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Are Pure Hydrocarbons the Future of Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes ?

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Abstract

The fantastic development of phosphorescent organic light-emitting diodes (PhOLEDs) has been undoubtedly driven by the molecular design of high-efficiency host materials for red, green and blue phosphors. Fine tuning the electronic and physical properties of the host materials have allowed to reach very high External Quantum Efficiency (EQE), reported nowadays above 30% for the three colours. The most used molecular design strategy consists to judiciously assemble small functional units to maintain a high triplet energy level (E_T), essential to insure efficient energy transfer from the host to the guest phosphor. To adjust the molecular orbitals energy levels and the charge transport, these functional units display electron-donating (for hole transport) and electron-accepting (for electron transport) capabilities. Hundreds of host materials have been reported in the literature since the discovery of PhOLEDs in 1998. However, they all have a common characteristic: they incorporate heteroatoms. However, if these functional units are highly beneficial for the device performance, several works have highlighted their potential instability in the device. As the stability of blue-emitting PhOLEDs is a central concern in the field, finding alternatives to heteroatoms-based hosts is a mandatory step. In recent years, pure hydrocarbons (PHC) materials, only built with carbon and hydrogen atoms have shown a real potential for the next generation of PhOLEDs. In the light of literature, it appears nowadays that the PHC design strategy is very promising for the future development of OLED industry as a high-performance and low-cost option. This is the purpose of the present *Chemistry Frontiers*.

Introduction

Designing high efficiencies host materials for the emerging technologies of Phosphorescent Organic Light-Emitting Diodes (PhOLEDs) has been, since their discoveries in 1998, one of the main driving force of the field.¹ The EMitting Layer (EML) of a PhOLED consists in a triplet emitter (Guest) disperse into an appropriate Organic Semi-Conductor (Host). This technique allows to reach 100% internal quantum efficiency by recovering both singlet and triplet excitons.¹ Bipolar hosts²⁻³ constructed on the assembly of electron-rich, and electron-poor units, see examples selected among the most efficient materials in each colour in Chart 1,⁴⁻¹⁰ have appeared as the most efficient host materials. Over the years, their designs have been finely tuned in order to reach very high PhOLED performance. Nowadays, the design techniques are rather well-known and the most efficient host materials achieved very high external quantum efficiency (EQE) for red, green and even blue PhOLEDs (>30%).³⁻¹⁰ One of the advantages of donor/acceptor host materials is their capability to efficiently transport both electrons and holes. For example, **SPA-2,7-F(POPh₂)₂** host, reported in 2020, displays rather well-balanced mobilities between holes ($8.2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electrons ($2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),^{8, 11} which favour a good charges recombination in the centre of the EML of the device. Thanks to this

property, **SPA-2,7-F(POPh₂)₂** has been efficiently incorporated in simplified single-layer PhOLEDs (EQE of 18%), in which the additional functional transporting layers have been removed.^{8, 11}

Despite very high performances have been reached, PhOLED technology still suffers from many issues, and the stability of blue PhOLEDs is one of the most important. Reaching high efficiency and stable blue PhOLEDs is undoubtedly the next important barrier to lift towards their industrial exploitations. From a general point of view, blue OLEDs (either fluorescent, phosphorescent, TADF or hyperfluorescent)¹²⁻¹⁵ have always been the weakest link of the technology both in term of efficiency (due to the large gap of blue emitting materials) and stability.^{3, 16-22} The instability of blue PhOLEDs has been the subject of intense research.²³⁻²⁵ It is now widely known that FIrpic, the most used blue phosphor, is involved in the PhOLED degradation processes.²⁴ However, the host material is also an important piece of the puzzle and also involved, at least partially, in the degradation processes. Thus, heteroatoms-based host materials, despite their very high performances present several drawbacks.

First, their molecular structures can be complicated due to the assembly of different donor and acceptor fragments, which increases the synthetic complexity, the environmental footprint and production costs. As different building units are used, many issues can occur. For example, diazafluorene building block is, a good electron accepting fragment but appears to be difficult to handle due to chelating and solubility issues.²⁶⁻²⁷ Quinolinophenothiazine is a recently discovered electron-rich fragment built on a phenylacridine core bridged by a sulphur atom.²⁸ This fragment has recently provided very high performance in simplified PhOLEDs.²⁹ Despite a high HOMO level and stable radical cation species,²⁸⁻²⁹ this fragment suffers from the inversion of the nitrogen atom leading to diastereoisomeric features.³⁰ It is obvious that for the next step of the OLED technology, very simple molecular structures, which can be easily and cleanly synthesized, should be considered. This is a key consideration for the future to provide a new generation of electronics, essential for the ecological transition.

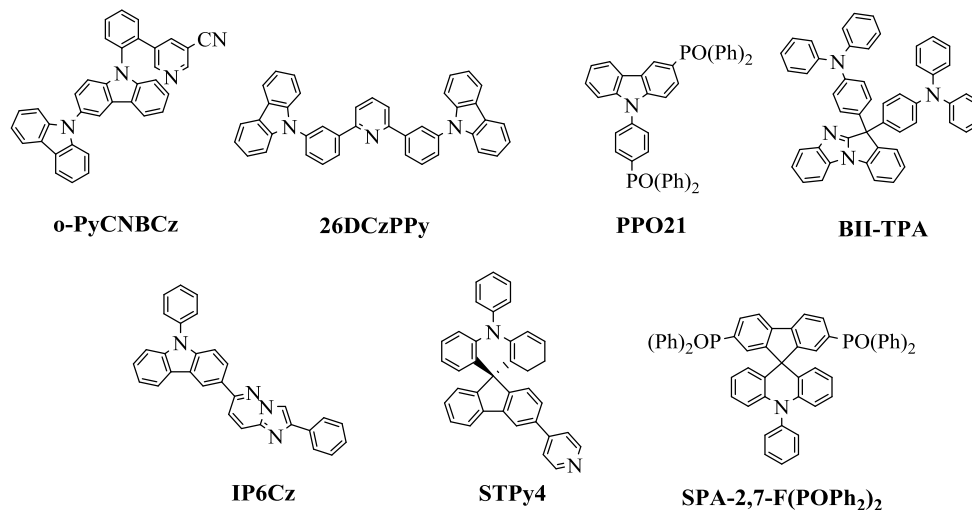


Chart 1: Selected examples of state of the art of heteroatoms-based host materials.⁴⁻¹⁰

Second, regarding the stability, it has been shown that the C–N, C–P and C–S bonds, particularly in their excited states, can be easily broken by the energy of excitons formed in blue PhOLEDs (which is around 3 eV).³¹⁻³³ Indeed, the dissociation energies of the C–N, C–P or C–S bonds in common building units used in host materials lies in this range.³³ In 2013, König and coworkers have reported the key role played by the bond dissociation energies in the chemical degradations in OLEDs (*Exciton induced degradation process*).²⁵ Similarly, Bredas and coworkers have explored the bond dissociation processes in arylsulfones and arylphosphine oxides, two famous building units of host materials, and have shown that C–S and C–P bonds are significantly more vulnerable to dissociation in their first triplet state than in the ground state.³⁴

Thus, pure hydrocarbons (PHC), which are molecules free of heteroatoms, only built with carbon and hydrogen atoms have emerged as a possible solution to increase the stability of blue PhOLEDs (See the most efficient materials reported to date in Figure 1).³⁵ PHCs only use phenyl rings as building unit, which is one of the most inert and stable molecular fragment. Therefore, they do not possess any weak heteroatom-based bonds and can be, most of the time, very easily synthesized. The first example of PHC in PhOLED was reported in 2005 (Figure 2), using a low E_T red phosphor as emitter.³⁶

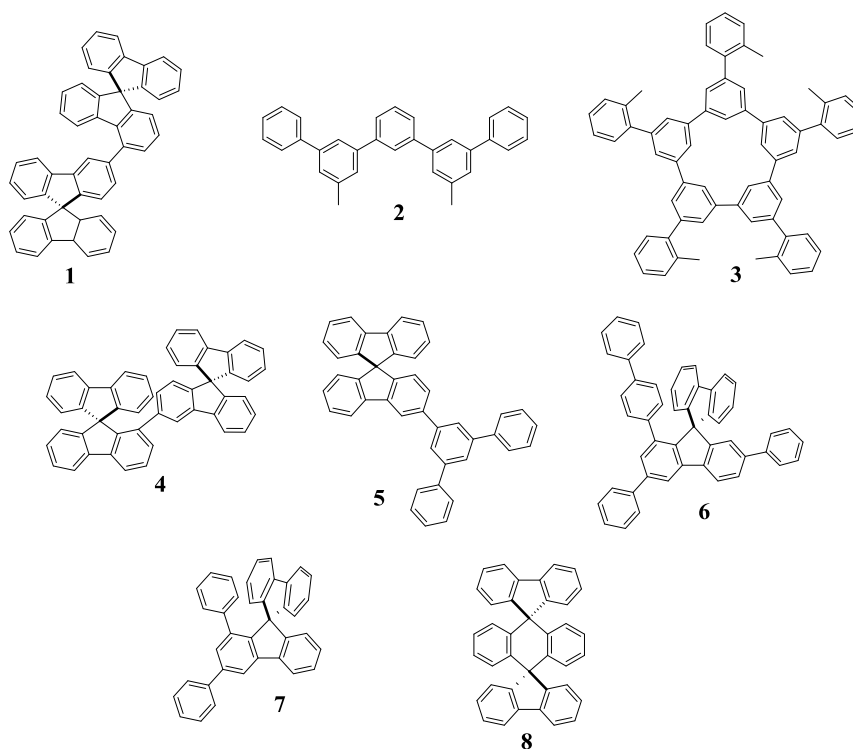


Figure 1. Selected examples of state of the art PHC-based hosts used in PhOLEDs.

Some key dates in the history of PHC are presented in Figure 2. However, elaborating efficient host materials with only phenyl rings appeared, at the beginning, as a very difficult task. Nowadays, this barrier has been lifted and in 15 years, the PHC design to host phosphors in PhOLEDs has become a credible alternative to bipolar hosts containing heteroatoms. Indeed, year after year, the performances of PHC-based devices have increased thanks to the different design tactics elaborated by chemists and in 2020, it has been shown that PHC hosts can overpass heteroatoms-based host materials (see below).³⁷

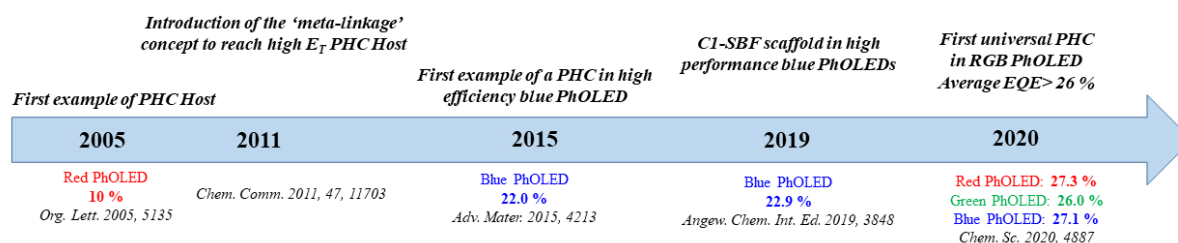


Figure 2. Important dates in the history of PHCs as host materials for PhOLEDs

So, how PHCs have become efficient host materials in PhOLEDs and what are the most efficient designs used to date? The first step was to judiciously assemble phenyl rings to reach high E_T

materials. In this context, an important date in the development of PHC hosts was 2011, when the electronic decoupling using *meta* linkage was introduced in PHCs.³⁸ This linkage has appeared as an efficient molecular tool to disrupt the conjugation of a π -system. This π -conjugation disruption is essential to keep a high E_T , which is a key property to host a blue phosphor. Many PHC hosts materials were then synthesised with the *meta* linkage as key characteristic.³⁹⁻⁴⁶ Despite the PhOLED performances were not always very high (EQE of blue PhOLED below 16%), all these works have significantly contributed to the development of PHC hosts and have undoubtedly opened the way to the high performance reported nowadays. In 2015, Jiang, Liao and their coworkers have reported the first PHC-based blue PhOLEDs (**1**) with an EQE above 20%, clearly opening new perspectives for this class of materials.⁴⁷ Very high efficiency white-emitting PhOLEDs (combination of FIrpic blue emitter and PO-01 yellow emitter) were also fabricated using **1** as host, displaying a very high EQE of 25.3%.

In 2016, a very high EQE of 24.8% was also obtained by Isobe and coworkers with PHC **3** in a simple green-emitting two-region phosphorescent device (structure: ITO/PEDOT:PSS/non-doped Host/Host:Ir(ppy)₃ 6%)/Cs/Al). Interestingly, they have highlighted the significant differences between linear (such as **2**) and cyclic (such as **3**) *meta*-linked PHCs when used as host for green phosphors.⁴⁴⁻⁴⁶ In 2020, the same group has reported an impressive value of 21.4 % with **2** as host in green emitting simplified single-layer PhOLEDs.⁴⁴ This performance is the highest reported to date for a green single-layer-PhOLED (including heteroatoms-based hosts). As single-layer devices^{2, 8, 11, 20, 29, 48} only built with electrodes and EML are nowadays more and more appealing for the future of the OLED technology, this work also shows the real potential of PHC materials in this emerging technology. For more details on SL-PhOLEDs, see the recent review published in 2021.²

In the elaboration of high efficiency PHC host materials, the building units used are of key importance. They should not only allow restriction of the π -conjugation to keep a high E_T but they should also possess very good thermal and morphological stabilities (high decomposition temperature T_d and high glass transition temperature T_g). Regarding the latter, the spirobifluorene (SBF) fragment is a 3D molecular scaffold, widely known in organic electronics for its capacity to highly increased T_d / T_g .^{40, 49 50} The impact of SBF substitution pattern on the electronic properties and particularly on the E_T is far more recent but has been an important step in the development of high efficiency PHCs as host.⁴⁰ Thus, the C1-substituted SBF scaffold reported in 2017,⁵¹ is appeared as an important building block to efficiently restrict the π -conjugation extension thanks to its *meta* linkage keeping in the meantime excellent thermal and morphological properties owing to its spiro bridge.⁴⁰ In 2019, the highly twisted SBF dimer **4** constructed on the C1-substituted SBF scaffold was incorporated as host in blue FIrpic PhOLEDs, **4** displaying an impressive EQE of 22.9%, which was, at that time, the highest reported in the literature for a PHC host.⁵² This device also displayed low turn-on voltages, below 3V. As turn-on voltages is one of the main issue in blue emitting devices, this work has shown that the PHC strategy can be compatible with a good charge injection. Despite this performance was very high and promising for the future of PHC, it was still incomparable with the best heteroatoms-based hosts in blue, green, and red OLEDs (these materials adapted for the three phosphors are called 'universal').²²⁻²⁵ In 2020, the full potential of PHC host materials has been released as the simple PHC host **5**, only constructed on a C3-SBF terphenyl assembly, has overpassed the performance reached by the best universal heteroatoms-based hosts.^{9, 53} This PHC has the huge advantage to be very easily synthesized in a single step with a very high yield at the multi-gram scale. This is undoubtedly of key importance for future industrialization.

Thus, PHC hosts hold nowadays two record performances in the field of PhOLEDs, the most efficient universal host (**5**)³⁷ and the most efficient host (**2**) in a green-emitting single-layer device.⁴⁴ Despite the state of the art performances in red, green and blue PhOLEDs are still hold by bipolar materials, the performances of PHC hosts get closer and closer and this is undoubtedly an important feature. However, their potentials in term of stability is difficult to evaluate as there is, to the best of our knowledge, no stability study published to date with PhOLEDs. There is, nevertheless, one study

published on the stability of a PHC-based device using a TADF emitter, which has shown very promising results (see below).⁴⁷ Such studies will be highly relevant in the coming years.

As the performances are now very high, the interest towards PHC continue to rise and improving the synthesis efficiency is an important step. In early 2021, Lan, You and their coworkers⁵⁴ have reported poly-substituted SBFs based PHCs as hosts for blue PhOLEDs (**6** and **7**, Figure 1). They report the first examples of diarylation/annulation of benzoic acids via an iridium catalyst system, providing a step-economic and efficient pathway to 1-aryl, 1,3-diaryl, 1,7-diaryl and 1,3,7-triaryl SBFs. This work not only shows the efficiency of the C-H activation for the development of PHC materials but also allows to reach poly-substituted SBFs, which are very difficult to synthesize. Thanks to the poly-substitution, **6** displays excellent thermal properties (T_g of 140°C) and a very high EQE of 27.3% when hosting a red phosphor. A very simple modification of the starting material leads to the 1,3-disubstituted SBF **7**, which displays a high E_T of 2.83 eV and a good EQE of 18.6% when incorporated as host in a blue PhOLED. Thus, the C-H activation will surely be an efficient tool in the future design of efficient PHC based materials.

In term of molecular design, increasing the E_T of PHCs is undoubtedly a key direction for the future in order to host deep blue phosphors, which are still missing. To reach this goal, molecular adjustments should be performed such as those very recently performed by Thompson and coworkers.⁵⁵ They have designed the PHC host **8** constructed on two fluorenyl units spirolinked to a dihydroanthracene core. The structural particularity of this PHC host is linked to the fact that there is no pending substituent, which allows to display a very high E_T of 2.92 eV and a very wide HOMO/LUMO difference above 5 eV. The PhOLED incorporates a barely used blue phosphor, namely Fac-tris(N,N-di-p-tolyl-pyrazinoimidazol-2-yl)iridium(III) Ir(tpz)₃, known to be more stable than FIrpic, and displays a high EQE of 18% and a low turn on voltage (2.9 V). Removing all the pending substituent is clearly the right way to increase E_T and a very interesting strategy for the future. However, it should be mentioned that this strategy has already been used notably with SBF, with nevertheless lower performance.⁵⁶ This also highlights the importance of the device engineering to reach high performance blue PhOLEDs

Conclusions and outlooks

PHC hosts, free of heteroatoms, represent nowadays a key evolution in the OLED technology. They can be a possible solution to the blue PhOLEDs instability and their simple structure and synthesis can be a solution to the production costs. The design of Donor/Acceptor host materials has attracted tremendous interest for the last twenty years but the interest towards PHC based materials is more recent. Despite the first example has been published in 2005, PHC hosts have not strongly influenced the scientific community at the beginning, surely because bipolar materials, notably based on the widely known carbazole or phosphine oxide functional units, were far more efficient. However, year after year, the molecular simplicity and easy synthesis of PHCs have attracted more and more attention from research groups involved in the design of host materials. As nowadays some PHC hosts have shown their very high potential, they can be key actors for the future of PhOLED technology.

What are now the next challenges the PHC materials will have to face?

First, as the blue PhOLEDs technology is still the weakest link of the technology, improving the blue PhOLED performance with PHC hosts remains an important challenge. More importantly, in almost all the examples reported in the literature, the blue-greenish FIrpic emitter is used. However, FIrpic emission is not in the deep blue region (CIE of ca 0.15, 0.38) and other phosphors emitting at short wavelengths (deep blue and violet) should be investigated in the future. However, such emitters are

not highly developed in literature, which significantly increases the scientific challenge. For example, phosphor FIr6 possesses an emission at shorter wavelengths (CIE of ca 0.15, 0.32) and has only been tested in a very few instances with PHC hosts. This constitutes an interesting direction for the future of PHCs. However, the CIEs of FIr6 are still far to be in the deep blue region and other phosphors should be developed. To host such deep blue phosphors, the E_T of PHCs should be increased. Thus, the next challenge of PHC hosts will be to increase their E_T to efficiently host the new generation of deep blue phosphors. For that, novel molecular design approaches should also be developed, with for example no pending substituent. This strategy has recently been developed by Thompson and coworkers⁵⁵ and appears promising. The combination of deep blue phosphors and PHC hosts is surely of great interest for OLED technology.

The stability of the blue emitters should also be significantly improved. As FIrpic is unstable and degrades through the loss of the picolate ancillary ligand, finding stable alternative to this widely used phosphor is a key requirement.²⁴ Ir(tpz)₃, a cyclometalated N-heterocyclic carbene, more stable than traditional Ir complexes with datively bound nitrogen ligands such as FIrpic⁵⁷ starts to show a great potential. This type of Ir complexes appears interesting for the future of this technology.⁵⁸ However, the CIE of this phosphorescent emitters (0.17-19, 0.37-0.40)⁵⁵ are roughly similar to those of FIrpic, being therefore inadequate for deep blue emission.

With the new generations of PHC hosts, it will also be important to precisely investigate the stability of the corresponding devices, which is not systematically performed in the PhOLED field. This will be a key in the development of PHC-based PhOLEDs. Thus, in the blue PhOLED technology, the combination of PHC hosts with a more stable Ir complex, such as Ir(tpz)₃, appears as a promising strategy. Another key perspective of PHC-based PhOLEDs lies in white emitting PHC-based devices, which are almost absent from literature. As far as we know, there is only one example reported to date.⁴⁷ As white light emission can be obtained by the combination, in a single EML, of two complementary emissions (*ie* association of a blue and a yellow phosphorescent emitter), a high E_T PHC host could be, in principle, used. This is an interesting direction for the production of low-cost white-emitting devices for lighting applications.

Finally, the potential of PHC hosts could be extended to other generations of OLED, such as TADF OLEDs. Indeed, in 2015, Jiang and coworkers have shown that PHCs can also efficiently host green TADF emitters such as (2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile, 4CzIPN) with a very high EQE of 22.3%.⁴⁷ Beside the very high EQE reached, the group has shown that the device lifetime was also significantly improved compared to that using the well-known 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) as host. This has been an important step but remains nevertheless, to date, one of the rare stability study reported with PHC hosts.

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