the TADF molecule and the $S_1$ CT state being more polar subsequently gained some stabilization. The triplet state was almost unaffected due to nonpolar nature of the concerned excited state. Thus, the singlet–triplet separation was minimized to some extent by the addition of a secondary polar inert material. Based on a spiroacridine based TADF emitter, 10-phenyl-10H-spiro[acridine-9,9'-fluorene]-2',7'-dicarbonitrile, Adachi and co-workers demonstrated that the choice of host for a TADF OLED was crucial to realize optimal device performance. The authors indicated that exciplex formation between the host and the emitter could be possible and one should take care of this phenomenon.

The well characterized host materials have several benefits over the new materials and therefore, majority of the TADF OLEDS are based on the conventional host materials such as those depicted in Scheme 1. These materials can be produced in bulk quantities at relatively low cost and their physical and chemical properties have been well documented since early days. Consequently, most of the TADF and PhOLEDs tend to employ these materials as the hosts. A collection of the various properties of these materials can be found in a recent review article by Wong and Eli Zysman-Colman.

CBP has a low triplet energy of about 2.6 eV and has been mostly employed in red TADF devices. The main concern of CBP is its highly symmetrical structure and low molecular weight which sometimes induce crystallization during the device operation, shortening the device lifetime. Triplet energies of mCP and 3,3-Di(9H-carbazol-9-yl)biphenyl (mCBP) are experimentally determined to be ≈2.9 and ≈2.8 eV, respectively, which make them attractive for green emitting devices. DPEPO is quite popular for the blue TADF OLEDs, as it owes very high triplet energy of about 3.0 eV. However, it suffers from some considerable setbacks such as stability, poor charge transporting ability, etc., which reduce the device lifetime. The lowest unoccupied molecular orbital (LUMO) of DPEPO is quite shallow and so the TADF dopants typically have deeper LUMO than it. Some other blue TADF devices are also known, which used mCP[14,15] and 2,8-bis(diphenylphosphoryl) dibenz[d,f]thiophene (PPT)[16,17] as the hosts.

In this perspective, we wish to highlight the hosts for TADF OLEDs. Though majority of the original research articles in this area contribute to development of new emitter materials, the hosts have so far drawn less research attention. Till the time of writing this article, there are only a handful number of publications that demonstrate newly synthesized host materials for already known TADF emitters. Molecular structures of the TADF emitter materials described in this article are
Among the various TADF emitters reported so far, the green emitter 2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile (4CzIPN, Scheme 2) has received most attention for some obvious reasons. Consequently, a large number of publications that demonstrate new hosts for TADF OLEDs are based on this emitter material. Similarly, majority of the bipolar hosts are either carbazole or phosphine oxide based and there is less structural diversity among the materials reported so far. However, in order to simplify the content of this article and to make an easier discussion, we have categorized the hosts into a few subgroups based on their molecular structures. The various devices and their configurations as described in the relevant original articles are collected in Table 1. We have further arranged this table according to the emitters so as to give the reader a clear picture about the structure–property relationship of the TADF hosts. We systematically analyzed only those papers which demonstrated employment of new host materials in OLEDs based on TADF dopants and excluded those for fluorescent and phosphorescence based dopants.

2. Carbazole-Based Hosts for TADF OLEDs

2.1. Carbazole-Based Unipolar Hosts

Needless to mention that manufacturing of OLEDs through solution process is attractive because of the simplicity of the process and low manufacturing cost than the vacuum processing. However, the latter method dominates in the present day display industry because the solution-processed OLEDs usually suffer from some negative issues such as low reproducibility, lower EQE, etc. Adachi and co-workers recently demonstrated a solution processed OLED using a new host material 1,3-bis[3-(9-carbazolyl)phenyl]-9-carbazolyl]benzene (CPCB, Scheme 3) and green-emitting 4CzIPN as the emitter. The material was synthesized by Pd-catalyzed Suzuki–Miyaura coupling between 3-(9-carbazolyl)phenylboronic acid and 3-bromocarbazole followed by Ullmann coupling with 1,3-diodobenzene. The material has a high triplet energy of about 2.8 eV and a high glass transition temperature of 165 °C, which are considerably higher than those of CBP (2.6 eV, 62 °C). CPCB is appreciably soluble in many solvents such as toluene, tetrahydrofuran, dichloromethane, etc. The spin-coated film of 6 wt% 4CzIPN:CPCB shows a high PLQY of 86%. The solution-processed OLED comprising 4CzIPN emitter and CPCB host exhibits 10% external quantum efficiency and a half-life of about 200 h at 1000 cd m\(^{-2}\) luminescence.

2.2. Carbazole-Dibenzothiophene Based Bipolar Hosts

Both carbazole and dibenzothiophene are promising building blocks for OLED host materials because of their high triplet energy. Koch and co-workers recently synthesized a series of host materials (LK3-7) featuring these heterocycles in differing connection topology and compared their performance with a well-known host, CBP. Molecular structures of these materials are summarized in Scheme 4. All these materials exhibit good thermal and morphological stability, their absorption spectra are CBP alike and the highest occupied molecular orbital (HOMO) levels as measured through ultraviolet photoelectron spectroscopy are similar to that of CBP. OLEDs were fabricated using these materials as host and 4CzIPN as the emitters. The device with LK4 exhibits highest performance with maximum current efficiency 68.0 cd A\(^{-1}\) corresponding to a power efficiency of 60.3 lm W\(^{-1}\) and EQE of 21%. The authors found that introduction of the dibenzothiophene functionality augmented electron transport ability of the relevant materials, where the materials with 1:1 carbazole to dibenzothiophene ratio exhibited optimal carrier balance in the electroluminescence devices, thereby, increasing the device performance. It was also noted that the charge transport ability of the relevant bipolar host materials increased with shortening the spacer length between carbazole and dibenzothiophene. Though the devices with LK4 as the host outperformed other host based devices. However, LK4 has a low glass transition temperature which could negatively impact its application in electroluminescence (EL) devices. After incorporating all these factors, it emerged that LK3, which
is comprised of one carbazole and one dibenzothiophene linked through a biphenyl spacer, could be the optimal material among the other members of the series. This study nevertheless reveals that introduction of neutral functional groups such as dibenzothiophene at the backbone of carbazole based TADF host materials could be effective to fine-tune electron transport property of the pertinent materials. Thus, the carbazole-dibenzothiophene based hosts appear to be promising both in terms of their thermal and morphological stability and device performance (Table 1). All these devices have low efficiency roll-off, though the turn-on voltages of the relevant devices are a slightly higher than those of other 4CzIPN based devices.

2.3. Carbazole-Polyaromatic Hydrocarbon Based Bipolar Hosts

According to Duan and co-workers, bipolar hosts with equal electron and hole mobilities might not be the best for optimal device performance. Usually, the hole mobility of the most hole-transporting materials is higher than the electron mobility of the conventional electron-transporting materials. It has been demonstrated that blue TADF OLEDs could be more stable if the emitters are dispersed in electron transport type host instead of hole transport type materials because of lesser degree of electrochemical and photochemical oxidation processes. Therefore, there is a demand to improve electron mobility of

Scheme 2. Molecular structures of the TADF dopants mentioned throughout this article.
Table 1. Summary of the various TADF OLED device structures and performance as described in this article.

| Emitter | Host     | Device structure                                                                 | $V_{on}$ [V] | $\lambda_{max}$ [nm] | EQE$^a$ [%] | CE$^b$ [cdA$^{-1}$] | PE$^c$ [lmW$^{-1}$] | $\tau^d$ [h] | Ref. |
|---------|----------|---------------------------------------------------------------------------------|-------------|------------------------|-------------|----------------------|---------------------|------------|-------|
| 4CzIPN  | CPCB     | ITO/PEDOT:PSS (40 nm)/6 wt% emitter:host (30 nm)/T2T (10 nm)/Bpy-TP2 (40 nm)/LiF (0.8 nm)/Al (80 nm) (solution processed) | 3.4         | 510                    | 9.9 (9.8)   | –                     | –                   | 184        | (LT50) |
| LX3     | ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)/6 wt% emitter:host (20 nm)/TmPyPB (40 nm)/Liq (2.5 nm)/Al | 4.7         | –                      | 19.4 (18.2) | 66.0 (62.0)          | 51.8 (41.5) | –                     | –          | [38]  |
| LK4     | 4.0      | –                                 | 4.7         | –                      | 21.0 (19.9) | 68.0 (64.5)          | 60.3 (49.7) | –                     | –          | [38]  |
| LK5     | 5.0      | –                                 | 5.0         | –                      | 19.0 (17.6) | 64.5 (60.0)          | 47.0 (37.5) | –                     | –          | [38]  |
| LK6     | 4.9      | –                                 | 4.9         | –                      | 18.2 (17.4) | 61.5 (58.8)          | 45.1 (37.4) | –                     | –          | [38]  |
| LK7     | 4.5      | –                                 | 4.5         | –                      | 17.7 (16.7) | 60.0 (56.6)          | 50.9 (40.8) | –                     | –          | [38]  |
| D1      | ITO/HAT-CN (20 nm)/NPB (40 nm)/TCTA (10 nm)/10 wt% emitter:host (25 nm)/Bphen (35 nm)/LiF (1 nm)/Al (150 nm) | 3.5         | 533                    | 16.3        | 51.8                  | 36.4              | –                     | –          | [39]  |
| D2      | 3.1      | –                                 | 3.1         | 533                    | 15.9        | 50.7                  | 41.4                | –          | –     |
| D3      | 2.9      | –                                 | 2.9         | 547                    | 5.5         | 15.4                  | 13.3                | –          | –     |
| D4      | 3.3      | –                                 | 3.3         | 533                    | 15.4        | 49.2                  | 37.5                | –          | –     |
| D5      | 3.6      | –                                 | 3.6         | 533                    | 15.5        | 49.3                  | 35.4                | –          | –     |
| D6      | 2.7      | –                                 | 2.7         | 550                    | 12.3        | 37.4                  | 34.8                | –          | –     |
| DCzDCN  | ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/3 wt% emitter:host (25 nm)/TSPO1 (35 nm)/Liq (1 nm)/Al (200 nm) | 3.0         | –                      | 26.7 (25.9) | –                     | –                   | 200        | –       | [41]  |
| 4CN34BCz| ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/1 wt% emitter:host/TSPO1 (5 nm)/TPBi (30 nm)/Liq (1 nm)/Al (200 nm) | –           | 496                    | 21.8 (19.5) | –                     | –                   | –          | –       | [43]  |
| oCzB-2CN| ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/5 wt% emitter:host (25 nm)/TSPO1 (35 nm)/Liq (1 nm)/Al (200 nm) | –           | 502                    | 20.9 (17.5) | –                     | 46.6                | –          | –       | [45]  |
| mCzB-2CN| –        | –                                 | –           | 508                    | 26.0 (22.5) | –                     | 71.4                | –          | –     |
| pCzB-2CN| –        | –                                 | –           | 510                    | 22.9 (19.9) | –                     | 64.5                | –          | –     |
| Sy      | ITO/4% ReO$_3$/CzSi (60 nm)/CzSi (15 nm)/10 wt% emitter:host (20 nm)/PO-T2T (50 nm)/Liq/Al | 2.6         | –                      | 24.0 (22.1) | 74.4                  | 81.3                | –          | –       | [46]  |
| Asy     | 2.6      | –                                 | 2.6         | –                      | 22.5 (20.4) | 65.0                  | 53.8                | –          | –     |
| PPD2    | ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/2 wt% emitter:host/TSPO1 (35 nm)/TPBi (30 nm)/Liq (1 nm)/Al (200 nm) | –           | 492                    | 21.1 (18.1) | –                     | 42.1 (20.2)         | –          | –       | [47]  |
| PzCz    | ITO/α-NPD (35 nm)/mCP (10 nm)/3 wt% emitter:host (20 nm)/PPT (40 nm)/Liq (0.8 nm)/Al (80 nm) | 4.5         | 506                    | 18.2        | 60.2                  | 38.6                | –          | –       | [53]  |
| o-mCPB1 | ITO/MoO$_3$ (5 nm)/TAPC (65 nm)/8 wt% emitter:host (15 nm)/TmPyPB (35 nm)/Liq (1 nm)/Al (100 nm) | 3.4         | –                      | 18.7 (18.5) | 60.4                  | 42.0                | –          | –       | [58]  |
| o-CzDPz | ITO/PEDOT:PSS (40 nm)/TAPC (20 nm)/6 wt% emitter:host (20 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (200 nm) | 4.8         | –                      | 13.7 (11.4) | 39.6 (33.1)          | 23.7 (13.9)         | –          | –       | [59]  |
| m-CzDPz | 4.5      | –                                 | 4.5         | –                      | 12.1 (10.9) | 37.5 (33.7)          | 22.0 (13.3)         | –          | –     |
| 3-CzDPz | 3.8      | –                                 | 3.8         | –                      | 13.3 (12.7) | 41.1 (39.1)          | 32.2 (17.8)         | –          | –     |
| mCPDPz  | 4.9      | –                                 | 4.9         | –                      | 13.1 (9.8)  | 37.9 (28.3)          | 19.8 (9.8)          | –          | –     |
| mCP:SOB | ITO/MoO$_3$ (15 nm)/Poly-TriCz (50 nm)/3 wt% emitter:host (25 nm)/TPBi (60 nm)/Liq (1 nm)/Al (100 nm) | 3.2         | –                      | 26.5 (21.5) | 81 ± 2                | 79 ± 2              | –          | –       | [54]  |
| 3TPAPP  | ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/2 wt% emitter:host (25 nm)/TSPO1 (35 nm)/Liq (1 nm)/Al (200 nm) | –           | –                      | 21.2        | –                     | –                   | –          | –       | [74]  |
| 4TPAPP  | ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/2 wt% emitter:host (25 nm)/TSPO1 (35 nm)/Liq (1 nm)/Al (200 nm) | –           | –                      | 6.6         | –                     | –                   | –          | –       | [74]  |
| DBTTP1  | ITO (120 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/3 wt% emitter:host (25 nm)/TSPO1 (5 nm)/TPBi (30 nm)/Liq (1 nm)/Al (200 nm) | 4.0         | –                      | 18.7        | –                     | >250                | 250        | –       | [78]  |
| DBTTP2  | –        | –                                 | –           | 20.0 (17.5)           | –          | –                   | >100                | –          | <100  |
| mCP:B3PYPM # (1:1) | ITO (70 nm)/(4 wt% ReO$_3$):mCP (A nm)/mCP (15 nm)/5 wt% emitter:host (30 nm)/B3PYPM (20 nm)/(4 wt% Rb$_2$CO$_3$):B3PYPM (8 nm)/Al (100 nm) | 3.0         | –                      | 29.6 (27.8) | 94.5 (88.0)          | 88.6 (49.0)         | –          | –       | [86]  |
### Table 1. Continued.

| Emitter Host Device structure | $V_{on}$ [V] | $\lambda_{EL,max}$ [nm] | EQE [%] | CE $[^{\circ}]$ | PE $[^{\circ}]$ | $\tau$ [h] | Ref. |
|------------------------------|--------------|--------------------------|---------|---------------|--------------|-----------|------|
| TAPC:TPBI (1:1) ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/3 wt% emitter:host (25 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm) | – | – | 3.3 | – | 8.2 | – | [87] |
| TCTA:TPBI (1:1) | – | | | | | | |
| CBP:TPBI (1:1) | – | | | | | | |
| mCP:TPBI (1:1) | – | | | | | | |
| mCP:BmPyPb (1:1) | – | | | | | | |
| Cz-PO ITO (100 nm)/HATCN (10 nm)/TAPC (40 nm)/6 wt% emitter:host (20 nm)/TPBi (50 nm)/LiF (1 nm)/Al (80 nm) | – | | | | | | |
| Cz-PS | – | | | | | | |
| 2CzPN o-CzCN ITO/PEDOT:PSS (40 nm)/TAPC (20 nm)/TCTA (5 nm)/4 wt% emitter:host (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (200 nm) | 5.1 | – | 14.5 | 29.2 | 18.4 | – | [44] |
| m-CzCN | – | | | | | | |
| p-CzCN | – | | | | | | |
| CzDPpy ITO/MoO$_3$ (1 nm)/TAPC (40 nm)/TCTA (5 nm)/5 wt% emitter:host (20 nm)/DPEPO (5 nm)/TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm) | 3.4 | | 480 | 16.0 | 34.8 | 33.1 | [55] |
| tCzDPpy | – | | 488 | 11.7 | 28.9 | 23.3 | [55] |
| o-mCPBI ITO/MoO$_3$ (5 nm)/TAPC (65 nm)/8 wt% emitter:host (15 nm)/TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm) | 3.6 | – | 10.2 | 6.5 | 21.4 | 17.7 | [58] |
| o-CzDPz ITO/PEDOT:PSS (40 nm)/TAPC(20 nm)/3 wt% emitter:host (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (200 nm) | 4.5 | – | 14.5 | 5.0 | 26.2 | 16.5 | 26.2 | [59] |
| m-CzDPz | – | | | | | | |
| 3-CzDPz | – | | | | | | |
| mCPDPz | – | | | | | | |
| tBu-OXD-o-L-TPA ITO/MoO$_3$ (5 nm)/TAPC (65 nm)/8 wt% emitter:host (15 nm)/TmPyPB (35 nm)/LiF (1 nm)/Al (100 nm) | – | | | 7.6 | 22.8 | 20.6 | – | [75] |
| tBu-OXD-o-L-TPA | – | | | 7.2 | 22.1 | 15.9 | – | [75] |
| tBu-OXD-p-L-TPA | – | | | 8.7 | 25.2 | 26.0 | 8.7 | [75] |
| ZDZ ITO (50 nm)/HATCN (7 nm)/TAPC (75 nm)/6 wt% emitter:host (20 nm)/TmPyPB (50 nm)/LiF (1.5 nm)/Al (100 nm) | – | | 489 | 18.5 | 49.8 | 31.8 | – | [77] |
| ZDN | – | | 494 | 25.7 | 6.0 | 53.0 | – | [77] |
| NDN | – | | 494 | 23.9 | 4.7 | 47.4 | – | [77] |
| BT-01 ITO/10 (nm)/mCP (20 nm)/10 wt% emitter:host (30 nm)/TmPyPB (60 nm)/LiF (0.8 nm)/Al (100 nm) | 3.0 | | 25.5 | 10.0 | 53.0 | 20.2 | 47.5 | [83] |
| BT-02 | 3.4 | | 22.3 | 6.2 | 47.5 | 13.3 | 42.6 | 5.9 | [83] |
| 5CzCN o-PhCzCNCz ITO (120 nm)/DNTPD (60 nm)/BPBPA (20 nm)/PCzAc (10 nm)/15 wt% emitter:host (25 nm)/DBFTrz (5 nm)/NAPIm (30 nm)/LiF (1.5 nm)/Al (200 nm) | – | | – | – | 16.4 | – | – | [66] |
| m-PhzCzCNCz | – | | – | – | 15.0 | – | – | [66] |
| DBT2CzCN ITO (120 nm)/DNTPD (60 nm)/BPBPA (20 nm)/PCzAc (10 nm)/30 wt% emitter:host (30 nm)/DBFTrz (5 nm)/ZADN (30 nm)/LiF (1.5 nm)/Al (200 nm) | 5.6 | – | 11.1 | – | – | 66 | [67] |
| DBTCzCzCN | 5.2 | – | 14.9 | – | – | 80 | [67] |
| DBTPCzCzCN | 4.9 | – | 15.7 | – | – | 53 | [67] |
| DPOBBPE ITO (150 nm)/MoO$_3$ (15 nm)/Poly-TPD (15 nm)/PVK (70 nm)/25 wt% emitter:host (40 nm)/TSPO1 (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al (200 nm) | – | – | 25.8 | 27.1 | 52.3 | – | [72] |
| DMAC-DPS 9CzFDPEPSPO ITO/MoO$_3$ (5 nm)/NPB (70 nm)/mCP (5 nm)/10 wt% emitter:host (20 nm)/DPEPO (5 nm)/BPhen (40 nm)/LiF (1 nm)/Al | 3.5 | | 472 | 16.7 | 11.0 | 31.3 | 20.7 | 28.1 | 8.1 | [49] |
| Emitter Host Device structure | $V_{\text{on}}$ [V] | $\lambda_{\text{EL max}}$ [nm] | EQE [%] | CE [cdA$^{-1}$] | PE [lmW$^{-1}$] | $\tau$ [h] | Ref. |
|-------------------------------|-----------------|-----------------|--------|-----------------|----------------|---------|------|
| 9CzFDPPO ITO/MoO$_3$ (6 nm)/NPB (70 nm)/mCP (5 nm)/10 wt% emitter:host (20 nm)/SFXSPO (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al | 3.5 | 472 | 13.2 (8.3) | 25.1 (15.8) | 22.4 (6.7) | – | [49] |
| SFXSPO ITO/MoO$_3$ (6 nm)/NPB (70 nm)/mCP (5 nm)/10 wt% emitter:host (20 nm)/SFXSPO (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al | 3.1 | – | 17.9 (14.9) | 30.3 (25.1) | 30.7 (11.4) | – | [68] |
| DPDPO2A ITO/MoO$_3$ (6 nm)/NPB (70 nm)/mCP (5 nm)/10 wt% emitter:host (20 nm)/DPDPoA (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al | 2.5 | – | 22.5 (18.2) | 42.1 (34.1) | 52.9 (21.7) | – | [69] |
| DBTDOPO ITO/MoO$_3$ (6 nm)/TAPC (70 nm)/10 wt% emitter:host (20 nm)/DBTDPO (10 nm)/46DBSOPO (30 nm)/LiF (1 nm)/Al | 3.0 | 476 | 16.1 (12.4) | 31.5 (24.2) | 32.9 (9.5) | – | [70] |
| 22'DPEPO ITO/MoO$_3$ (6 nm)/NPB (70 nm)/mCP (5 nm)/10 wt% emitter:host (20 nm)/mDPEPO (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al | 3.7 | 460 | 16.7 (8.4) | 25.3 (12.7) | 21.5 (5.4) | – | [71] |
| 24DPEPO | 4.3 | 460 | 3.7 | 5.7 | 4.2 | – | [71] |
| 24'DPEPO | 3.5 | 460 | 20.1 (13.7) | 30.6 (20.5) | 27.5 (9.4) | – | [71] |
| 44'DPEPO | 3.6 | 460 | 13.1 (9.2) | 20.8 (14.6) | 18.1 (8.5) | – | [71] |
| DPETPO ITO/MoO$_3$ (6 nm)/NPB (70 nm)/mCP (5 nm)/10 wt% emitter:host (20 nm)/DPEPO (10 nm)/Bphen (30 nm)/LiF (1 nm)/Al | 3.1 | 464 | 23.0 (19.6) | 39.7 (33.7) | 44.4 (17.8) | – | [73] |
| DPEQPO | 3.5 | 472 | 11.6 (3.0) | 22.0 (5.7) | 19.4 (1.9) | – | [73] |
| PPO2 ITO/HATCN (7 nm)/TAPC (40 nm)/DCDPA (10 nm)/20 wt% emitter:host (25 nm)/TSPO1 (5 nm)/TPBi (30 nm)/LiF (1.5 nm)/Al (100 nm) | 3.0 | 471 | 27.8 (21.8) | 36.1 (28.4) | – | – | [50] |
| 3DCPO | 2.8 | 473 | 23.1 (17.0) | 32.5 (23.9) | – | – | [50] |
| tBCzHDPO ITO/MoO$_3$ (6 nm)/NPB (40 nm)/mCP (10 nm)/10 wt% emitter:host (20 nm)/DPEPO (3 nm)/DBTDPO (30 nm)/LiF (1 nm)/Al (100 nm) | 3.0 | 476 | 15.2 | 30.4 | 38.2 | – | – |
| TCzTrz SiCz3Py1 ITO (50 nm)/HATCN (7 nm)/TAPC (50 nm)/DCDPA (10 nm)/20 wt% emitter:host (25 nm)/TSPO1 (5 nm)/TPBi (25 nm)/LiF (1.5 nm)/Al (100 nm) | 4.4 | 476 | 15.1 (7.5) | 25.4 (13.8) | – | – | [40] |
| SiCz2Py2 | 4.4 | 478 | 18.7 (7.6) | 32.7 (15.9) | – | – | [40] |
| SiCz1Py3 | 4.0 | 479 | 18.8 (7.4) | 34.0 (16.4) | – | – | [40] |
| BDpyInCz mCBP-CN ITO/HAT-CN (10 nm)/NPB (50 nm)/mCP (10 nm)/20 wt% emitter:host (30 nm)/DBFPO (10 nm)/50:50 Liq:DBFPO (30 nm)/Liq/Al (100 nm) | 4.7 | 472 | 11.2 | – | – | 21 (LT80) | [42] |
| 2CzTPN Sy ITO/4% ReO$_x$/CzSi (60 nm)/CzSi (15 nm)/10 wt% emitter:host (20 nm)/PO-T2T (50 nm)/Liq/Al | 2.6 | – | 20.4 (16.9) | 47.7 | 46.8 | – | [46] |
| 2CzTPN Asy | 2.6 | – | 15.0 (12.7) | 37.6 | 42.2 | – | [46] |
| PXZDSO2 CzPO ITO (95 nm)/PEDOT:PPS (40 nm)/PVK (25 nm)/6 wt% emitter:host (40 nm)/TmPyPB34 (50 nm)/LiF (1 nm)/Al (100 nm) | 7.6 | 561 | 5.4 | 14.3 | 4.9 | – | [48] |
| DCzPO | 4.3 | 561 | 11.3 (8.9) | 32.3 | 18.8 | – | [48] |
| TCzPO | 4.0 | 561 | 12.3 (10.1) | 35.5 | 21.5 | – | [48] |
| FCzPO | 4.0 | 561 | 13.6 (10.9) | 39.1 | 23.8 | – | [48] |
| 2CzTPN PzCz ITO/α-NPD (35 nm)/mCP (10 nm)/3 wt% emitter:host (20 nm)/PO-T2T (50 nm)/PO-T2T (50 nm)/Liq/Al (80 nm) | 4.2 | 494 | 15.0 | 37.2 | 24.4 | – | [53] |
| DPAC-TRZ 29Cz-BID-BT ITO/HAT-CN (10 nm)/TAPC (35 nm)/10 wt% emitter:host (20 nm)/TSPO1 (10 nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (120 nm) | – | – | 20.8 | – | – | – | [56] |
| 39Cz-BID-BT | – | – | 20.4 | – | – | – | [56] |
| 4CzCNPy SFXSPO ITO/MoO$_3$ (6 nm)/NPB (70 nm)/mCP (5 nm)/5 wt% emitter:host (20 nm)/SFXSPO (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al | 3.5 | – | 19.7 (16.0) | 60.9 | 54.6 | – | [68] |
| 4CzTPN | 3.6 | – | 19.6 (16.9) | 62.9 | 54.9 | – | [68] |
| 4CzPNPh | 3.7 | – | 22.5 (20.9) | 63.3 | 53.7 | – | [68] |
| 4CzTPNPh | 3.8 | – | 13.9 (12.2) | 32.4 | 26.8 | – | [68] |
| DACT-II 23αICTRZ ITO/TAPC (30 nm)/TCTA (10 nm)/15 wt% emitter:host (25 nm)/Bphen (30 nm)/LiF (0.5 nm)/Al (150 nm) | 3.7 | 494 | 21.2 | – | 56.6 | – | [76] |
| 23βICTRZ | 3.5 | – | 19.2 | – | 53.5 | – | [76] |
| 32αICTRZ | 3.7 | – | 26.2 | – | 69.7 | – | [76] |
the bipolar hosts where the intermolecular interactions such as π–π stacking, etc., play a major role. Polycyclic aromatic hydrocarbons, e.g., triphenylene, are special in this respect because of their stacked packing that leads to 1D charge transport behavior, and modulation of the frontier molecular orbitals because of their stacking that leads to 1D charge transport behavior, and modulation of the frontier molecular orbitals through variations of the attached functionalities.

Duan and co-workers recently synthesized a series of triphenylene and carbazole based bipolar hosts materials for TADF and phosphorescence OLEDs (D1–D5, Scheme 5) through Suzuki–Miyaura coupling reactions. \[39\] These materials exhibit good thermal and morphological stabilities and very similar absorption and emission spectra. All of them possess triplet energy higher than 2.6 eV, which makes them suitable for green dopants.

Table 1. Continued.

| Emitter | Host | Device structure | \( V_{in} [\text{V}] \) | \( \lambda_{max} [\text{nm}] \) | EQE\(^a\) [%] | CE\(^b\) [cdA\(^{-1}\)] | PE\(^c\) [lmW\(^{-1}\)] | \( \tau \) [h] | Ref. |
|---------|------|------------------|----------------|----------------|--------------|----------------|----------------|---------|------|
| STCzBN  | DMIC-TRZ | ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/30 wt% emitter:host (30 nm)/B3PyPM (40 nm)/LiF (1 nm)/Al (150 nm) | 2.8 | – | 19.2 | – | 38.8 | – | \[84\] |
| DMIC-BP | ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/12 wt% emitter:host (30 nm)/B3PyPM (40 nm)/LiF (1 nm)/Al (150 nm) | 2.8 | – | 21.0 | – | 52.9 | – | \[84\] |
| 4TCzTPN | ITO/HATCN (5 nm)/NPB (40 nm)/TCTA (10 nm)/emitter:host (30 nm)/Bphen (40 nm)/LiF (1 nm)/Al (150 nm) | 2.6 | – | 23.2 | – | 70.1 | – | \[84\] |
| HAP-JTPA | 3PCzPFP | ITO (150 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/1 wt% emitter:host (25 nm)/TSPO1 (5 nm)/TPBI (40 nm)/LiF (1.5 nm)/Al (200 nm) | – | 580 | 24.3 (9.8) | – | 70.4 (16.8) | – | \[57\] |
| Self | tbCz-SO | ITO/PEDOT:PSS/tbCz-SO/TmPyPB/Cs\(_2\)CO\(_3\)/Al (solution processed) | 5.1 | 464 | 2.6 | 4.0 | – | – | \[79\] |
| Self | poCz-SO | ITO/PEDOT:PSS/poCz-SO/TmPyPB/Cs\(_2\)CO\(_3\)/Al (solution processed) | 6.1 | 480 | 6.2 | 10.5 | – | – | \[79\] |
| Self | Cz-CzCN | ITO/PEDOT:PSS (40 nm)/Cz-CzCN (60 nm)/PhPO (40 nm)/Al (solution processed) | 3.1 | 510 | 15.5 | 46.3 (39.0) | 39.3 | – | \[80\] |
| Self | POCz-DPS | ITO/PEDOT:PSS (25 nm)/POCz-DPS (35 nm)/TPBI (35 nm)/Cs\(_2\)CO\(_3\) (2 nm)/Al (100 nm) (solution processed) | 5.4 | 480 | 7.3 | 12.6 | – | – | \[81\] |
| Self | TZ-Cz | ITO/PEDOT:PSS (25 nm)/TZ-Cz (35 nm)/TPBI (35 nm)/Cs\(_2\)CO\(_3\) (2 nm)/Al (100 nm) | 4.0 | 520 | 6.5 | 20.0 | – | – | \[82\] |
| Self | TZ-3Cz | ITO/PEDOT:PSS (25 nm)/TZ-3Cz (35 nm)/TPBI (35 nm)/Cs\(_2\)CO\(_3\) (2 nm)/Al (100 nm) | 3.6 | 520 | 10.1 | 30.5 (29.0) | – | – | \[82\] |

\(a\)External quantum efficiency; \(b\)Current efficiency; \(c\)Power efficiency. Maximum values, those at the parenthesis are of data obtained at 1000 cd m\(^{-2}\); \(d\)Device lifetime.

2.4. Carbazole-Based Bipolar Hosts Containing a Silane Core

Choi and co-workers reported three silane core containing hosts for blue TADF OLEDs, namely, 9,9’\(^{9}\)*-((4-(pyridin-3-yl)phenyl)silanelanetrilyl) tris(benzene-4,1-diyli)tris(9H-carbazole) (SiCz3Py1), bis(4-(9H-carbazol-9-yl)phenyl)bis(4-(pyridin-3-yl)phenyl)silane (SiCz2Py2), and 9-(4-(tris(4-(pyridin-3-yl)phenyl)silyl)phenyl)-9H-carbazole (SiCz1Py3) (Scheme 6). \[80\] In these materials, carbazole donor and pyridine acceptor functionalities were attached to tetraphenylsilane core at different molecular
ratios. As the authors aimed at designing hosts for blue TADF OLEDs, materials with high optical energy gap and high triplet energy were essential. A crucial design strategy is to insulate the donor–acceptor electronic communication. They opted for the tetraphenylsilane core as the conjugation blocking unit because of its unique features such as its capability toward resulting in wide optical energy gap due to the nonconjugated tetrahedral molecular geometry, high \( T_1 \) energy, etc. Moreover, the title molecules have bipolar character which makes them attractive as hosts. All these materials owe high triplet energy of about 2.9 eV where the compound SiCz3Py1 containing three carbazole units has relatively higher triplet energy than the others. The ability of these materials to host blue TADF OLEDs was tested using 9,9',9''-(5-(4,6-diphenyl-1,3,5-triazin-2-yl)benzene-1,2,3-triy1)tris(9H-carbazole) (TCzTrz) as a blue dopant. Interestingly, maximum EQEs of 15.1%, 18.7%, and 18.8% were realized from the devices based on SiCz3Py1, SiCz2Py2, and SiCz1Py3, respectively. Performances of these silane core containing hosts were found to be better than the reference bis(4-(N-carbazole)phenyl)-dimethylsilane (2MCBP) hosted device which exhibited only 11.6% EQE. The authors attempted to rationalize the performance difference on the basis of the various photophysical rate constants. The measured \( k_{RISC} \) for the doped films based on the title hosts were found to be about two-times higher than that of 2MCBP probably due to smaller singlet–triplet gap of the dopant in these silane based hosts. The higher \( k_{RISC} \) values of the SiCz2Py2 and SiCz1Py3 hosted films suppressed the nonradiative pathways of the dopant triplet excited state and together with the high PLQY resulted in better performance of the relevant host based devices as compared to the 2MCBP based one. However, the inferior performance of the SiCz3Py1 based device among the three congeners hosts was attributed to lower PLQY of the dopant plausibly due to higher triplet nonradiative rate constant. Thus, the idea of introducing a relatively less conventional conjugation insulator, silane core, between donor and acceptor counterparts to generate bipolar hosts is appreciable. Though these host based OLED devices yield notable maximum efficiencies, the roll-offs are pretty significant and this could be possibly improved either through modification of the device structures or through variation of the molecular structures.

2.5. Carbazole-Based Bipolar Hosts Containing CN Substituted Acceptor

The host material for both TADF and phosphorescence based OLEDs has several common features. However, the host for TADF emitters should meet some additional

**Scheme 4.** Molecular structures of the carbazole-dibenzothiophene based bipolar hosts.

**Scheme 5.** Structures of the carbazole-polyaromatic hydrocarbon based hosts.
criteria, such as deeper frontier molecular orbitals, higher singlet and triplet energies than that of the TADF dopant, etc. The higher singlet and triplet excitation energies of the host suppress singlet energy quenching of the TADF emitter and prevent exciton leakage from the emission layer. However, a high triplet energy is a consequence of higher singlet energy and a wide optical energy gap which have a negative impact on the driving voltage of the device. Lee and co-workers demonstrated a universal host material, \(3',5'\text{-di(carbazol-9-yl)-[1,1'-biphenyl]-3,5-dicarbonitrile} \) (DCzDCN, Scheme 7) for both TADF and phosphorescent OLEDs a couple of years ago.\(^{[41]} \) The bipolar host DCzDCN has a narrow optical energy gap, singlet energy of \(\approx 3.0 \text{ eV} \), and triplet energy of \(2.7 \text{ eV} \), which are sufficient for energy transfer to Ir(ppy)\(_3\) and 4CzIPN emitters. Green OLEDs were then fabricated using TADF emitter 4CzIPN and phosphorescent emitter Ir(ppy)\(_3\). In both the TADF and PhOLED cases, current density, luminance, and turn-on voltages of the DCzDCN based devices are found to be better than that of the model CBP based devices. The deep LUMO of the host assists electron injection and transport which reduces the turn-on voltage. Interestingly, high EQE of about 25\% could be realized for both the TADF and phosphorescent OLEDs employing the same host. Additionally, the device lifetime of the DCzDCN based device was found to be longer than that of CBP based device.

Development of pure blue TADF OLED has been a challenging goal to many researchers since the early days. Apart from the emitter related issues, finding of appropriate host materials for blue TADF emitters is another critical task. The

![Scheme 6. Carbazole based bipolar hosts containing a silane core.](image)

![Scheme 7. Carbazole based bipolar hosts comprising of CN substituted acceptor.](image)
most popular host for blue TADF is DPEPO which suffers from major drawbacks such as stability and poor charge transporting ability, which reduce the device lifetime. Lee and co-workers recently reported an OLED fabricated using an alternative host material \( \text{3',5'-di[(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (mCBP-CN, Scheme 7)]} \) and the blue TADF emitter 5,8-bis(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5,8-dihydroindolo[2,3-c]carbazole (BDpyInCz, Scheme 2).\(^{2,3}\) The mCBP-CN hosted device exhibited a slight blue shifted spectrum as compared to the DPEPO hosted one. Also, increasing the doping ratio of the emitter caused a little bathochromically shifted electroluminescence. Interestingly, the mCBP-CN containing device showed improved driving voltage and a lower efficiency roll-off than that of the DPEPO based device though the latter device exhibited higher EQE\(_\text{max}\). The authors suggested that smaller optical energy gap and deeper LUMO of mCBP-CN and the hole-transporting character of the emitter, BDpyInCz, contributed toward lower operating voltage of the mCBP-CN hosted device. However, an elongated excited state lifetime of the emitter influences triplet–triplet annihilation and singlet–triplet annihilation, which negatively impacts the efficiency roll-off. Most interestingly, the device based on BDpyInCz:mCBP-CN as emitting layer exhibited more than 40 times longer device lifetime than the relevant DPEPO based device possibly due to lower operating current density at the same luminance and higher stability as compared to DPEPO.

Lee and co-workers designed and synthesized a new bipolar host \( 4,4'\text{-(}[3,4'\text{-bicarbazole}]\text{9,9'-diyl})\text{ dibenzonitrile (4CN34BCz, Scheme 7)} \) comprising of two hole-transporting carbazole moiety's linked together at 3 and 4 positions and two electron-transporting benzonitrile fragments connected at the N(9) positions of the two carbazole units.\(^{4,5}\) The effect of cyano group positioning on the overall device performance was also studied by synthesizing another model compound \( 3,3'\text{-(}[9H,9'H\text{-}[3,4'\text{-bicarbazole}]\text{9,9'-diyl})\text{ dibenzonitrile (3CN34BCz)} \) where the CN groups were placed at meta-positions with respect to the carbazole-phenyl linkages instead of para-topology of 4CN34BCz. Both the materials have high triplet energy of more than 2.9 eV and are suitable for hosting the green TADF emitter 4CzIPN. OLEDs were then fabricated using a low doping concentration of 1% 4CzIPN in the relevant hosts. It was found that the electron current density was higher in the 4CN34BCz-hosted device and hole current density was higher in the 3CN34BCz-hosted device. However, the total current density of the TADF device was dominated by the hole current density because of strong electron trapping by the 4CzIPN dopant. Therefore, the current density and luminance of the 3CN34BCz-hosted device were found to be higher than that of the 4CN34BCz-hosted device. Interestingly, the 4CN34BCz-hosted device achieved a higher external quantum efficiency of 21.8% in comparison to the CBP-based device which achieved 19.3%. The efficiency enhancement was attributed to balanced hole and electron density in the emission layer. The maximum quantum efficiency of the 3CN34BCz-based device was found to be only 13.9%.

Li et al. demonstrated a series of small molecule isomeric bipolar host materials, viz., o-CzCN, m-CzCN, and p-CzCN (Scheme 7) and their efficiency to host blue PhOLEDs and TADF OLEDs.\(^{6,7}\) The different connection topologies of the n-type and p-type fragments of the relevant bipolar materials tuned their triplet energy, charge mobility, and the morphological stability. Moreover, these materials were readily available through Suzuki–Miayaura coupling between 3,5-dibromo-benzonitrile and the appropriate carbazole boronic acid. The o-CzCN and m-CzCN isomers were found to have higher triplet energy and better charge transport than the other isomer, p-CzCN. The efficiency of these hosts in OLED was tested by fabricating blue PhOLED using iridium(III) bis(4,6-difluorophenyl)pyridinato-N,C picolinate (FIrpic) and blue TADF OLED using 2CzPN as the emitters. The TADF devices owed turn-on voltages ranging from 3.8–5.1 V. Both the PhOLED and TADF OLED based on o-CzCN and m-CzCN performed better than p-CzCN. The outperformance of m-CzCN-hosted device was attributed to its balanced charge transport, efficient energy transfer from the host to the dopant, and effective confinement of the triplet excitons in the emitting layer due to good spectral overlap between the emission spectrum of the host and the absorption spectrum of the dopant. Notable result was also obtained using o-CzCN as the host. The o-CzCN and m-CzCN-hosted TADF devices exhibited maximum efficiencies \( \eta_{\text{el}} \) of 29.23 cd A\(^{-1}\) (corresponding to \( \eta_{\text{el}} \) of 18.36 lm W\(^{-1}\) and \( \eta_{\text{tot}} \) of 14.52%), and 26.37 cd A\(^{-1}\) (corresponding to \( \eta_{\text{el}} \) of 16.56 lm W\(^{-1}\) and \( \eta_{\text{tot}} \) of 14.98%), respectively. Though the p-CzCN-hosted device was found to exhibit high current density, it suffered from brightness related issue.

Lee and Lee reported a series of donor–acceptor type host materials with different connection topologies, 4-(9-carbazolyl)-[1,1'-biphenyl]-3,5-dicarbonitrile (pCzB-2CN), 3-(9-carbazol-9-yl)[1,1'-biphenyl]-3,5-dicarbonitrile (mCzB-2CN), and 2-(9-carbazol-9-yl)[1,1'-biphenyl]-3,5-dicarbonitrile (oCzB-2CN) (Scheme 7).\(^{8,9}\) These host materials possessing carbazole donor and isophthalonitrile acceptor units were obtained by simple Pd-catalyzed Suzuki coupling reaction between appropriate carbazole boronic acid and brominated isophthalonitrile. The 4CzIPN doped films of these materials exhibited delayed luminescence which made them suitable for fabricating TADF OLEDs. The relevant devices exhibited current density in the order of pCzB-2CN > mCzB-2CN > oCzB-2CN that corroborated well with the sequence of ionization potential (IP)–electron affinity (EA) gap of these materials. The authors explained that due to extended skeleton of pCzB-2CN, charge transport was facilitated through orbital overlap which enhanced the current density. However, in case of oCzB-2CN, a twisted structure perturbed the orbital overlap between adjacent molecules that decreased the current density. Interestingly, the mCzB-2CN based device exhibited maximum EQE of 26.0% and 22.6% at 1000 cd m\(^{-2}\). In cases of the pCzB-2CN-based and oCzB-2CN-based devices, reduced EQEs of 22.9 and 20.9% were observed. This observation matched with the observed PLQY of the relevant films. Nevertheless, the power efficiencies of the pCzB-2CN-hosted and mCzB-2CN-hosted devices were alike, though relatively low quantum efficiency of the pCzB-2CN-hosted device was observed. The authors connected this result with the low driving voltage of the pCzB-2CN based device that originated because of narrow IP–EA gap of the host material. The EL emission of 4CzIPN was host dependent, where a red-shift of the EL emission spectrum was observed in the pCzB-2CN and mCzB-2CN based devices, which was attributed to strong dipole interaction between the host and the dopant.
In a recent article, we demonstrated green and blue TADF OLEDs using two isomeric hosts comprising of cyanopyrimidine acceptor and carbazole donor (Sy and Asy, Scheme 7). The unsymmetrical structural feature of pyrimidine is beneficial to tune the donor–acceptor linkage topology which could result in various isomers with distinct electronic distribution and photophysical properties. The relevant target materials were obtained by controlling the ratio of deprotonated carbazole and trichloropyrimidine followed by cyanylation. These materials owed triplet energy of higher than 3.0 eV and high decomposition temperature (270–280 °C) and high glass transition temperature (150 °C for Sy, not detected for Asy). The electrochemical studies revealed weaker electron withdrawing character of 2-cyanopyrimidine as compared to that of 4-substituted analogue. The absorption spectra of these hosts illustrated typical characteristics of π–π* and charge transfer transitions where the nature of the latter band was apparently different for the two materials due to their differing structures. Though the room temperature fluorescence spectra of Sy and Asy were typical to charge transfer emission, interestingly, their phosphorescence spectra (77 K) illustrated a localized triplet for Asy and CT character of Sy triplet. Quantum chemical structural simulations of these compounds were interesting too. The HOMO of Sy was found to be composed of both the carbazole sub-units, whereas that of Asy was found to consist of only one carbazole unit. This different behavior of orbital distribution probably caused different photophysical characteristics of the two materials. Though the singlet–triplet gap for both the materials was measured to be around 100 meV, none of them exhibited evident TADF character. However, they performed well in blue and green TADF OLEDs based on 2CzTPN (blue) and 4CzIPN (green) dopants, the efficiency of devices using Sy as the host outperforming that of the Asy-hosted devices. The Sy-hosted devices realized η_{ext}max as high as 24.3% for green devices and 20.4% for blue devices. The high performance of these devices was due to high PLQY of the relevant thin films and improved light out-coupling due to horizontal dipole orientation preference (θ = 88%) of these emitters.

It is needless to mention that the cyano substitution is attractive in optical materials because of many exciting properties such as good electron withdrawing ability, low reorganization energy, etc. This is simply reflected by more entries of materials in this category as compared to the previous sections. Significantly, most of this class of hosts exhibit excellent device performance as far as their device efficiencies are concerned though, some of them have turn-on voltages higher than 4.0 V. However, optical (and other physicochemical) properties of these hosts are easily tuned through straightforward structural modification which is advantageous.

2.6. Carbazole-Phosphine Oxide Based Hybrid Hosts

Kim and Lee developed a bipolar type host 2,7-bis(diphenylphosphoryl)-9-phenyl-9H-carbazole (PPO27) for apparent improvement of the 4CzIPN-based devices (Scheme 8). As the photophysical properties of PPO27 were suitable for application of this material as the host for 4CzIPN, green TADF OLEDs were fabricated using the relevant host and dopant. Interestingly, the current density of the devices based on PPO27:4CzIPN as emitting layer was lowered as a doping concentration of 2% but a rise at 5%. This was possibly due to charge trapping by the emitter. The enhancement of current density at 5% doping concentration was attributed to facile charge hoping. Therefore, the optimum doping concentration was found to be 2% and a maximum quantum efficiency of 21.1% could be realized from the relevant device.

Su and co-workers reported a series of polarity-tunable host materials based on diphenylphosphine oxide and oligocarbazoles (CzPO, DCzPO, TCzPO, and FCzPO) (Scheme 8). The diphenylphosphine oxide was chosen as the electron-accepting unit due to its excellent electron injection and transport ability and the oligocarbazoles formed by linkages through the 3(9) position were employed as the donor units. The 3(9) linkage topologies of oligocarbazoles were expected to maintain high triplet energy levels of the target compounds, since N-heteroatoms together with large dihedral angles between adjacent carbazoles would minimize their conjugation. The TADF emitter 2-(4-phenoxazinophenyl) thianthrene-9,9′,10,10′-tetraoxide (PXZDSO2, Scheme 2) was employed as the dopant in the relevant study. All these oligocarbazole-based host materials owed different polarities as indicated by their PL spectra in different polar solvents. Interestingly, CZPO and DCZPO revealed greater polarities than those of TCZPO and FCZPO. At first, the authors fabricated solution-processed OLEDs by doping 6 wt% PXZDSO2 in these hosts with a device configuration: ITO (95 nm)/poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT:PSS) (40 nm)/poly(9-vinylcarbazole) (PVK) (25 nm)/PXZDSO2: host (6 wt%, 40 nm)/TmPyPB34 (50 nm)/LiF (1 nm)/Al (100 nm). The foremost important observation from the obtained device data was that performance of the devices improved as the number of carbazole units in the relevant hosts increased. This was attributed to the better charge balance in the higher oligomers. Significantly, the CZPO-based device performed poorest among the series with a maximum EQE of only 5.4% and maximum luminance of 693 cd m⁻². Also the relevant device had a large driving voltages of 12.2 V at the luminance of 100 cd m⁻² probably due to large electron injection barrier. Notably, the FCzPO-based device had the lowest turn-on voltage in the series (4.0 V) and high external quantum efficiency of 13.6% and a low efficiency roll-off. OLEDs were also prepared through vacuum sublimation using CZPO and DCZPO as the hosts, as these materials could be sublimed. The relevant device structure was ITO/4,4′-cytohydroxylidenedicis[N,N-bis(4-methylphenyl)benzamine] (TAPC) (25 nm)/PXZDSO2: host (6 wt%, 35 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (100 nm). The device performances of these co-deposited devices were similar to those of the solution processed devices.

Xu and co-workers reported two quaternary ambipolar phosphine oxide host materials, namely, 9-(4-(9-(4-(diphenylphosphoryl) phenoxy)-biphenyl-4-y1)-9H-fluoren-9-yl) phenyl)-9H-carbazole (9CzFDPESPO) and 9-(4-(9-(30-(diphenylphosphoryl))-40-(2-(diphenylphosphoryl) phenoxy)biphenyl)-4-y1)-9H-fluoren-9-yl) phenyl)-9H-carbazole (9CzFDPEPO) (Scheme 8). They were synthesized to investigate the spatial effect of high-energy-gap hosts on the electroluminescence performance in blue PHOLEDS and TADF OLEDs. For ready comparison, the authors also prepared a ternary analogue 9-(4-(9-(4-(diphenylphosphoryl)phenyl)-9H-fluoren-9-y1)
phenyl)-9H-carbazole (9CzFSPO). As fluorene is known to have electron-transporting character, the short carbazole-triphenylphosphineoxide distance in 9CzFSPO was expected to hinder the hole transportation by the carbazoles across the bulk material. Consequently, the diphenylene π-extender was introduced in the title materials to increase the distance between the n-type and p-type fragments. This design strategy further improved the thermal and morphological stability of the concerned materials. Based on the photophysical characteristics of the title materials, the authors excluded the possible influence of the π-extender on the optical properties of the materials and the host–dopant energy transfer process, and selectively aimed to study the influence that the π-extender might have on the electrical properties of the relevant hosts. Blue TADF OLEDs were prepared using 10,10′-(4,4′-sulfonylbis(4,1-phenylene)) bis(9,9-dimethyl-9,10-dihydroacridine) (DMAC-DPS, Scheme 2) as the emitter. The driving voltages of all these devices were found to be similar. Interestingly, the variation of current density in these devices corroborated with the trend of the relevant electron-only devices, though the luminances of these devices were a bit different. The 9CzFDPESPO and 9CzFDPEPO based devices achieved about 50% higher brightness than that of 9CzFSPO-based one. The 9CzFDPESPO based device performed best among the three hosts with maximum EQE of 16.7% (31.3 cd A⁻¹, 28.1 lm W⁻¹). However, performances of the 9CzFDPEPO and 9CzFSPO based devices were rather comparable with the maximum efficiencies of 13.2% (25.1 cd A⁻¹, 22.4 lm W⁻¹) and 12.2% (21.4 cd A⁻¹, 19.2 lm W⁻¹) which were in line with the D–A distances in the relevant hosts. This was the direct consequence of the highest hole mobility of 9CzFD-PESPO among others in the series.

Kwon and co-workers reported two carbazole and phosphine oxide containing bipolar hosts, namely, (9-phenyl-9H-carbazole-3,6-diyl)bis(diphenylphosphineoxide) (PPO2) and phenyl bis(9-phenyl-9H-carbazol-3-yl)phosphine oxide (3DCPO) (Scheme 8) for blue TADF OLEDs. The material PPO2 contains one carbazole and two phosphine oxide fragments and 3DCPO comprises of two carbazole subunits and one phosphine oxide unit. The different molecular structures of the two hosts impart different polarity. Based on simulation studies, the authors calculated the dipole moments of the materials to follow the order 3DCPO (4.5 D) > PPO2 (3.4 D) > DPEPO (2.2 D). The donor–acceptor structures of these materials induce larger dipole moments than that of DPEPO which contains only the electron deficient component in its molecular structure. Notably, both the hosts exhibit high triplet energy of about 3.0 eV, which are

Scheme 8. Carbazole-phosphine oxide based bipolar hosts.
suitable for hosting a blue emitter. Consequently, DMAC-DPS was chosen as the preferred emitter. The emitter doped films of the newly synthesized materials exhibit typical long-lifetime component characteristic of the delayed luminescence in the time resolved fluorescence spectra. Though the prompt fluorescence in both the films were observed to have similar time scales, the delayed component was found to vary with the host (DPEPO > PPO2 > 3DCPO). The carrier-only devices indicated that the hole current density followed the order of 3DCPO > PPO2 > DPEPO and the electron current density followed the order of PPO2 > 3DCPO > DPEPO. It was apparent that 3DCPO had better carrier balanced property than other congeners which was reflected in higher current density and luminance of the 3DCPO-based TADF device. However, the PPO2-based device realized EQE of 27.8% which was higher than those of the 3DCPO-based TADF device. The authors concluded that with the increment of the operating voltage, the tBCzHDPO adopts a low polarity conformation which caused the allochromism (Figure 2).

Han et al. recently demonstrated an allochroic OLED (that changes color with the applied voltage) using a carbazole-phosphine oxide hybrid host 3,6-di-tert-butyl-1,8-bis(diphenylphosphoryl)-9H-carbazole (tBCzHDPO, Scheme 8).[51] Here the central topic of discussion is the intramolecular N–H⋯O hydrogen bonding between carbazole and diphenylphosphine oxide that locks the molecular geometry in an unusual way. The two P=O bonds could theoretically orient themselves either in outward–outward, outward–inward, or inward–inward fashion out of which the last conformation should have higher energy than the two others. However, existence of the intramolecular hydrogen bond causes the molecule to adopt the theoretically higher energy conformation. Interestingly, quantum chemical simulation studies revealed that the dipole moments of the conformers were different from each other. The authors also investigated three other congeners of tBCoHDPO, viz., one P=O unit containing (tBCzHSPO) and their N–Me analogues, tBCzMSPO and tBCzMDPO (Scheme 8), to establish the role of intramolecular hydrogen bonding on the overall performance. Both the N–H and N–Me analogues displayed almost identical spectral characteristics with triplet energies higher than 2.9 eV which was suitable for a blue dopant. The selected dopant was DMAC-DPS. The tBCzHDPO and tBCzMDPO based devices exhibited turn-on voltage of 3.0 V which was slightly lower than the tBCzHSPO-based and tBCzMSPO-based devices (3.5 V). The tBCzHDPO based device was found to outperform others with the maximum EQE of 15.2% corresponding to current efficiency of 30.3 cd A−1 and power efficiency of 38.2 lm W−1. Interestingly, EL maximum of the relevant device was found to shift with applied voltage from 480 nm (bluish-green) at 3.5 V to 460 nm (blue) at 10 V (Figure 2). This result was similar to a solvatochromic shift of the emission maximum. The authors concluded that with the increment of the operating voltage, the tBCzHDPO adopts a low polarity conformation which caused the allochromism (Figure 2).

Yasuda and co-workers developed bipolar hosts comprising of hole-transporting carbazole and electron transporting diphenylphosphineoxide fragments bridged by a nonconjugating cyclohexane moiety (Cz-PO, Scheme 8).[52] For ready comparison, the authors also synthesized the P=S analogue (Cz-PS, Scheme 8). These materials exhibit impressive thermal (5% weight loss temperature >400 °C) and morphological (Tg >100 °C) stability and high triplet energy of ~3.0 eV. 4CzIPN was chosen as the TADF dopant which exhibited very high photoluminescence quantum yield (>95%) and characteristic delayed fluorescence in these hosts. These devices exhibited impressive performance with maximum EQE of 20.5–21.7% (62.1–68.7 cd A−1 and 51.3–59.5 lm W−1).

Phosphine oxide is an important building block for optoelectronic materials, especially as the electron-transporting functionality in host materials. Both the unipolar and bipolar phosphine oxide based hosts are popular among academic researchers where a desired host is picked up based on its property and device need. A large number of entries in this category of hosts reveal popularity of the concerned functionality. The high triplet energy of such materials together with the diverse scope of material development makes these materials even more interesting. Device stability might be an issue for these materials. However, due to absence of device lifetime data, such analysis would be difficult to perform.

Figure 2. (Left) Electroluminescence spectra of the tBCzHSPO, tBCzHDPO, tBCzMSPO, and tBCzMDPO devices in the operation voltage range of 3.5–10 V. (Right) Variation of CIE coordinates of the relevant devices in the mentioned voltage range and mechanism of the allochromism. Reproduced with permission.[51] Copyright 2017, American Association for the Advancement of Science.
2.7. Other Acceptor Containing Carbazole Based Bipolar Hosts

Adachi and co-workers reported a six-carbazole cyclotriphosphazene host material, hexakis(9H-carbazol-9-yl)cyclotriphosphazene (PzCz, Scheme 9), which had a high triplet energy of 3.0 V and very high decomposition temperature (>470 °C).[53] Interestingly, these properties were notably better than those of the common host materials, mCP ($E_T = 2.9$ eV, $T_d = 370$ °C) and CBP ($E_T = 2.7$ eV, $T_d = 440$ °C). The cyclotriphosphazene core was chosen, as it has a rigid planar structure and excellent chemical and thermal stability. PzCz was easily synthesized from hexachlorocyclotriphosphazene ($P_3N_3Cl_6$) via a one-pot nucleophilic substitution. The X-ray crystal structure of the host material revealed quasi-tetrahedral arrangement of the peripheral carbazole heterocycles around the phosphorous atoms of the planar central $P_3N_3$ ring. The highly twisted structure hindered conjugation between the carbazoles, which leads to the high triplet energy of the material. The absorption and emission bands of PzCz appeared at the ultraviolet region and the emission in the solid state is bathochromically shifted. Blue-green OLEDs were then fabricated using 5-bis(carbazol-9-yl)-1,4-dicyanobenzene (CzTPN) as the emitter and PzCz as host.

Scheme 9. Other acceptor containing carbazole based hosts.
For a ready comparison, OLED was also fabricated using mCP as the host. Importantly, the current density and luminance of the PzCz-hosted device were found to be appreciably higher than those of the mCP-hosted device at the same driving voltage and the former has a lower turn-on voltage (4.2 V) than that of later. The PzCz hosted device displayed a maximum current efficiency of 37.2 cd A\(^{-1}\) and power efficiency of 24.4 lm W\(^{-1}\), corresponding to a maximum EQE of 15.0% that was higher than that of the mCP hosted device over the whole current density range. The PzCz was also tested for a green TADF-OLED using 4CzIPN as the emitter. The subsequent device achieved a high luminance of up to 49 200 cd m\(^{-2}\) and high EQE of 18.2%.

Kippelen and co-workers fabricated a TADF OLED using an ambipolar host material 3,5-di[carbazol-9-yl]-1-phenylsulfonylbenzene (mCPSOB, Scheme 9) comprising of carbazole as hole-transporting moiety with a phenylsulfone as electron-transporting moiety and the TADF emitter 4CzIPN.\(^{[54]}\) The relevant devices turned-on at 3.2 V at 10 cd m\(^{-2}\) and 4.8 V at 1000 cd m\(^{-2}\) and achieved EQEs of 26.5% (80.6 cd A\(^{-1}\)), 24.3% (73.7 cd A\(^{-1}\)), and 21.5% (67.1 cd A\(^{-1}\)) at 10, 100, and 1000 cd m\(^{-2}\), respectively, with a doping concentration of 5 wt% 4CzIPN. These data showed significant improvement with respect to the device fabricated from CBP as host. The CBP based TADF device exhibited an EQE of only 8.2% at 10 cd m\(^{-2}\) and 12.6% at 1000 cd m\(^{-2}\). Also, higher turn-on voltage of 3.8 V was noted for the CBP based device as compared to 3.2 V for mCPSOB based devices. The mCPSOB device exhibited low efficiency roll-off at high luminance, e.g., EQE > 22% at 1000 cd m\(^{-2}\) compared to only 9.2% at 1000 cd m\(^{-2}\) for the CBP-hosted device. The improved device performance of mCPSOB as compared to CBP was attributed to better energetic alignment of the adjacent layers in case of the former which resulted in facile charge transfer from the host to the dopant. Also, the lower efficiency roll-off of the mCPSOB based device was attributed to a) lowering of the triplet exciton quenching due to high triplet energy of the host and b) ability of the title host to maintain charge balance across a larger range of applied voltage as compared to CBP.

Pei et al. recently demonstrated two highly twisted bipolar host materials, namely, 2,6-bis[2-(9H-carbazol-9-yl)phenyl]pyridine (CzDPPy) and 2,6-bis[2-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl]pyridine (tCzDPPy) (Scheme 9).\(^{[55]}\) The materials were obtained in moderate to good yield by simple Ullmann coupling reactions between 2,6-bis[2-bromophenyl]pyridine and carbazole/3,6-di-tert-butyl-carbazole. Highly twisted structures of the compounds were revealed by the single crystal structure of CzDPPy. Both these materials exhibited excellent thermal (T\(_g\) = 300 °C) and morphological (T\(_m\) > 100 °C) stability. The absorption and emission due to the materials obeyed similar spectral profile with a slight red-shift in case of tCzDPPy possibly due to the electron donating nature of the tert-butyl group. Quantum chemical calculations indicated that the occupied orbitals of CzDPPy were slightly raised in energy due to the positive induction effect of the tert-butyl group as compared to CzDPPy which might have contributed to the red-shift. Both these materials exhibited triplet energies higher than 2.6 eV, which made them suitable for sky-blue TADF OLEDs. The single-carrier devices of these hosts depicted higher hole current than electron and tCzDPPy appeared to possess better balanced carrier-transporting property than CzDPPy. Consequently, 2CzPN was chosen as the emitter and OLEDs were fabricated. Both the devices exhibited low turn-on voltages of 3.4 and 3.9 V, respectively, for CzDPPy and tCzDPPy and emission solely from the TADF emitter. The EL emission spectra of the two doped films were slightly shifted in their wavelengths, as ascribed to different exciton recombination zone within the emission layer. Unlike the other Cz2PN based reports, the title devices realized relatively low luminance. However further insight of the device data revealed some interesting pattern. Though the electron and hole-only devices revealed better charge transporting ability of tCzDPPy, the device based on CzDPPy (16.0%, 34.8 cd A\(^{-1}\), 33.1 lm W\(^{-1}\)) was found to outperform that based on tCzDPPy (11.7%, 28.9 cd A\(^{-1}\), 23.3 lm W\(^{-1}\)). This anomalous behavior of tCzDPPy was attributed to the bulkier tert-butyl group which might cause a different molecular orientation in the emitting film and incomplete energy transfer to the dopant.

Adachi and co-workers reported a rigid acceptor unit, benzimidazobenzothiazole (BID-BT), with electron-transporting benzimidazole and benzothiazole as the backbone linked by a tertiary nitrogen atom.\(^{[56]}\) Two BID-BT derivatives, viz., 2,9-di(9H-carbazol-9-yl)benzo[db]imidazo[2,1-b]thiazole (29Cz-BID-BT) and 3,9-di(9H-carbazol-9-yl)benzo[db]imidazo[2,1-b]thiazole (39Cz-BID-BT), were developed (Scheme 9) as hosts for blue TADF and phosphorescent OLEDs. The materials were synthesized by copper-catalyzed Ullmann coupling between halogenated benzimidazo[2,1-b]benzothiazole and carbazole. The absorption spectra of both the compounds were quite similar, exhibiting intense bands at 270–300 nm due to \(\pi-\pi^*\) transitions and weak bands at 325–340 nm region due to \(n-\pi^*\) transitions. Both of the materials exhibited structureless emission at about 360 nm indicating some charge transfer character in their excited states due to spatially separated frontier molecular orbitals. The triplet energies of these materials were reported to be as high as \(\approx 3.0\) eV. Two doped films of 29Cz-BID-BT and 39Cz-BID-BT with the blue TADF material 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-di-phenyl-9,10-dihydroacridine (DPAC-TRZ, Scheme 2) exhibited characteristic prompt and delayed luminescence at room temperature. Based on the carrier-only devices, it was found that the current density of the hole-only devices with 29Cz-BIDBT and 39Cz-BID-BT was a little greater than that of mCBP, which was probably because of the rigidity of BID-BT. By contrast, the current densities of the electron-only devices were found to be much higher than that of mCBP which could be due to the electron withdrawing ability of BID-BT. This difference in current density between the carrier-only devices was much smaller in case of BID-BT hosts than that of mCBP at the same voltage which indicated excellent bipolar transport and lower efficiency roll-off in the BID-BT based devices than that with mCBP. Blue TADF OLEDs were then fabricated using the blue TADF material, 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-di-phenyl-9,10-dihydroacridine (DPAC-TRZ). The 29Cz-BID-BT and 39Cz-BID-BT based devices attained EQEs of 20.8% and 20.4%, respectively, which were the highest reported for blue TADF OLEDs at the time of the report. The devices also exhibited lower efficiency roll-off than that of the mCBP-based device probably due to the well-balanced electron/hole-transport in the emission layer.
Lee and co-workers recently developed an ambipolar host 3-(9-phenyl-9H-carbazol-3-yl)furo[2,3-b]pyridine (3PCzPP, Scheme 9) comprising of phenylcarbazole and pyridofuropyridine donor and acceptor counterparts, respectively.[57] The relevant material was obtained by Suzuki coupling reaction between appropriate 9-phenylcarbazole and benzo[furo]pyridine intermediates. Photophysical studies indicated a triplet energy of approximately 2.7 eV which was suitable for hosting red-emitting dopants. Consequently, a red emitter HAP-3TPA (Scheme 2) was selected as the dopant to fabricate TADF OLED. The relevant HAP-3TPA doped film exhibited characteristic delayed luminescence of the emitter, though at a shorter emission lifetime than that obtained in CBP film. Based on the carrier-only device data ambipolar charge transport property of 3PCzPP was revealed, though the title host material owed higher hole current density than electron current. Interestingly, the current density of the HAP-3TPA:3PCzPP based device was found to reduce with increasing the doping concentration which was attributed to the carrier trapping effect of the emitter. However, both the luminance and current density of the 3PCzPP hosted device were found to be appreciably higher than those of the CBP based device. At the optimal 1% doping concentration, the maximum EQE was found to be 24.3% (70.4 lm W$^{-1}$) as compared to 18.6% (46.1 lm W$^{-1}$) realized in CBP based device. Interestingly, a slight red-shift of the electroluminescence maximum was found with increasing doping concentration from 1% to 3% that was probably due to strong intermolecular interactions between the emitter molecules at higher doping concentration. However, the efficiency roll-off of the relevant device was found to be significant (9.8%, 16.8 lm W$^{-1}$ at 1000 cd m$^{-2}$).

Ma and co-workers reported three new bipolar host materials, 9,9′-(’2′-(1H-benzoimidazol-1-yl)-1,1′-biphenyl)-3,5-diyl)bis(9H-carbazole) (o-mCPBI), 9,9′-(’3′-(1H-benzoimidazol-1-yl)-1,1′-biphenyl)-3,5-diyl)bis(9H-carbazole) (m-mCPBI), and 9,9′-(’4′-(1H-benzoimidazol-1-yl)-1,1′-biphenyl)-3,5-diyl)bis(9H-carbazole) (p-mCPBI) by integrating mCP with benzoimidazole moiety via the ortho-, meta-, and para-positions of N-phenyl group (Scheme 9).[58] The rigid molecular structures of these hosts resulted in high thermal and morphological stability. All the three compounds have similar absorption spectral characteristics. However, their phosphorescence spectra were appeared to be quite different. The three benzoimidazole-based hosts were found to exhibit lower hole current density but drastically enhanced electron current density than mCP, illustrating enhanced bipolar character than mCP. The authors employed these hosts in TADF OLEDs using the dopants, 2CzPN (blue) and 4CzIPN (green). The 4CzIPN-o-mCPBI based device attained a peak EQE of 18.7% with almost no efficiency roll-off. Similarly, the maximum EQE of the o-mCPBI-2CzPN based device was 10.2%. The authors also utilized these hosts in multicolor phosphorescence OLEDs with impressive device performance.

Li et al. synthesized a series of bipolar hosts, namely, 5-(2-(9H-carbazol-9-yl)-phenyl)-1,3-dipyrrozolbenzene (o-CzDPz), 5-(3-(9H-carbazol-9-yl)-phenyl)-1,3-dipyrrozolbenzene (m-CzDPz), 5-(9-phenyl-9H-carbazol-3-yl)-1,3-dipyrrozolbenzene (3-CzDPz), and 5-(3,5-di(9H-carbazol-9-yl)-phenyl)-1,3-dipyrrozolbenzene (mCPDPz) for phosphorescent and TADF OLEDs (Scheme 9).[59] All these materials contain pyrazole as the n-type unit and carbazole as the p-type fragment. The four compounds were synthesized through Suzuki cross-coupling reaction between 3,5-dipyrrozolyl-1-bromobenzene and the corresponding carbazole-containing boronic acid. The absorption spectra of the compounds illustrated typical features of \( \pi-\pi^* \) transitions and were slightly structure dependent. The absorption spectrum of 3-CzDPz in the range of 280–350 nm has stronger intensity than the other compounds in the series. The authors attributed this to the reversal of the energy of the \( \pi-\pi^* \) and \( n-\pi^* \) excited states in case of this material. This was further supported by theoretical calculations. A small bathochromic shift of about 6 nm for the emission spectrum of m-CzDPz as compared to that of o-CzDPz was ascribed to the fact that minimization of steric hindrance and less twisted molecular backbone for m-CzDPz resulted in stabilization of the \( S_1 \) state. However, the triplet energy of o-CzDPz was found to be larger than the others possibly because of localization of the triplet excited state on carbazoles due to highly twisted structures. The simulation studies revealed that the spin density distribution of o-CzDPz was mainly on the carbazoles. Based on single-carrier devices, it was found that 3-CzDPz owed higher hole and electron mobility than the two other congeners, viz., o-CzDPz and m-CzDPz. The authors attributed this observation to a) more coplanar stacking of 3-CzDPz molecules in the solid state (based on crystal structures) which facilitated charge transport and b) enhanced hole transportation behavior of the carbazole containing materials when carbazole is substituted at the C(3) position instead of the N(9) position. It was further observed that the increment of the ratio of p-type and n-type fragments to 1:1 in mCPDPz had resulted in higher hole current than all three materials o-CzDPz, m-CzDPz, and 3-CzDPz. Sky-blue PhOLEDs were fabricated using Flrpic as the emitter which exhibited excellent device performance. Furthermore, TADF devices were fabricated using 2CzPN (sky-blue) and 4CzIPN (green) as emitters. The sky-blue device with 3-CzDPz host realized good performance with the maximum efficiencies of 26.2 cd A$^{-1}$, 20.6 lm W$^{-1}$, and 15.8%. The o-CzDPz, m-CzDPz, and mCPDPz based blue TADF devices also performed well. For example, the o-CzDPz hosted device exhibited maximum efficiencies of 26.2 cd A$^{-1}$, 15.6 lm W$^{-1}$, and 14.5%. The EQE of these devices correlated well with the PLQY of the doped films. The green TADF devices also exhibited notable performance with high brightness, high efficiencies, and low efficiency roll-off. For example, the m-CzDPz based device exhibited a maximum brightness of 24,050 cd m$^{-2}$. The maximum efficiencies of 41.1 cd A$^{-1}$, 32.2 lm W$^{-1}$, and 13.3% were achieved by 3-CzDPz based device.

Device performance of this class of hosts clearly leaves a footprint of the diversity of material design and the scope of developing new materials. Though many of the acceptor functionalities are less popular than cyano or diphenylphosphine oxide in hosts, nevertheless, it is appreciable to test new materials in optoelectronic devices.

### 2.8. Cyanocarbazole-Based Hosts for TADF OLEDs

Simple modification of the carbazole backbone by introducing electron-accepting cyano (CN) functionality enhances its
electron affinity and thus improves the electron-transporting ability.\cite{60,61} Using this idea we developed a simple and yet elegant host 9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazole-3-carbonitrile (mCPCN, Scheme 10), which is a slight alteration of the structure of mCP.\cite{62} However, this modification dramatically altered the physicochemical properties of the relevant material \(T_g = 97\,^\circ\mathrm{C},\ T_d = 313\,^\circ\mathrm{C},\ E_T = 3.0\,\mathrm{eV}\). The compound mCPCN was synthesized by a simple two-step synthetic approach starting with mCP, mono-bromination at the 3- position of one of the carbazole fragment followed by cyanation. Initially we tested the ability of the newly synthesized material in blue PhOLED employing FIrpic as the emitter which exhibited maximum \(\eta_{\text{ext}}\) of 26.4% (58.6 cd A\(^{-1}\), 57.6 lm W\(^{-1}\)). Recently we developed a series of small molecule pyridine and pyrimidine containing TADF emitters.\cite{63} These emitters together with mCPCN as the host in blue-green to yellow TADF OLEDs realized high EQE of 23–31%. In another recent report, we demonstrated above 37% EQE from a cyan TADF OLED based on a spiroacridine-triazine emitter and mCPCN host.\cite{64} The mCPCN doped film of another acridine-triazine hybrid (DMAC-TRZ) as the emitting layer in a blue-green TADF OLED exhibiting excellent device performance (26.5%, 66.8 cd A\(^{-1}\), 65.6 lm W\(^{-1}\)).\cite{16} Very recently Zeng et al. reported two orange-red TADF OLEDs based on mCPCN as the host and two acridine-1,8-naphthalimide based TADF emitters.\cite{65} The relevant devices achieved very high EQE of 21–29.2%.

Lee and co-workers developed two analogous CN-modified host materials, 9-(2-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-carbazole-3-carbonitrile \(\text{o-PhCzCNCz}\) and 9-(3-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-carbazole-3-carbonitrile \(\text{m-PhCzCNCz}\) (Scheme 10), which comprised of two differently substituted carbazole heterocycles linked through a phenyl spacer at different connection topology.\cite{66} Both the fluorescence and phosphorescence spectra of o-PhCzCNCz were found to be blue-shifted as compared to those of m-PhCzCNCz possibly due to twisted structure by steric hindrance. These materials possess high triplet energy \((\approx 2.8\,\mathrm{eV})\), deep LUMO, bipolar charge transport nature, which make them suitable for blue TADF OLED. Consequently devices were fabricated using 2,3,4,5,6-penta(9H-carbazol-9-yl) benzonitrile \(5\mathrm{CzCN}\) at a doping concentration of 15%. Interestingly, it was found that the successive devices based on these hosts exhibit better current density and luminance than that of mCBP based device. However, the current density and luminance of the m-PhCzCNCz-based device were better than those of o-PhCzCNCz hosted device possibly due to higher carrier density in the former device. According to the authors, the sterically crowded o-PhCzCNCz hinders electron and hole transport due to diminished orbital overlap between the molecules. Interestingly, the EQEs of the o-PhCzCNCz and m-PhCzCNCz hosted devices were 16.4% and 15.0%, respectively, which were considerably lower than 9.3% of the mCBP hosted device. In the mCBP-based device, strong electron trapping by 5CzCN hinders carrier balance, but in the o-CzCN and m-CzCN devices the carrier balance is improved because of diminished LUMO gap between hosts and emitter. The m-PhCzCNCz-based device was found to have higher operational stability than mCBP and o-PhCzCNCz based devices possibly due to wide emission zone, carrier path separation, and electron stability of m-PhCzCNCz. The bipolar charge transport property induces wide emission zone which enhances the device lifetime by minimizing triplet-triplet annihilation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme10.pdf}
\caption{Molecular structures of the cyano substituted carbazole based TADF hosts.}
\end{figure}
Also, separation of the charge carriers in the emission layer by the n-type and p-type hosts reduces the effect of degradation of each host material thereby enhancing the lifetime.

Lee and co-workers reported three host materials based on a dibenzothiophene moiety, namely, 9,9’-(dibenzo[b,d]thiophene-2,8-diyl)bis(9H-carbazole-3-carbonitrile) (DBT2CzCN), 9-(8-(9H-carbazol-9-yl)dibenzo[b,d]thiophen-2-yl)-9H-carbazole-3-carbonitrile (DBTCzCzCN), and 9-(8-(9-phenyl-9H-carbazol-3-yl)dibenzo[b,d]thiophen-2-yl)-9H-carbazole-3-carbonitrile (DBTPCzCzCN) (Scheme 10). The absorption spectra of these materials consisted of typical π-π* and n-π* bands. The estimated singlet energy of DBTPCzCzCN was slightly lower possibly due to extension of conjugation and weak D–A character. Triplet energy of DBTPCzCzCN was found to be lower than the other member of the series due to extended degree of conjugation through 3-position of the carbazole moiety. Blue TADF OLEDs were fabricated using 5CzCN as the emitter. The relevant devices were aimed at higher operational stability rather than higher efficiency. The operating voltages at 1000 cd m⁻² were observed in the range of 4.94–5.60 V and the J and L values of the relevant host-based devices were found to be higher than those of mCBP based device because of deeper LUMO of these hosts as compared to mCBP. Among the other members of the series, the DBTPCzCzCN based device achieved higher current density because of its shallower HOMO than others. The maximum EQEs of the relevant devices were 11.1, 14.9, and 15.7% at 30 wt% concentration of 5CzCN in DBT2CzCN, DBTCzCzCN, and DBTPCzCzCN, respectively. The high EQE of the DBTPCzCzCN based device as compared to other host based devices was possibly due to balanced hole and electron transport, as observed in the single carrier devices. The operational lifetimes of the DBT2CzCN-, DBTCzCzCN-, and DBTPCzCzCN-based devices were observed to be 66, 80, and 53 h (up to 60% of initial luminance), respectively. The operational stability of DBTCzCzCN was found to be better than that of other members of the series and mCBP. Based on bond dissociation energy (BDE) calculation, the authors concluded that the operational stability of DBTCzCzCN was partly due to the higher BDE of the C–N bond between dibenzothiophene and cyanocarbazole than that of DBTPCzCzCN and mCBP in negative polaron state. Another reason for the longer operational stability of DBTCzCzCN was assigned to balanced carrier transportation as compared to the others that led to widely spread recombination zone and longer lifetime.

Cyanocarbazole-based hosts are interesting materials because of their excellent photophysical and physicochemical properties. A little modification of carbazole by introducing a cyano functionality greatly alters its electronic properties, which in turn modifies device performance of the relevant hosts. Our modification of mCP to mCPCN is a great example for this. Though cyano-functionalized acceptor units have been heavily used in OLED hosts, the cyano-functionalized donor units are relatively less popular and this leaves a great scope of new material development.

3. Phosphine Oxide-Based Hosts

Xu and co-workers developed a highly twisted and asymmetrical spiro[fluorene-9,9’-xanthene] (SFX) phosphine oxide host substituted with a single diphenylphosphine oxide (DPPO) group at its 4’-position (SFXSPO) (Scheme 11). This material was prepared at a good yield from SFX through a successive two-step lithiation and phosphorylation reactions. The twisted structure of the compound enhances molecular rigidity resulting in a high glass transition temperature (Tg) over beyond 180 °C indicating good morphological stability. The atomic force microscopy (AFM) images of codeposited films of SFXSPO doped with the blue, green, yellowish green, yellow, and orange TADF emitters bis[4-(9,9-dimethyl-9,10-dihydroacridine)phenyl]sulfone (DMAC-DPS); 2,3,5,6-tetracarbazole-4-cyano-pyridine (4CzCNPy); 2,3,5,6-tetrakis(carbazol-9-yl)-1,4-dicyanobenzene (4CzTPN); 3,4,5,6-tetrakis(3,6-diphenylcarbazol-9-yl)-1,2-dicyanobenzene (4CzPNPh); and 2,3,5,6-tetrakis(3,6-diphenylcarbazol-9-yl)-1,4-dicyanobenzene (4CzTPNPh), respectively, illustrated smooth surface with root mean square roughness of =0.3–0.4 nm, indicating good compatibility of these emitters in the host matrix. TADF OLEDs were then prepared to examine the materials potentiality as a universal TADF host. The blue device achieved maximum EQE of 17.9% (30.3 cd A⁻¹, 30.7 lm W⁻¹) with low efficiency roll-off. Though the external quantum efficiency of the green device was found to be higher (19.7% corresponding to 60.9 cd A⁻¹ and 54.6 lm W⁻¹) than the blue device, the former suffered from greater extent of efficiency roll-off than the latter. This could be ascribed to the quenching of triplet excitons of the green emitter 4CzCNPy due to its longest lifetime. The shorter lifetime of 4CzTPN caused reduced efficiency roll-off. Notably, the yellow device based on SFXSPO exhibited great efficiency (EQEmax up to 22.5% (corresponding to 63.3 cd A⁻¹ and 53.7 lm W⁻¹) with negligible EQE roll-off. The corresponding orange device also attained a good EQEmax of 13.9%, maximum current efficiency and power efficiency of 32.4 cd A⁻¹ and 26.8 lm W⁻¹, respectively, that were better than the relevant CBP-based device. Based on the good performance of these monochromatic TADF OLEDs, the authors further attempted to fabricate single host nearly white OLED (WOLED) using DMAC-DPS and 4CzPNPh as blue and yellow emitters, respectively. Unfortunately, the driving voltage of the WOLED was slightly higher than the pertinent blue and yellow devices due to thicker device architecture of the WOLED. However, the white device achieved a maximum EQE of 19.1% (50.5 cd A⁻¹, 40.6 lm W⁻¹) corresponding to a ηlight as high as 95.5%.

The major problem associated with the hitherto known blue TADF OLEDs is the driving voltage. In order to achieve a lower driving voltage at practical luminance, both the carrier injecting and transporting ability of the host should be optimal with concomitant reduction of the exciton quenching. Xu and co-workers realized that crystal packing of the host molecules played an important role in carrier transportation and an optimum intermolecular interaction would not quench the excitons induced by intermolecular interactions. The research group considered that close packing motif would lead to balanced carrier transportation and quenching suppression, as this packing pattern resulted in closest and regular molecular arrangement. Consequently, the authors developed a phosphine oxide host 5,10-diphenylphosphathrene 5,10-dioxide (DPPDO2A) (Scheme 11), which exhibited spheroidal configuration and spherical packing mode through intramolecular and intermolecular hydrogen bonds (Figure 3). Two other
Scheme 11. Molecular structures of the phosphine-oxide based hosts.
compounds, 5,10-disulfide congener DPDPS2A and 5-oxide 10-sulfide congener DPDPSOA, were also demonstrated which illustrated disordered packing modes. All these materials depicted almost identical absorption and photoluminescence spectral profile owing to the insulating effect of the sp³ phosphorous atom and the negligible influences of P = X (X = S and O) on the electronic states. The triplet energy of these hosts is impressively high (≈3.0 eV) to support blue TADF dopants. DMAC-DPS doped films of these hosts revealed TADF character of the dopant and the DPDPO2A based film achieved PLQY of 84% which was the highest among the other films illustrating most effective quenching suppression. Interestingly, among the congeners, the material, DPDPO2A, with a spherical packing pattern achieved excellent electron and hole mobility and highest PLQY from its DMAC-DPS-doped film. Blue TADF OLEDs were then fabricated where the DPDPO2A-based device achieved low driving voltage and maximum EQE of more than 20%.

Huang and co-workers reported simplified highly efficient blue TADF OLEDs utilizing phosphineoxide based hosts, namely, 4,6-bis(diphenylphosphoryl) dibenzothiophene (DBTDPO) and 4-diphenylphosphoryl dibenzothiophene (DBTSPPO) (Scheme 11) and DMAC-DPS as the dopant. The authors also synthesized three electron transport materials (ETMs), 2-(diphenylphosphoryl)dibenzothiophene sulfone (2DBSOSPO), 3-(diphenylphosphoryl)dibenzothiophenesulfone (3DBSOSPO), and 4-(diphenylphosphoryl)dibenzothiophene sulfone (4DBSOSPO), which were collectively named mDBSODPO. The authors optimized the compatibility between DBTDPO and mDBSODPO with respect to structural configuration, packing mode, and interfacial interaction by adjusting the substitution positions of DPPO groups in mDBSODPO. They also tried another ETM, namely, 4,6-bis-(diphenylphosphoryl) dibenzothiophene sulfone (46DBSODPO). Though the electron injecting and transporting ability of 46DBSODPO was found to be rather inferior, its DMAC-DPS-based blue TADF device exhibited high EQE of 16.1% with low efficiency roll-off. This was because of the highest compatibility of the material with DBTDPO host and the suppression of effect on interfacial exciplex. Therefore, apart from optoelectronic properties, material compatibility is also an important parameter to consider while developing light emitting devices.

The host molecules in a TADF OLED function a crucial role in exciton harvesting. Though DPEPO is a popular host for blue TADF OLEDs, it has a drawback of efficiency roll-off due to its weak electronic activity. Xu and co-workers
of 22′DPEPO to the effective suppression of collision-induced quenching through reduced host–dopant interactions and strong steric effect of its ortho-DPPOs. Also, the unsymmetrical structure of 24′DPEPO further weakened the intermolecular interactions, leading to maximum efficiencies of 30.6 cd A\(^{-1}\), 27.5 lm W\(^{-1}\), and 20.1\% EQE. By contrast, the maximum efficiencies of 24DPEPO-based devices were the lowest among the series.

Lee and co-workers recently developed a soluble high triplet energy host material (oxybis(3-(tert-butyl)-6,1-phenylene) bis-(diphenylphosphine oxide) (DPOBBPE, Scheme 11) for solution-processed blue TADF and hyper fluorescence OLEDs.\(^{[72]}\) The relevant TADF OLED utilized the blue emitting 5CzCN as the dopant and the hyper fluorescence OLED involved codoping of 5CzCN and 2,5,8,11-tetra-tertbutylperylene. The tert-butyl group was introduced in the diphenylphosphine oxide backbone to improve solubility of the host as well as to suppress the magnitudes of the intermolecular interactions. This simple design strategy retained the high triplet energy of the host (\(\approx 3.0\) eV), as the tert-butyl group was not expected to undergo strong electronic coupling with the diphenylphosphine oxide. The 5CzCN-doped film of DPOBBPE clearly exhibited the delayed luminescence characteristic of the emitter. Interestingly, the PL spectrum of the dopant in DPOBBPE host was slightly blue shifted as compared to that of the DPEPO based film which was attributed by the authors to suppression of the host–dopant intermolecular interactions by the tert-butyl groups in DPOBBPE. The solution-processed TADF OLEDs achieved an impressive 25.8\% maximum EQE (52.3 cd A\(^{-1}\), 27.1 lm W\(^{-1}\)).

Another strategy to improve the performance of the DPEPO type host based devices is to modify the structure of the phosphine oxide hosts. The multi-insulating linkage strategy as demonstrated by Xu and co-workers is effective, as it blocks conjugation between the various counterparts. This group developed a tris-phosphine-oxide host material, 2,2′,4-tris(di(phenyl) phosphoryl)-diphenylether (DPETPO) and a tetra-phosphine-oxide host 2,2′,4,4′-tetra(di(phenyl) phosphoryl)-diphenylether (DPEQPO) to prove this concept (Scheme 11).\(^{[73]}\) The famous host material DPEPO, having two DPPOs at 2- and 2′-positions, attains a symmetrical structure which renders the DPE completely exposed to intermolecular interactions. However, the extra DPPO at 4-position in DPETPO reduces molecular symmetry and partially blocks its DPE core. In case of DPEQPO, the fourth DPPO at 4-position restores the symmetry. Interestingly, the electron and hole mobilities of DPETPO were found to be 1.96 \(\times\) 10\(^{-6}\) and 2.96 \(\times\) 10\(^{-8}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively, which were higher than...
those of DPEPO and DPEQPO-based devices. The higher carrier mobility of DPETPO was attributed to its higher electron affinity, properly exposed DPE as carrier transporting channel, and regular molecular alignment; whereas the poorer mobility of DPEQPO was owing to its completely surrounded DPE core. Blue TADF OLEDs were then fabricated employing DMAC-DPS as the dopant. Interestingly, the DPETPO based devices exhibited the best performance with the lowest driving voltages of 2.8 V and the highest efficiencies of 23.0% for EQE which are comparable to those of the phosphorescent counterparts.

Phosphine oxides are celebrity in optoelectronic research. A majority of this class of materials are used in blue OLEDs because of the high triplet energy of the hosts. As can be seen from data in Table 1, considerable attention has also been paid to test the phosphine oxide based hosts in blue TADF OLEDs and impressive device performance could be realized. Though DPEPO has remained the most popular host in this category, the peripherally modified diphenylphosphine oxides have gained popularity among researchers. However, a concern of these host based devices is the significant roll-off for power and current efficiencies.

Han et al. recently demonstrated influence of host excited state dipole field on the quenching of excitons of the blue TADF emitters by synthesizing three different series of bipolar dibenzothiophene bridged carbazole–phosphine oxide hybrid hosts (DBTPOCz, DBTPOPhCz, and DBTPOFAr (Scheme 11). In these hosts, the dipole moment was modulated either through increasing separation between the D/A counterparts by introducing phenyl spacer or by blocking the conjugation by incorporating a σ-bridge. The materials exhibited routine spectroscopic behavior and triplet energy as high as ≈ 3.0 eV so as to host blue dopants such as DMAC-DPS. Performance of the relevant devices exhibited good correlation with the excited state dipole moment of the host. The DBTPOFAr based devices realized highest efficiencies, whereas performances of the DBTPOPhCz hosted devices were inferior. Suppression of the intramolecular charge transfer by incorporating a σ-blocking functionality in DBTPOFAr resulted in local excited state that caused reduced excited state dipole moment (≈ 2 Debye), minimized the exciton quenching, and better device outcome.[18b]

4. Triphenylamine Based Bipolar Hosts

The design of bipolar hosts for TADF OLEDs is not only limited to carbazoles as the hole-transporting and common electron-withdrawing groups such as phosphine oxide, etc., as the electron-transporting group, but also many other heterocyclic subunits have been successfully tested for the construction of TADF hosts. For example, Im and Lee reported a 4CzIPN based TADF OLED using triphenylamine–furodipyridine functionalized bipolar host materials, namely, 3-(furo[2,3-b:5,4-b’]-dipyridin-3-yl)-N,N-diphenylaniline (3TPAPFP) and 4-(furo[2,3-b:5,4-b’]-dipyridin-3-yl)-N,N-diphenylaniline (4TPAPFP) (Scheme 12). The furodipyridine moiety was chosen because of its high electron deficiency due to the presence of two pyridine units, which make it a good electron-transporting functionality and it possessed a high triplet energy. Similarly, triarylamines is also known as a good hole transport moiety and owes a high triplet energy alike carbazole. Therefore, their combination was expected to yield a bipolar host material with high triplet energy which was indeed the case (E_T ≈ 2.8 and 2.6 eV for 3TPAPFP and 4TPAPFP, respectively). Interestingly, the emission due to 3TPAPFP:4CzIPN film exhibited similar spectral profile to that of 4CzIPN, whereas that of the 4TPAPFP:4CzIPN film was broad and featureless indicating inefficient host to dopant energy transfer in the latter case. TADF OLEDs were fabricated using 4CzIPN as the dopant. The current density of the 3TPAPFP-based device was found to be lower than that of the 4TPAPFP-based device. However, both devices exhibited higher current density than the CBP-based device. This was attributed to a) bipolar carrier transporting properties of the host, b) low charge injection energy barrier due to appropriate HOMO and LUMO, and c) formation of intermolecular CT complex. The external quantum efficiency of the 3TPAPFP-based device (21.2%) was found to be higher than that of the 4TPAPFP based device possibly due to the above reasons.

Ma and co-workers developed three nonconjugated host materials, tBu-OXD-o-L-TPA, tBu-OXD-m-L-TPA, and tBu-OXD-p-L TPA by utilizing 2,5-biphenyl-1,3,4-oxadiazole (OXD) donor and triphenylamine (TPA) acceptor (Scheme 12). As compared to carbazole, which is the most famous heterocyclic electron-donating fragment in OLED, triphenyl amine is also an attractive donor group because of its high triplet, good hole-transporting ability, and shallow HOMO. Similarly, oxadiazole is an effective electron-withdrawing functionality in OLEDs. The effective
conjugation between the donor and acceptor constituents in the relevant hosts is broken by the introduction of nonconjugated alkyl chains which preserved the triplet energies of the materials and caused similar photophysical and electrochemical properties. The flexible linkage was introduced between the donor and acceptor constituents with the aim of enhancing the morphological stability. The absorption and emission spectra of the three compounds were found to be almost identical and depicted decoupled donor and acceptor counterparts. TADF OLEDs were then prepared using these hosts and the blue emitter 2CzPN. Notably, the relevant blue devices exhibited similar current density–voltage–luminance (J–V–L) characteristics and device efficiencies. The maximum EQEs of the TADF blue devices were 7.6%, 7.2%, and 7.5% for the o-, m-, and p-hybrids, respectively. Based on the single carrier devices, it was apparent that the tBu-OXD-m-L-TPA containing devices illustrated the lowest hole and electron current densities at the same voltage, causing relatively lower OLED device efficiencies.

Though some interesting materials have been developed in this category using triphenylamine as the hole-transporting moiety instead of the immensely popular carbazole, unfortunately, external quantum efficiencies of these hosts based devices are rather found to be inferior. However, we believe, this opens a great scope for developing new materials through structural modifications for better performing devices.

5. Other Heterocycle-Based Hosts

Duan and co-workers reported a series of indolocarbazole derivatives 23aICTRZ, 23bICTRZ, and 32aICTRZ (Scheme 13) for low efficiency roll-off TADF OLEDs. The crystal structures of these materials illustrated moderately twisted structures and did the quantum chemical calculations. The absorption and fluorescence spectra of all these compounds revealed CT transitions, whereas the phosphorescence spectra were typical to those of locally excited states. This was further confirmed on the basis of simulation studies which manifested large overlap between the hole and particle of the triplet states. However, as compared to 32aICTRZ, the $\Delta E_{ST}$ values of 23aICTRZ and 23bICTRZ were found to be relatively larger probably due to weak coupling between the D–A fragments. As these compounds exhibited relatively small singlet–triplet gap, their doped films in DPEPO illustrated TADF characteristics. The materials were utilized both as emitters and hosts in TADF OLEDs. The performances of the ICTRZs as emitters were examined on the basis of devices with the structures of ITO/TAPC (30 nm)/TCTA (10 nm)/mCP (10 nm)/DPEPO:emitters (25 nm)/Bphen (30 nm)/LiF (0.5 nm)/Al (150 nm). In these cases, DPEPO was chosen as the host, as it owed a high triplet energy which would confine the excitons within the dopant. The EL spectra of the relevant devices had their maxima at 489, 492, and 512 nm for devices with 23aICTRZ, 23bICTRZ, and 32aICTRZ as the emitters, respectively. EQE$_{max}$ of higher than 25% could be realized from the 32aICTRZ-based device which exhibited only a limited efficiency roll-off at high brightness. By contrast, though the films of 23aICTRZ and 23bICTRZ exhibited high photoluminescence quantum yield, their devices could realize low EQE$_{max}$ of only 13.6% and 9.8%, together with significant efficiency roll-off. The efficiency roll-off was attributed to the significant TTA. These materials were also employed as hosts in the TADF devices. In these devices, 9-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-N,N,N’,N’-tetraphenyl-9H-carbazole-3,6-diamine (DACT-II, Scheme 2) was utilized as the TADF emitter.
because of its very high PLQY close to 100%. Interestingly, low driving voltages in the range of 3.52–3.74 V at a high brightness of 5000 cd m\(^{-2}\) were observed which were significantly lower than that of the CBP-based device (5.06 V). The authors noted that, due to high bipolar charge transporting ability and small energy barrier for ICTRzs based devices, carriers were directly transported on the hosts. However, large energy gap for the CBP-based device hindered carrier injection into the host under low voltages and the charges were directly injected into the TADF emitter. Interestingly, a high EQE\(_{\text{max}}\) of 27% could be obtained from the ZDZ-based device with very low efficiency roll-off.

Choi and co-workers synthesized three host materials with carbazole, carboline, and DBT moieties, viz., 2,8-di(9H-carbazol-9-yl)dibenzo[b,d]thiophene (ZDZ), 9-(8-(9H-carbazol-9-yl)dibenzo[b,d]thiophen-2-yl)-9H-pyrido[2,3-b] indole (ZDN), and 2,8-bis(9H-pyrido[2,3-b]jindol-9-yl)dibenzo-b,d]thiophene (NDN) (Scheme 13). In these materials, carbazole and carboline units were directly attached to the 2,8-positions of the dibenzothiophene unit. ZDZ has two carbazole units, ZDN has one carbazole and one carboline unit, and NDN has two carboline units. This difference in molecular structures enables them to display different bipolar characters. The electrochemical studies revealed that both HOMO and LUMO of ZDZ and ZDN were slightly raised as compared to NDN indicating alteration of the FMOs with the number of carboline units present in the host. All these materials exhibited almost similar absorption and emission characteristics and relatively high triplet energy (=2.9 V) to confine the triplet energy of the blue emitter, 2CzPN (2.5 eV). The 2CzPN doped films of these hosts realized delayed exciton lifetimes of 228.85, 208.82, and 135.41 µs, respectively, for the ZDZ, ZDN, and NDN host materials indicating variation of the exciton lifetimes with the host structure. The lifetime of 2CzPN was found to be shorter in the DBT-based host materials than that as mCP serves as host. Also the exciton lifetime shortened with the increment of the number of carboline units in the host. The emission spectra of the dopant were observed to be slightly bathochromically shifted as compared to that in mCP possibly due to the polarity effect. Interestingly, estimation of the RISC rate constant revealed larger values as compared to mCP and alteration of the parameter with the host structure. Blue TADF OLEDs were prepared using 2CzPN as the blue dopant. The operating voltages for the ZDZ, ZDN, and NDN based devices were found to be 5.0, 4.7, and 4.8 V, respectively, at 1000 cd m\(^{-2}\) and these values were lower than that of the mCP based control device (6.2 V). At the same brightness, the respective devices (mCP, ZDZ, ZDN, and NDN) delivered EQE of 4.0%, 4.9%, 6.0%, and 4.7%, respectively. The ZDN-based device realized best performance among the other congeners of the series. The maximum EQE of 25.7% was observed for the ZDZ-based device. The NDN-hosted device also exhibited noteworthy QE of 23.9% at the current density of 0.05 mA cm\(^{-2}\). The authors attributed the outperformance of ZDN- and NDN-based devices to the larger \(k_{\text{RISC}}\) of the 2CzPN dopant in both of the host materials and proper charge balance in the emission layer. Similarly, the overall better efficiency of the ZDN-hosted device than that of the NDN-based device was because of the larger \(k_{\text{nrT}}\) of the latter than the former which caused a drop in efficiency at higher current density for the NDN-based device. It was however found that the EL spectra of the relevant OLEDs in the title hosts were slightly red-shifted than that of the mCP based reference device which matched the trend of their PL spectra.

Lee and co-workers developed two dibenzothiophene-based host materials, namely, 4-(3-(triphenylen-2-yl)phenyl)dibenzo-b,d]thiophene (DBTTP1) and 4-(5′-phenyl-[1,1′:3′,1″terphenyl]-3-yl)dibenzo-b,d]thiophene (DBTTP2) for green TADF emitters to investigate the effect of molecular structure of the host materials on the efficiency and lifetime of the green TADF devices (Scheme 13). The authors chose dibenzothiophene due to its planar structure and aimed to study the device lifetime based on two substituents, i.e., triphenylene and terphenyl. Quantum chemical calculation illustrated localization of HOMO on the dibenzothiophene unit and LUMO on the triphenylene unit in case of DBTTP1. However, both the HOMO and LUMO of DBTTP2 were based on dibenzothiophene. This pointed to the involvement of both the dibenzothiophene and the triphenylene moieties for charge transport in case of DBTTP1, whereas for DBTTP2 the carrier transportation mainly involved the dibenzothiophene unit. The estimated triplet energy of DBTTP2 was slightly higher than that of DBTTP1 probably due to slightly distorted structure. Both of the materials were examined as hosts for a well-known TADF dopant, 4CzIPN. The current density and luminance of the DBTTP1-based device were found to be higher than that of the DBTTP2-based device. The driving voltages at 1000 cd m\(^{-2}\) for the DBTTP1 and DBTTP2 hosted devices were 4.0 and 5.7 V, respectively. The low driving voltage for the former was due to the differences in their electron-transporting moiety, triphenylene in the former versus terphenyl in the latter. The authors noted that, as compared to the terphenyl moiety, the triphenylene unit could enhance the electron density in the emission layer contributing to the high current density of the DBTTP1-based device. Similarly, the quantum efficiency of DBTTP2-based device was 17.5% at 1000 cd m\(^{-2}\) which was higher than that of the DBTTP1-hosted device. Both of the devices were then tested for lifetime which revealed that the lifetime of the DBTTP1-based device was longer than that of the DBTTP2-based device at the same initial luminance of 1000 cd m\(^{-2}\). This was attributed to the difference in structures of the dibenzothiophene attached functionalities. The planar triphenylene moiety in case of DBTTP1 versus the twisted terphenyl moiety for DBTTP2 was attributed for the performance difference.

6. TADF Self-Hosts

Though the vapor deposition technique is mostly used in fabricating OLEDs at present, the solution process technique is another interesting device fabrication technique mainly because of device structure simplification, cost effectiveness, and large-scale production. It is generally accepted that solubility of the components largely influences performance of solution-processed devices. Many small molecules have been tested for solution-processed OLEDs but the major disadvantage of them is poor solubility and crystallization tendency. Also, the neat films of the small molecules suffer from negative effects such as concentration quenching, unwanted excimer emission, etc.
The small molecule OLEDs are thus mostly fabrication through chemical vapor deposition technique where the emissive layer consists of the emitter molecules dispersed in a suitable host matrix. As would be reviewed in this section, dendritic materials are good candidates for solution-processed OLEDs.

Jiang and co-workers reported two alkyl chain containing molecules, tbCz-SO and poCz-SO (Scheme 14), with solution process feature, blue TADF, and self-host behavior. The relevant materials consist of tert-buty carbazole (tbCz) or phosphine oxide carbazole (poCz) moieties connected with a well-known TADF blue emissive core. The alkyl chain connectivity made these materials soluble in common organic solvents. The absorption spectra of these materials are quite similar with a charge transfer band due to the central TADF core near 350 nm and some high energy bands due to other electronic transitions. The time-resolved fluorescence of these materials exhibits a prompt and a delayed component in their spectra. The carrier-only devices revealed that the hole current density of tbCz-SO was higher than that of poCz-SO. However, the electron current density of tbCz-SO was found to be lower than the other counterpart. Solution-processed OLEDs were then fabricated using these self-host TADF emitters. The current densities of the two devices were found to be dependent upon the peripheral host functionality. The tbCz-SO-based devices exhibited a lower turn-on voltage than the poCz-SO-based device presumably due to higher HOMO of tbCz-SO. Based on these observations, the authors suggested that the exciplexes were primarily formed at the peripheral subunits and the excitation energy was then transferred to the central TADF functionality. The poCz-SO-based device exhibited best efficiency with an EQE of 6.2%, whereas the relevant parameter for tbCz-SO-based device was only 2.6%. The authors suggested that the poorer performance of tbCz-SO-hosted device was probably due to weaker carrier balance in the relevant device owing to dominant hole mobility of the material. Similarly, the enhanced device performance of tbCz-SO-based device was attributed to a) improved charge balance due to bipolar character of the material, b) effective confinement of the triplet of the core TADF emitter due to high triplet energy of poCz, etc.

In another report, Ban et al. depicted a dendritic self-host TADF emitter Cz-CzCN (Scheme 14), which was synthesized by simple aromatic nucleophilic substitution reaction. The alkyl chains in Cz-CzCN help to encapsulate the central TADF emitter core and minimize the intermolecular interactions induced exciton quenching. The solution process feature of the relevant material was tested based on performance of four types of devices, as shown in Figure 5. In these devices, PEDOT:PSS and Cs2CO3 served the roles of hole- and electron-injection layers, tris(4-(diphenylphosphoryl)phenyl) benzene (PhPO) was used as an alcohol-processable electron-transporting material. Device A was the control device with vacuum deposited 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl) benzene (TPBI) and Device C was another control device with a vacuum-deposited PhPO. The authors also fabricated Device D without the electron-transporting layer for comparison. The relevant findings show that the material was resistant toward isopropyl alcohol. The Cz-CzCN-based solution-processed device exhibited an impressive ηext of 46.3 cd A−1 and ηCE of 15.5% showing the potentiality of the self-host TADF emitters for solution-processed OLEDs. Another interesting feature of the pertinent study is the simplicity of material construction. Wrapping a core TADF emitter with peripheral functionalities linked by alkyl chains opens up new possibilities for solution-processed OLEDs.

Sun and co-workers reported a bipolar blue TADF self-host dendrimer, POCz-DPS (Scheme 14), where the blue emitter bis[4-(3,6-dimethoxycarbazole)phenyl] sulfone (DMOC-DPS) was used as the TADF emissive core and phosphine oxide substituted carbazole served the role of bifunctional dendrons. To preserve the blue emission from the TADF emitter core and thus to avoid any color impurity, the dendrons were linked to the core through flexible nonconjugated linkers instead of π-conjugated spacers which would spread the frontier molecular orbital distribution throughout the dendrimer. This design strategy makes the TADF emitter core to fluoresce independently with simultaneous encapsulation that suppresses the concentration quenching. Interestingly, this makes the material, POCz-DPS, well soluble in conventional organic solvents, which facilitates the spin-coating process. The single carrier devices based on the POCz-DPS dendrimer and its analogue DMOC-DPS revealed that the former owned almost equal electron and hole mobility, whereas the electron current density of the latter case was inferior to the hole current density. The authors then went to prepare solution-processed nondoped OLEDs with the configuration: ITO/PEDOT:PSS (25 nm)/POCz-DPS (35nm)/TPBI (35 nm)/Cs2CO3 (2 nm)/Al (100 nm). Another control device was also prepared using 10 wt% DMOC-DPS doped in PPO2 as the emissive layer under the same condition. Interestingly, an EQE of 7.3% could be extracted from the solution-processed nondoped device.

Sun and co-workers developed two self-host TADF dendrimers, TZ-Cz and TZ-3Cz (Scheme 14), for solution-processed nondoped fluorescent OLEDs. The 1st and 2nd generation carbazole dendrons in these dendrimers are attached with the TADF core subunit by nonconjugated aliphatic spacers, which preserve the fluorescence due to the TADF core. Like the previous examples, this type of encapsulation suppressed the concentration quenching of the TADF chromophore. The abilities of the two dendrimers in nondoped self-host devices were examined by fabricating OLEDs with the configuration of ITO/PEDOT:PSS/TZ-Cz or TZ-3Cz/TPBI/Cs2CO3/Al through spin-coating. Control device with the TADF emitter TZ was also prepared under the same condition that revealed similar EL spectral characteristics of all the three devices. Interestingly, though the EL spectra of TZ showed an aggregation characteristic that of TZ-Cz and TZ-3Cz had better color purity and were independent of the applied voltage. Among the three devices, the TZ-3Cz-based device exhibited a lower turn-on voltage of 3.6 V, maximum CE of 30.5 cd A−1, and a ηCE of 10.1%, which were significantly higher than those of TZ-Cz (4.0 V, 20.0 cd A−1, and 6.5%) and only TZ-based devices (4.7 V, 3.4 cd A−1, and 1.1%). The authors attributed the superior performance of TZ-3Cz-based device to the following facts: a) better hole injection and transportation of TZ-3Cz than the others due to its higher HOMO, b) improved charge injection and transportation properties of TZ-3Cz due to the bulky tricarbazole, and c) stronger encapsulation in case of TZ-3Cz. These observations established that the selection of appropriate peripheral dendron was absolutely necessary for superior performing self-host dendrimer.
Scheme 14. Molecular structures of the TADF self-host dendrimers.
Developing self-host TADF emitters is appreciable effort. However, sometimes the synthesis and separation of the compounds might become complex which might affect their practical usage in the devices. Solution process technology is simple yet promising. Though the present device data for self-host TADF emitters (Table 1) are fairly basic as compared to other high-performing devices, the efforts to develop more such materials with the anticipation of better performing devices is praiseworthy.

7. TADF Materials as Host

7.1. Conventional TADF Emitters as Hosts for TADF OLEDs

Apart from developing new host materials for TADF emitters, development of new TADF materials as hosts for blue light emitting devices is considerably challenging. Though a majority of the TADF emitter based hosts have been applied in electrophosphorescence devices, there are some reports of their applications in TADF OLEDs. For example, Cheng and co-workers reported two TADF-based host materials, 9-(2,2′-dimethyl-4′-(phenylsulfonyl)-[1,1′-biphenyl]-4-yl)-9H-carbazole (BT-01) and 9-(2,2′-dimethyl-4′-(phenylsulfonyl)-[1,1′-biphenyl]-4-yl)-9H-carbazole-3-carbonitrile (BT-02) (Scheme 15), consisting of a carbazole with or without a cyano moiety and diphenylsulphone linked through a twisted biphenyl \( \pi \) bridge.[83] Both of the materials exhibit high triplet energy (\( \approx 3.0 \) eV) and small \( \Delta E_{ST} \) which made them suitable for blue phosphorescence and TADF devices. Both of the materials exhibited similar absorption spectra with strong \( \pi - \pi^* \) and weak \( n - \pi^* \) characters, though their emission spectra appeared to exhibit a difference because of the different carbazole groups. The estimated \( \Delta E_{ST} \) for the two materials were 0.45 and 0.52 eV for BT-01 and BT-02, respectively. Both of the BT-01 and BT-02 films show two decay components, viz., a prompt component of nanosecond time scale and a delayed component in microsecond time scale. Though the materials have relatively higher singlet–triplet gaps compared to the available \( k_B T \) energy (\( k_B = \) Boltzmann constant) of \( \approx 25 \) meV in the surroundings at 298 K, the authors excellently described the origination of the delayed luminescence in these materials based on excitation power dependent studies. A linear dependence of the delayed emission intensity from the relevant neat films with the excitation power indeed confirms a TADF pathway but that was attributed to intermolecular charge transfer among the adjacent D–A molecules. PhOLED and TADF OLED were then fabricated using Flrpic and 2CzPN as the emitters, respectively. Alike the PhOLED, the 2CzPN-based TADF OLED exhibited best performance for BT-01 hosted device with low driving voltage, maximum EQE of 25.5% corresponding to a current efficiency of 53.0 cd A\(^{-1}\), and power efficiency of 47.5 lm W\(^{-1}\). The corresponding data for BT-02 hosted devices were EQE = 22.3%, CE = 47.5 cd A\(^{-1}\), and PE = 42.6 lm W\(^{-1}\). The outperformance of BT-01-hosted device compared to that of BT-02 was attributed to higher PLQY of the 2CzPN in the former host (99% in BT-01 vs 91% in BT-02).

Duan and co-workers demonstrated employment of a TADF bipolar host material, 11-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-12,12-dimethyl-11,12-dihydroindenolo[2,1-a]carbazole (DMIC-TRZ, Scheme 15), for OLEDs based on the sky-blue TADF emitter 2,3,4,5,6-pentakis-(3,6-di-tert-butyl-9H-carbazol-9-yl)benzonitrile (5TCzBN), green TADF emitter bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)methanone (DMAC-BP), and orange TADF emitter 3,4,5,6-Tetrakis(3,6-ditert-butyl-9H-carbazol-9-yl)benzene-1,2-dinitrile (4TCzTPN).[84] The electron mobility of DMIC-TRZ was found to be 1.03 \( \times \) 10\(^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at an electric field of 1.2 \( \times \) 10\(^6\) V cm\(^{-1}\) and the hole mobility was measured as 1.03 \( \times \) 10\(^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). The relevant orange TADF device using 4TCzTPN as the dopant in DMIC-TRZ had the

Figure 5. Device configurations and fabrication processes of the Cz-CzCN based devices. Reproduced with permission.[80] Copyright 2017, American Chemical Society.
7.2. Exciplex Based TADF Emitters as Hosts for TADF OLEDs

Exciplexes are attractive both as emitters and hosts in TADF OLEDs. In terms of photoluminescence, exciplex is an excited state charge transfer complex between an electron rich and an electron deficient counterpart. Due to the strong intermolecular charge transfer nature, emission from the exciplex is usually broad and is thus less attractive toward obtaining color pure OLEDs. Nevertheless, the exciplexes have been revealed to be potential hosts because of their bipolar nature and TADF character leading to better exciton harnessing ability, efficient charge injection, balanced charge transportation, etc. In order to serve the role of hosts, the exciplexes should meet some obvious criteria such as: a) should possess lower triplet energy as compared to the components so as to confine the excita-
tion energy, b) higher triplet than the dopant to confine the
excitons solely within the guest, c) overlapping of the exciplex emis-
sion spectra with the absorption spectra of the dopant, etc. Alike the con-
tventional TADF emitters, majority of the exciplex hosts have been applied in PhOLEDs. However, there are a few examples for TADF OLEDs, which are summarized in this section.

The term “exciplex” has a slightly different meaning in elec-
troluminescence from that in photoluminescence. Exciplex formation in photoluminescence is a reversible bimolecular process and occurs through Coulombic attraction between the excited species and another ground state counterpart. A partial charge transfer from the donor-centered orbital ($D^0/D$) to an acceptor-centered orbital ($A/A^*$) imparts significant charge transfer character in the exciplex emission spectra. Interaction between the donor and acceptor molecules in the ground state is mostly repulsive and is attractive only in the electroni-
cally excited state. Consequently, the potential energy surface of the excited possesses a minimum. In solution, the exciplex formation is diffusion controlled. However, in the solid state, the molecules are locked in their positions. Under electrical excitation, the charge carriers are injected at the opposite electrodes which move up to the valence and conduction bands of the donor and acceptor in a field bias. As electrons and holes are Fermions, they can be transferred only as whole particles. Therefore, unlike photoluminescence there is no such concept such as partial charge transfer in electroluminescence. The complete charge separated heteromolecular exciton thus formed under the field bias is approximated as an exciplex in OLEDs. Exciplexes were tested in OLEDs as the emitting materials but unfortunately the device efficiency was found not to be impressive as typical TADF emitters. However, employ-
ments of the exciplexes as hosts in OLEDs have received some attention. We have recently reviewed this topic in a sepa-
rate article.[85] In this article we chose only those reports where exciplex based hosts were employed for TADF dopants. The relevant exciplex components cited in this article are summa-
ized in Scheme 16.

Kim and co-workers reported an OLED with 30% EQE based on 4CzIPN emitter and an exciplex host comprising of 1:1 mixture of mCP and 4,6-Bis(3,5-di-3-pyridylphenyl)-2-methylpyrimidime (B3PYMPM).[86] Interestingly, a 5 wt% doped film of 4CzIPN in the said exciplex host exhibited emission mainly from the dopant (515 nm) and a high PLQY of nearly 97%, indicating efficient energy transfer from the exciplex host to the dopant and blocking of the nonradiative decay channels. A large overlap between the exciplex emission and 4CzIPN absorption further confirmed the observation. The authors measured the angle dependent emission of the relevant film, which illustrated horizontal orientation of the dopant ($\Theta=0.73$). Consequently, TADF OLED was fabricated using 4CzIPN as dopant in the 1:1 mCP:B3PYMPM exciplex host. The relevant device had a turn-on voltage of 3.0 V and a driving voltage of 5.6 V was obtained at a luminance of 1000 cd m$^{-2}$. An impressive EQE$_{\text{max}}$ of 29.6% was reported by the authors.

Kim and Lee in another article described an efficient TADF OLED based on 4CzIPN emitter and an exciplex host consisting of 1:1 mixture of mCP and BmPyPb. The authors in the relevant article tried several other exciplex based hosts to optimize the device performance.[87] Four hole-transport type materials, viz., TAPC, TCTA, CBP, and mCP were tested with the electron-transport type materials 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benimidazole) (TPBI) and 1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (BmPyPb) in order to find the optimal combination. It was found that the film of 4CzIPN doped in mCP:TPBI host had stronger emission from the dopant than that in other mixed hosts. In particular, the emissions in TCTA:TPBI and TAPC:TPBI were too weak and host emission was observed, indicating incomplete energy transfer and exciton quenching. The photoluminescence quantum yield of the doped films corresponding to mCP:TPBI, CBP:TPBI, TCTA:TPBI, and TAPC:TPBI were found to be 97, 66, 15, and 6%, respectively. The authors attempted to calculate the energy transfer rates from the Förster radii and excited state lifetimes and the calculated values were found to be $1.5 \times 10^{15}$ and $1.3 \times 10^{16}$ s$^{-1}$ for CBP:TPBI and mCP:TPBI mixed hosts, respectively. When examined for delayed luminescence, it was found that the mCP:TPBI doped film exhibited stronger emission due to efficient energy transfer and suppressed exciton quenching, weak emission in CBP:TPBI based film and almost nonex-
istant emission in case of TAPC:TPBI and TCTA:TPBI films.
The authors commented that CBP:TPBI and mCP:TPBI mixed hosts activated the TADF emission of 4CzIPN dopant, whereas the TAPC:TPBI and TCTA:TPBI hosts deactivated it. Therefore, the mCP:TPBI host was thought to be effective in harvesting the triplet excitons and devices were fabricated using the 4CzIPN dopant. The maximum EQE of the mCP:TPBI device was 25.8%.

Undoubtedly, TADF materials are great hosts too. Their triplet harvesting ability makes them attractive as hosts. Apart from the conventional TADF materials as host, exciplex-forming hosts appear to be promising as the desired property could be readily tuned by simply mixing of appropriate commercially available donor and acceptor materials.

8. Conclusion and Outlook

At this stage we conclude that, though there has been significant progress in developing TADF emitting materials which is reflected by hundreds of research publications since the first report by Adachi and co-workers, the hosts for TADF OLEDs have been largely overlooked. Our database search yielded only a handful number of articles in this area. Although the presently commercialized OLEDs mostly utilize the organo-metallic phosphorescence emitters as the pixels, the promising aspects of TADF emitters are continuously ushering this generation of OLEDs toward industrialization. A quick
The device data table further illustrates the broad scope of research in this area that can be pursued to improve TADF OLED device efficiency. The majority of hosts developed for the TADF OLEDs were tested for the benchmark green emitter 4CzIPN, some for the blue emitters 2CzPN, 5CzCN, and DMAC-DPS, whereas there is still a void for other emission colors. It is worth noting that most of the host materials exhibit excellent device performance, which is surely a great achievement by the researchers in this community. However, industrialization demands a balance between efficiency and operational stability and this should be kept in mind while developing new materials.

Manufacturing cost is a great factor in commercial market where multistep organic synthesis often increases this parameter. Sometimes little modification of small molecules yields interesting results and a better performing material could be obtained at relatively same cost. Our effort to modify the benchmark host mCP to mCPCN is worth mentioning at this point. We have been using mCPCN in TADF OLEDs since we had reported it a couple of years back and the results are truly satisfactory. We encourage the researchers to consider this point while developing new host materials for TADF OLEDs.

Finally, we must mention that the exciplex based hosts sound promising both in terms of avoiding laborious synthetic efforts and cost. Though these materials were found not to be satisfactory as emitters in TADF OLEDs, their ready availability by mixing appropriate commercially available components and tunability of optical properties through alteration of the components together with their excellent capability of exciton harnessing make them favorable candidates as hosts in TADF OLEDs. Most of the exciplex based hosts till date have been tested for PhOLEDs, which leaves ample of scopes for TADF OLEDs.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
excitons, host materials, multifunctional materials, organic light emitting diodes, structure–property relationship, thermally activated delayed fluorescence

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