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# Pure hydrocarbons: An efficient molecular design strategy for the next generation of host materials for Phosphorescent Organic Light-Emitting Diodes

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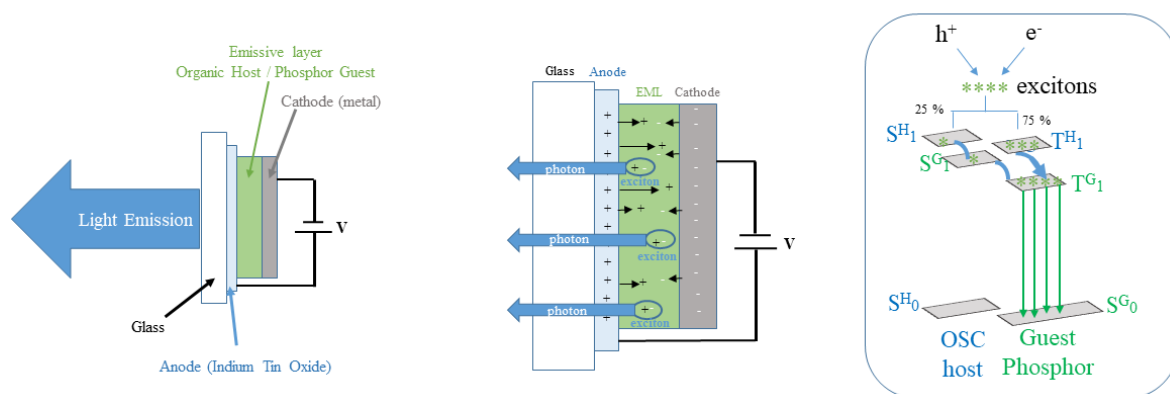
## CONSPECTUS

Fantastic progresses have been made since the discovery of phosphorescent organic light-emitting diodes (PhOLEDs) in 1998.<sup>1</sup> In the emissive layer of a PhOLED, a heavy-metal complex (emitter) is dispersed as a guest in an organic semiconductor (host) in order to harvest both singlet and triplet excitons. This host / guest technique is essential to reach high performance PhOLEDs. Undoubtedly, designing high-efficiency host materials for red, green and blue phosphors has been the main driving force of the field. Nowadays, the most efficient PhOLEDs report very high External Quantum Efficiency (EQE) above 27% for the three colours. The molecular design of these high-efficiency host materials is based on small functional units, which have a crucial role in the device performance. These functional units are constructed on the assembly of electron-rich and / or electron-poor molecular fragments (such as carbazole, phenylamine, phosphine oxide, oxadiazole, pyridine, sulfone etc), which allows to finely tune the molecular orbitals energy levels (HOMO and LUMO) and the mobility of the charge carriers (hole and electrons). However, these molecular fragments incorporate heteroatoms, which in turn increase the molecular design complexity and production cost of the target materials and also create potential instability in the device. Indeed, the fragile C–N, C–P and C–S bonds of such heteroatoms-based hosts are involved, in part, in the OLED instability. As the instability of OLEDs is one of the most important problem to address at the current stage of development, developing new generations of host materials, without heteroatoms, has appeared as an important challenge in the field. In recent years, this new generation of host materials, called Pure HydroCarbons (PHC), only incorporating carbon and hydrogen atoms has drawn the attention of the scientific community. PHC host materials only contain benzene rings, one of the most robust and inert building unit, which are assemble with suitable linkages to adjust their energy levels. However, reaching high performance PhOLEDs with PHC-based hosts has been a real challenge. In the present account, thanks to a structure-properties relationship study, we recount the history of PHC-based host materials for PhOLEDs from the first example published in 2005,<sup>2</sup> to the recent advances, which have shown that PHC hosts can overpass the performance of heteroatoms-based hosts.<sup>3</sup> Our group has contributed over the years to unravel the design principles of PHC hosts in order to improve the devices performance. In the light of recent results, PHC hosts now enter a new era and this work shows that the PHC design strategy is promising for the future development of OLED industry as a high-performance and low-cost option.

## Introduction

In the emerging Organic Electronic (OE) technologies for lighting and display, Phosphorescent Organic Light-Emitting Diodes (PhOLEDs) are the 2<sup>nd</sup> generation of OLEDs (after fluorescent OLEDs) and have encountered a fantastic development (Figure 1).<sup>1</sup> Therefore, PhOLED technology is more mature than the recent 3<sup>rd</sup> generation of OLEDs based on Thermally Activated Delayed Fluorescence (TADF).<sup>4</sup> A PhOLED uses a host-guest EMitting Layer (EML) which consists in a triplet emitter (Guest) dispersed into an appropriate Organic SemiConductor, OSC, (Host). The 100% internal quantum efficiency is fulfilled through harvesting both the singlet (25%) and triplet (75%) excitons (Figure 1, right).<sup>1</sup> During the past two decades, intense research has been focused on developing very high-efficiency hosts. Many molecular design strategies have been developed to gather within a single host all the required properties to fit with a phosphor within a device. An ideal PHC host for a PhOLED should indeed fulfil several precise criteria: (i) a triplet energy ( $E_T$ ) above that of the phosphor used (ca 2.2 eV for red, 2.5 eV for green and 2.7 eV for blue phosphor) to confine the triplet excitons within the phosphorescent guest, (ii) HOMO/LUMO levels adapted to the phosphor used and to the Fermi level of the electrodes to insure an efficient charge injection, (iii) good mobility of electron and hole for efficient charge recombination, (iv) thermal and morphological stabilities to extend the lifetime of the device. In addition, the next generation of host materials should be highly

simple in order to simplify the synthetic access and to provide a clean and simple electronics, essential for the ecological transition. These molecular engineering works of host materials have undoubtedly driven the field. The most efficient are the bipolar hosts constructed on a ‘Donor/Acceptor’ molecular design.<sup>5-6</sup> This design is widely known and consists to judiciously assemble electron-rich (such as carbazole,<sup>7</sup> *N*-phenylacridine,<sup>8-9</sup> quinolinophenothiazine,<sup>10-12</sup> indoloacridine<sup>13</sup> etc) and electron-poor (such as pyridine,<sup>14</sup> dioxothioxanthene,<sup>15-16</sup> phosphine oxide,<sup>8-9</sup> diazafluorene<sup>13, 17</sup> etc) fragments to gather the above mentioned properties within a single molecule. The best host materials achieved over 27% external quantum efficiency (EQE) in red, green or blue PhOLEDs, the three prominent emission colours in this technology.<sup>6</sup> However, the complicated structure of these molecules increases the synthetic complexity, the environmental footprint and production costs. In addition, the fragile C–N, C–P and C–S bonds of such heteroatoms-based hosts are also involved, in part, in the OLED instability.<sup>18-22</sup> Thus, as the instability of OLEDs is one of the most important problem to address at the current stage of development, developing new generations of host materials, without heteroatoms, has appeared as an important challenge in the field. In 2005, a new molecular design approach of host materials without any heteroatoms, so-called pure hydrocarbon (PHC), was introduced in literature.<sup>2</sup> At the beginning, the device performance was very poor because designing an efficient host free of heteroatoms is a very difficult task. Indeed, the functional building blocks such as carbazole or phosphine oxide are very important in the device performance as they allow to respectively adjust the HOMO and LUMO energy levels and increase in the meantime the charge carrier mobilities. Without these functional groups, the task is far more difficult. However, year after year, the performances of PHC-based devices have increased thanks to the different design tactics elaborated by chemists. Thanks to precise structure-properties relationship studies, our group has strongly contributed to the development of this research field. In 2020, an important barrier has been lifted as we have shown that PHC host can overpassed heteroatoms-based host materials.<sup>3</sup> This is the story we want to tell herein.



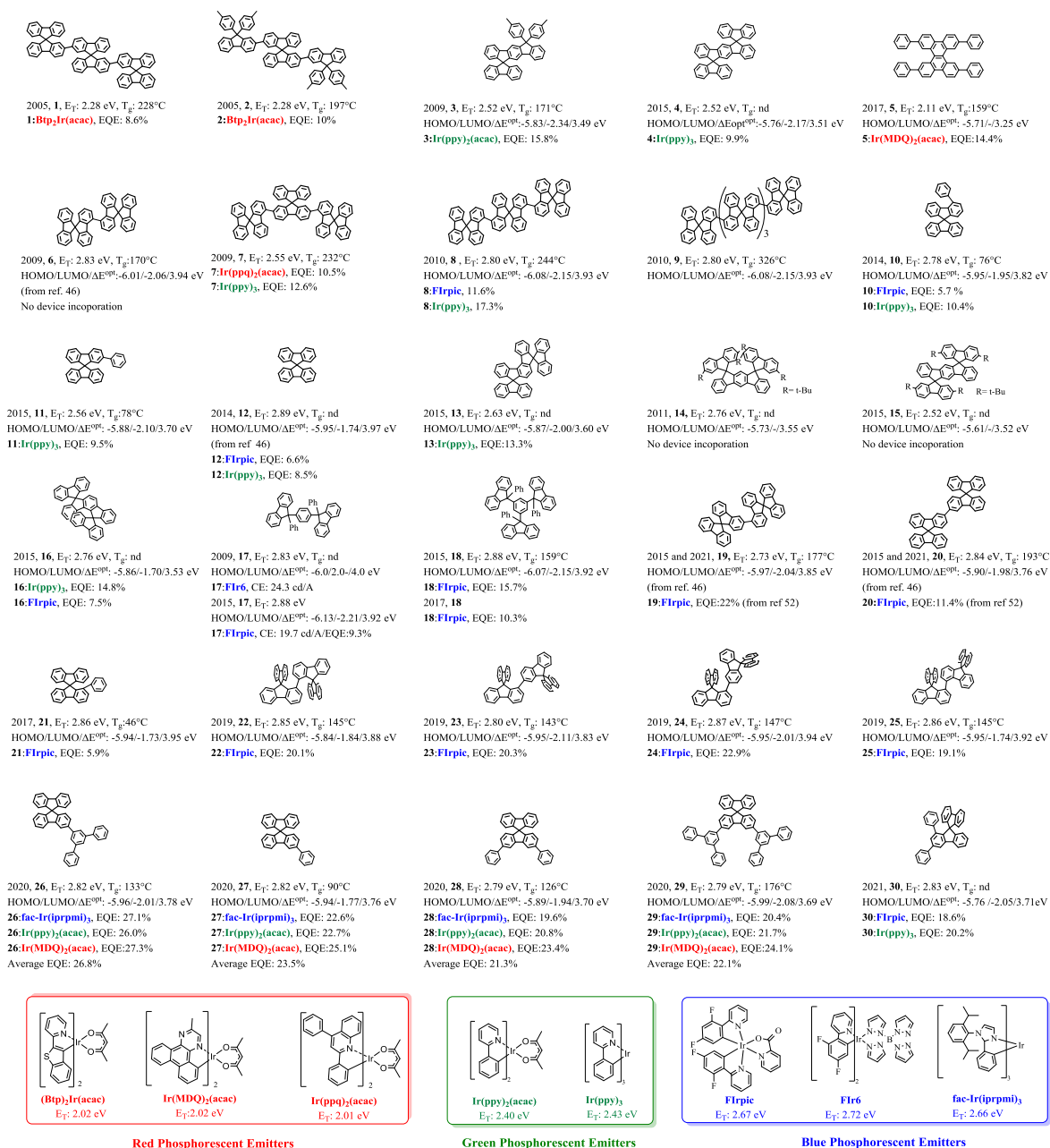
**Figure 1.** OLED simplified working principle (Left and middle). Energy transfer cascade within a PhOLED (Right).

### PHCs as host for PhOLEDs: The first advances.

The first examples of PHC-based materials displayed a low  $E_T$ , and were then only suitable for red PhOLEDs. The first work published in 2005 by Wong and coworkers, has attracted little attention because of the moderate device performance.<sup>2</sup> This work was however an important milestone. The two hosts investigated, **1** and **2**, possess a central spirobifluorene (SBF) connected via a *para* linkage to either another SBF (**1**) or to a 9,9-ditoly-fluorene (**2**), Figure 2. This linkage allows an efficient  $\pi$ -conjugation extension leading to a low  $E_T$  (2.28 eV for both). The host **2** achieved a 10% EQE in red PhOLED using  $\text{btp}_2\text{Ir}(\text{acac})$  ( $E_T = 2.02$  eV) as emitter, which was an interesting performance at that time. The device displayed low turn-on voltage of 2.5-3.0 V, indicating an effective charge injection and showing for the first time that PHC hosts may be used in red PhOLEDs. PHCs have then

continued to hold the attention of many research groups worldwide. The SBF unit was then extended to a dihydroindeno[1,2-*b*]fluorene backbone (**3**) and used as host for the green phosphor Ir(ppy)<sub>2</sub>acac ( $E_T = 2.40$  eV in 2MeTHF at room temperature<sup>10</sup>) in a PhOLED, displaying an EQE of 15.8%.<sup>23</sup> Our group has followed a similar strategy and has designed, several years later, a structurally related host, **4**, also based on the dihydroindeno[1,2-*b*]fluorene backbone. With an  $E_T$  of 2.52 eV, **4** was suitable to host the green phosphor, Ir(ppy)<sub>3</sub> ( $E_T = 2.43$  eV in 2Me-THF at room temperature)<sup>9</sup> reaching an EQE of ca 10%. In these two works, it was interesting to note, that despite an extended bridged terphenyl unit is constructed, namely dihydroindeno[1,2-*b*]fluorene fragment, the  $E_T$  remain higher than 2.5 eV. The study of positional isomers of dihydroindenofluorenes has provided, several years later, a response to this intriguing feature (see below).<sup>15, 24-26</sup> In 2017, tetraphenyldibenzochrysene **5** was successfully incorporated in a red PhOLED (Ir(MDQ)<sub>2</sub>(acac),  $E_T = 2.02$  in 2Me-THF at room temperature<sup>9</sup>) with a high EQE of 14.4%. The highly conjugated dibenzochrysene core nevertheless leads to an  $E_T$  of 2.11 eV that does not allow to host green or blue phosphor.<sup>27</sup>

Despite interesting molecular structures were constructed and the proof of concept highlighted, all these works suffer from a strong limitation; their  $E_T$  are kept very low due to the molecular arrangement, which maintains an extended  $\pi$ -conjugation. Indeed, increasing the  $E_T$  was a mandatory step in order to host blue phosphors, which are still nowadays the weakest link in this technology.<sup>6</sup> Thus, different molecular design strategies have been then established in order to rise the  $E_T$  of this new generation of PHC materials (see below).

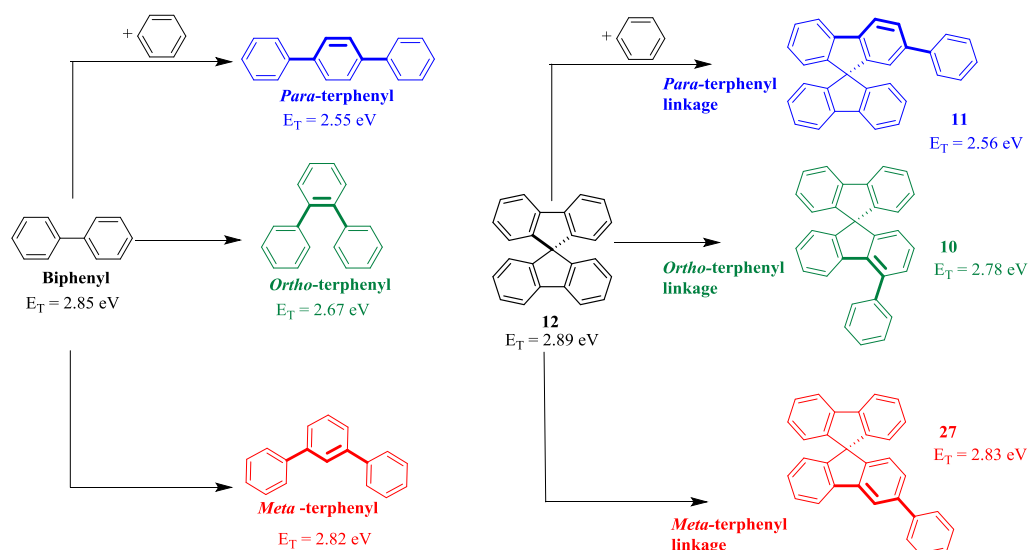


**Figure 2.** Selected PHCs designed to host phosphors in PhOLEDs and molecular structures of corresponding phosphorescent emitters. nd: Not detected.

### $\pi$ -Conjugation disruption: A tool to increase the $E_T$ .

In 2009, the substitution pattern of SBF was approached as an efficient tool to disturb the  $\pi$ -conjugation of PHC hosts and the first C4-substituted SBFs were synthesized.<sup>28</sup> A dimer and a trimer, **6** and **7**, were reported showing, for the first time, the potential of the C4 position to strongly disturb the  $\pi$ -conjugation. The C4 position of SBF was particularly interesting as it is at *ortho* position of the biphenyl linkage (Figure 3-right) whereas the C2 position, found for example in **1**, is located at *para* position. One of the main characteristics of an *ortho* linkage is its strong steric hindrance, which significantly disturbs the conjugation. Thanks to this sterically hindered *ortho* linkage, **6** displays a very high of  $E_T$  of 2.79 eV. However, despite this *ortho* linkage, **7** has a lower  $E_T$ , 2.55 eV, due to the *para* linkages with the two other SBFs. One can note that compared to the first generation of materials **1** and **2**, the  $E_T$  was nevertheless increased and has allowed to use **7** as host for both red (Ir(ppq)<sub>2</sub>(acac)) and green (Ir(ppy)<sub>3</sub>) phosphor with EQE of 10.5 and 12.6% respectively. This molecular design strategy has paved the way to the design of C4-SBF-based hosts, which are nowadays

an important class of host materials for PhOLEDs.<sup>7, 29-32</sup> The origin of this  $\pi$ -conjugation disruption is briefly discussed below and is detailed in other works.<sup>31-32</sup> However, it should be mentioned that despite its high  $E_T$ , **6**, was not tested at that time in blue PhOLEDs. The potential of 4-substituted SBFs and more generally of PHCs in blue PhOLEDs was then delayed.

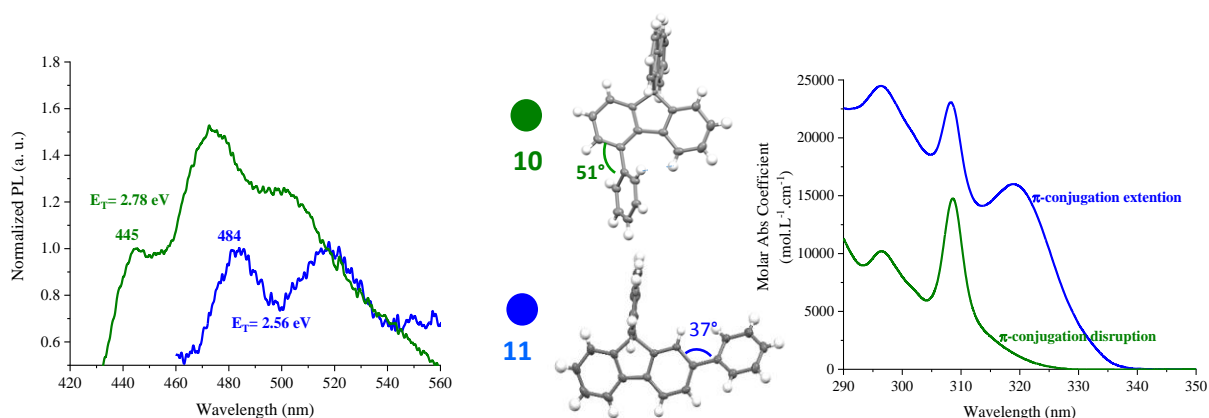


**Figure 3.** Evolution of  $E_T$  in oligophenylys and in phenyl substituted SBF analogues.

The efficiency of the PHC design strategy has been then developed on structurally related structures by the same group.<sup>33</sup> Longer oligospirobifluorenes with three (**8**) or five (**9**) SBF units all connected by C4 linkages were then synthesized. These molecules possess an optical gap of 3.93 eV, independent of the number of SBF units, identical to that of **6**.<sup>28</sup> This shows that the conjugation between the SBF units is efficiently broken.

In 2010, the trimer **8** was only the second example of a PHC incorporated as a host in a blue PhOLED<sup>33</sup> (the first example was reported by Liu and coworkers,<sup>34</sup> in 2009, with host **18**, see below). The device used FIrpic as emitter ( $E_T$ : 2.67 eV in 2Me-THF at room temperature)<sup>9</sup> and displayed an EQE of 11.6%, a Current Efficiency (CE) of 25 cd/A and a Power Efficiency (PE) of 17 lm/W. These values were, at that time, very promising.

In order to well establish the origin of the  $\pi$ -conjugation disruption in C4-SBFs, our group has designed in 2014, another very basic PHC-based host material constructed on the C4-SBF scaffold, namely 4-phenyl-spirobifluorene **10** and has precisely compared its properties to its positional isomer **11** (Figures 3 and 4).<sup>35</sup> The  $E_T$  of **10** was significantly increased compared to its 2-counterpart **11** (2.78 vs 2.56 eV, Figure 4, left), confirming the efficiency of the C4 position to rise the  $E_T$ . In **10**, the phenyl is attached at *ortho* position of the biphenyl linkage whereas in **11**, it is located at *para* position. The latter leads to a relaxed system, with a small dihedral angle between the fluorene and the phenyl ring ( $37^\circ$ ) whereas the former leads to a sterically hindered environment with a high dihedral angle between the fluorene and the phenyl ring ( $51^\circ$ ) (Figure 4, middle). This structural feature has been assigned to the interaction between the hydrogen atoms in *ortho* position of the pendant phenyl ring and those of the fluorenyl core,<sup>35</sup> and is at the origin of the  $\pi$ -conjugation breaking observed in **10** (detected thanks to the modification of the absorption spectrum, see Figure 4, right) and more generally in all the SBFs substituted at C4 such as **6**.



**Figure 4.**

Phosphorescence spectra (2Me-THF, 77K, Left), X-Ray structures (Middle) and absorption spectra (cyclohexane, Right) of **10** and **11**.

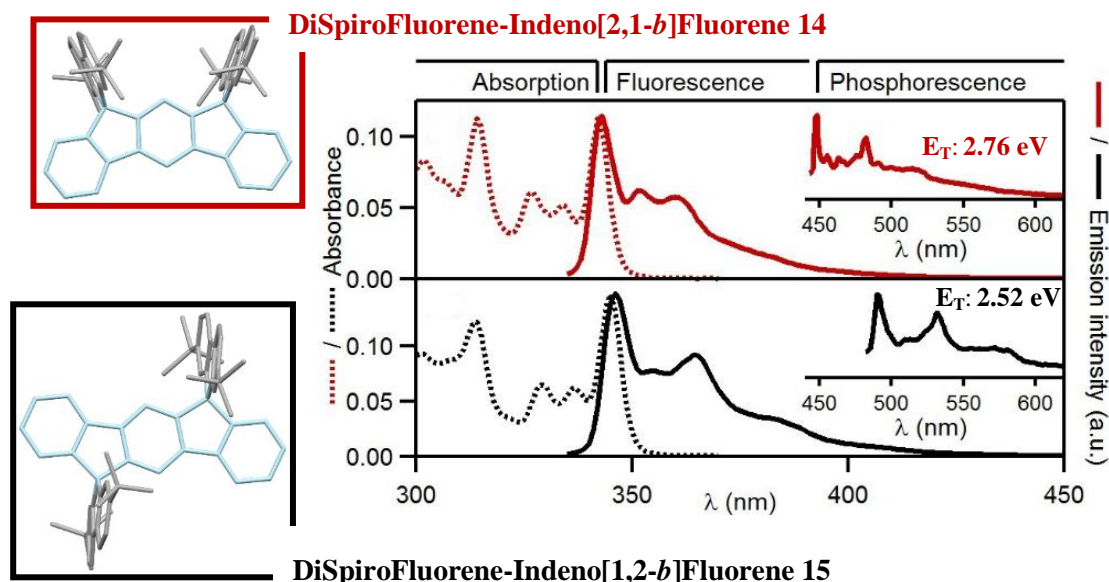
For the positional isomers, **10** and **11**, the influence of the linkage on the  $E_T$  can be understood with the terphenyl molecules possessing either a *para* or an *ortho* linkage (Figure 3, Left). Adding one phenyl unit either in *ortho* or in *para* position of the biphenyl molecule ( $E_T$ : 2.85 eV),<sup>36</sup> considerably reduces this  $E_T$  due to the  $\pi$ -conjugation extension, however not with the same amplitude. Thus, in the *para*-terphenyl, the conjugation between the three phenyl rings is maximized due to the *para* linkages and the  $E_T$  significantly drops to 2.55 eV. The *ortho* linkages of the *ortho*-terphenyl core provides a different result as they lead to a strong steric hindrance, which maintains the  $E_T$  at 2.67 eV, closer to that of biphenyl and therefore higher than that of the *para*-terphenyl.<sup>26, 36</sup>

Thanks to its high  $E_T$ , **10** has been incorporated as a host in green and more importantly in blue PhOLEDs with nevertheless moderate performance (EQE of 10.4 and 5.7% respectively).<sup>35</sup> Interestingly, in this work, the simple 9,9'-spirobifluorene **12** was also tested as host and has displayed modest EQEs of 6.6 / 8.5% for FIrpc / Ir(ppy)<sub>3</sub> PhOLEDs respectively, showing the necessity to decorate the SBF core to reach high performance PHCs. This is the strategy our group has then followed. These works have paved the way to the further design of PHC host materials constructed on a C4-SBF (or C4-fluorene) scaffold and other examples have been reported afterwards. For example, the dispirofluorene-indeno[2,1-*c*]fluorene **13** may be seen as a bridged 4-SBF.<sup>26</sup> In this work, it has been shown that, thanks to its *ortho* linkage, and despite its planar structure, the  $E_T$  is maintained high, at ca 2.63 eV. Other examples of high  $E_T$  materials constructed on an *ortho* linkage have been published by other groups showing the efficiency of this molecular design strategy.<sup>37</sup> However, the device characteristics using **13** as host were rather modest for a green PhOLED (EQE: 13.3%) and improving the device performance remained the major issue. The modification of the linkage (*ortho* to *meta*) has been one of the key to the success. This strategy is described below.

In this quest for robust PHC derivatives with very high  $E_T$ , we have reported, in 2011, a unique molecular design based on a *meta*-substituted terphenylene core, namely dihydroindeno[2,1-*b*]fluorene, flanked with two 2,7-*t*-Bu-fluorene units (**14**, Figure 5).<sup>38</sup> Despite the bridged structure, which should maximize the  $\pi$ -electronic delocalization, this molecular design has revealed an impressive increase of the  $E_T$  compared to the *para* counterpart **15** (2.76 eV for **14** vs 2.52 eV for **15**), keeping however excellent morphological and thermal properties thanks to the two spirofluorene units. Thus, the *meta*-substituted terphenyl backbone found in **14** has led to a remarkable increase of the  $E_T$  value compared to the *para*-substituted terphenyl backbone found in **15**. This work was the first example of a dihydroindeno[2,1-*b*]fluorene based OSC for organic electronic applications and has shown the potential of *meta* linkages to increase the  $E_T$  of PHCs (Note that regioisomers of dihydroindeno[2,1-*b*]fluorene are versatile fragments also used in the field of field-effect transistors<sup>39-41</sup> or that of fluorescent OLEDs<sup>42-45</sup>). In these pioneer works, an important characteristic was particularly



highlighted. Indeed, the absorption and fluorescence spectra of **14** and **15** are very similar with almost the same maxima (Figure 5). Oppositely, the first peak of the phosphorescence spectra is strongly blue shifted in the case of **14** vs **15** leading to different  $E_T$  values. This is due to the different impact of the nature of the linkage (*para* vs *meta*) and the dihedral angle between the different phenyl units (herein almost nul due to the bridges, which planify the  $\pi$ -system). This has been rationalized by our group several years later with SBF dimers.<sup>46</sup> This design tool appears to be very efficient to selectively tune the  $E_T$ , keeping the  $E_s$  unaltered, of great interest in the TADF OLED technology.



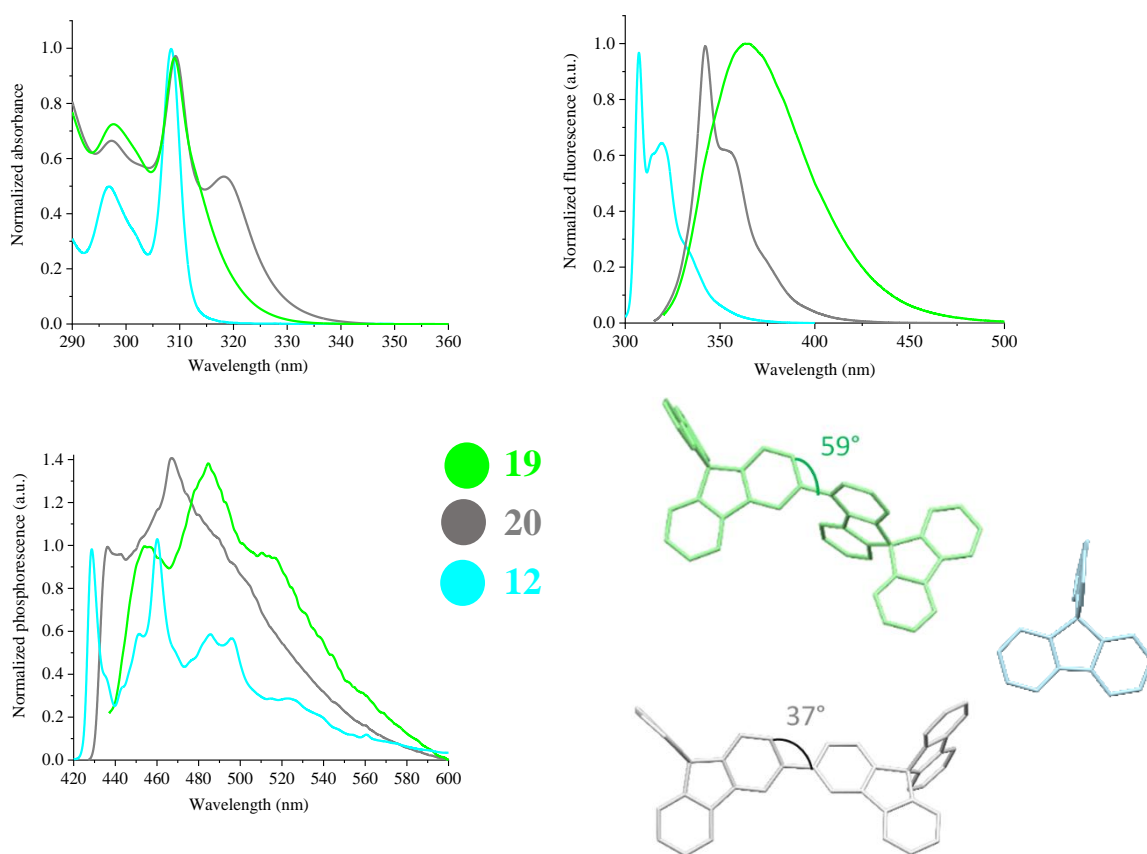
**Figure 5.** DiSpiroFluorene-Indeno[2,1-*b*]Fluorene **14** vs DiSpiroFluorene-Indeno[1,2-*b*]Fluorene **15**: X-ray structures, absorption and fluorescence emission at room temperature and at 77 K (in methylcyclohexane/2-methylpentane 1:1). Adapted from Ref. 38 with permission from the Royal Society of Chemistry.

The electronic decoupling arising from a *meta* linkage has then significantly changed the deal in the field. Indeed, as can be seen in Figure 3, the  $E_T$  of *meta* terphenyl is very high, 2.82 eV, significantly higher than those of *para* and *ortho* counterparts and has allowed the construction of high  $E_T$  PHC-based materials based on this fragment. In 2015, this molecular design strategy has been applied in PhOLEDs and a high  $E_T$  PHC material constructed on another *meta*-dihydroindenofluorene, namely dihydroindeno[1,2-*a*]fluorene **16** ( $E_T$ = 2.76 eV) has been incorporated as host in blue (FIrpic) and green (Ir(ppy)<sub>3</sub>) PhOLEDs with interesting EQEs of 7.5 and 14.8% respectively and low turn-on voltages of 3.2 and 2.8 V respectively.<sup>26</sup> Thus, the green PhOLEDs performance increases with the rise of  $E_T$ , from an EQE of 9.9% with **4**, to 13.3% with **13** and to 14.8% with **16**.

*Meta* linkages have been then efficiently used, year after year, to improve the PHC design efficiencies. Many different phenyl and/or fluorene assemblies have been constructed using the electronic decoupling characteristic induced by the *meta* linkage.<sup>34, 37, 47-50</sup> Note that another efficient  $\pi$ -conjugated breaker has also been used in these designs, namely the carbon bridge of the fluorene, which has been interestingly developed in several designs, such as in **17** and **18**, allowing to maintain a high  $E_T$ .<sup>34, 37, 47, 51</sup> Thus, since the first PHC host **17** for blue (FIr6) PhOLED published in 2009,<sup>34</sup> many research groups worldwide have tried to improve the performance of blue PhOLEDs, reaching 15.7% in 2015 with **18**:FIrpic as EML.

However, the performance of PHC-based blue PhOLEDs, has remained lower than 16% until 2015 when two SBF dimers, **19** and **20**, have shown the crucial importance of the *meta*-linkage for

constructing the next generation of high performance PHC hosts (Figure 6).<sup>52</sup> It was an important step in the field. Thus, two SBF dimers substituted at position C4 or at position C3, **19** (C4/C3) and **20** (C3/C3) were synthesized and used as host in blue and white PhOLEDs. In order to unravel their intriguing properties, our group has also investigated these molecules several years later.<sup>46</sup> The two isomers display very different optical properties due to their different linkages (*meta/ortho* vs *meta/meta*) and different steric congestions (fluorene/fluorene angle of 59° for **19** vs 37° for **20**, Figure 6). The absorption spectra clearly show that the  $\pi$ -conjugation is less extended in the case of **19** as **20** displays an intense band at ca 320 nm (Figure 6, Top-left). The fluorescence highlights very different molecular rearrangements occurring between the ground and the first excited states for the two compounds, the spectrum of **20** being thin, structured and blue shifted whereas that of **19** is unresolved large and red shifted. This can be partially assigned to the different fluorene/fluorene angle in S1 state (determined by theoretical calculation), this angle is large for **19** (ca 30°) and very low for **20** (ca 4°).<sup>46</sup> The linkage also has a strong impact on the phosphorescence spectra with an  $E_T$  measured at ca 2.73 eV for **19** and at 2.84 eV for **20** (Figure 6, Bottom-Left).<sup>46</sup> These two dimers have displayed very different performance when incorporated as host in blue PhOLEDs, **19**:FIrpic based PhOLED displaying a very high EQE of 22% whereas that of **20**:FIrpic based PhOLED is of only 11.4%.

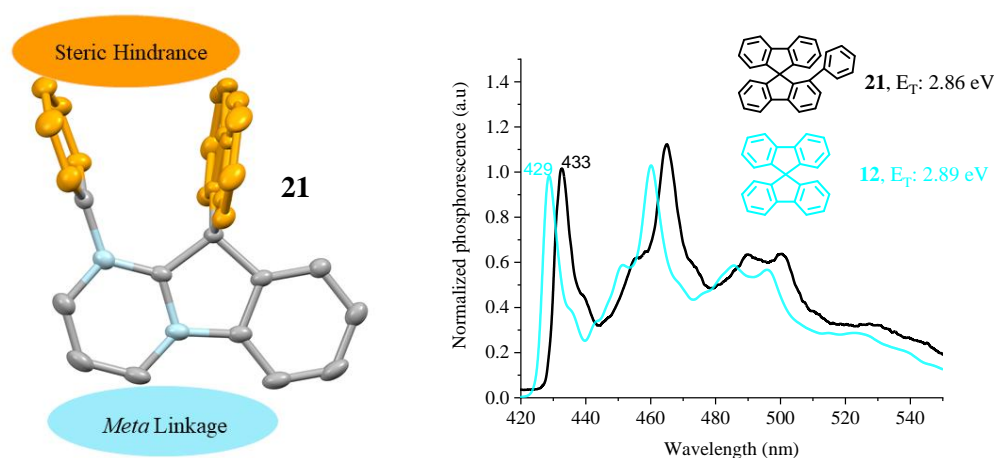


**Figure 6.** Spirobifluorene **12** and Spirobifluorene dimers **19** and **20**: X-Ray structures, absorption and emission at room temperature and at 77K (in 2Me-THF).<sup>46</sup>

SBF dimers have played a key role in the field of PHC hosts for PhOLEDs since they have often display the highest performance over the years.<sup>46, 52-53</sup> Two parameters control the electronic properties of these dimeric molecular structures (and OSCs in general): the electronic parameter (nature of the linkage, *i.e.* *ortho*, *meta* and *para*) and the steric parameter (relative position of the two SBF units one to the other, *i.e.* fluorene/fluorene dihedral angle). This is discussed in a recent article,<sup>46</sup> in which we have studied the ten dimeric structures of SBF and shown how the combination of these two parameters tunes the electronic properties of SBF dimers and how their respective weights are different as a function of the property considered (HOMO or LUMO energy, fluorescence,

phosphorescence). This is particularly important to control the electronic properties to accurately design efficient functional materials for a specified application.

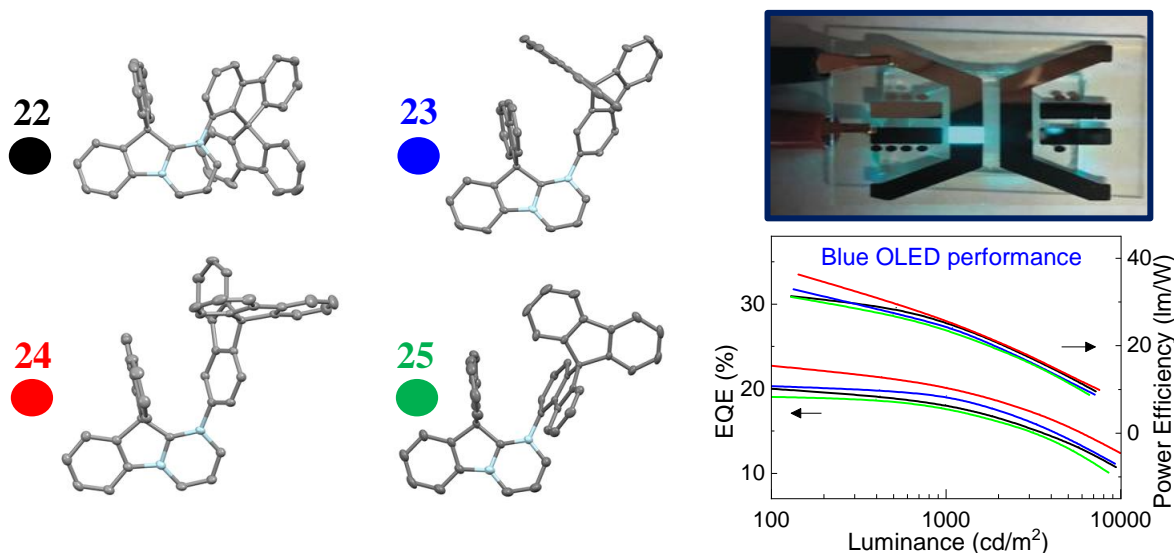
Following this work, an important breakthrough was made in 2017 with the development of the first C1-substituted SBF as PHC host materials for PhOLED, namely 1-Phenyl-Spirobifluorene **21**.<sup>54</sup> Despite low blue (Flrpic) PhOLED performances were obtained in these first works (EQE of 5.9% and corresponding CE and PE of 15.9 cd/A and 5.9 lm/W), this position was considered as ideal as it takes advantages from both C3 and C4 sites as previously described. Indeed, the  $\pi$ -conjugation breaking has been assigned to a combination of both the *meta* linkage (electronic parameter found in C3-SBFs) and the high dihedral angle formed between the substituent and the fluorene (steric parameter found in C4-SBFs) due to the cofacial arrangement. This particularity has been advantageously used to design high  $E_T$  host materials for blue PhOLEDs (see below with C1-linked SBF dimers **22-25**). Indeed, in **21**, the effect of the phenyl unit is vanished and the  $E_T$  remains almost identical to that of building block **12** (2.86<sup>54</sup> vs 2.89<sup>46</sup> eV, Figure 7, right).



**Figure 7.** Left: X-Ray structure of 1-Phenyl-Spirobifluorene **21**. Right: Phosphorescence contribution of **12** and **21** extracted from emission spectra at 77K (2Me-THF).

The next important step was made in early 2019, when our group and that of Jiang designed highly twisted SBF dimers possessing different phenyl connections, **22-25**, Figures 2 and 8.<sup>53</sup> The particularity of these dimers was their linkage derivatized from the C1 position, which appeared, as expose above, to be particularly efficient to maintain a high  $E_T$ . In these C1-linked dimers, there is a strong steric congestion (significantly more important than that of **21** exposed above) imposed by the two SBF units, which drives the physical and electronic properties.

These dimers present excellent thermal properties with a high decomposition temperature,  $T_d$ , above 310°C and a high glass transition temperature,  $T_g$ , above 143°C, highly beneficial for device lifetime. Thus, the thermal and morphological properties of the SBF dimers are much improved over their constituting block **12** ( $T_d=234^\circ\text{C}/T_g=135^\circ\text{C}$ ), highlighting the strength of the present dimer design: maintaining some excellent properties of **12** (such as its high  $E_T$ ) while enhancing others (such as the  $T_g/T_d$ ). The  $E_T$  of the four dimers, thanks to this  $\pi$ -conjugation breaking is maintained very high, between 2.80 eV for **23** and 2.87 eV for **24** (the difference is induced by linkage effects)<sup>46</sup> close to that of unsubstituted **12** ( $E_T$ : 2.89 eV). When incorporated as host in blue Flrpic PhOLEDs, the EQE were all very high, ie above 19%, and even reached 22.9% for **24** (Figure 8). This EQE was, at that time, the highest reported in the literature for a PHC host and was more and more closer to that of heteroatoms-based devices. The charge injection was also very good in these devices as the turn-on voltages were found below 3V. This is a low value for a blue emission, especially for PHC systems and the C1-SBF scaffold is undoubtedly at the origin of this very high performance.

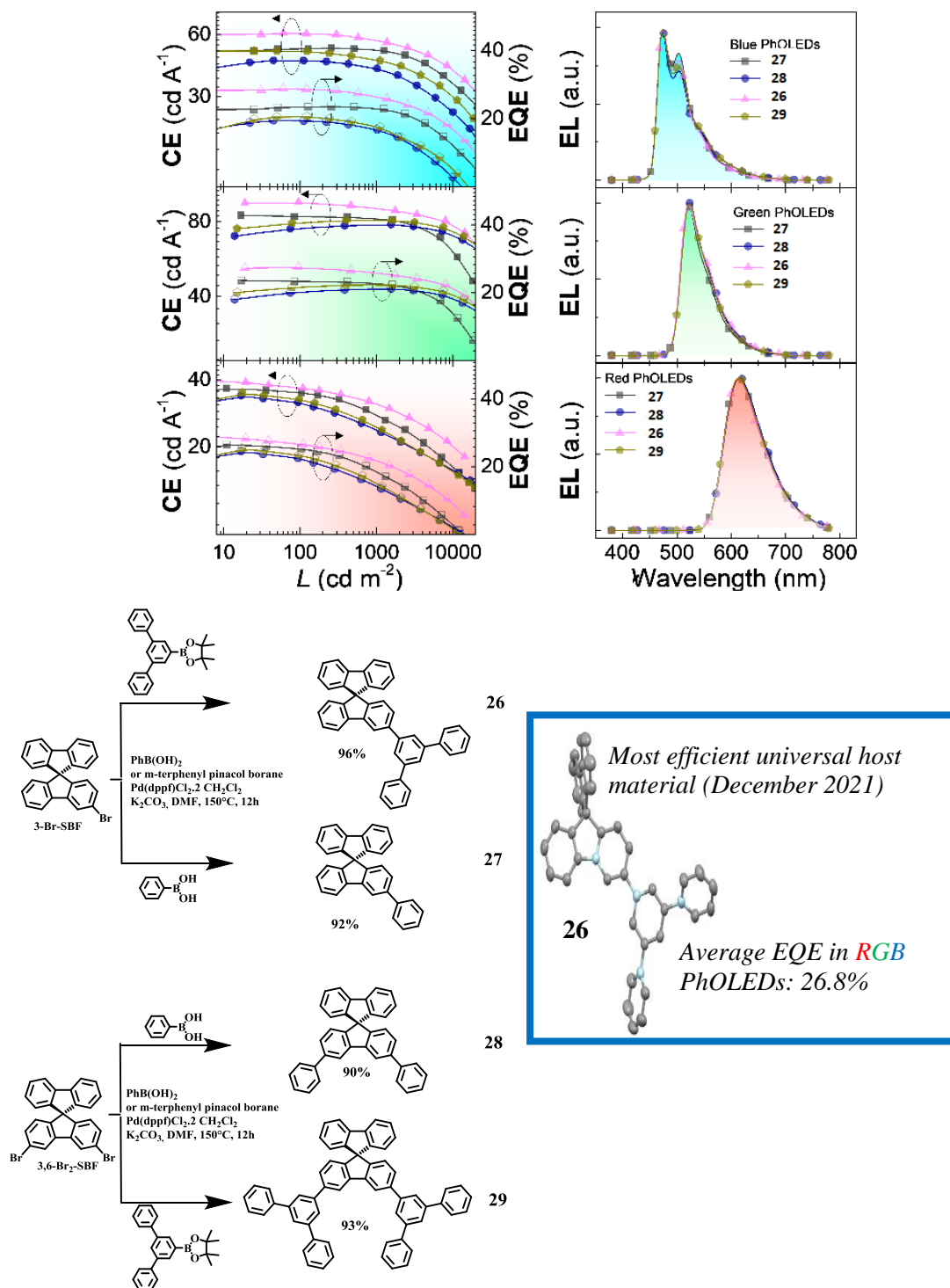


**Figure 8.** C1-substituted spirobifluorene dimers **22-25** as host for blue PhOLEDs (Flrpic)

Even so, this encouraging progress was still incomparable with the best heteroatoms-based hosts in blue, green, and red PhOLEDs.<sup>55-59</sup> In order to allow the PHC hosts to go one step forward, overpassing the performance reached by the best heteroatoms-based hosts was the next key step. In addition, reaching high performance in red (R), green (G) and blue (B) PhOLEDs using the same host was also a real challenge. Such a type of hosts is called ‘universal’ and is particularly difficult to design.<sup>5, 9-10</sup> Indeed, if a host with a high  $E_T$  (above 2.7 eV) can be, in principle, used with RGB phosphors, fitting the HOMO/LUMO energy levels is far from an easy task.

In 2020, a series of novel universal PHC materials **26-29**, featuring further simplified structures from SBF dimers to mono SBF derivatives were designed and successfully incorporated as host in high performance RGB PhOLEDs (Figure 9).<sup>3</sup> These molecules were constructed on a SBF scaffold substituted at C3/C6 positions thanks to an efficient one-step synthesis (Figure 9, Bottom-Left). Decreasing the number of synthetic steps is a key feature for future industrial applications. This approach should be short, high yielding and low cost. The present hosts were easily synthesized at the multi-gram scale through an extremely simple one-step approach from commercial precursors 3-bromo-spirobifluorene and 3,6-dibromo-spirobifluorene. The pendant substituents, phenyl or terphenyl, were efficiently grafted to the SBF core *via* simple Pd-catalysed coupling with yields over 90%.

The positions C3/C6 of the spirobifluorene fragment form a *meta* linkage with the constituted bridged biphenyl, leading to an electronic decoupling between the two fragments.<sup>53-54</sup> As the pending substituent itself also has a chief role in the PhOLED performance, two different side groups were investigated, phenyl and *meta*-terphenyl. The monosubstituted non-symmetric host, **26**, achieved excellent thermal and morphological stabilities ( $T_d=318^\circ\text{C}$ ,  $T_g=133^\circ\text{C}$ ), a high  $E_T$  of 2.82 eV, a well-balanced hole/electron mobility of 2.64 and  $3.55 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and has exhibited an outstanding average EQE of 26.8% when used as host in RGB PhOLEDs (Figure 9, Top). This PHC host presents the highest overall performance reported to date for a universal host (including heteroatoms-based hosts) and shows that the PHC design strategy is promising for the future development of OLED industry as a high-performance and low-cost opportunity. It is noteworthy to mention that the mobilities appear to be very low but well equilibrated, which shows that the charge balance in an OLED device is more important than the mobilities values themselves.



**Figure 9.** PHC **26-28**. Synthesis, X-Ray structure and performance as host in RGB PhOLEDs (Adapted from Ref. 3 with permission from the Royal Society of Chemistry)

The three other hosts in the series, **27-29**, also display very high EQE, despite lower than that of **26** (average value: 23.5% for **27**, 21.3% for **28** and 22.1% for **29**). To understand the high performance obtained in this series and particularly with **26**, lifetimes of the EMLs were investigated and have provided key data. The EMLs of 20 wt% blue emitting *fac*-Ir(iprpmi)<sub>3</sub> doped into the hosts show short lifetimes (**26**, **27**, **28** and **29** : 0.86, 1.18, 1.09 and 0.95  $\mu\text{s}$ , respectively). Of particular interest, the lifetime of the EML using **26**, 0.86  $\mu\text{s}$ , is considerably reduced compared to the others, which reduces the triplet density and the possibility of triplet-triplet annihilations, which are detrimental to the device

efficiency.<sup>60-61</sup> This feature is surely one of the key properties involved in the very high PhOLED performance obtained and should be kept in mind for further PHC molecular design. Therefore, the very high performance reached with **26** can be assigned to the combination of high  $E_T$ , well balanced mobility and short deactivation lifetime. This high performance was particularly important as it was the first time, that a PHC host overpassed the best heteroatoms-based hosts.<sup>57, 62</sup> It shows that deliberately introducing heteroatoms within molecular backbone of host materials (to adjust the HOMO/LUMO energy levels and to reach decent mobilities values) is not a mandatory step to obtain a high PhOLED performance. This was an important finding to construct the next generation of hosts. Finally, another important result was reported in this work. Indeed, this work reports a series of four molecules, all of them achieving high performance with average EQE of 26.8% for **26**, 23.5% for **27**, 21.3% for **28** and 22.1% for **29** (Figure 9) showing the efficiency of the whole design strategy and not only of one molecule.

PHCs now enter in a new era as several research groups start to deeply investigate the potential of these new generations of hosts. In this context, the C1-SBF scaffold, highlighted by our group, appears undoubtedly as one of the most efficient platform to build such materials. The recent works of Lan, You and their coworkers<sup>63</sup> on poly-substituted SBF based PHCs as hosts for RGB PhOLEDs (**30**, Figure 2) clearly confirm the high efficiency of this design strategy. Thus, when incorporated as host for blue and green phosphor, the high- $E_T$  PHC **30** (2.83 eV) displays a high EQE of 18.6 and 20.2% respectively.<sup>63</sup> The C1-SBF scaffold is undoubtedly at the origin of this performance.

## CONCLUSION

Since the first example reported in 2005, to the recent very high efficiency devices, PHC materials have started to conquer the world of host materials for PhOLEDs. These new generations of hosts, free of heteroatoms, only contain benzene rings, one of the most robust and inert building unit, which are assemble with suitable linkages to adjust their energy levels. Most of these materials display a large HOMO/LUMO difference, a high  $E_T$  and excellent thermal and morphological stabilities (in other words high  $T_g$ , and high  $T_d$ ), which are key data for PhOLED applications. Despite their low mobilities, recent examples have shown that ambipolar character (such as in **26**) can even be obtained with PHCs, which is a real advantage to favour the recombination in the centre of the device. Today, the most efficient universal host for RGB PhOLEDs is a PHC host (**26**), which displays an outstanding overall EQE of 26.8%.<sup>3</sup> This finding shows that the PHC design can really advance the field and it will undoubtedly drive future molecular designs. One of the most important characteristics of the PHC-based hosts is their facile, low cost and short synthesis, which are key requirements in OLEDs industrial production. The potential of PHC materials has also been shown in the field of simplified PhOLEDs (called single-layer PhOLEDs<sup>5</sup>) as the highest performance to date (EQE of 21.4%) in a green single-layer PhOLED has also been obtained with a PHC.<sup>48</sup> All these recent results suggest a bright future for PHC hosts in PhOLED technology and many groups worldwide are now involved in this field. The first stability studies using a PHC material as host have been performed on TADF OLEDs and have revealed the potential of this type of hosts in term of device lifetime.<sup>52</sup> However, to the best of our knowledge there is, to date, no stability studies on PHC-based PhOLEDs. Such studies should be investigated in the future. In term of molecular design, an important direction for the future of PHCs in PhOLEDs will be directed to the increase of the  $E_T$  in order to host deep blue phosphors, which are still the weakest link of the technology. To reach this goal, novel molecular approaches should be developed. We are currently working in this direction.

To conclude, it is only the dawn of the PHC hosts in PhOLED devices (and more generally for the other OLED technologies), but the efficiency of the molecular design strategy has clearly been highlighted. This straightforward design strategy avoids tedious molecular constructions and has therefore excellent potential for future OLEDs research and industrialization.

## BIOGRAPHICAL INFORMATION

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