Recent developments in AIEgens for non-doped and TADF OLEDs

Fabio Rizzo,*[a] and Fabio Cucinotta[b]

Abstract: The design of innovative and more efficient Aggregation-Induced Emission (AIE) chromophores has kept a very high scientific interest since the first report on 2001. Among the possible applications, the field of the organic electroluminescent diodes (OLEDs) is highly attractive. This review will focus on very recent development in the design of AIE molecules for OLEDs, with particular attention on the performance of different emitting devices. Another key point is the description of the new class of AIE luminogens showing Thermally Activated Delayed Fluorescence (TADF), which appears as possible solution to overcome the limitation of fluorescent dyes employed in electroluminescent devices.

Keywords: aggregation induced emission • AIEgens • OLED • organic dyes • thermally activated delayed fluorescence

1. Introduction

Since the first report of the concept of Aggregation-Induced Emission (AIE) in 2001,[1] the research activity in this area expanded tremendously. AIE provides a channel towards versatile luminescent organic materials. In fact, AIE chromophores are poor or non-emissive when solubilized in good solvent, whereas their luminescence enhances dramatically in poor solvent or in solid state. Such enhanced emission phenomena are acceptably interpreted as the restriction of intermolecular rotations and Twisted Intramolecular Charge Transfer (TICT), prevention of exciton diffusion, formation of special aggregates and intramolecular charge transfer. A huge amount of molecules showing AIE properties have been reported so far, and successfully employed in many application fields (Figure 1).

Figure 1. Typical examples of structural motifs of AIEgens and their technological applications. Reprinted with permission from reference 2a (Copyright 2018 American Chemical Society).

Several reviews on the application of AIE luminogens (AIEgens) on chemo- and biosensing as well on organic light-emitting diodes (OLEDs) have been published in the past years.[2]

However, highly efficient AIE-active material systems for application in electroluminescent devices are still desired. Therefore, it is important to keep up-to-date the scientific community about the development of AIEgens for OLEDs in order to suggest fruitful approaches increasing the performance of devices.

To avoid repetition, we focused this review on the very last progress by reporting compounds for non-doped OLEDs published between 2016 and end February 2018. Besides the description of chromophores applied in electroluminescent devices emitting different colours, we devote particular emphasis to a new class of AIEgens showing Thermally Activated Delayed fluorescence (TADF), which first appeared in 2015 and has not been reviewed yet. The combination of AIE and TADF phenomena in one single compound appears as an effective strategy to overcome the common limitations of fluorescent dyes.
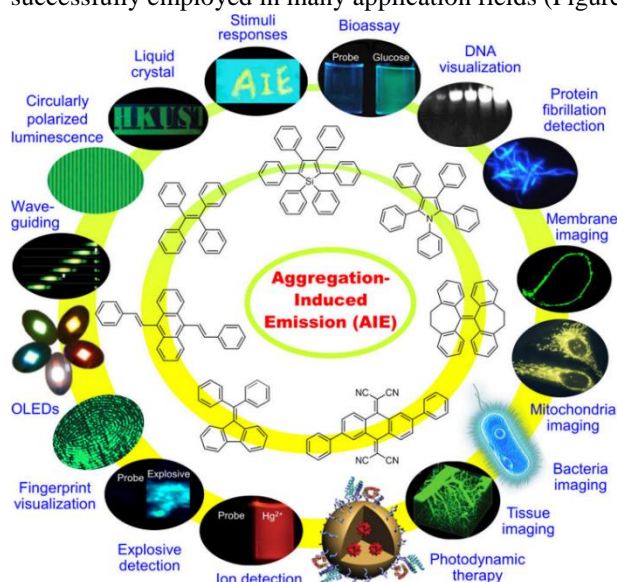
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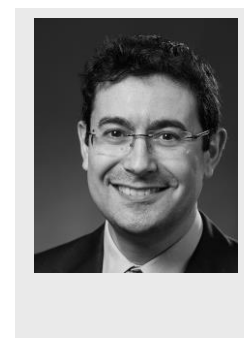
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dyes, organic compounds for OLEDs with TADF properties and functionalization of surfaces.

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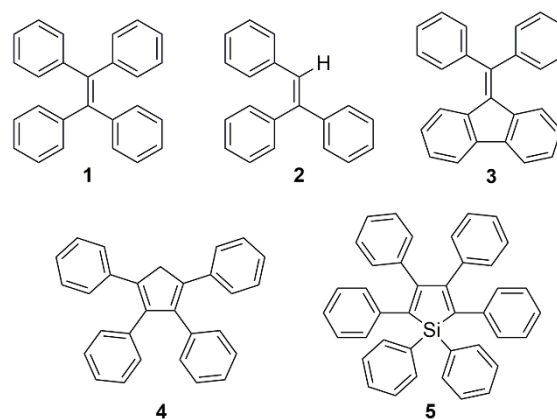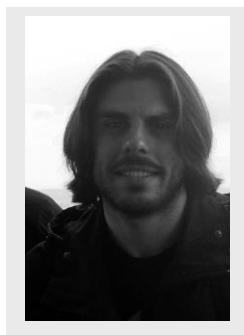

Chart 1. Examples of AIE-active core: tetraphenylethene (TPE, **1**), triphenylethene (tPE, **2**), diphenyldibenzofulvene (**3**), polyphenyl cyclopentadiene (CP, **4**) and silole (**5**).

2. Recent AIEgens emitters for non-doped OLEDs

2.1. Blue and green AIEgens emitters

Design and synthesis of blue-emitters particularly remain to be a challenge compared with the reported plethora of red- and green fluorophores with outstanding performances. Traditional blue-fluorophores, such as anthracene, pyrene, and triphenylamine derivatives, show high emission in dilute solutions, but they suffer from the notorious Aggregation-Caused Quenching (ACQ) effect in aggregate states such as their neat thin solid films, which severely limits their application in optoelectronic devices. To overcome the occurrence of ACQ, in the past decade, numerous organic dyes with AIE properties were externally designed based on special chromophores, such tetraphenylethene,[3] diphenyldibenzofulvenes and siloles (Chart 1).

The performances of non-doped OLEDs emitting blue-green fabricated with these structures are summarized in Table 1.

As versatile organic molecules, cyclopentadiene derivatives (CPs) have also been widely used for the fabrication of blue- and multicolour-OLEDs. Recently, Wang and co-workers[4] reported a systematic study on polyphenyl-substituted CPs in order to understand the relationship between their molecular structures and optoelectronic properties. The use of bulky substituents attached to the CP backbone helped reducing the formation of coplanar structures and suppressing the intermolecular π-π interactions that promote ACQ, resulting in the improvement of the emission intensity and electroluminescence efficiency. A non-doped blue-emitting OLED using a diphenyl-methoxynaphthyl-substituted CP showed a low turn-on voltage about 4.6 V, with a maximum luminance (L_{max}) of 3886 cd/m^2 and a maximum current efficiency (CE_{max}) of 2.12 cd/A at 10.6 V. The CE_{max} and the maximum power efficiency (PE_{max}) values of 2.06 cd/A and 1.04 lm/W were also achieved at the practical luminance of 100 cd/m^2.

Siloles are among the first discovered AIE luminogens, and due to their remarkable properties, a series of silole-based AIEgens have been developed and applied as biological probes, chemical sensors, and emitters in OLEDs.[5] Thanks to the Si-containing conjugated ring with the σ*–π* conjugation effect deriving from the σ* orbital of the exocyclic Si-C bond and the π* orbital of the butadiene segment, silole derivatives possessed high electron affinity and fast electron mobility, which offered them very high LED performance with external quantum efficiency (EQE) up to 8%, exceeding the theoretical limit.[6] However, also because of the good intramolecular conjugation including the σ*–π*, generally, silole derivatives gave strong green and yellow emissions, but scarcely blue ones. To overcome this limitation, Li et al. developed six new AIE-gens using as a core structure tetraphenylcyclopentadiene (TPCP), where the Si atom is replaced by a C atom. The new TPCP core was connected with tetraphenylethene (TPE) and triphenylethene (tPE) as peripheral moieties.[7]

The non-doped TPE-TPCP and tPE-TPCP based devices exhibited good performance with a L_{max} of 24096 and 35380 cd/m^2, a CE_{max} of 6.80 and 6.40 cd/A, and the EL spectra peaked at 492 and 508 nm, respectively, showing higher performances and blue-shifted emission than the corresponding silole-based devices (λ_{EL} of 552 nm). Further adjusting the conjugation degree by changing the linkage mode, a deep-blue emitting device was also obtained (λ_{EL} of 440 nm), with luminance and CE_{max} up to 8721 cd/m^2 and 3.40 cd/A.

Among the blue and green AIEgens, TPE is the most common example of a very versatile molecule because it can be incorporated into several chromophores as part of their core or peripheral structures and suppress ACQ in favour of AIE with high efficiency in the solid state. So far, TPE and its derivatives have been widely used to explore AIE phenomenon and develop high performance non-doped OLED materials.[8] In 2017, Ge et al. reported two multifunctional AIE emitters containing a TPE moiety. Multilayer non-doped OLEDs based on these emitters give maximum current efficiencies of 6.14 cd/A and 6.70 cd/A.[9] Wang et al. also synthesized two novel TPE derivatives,[10] with obvious AIE characteristics in the blue-green region and they were applied to fabricate non-doped OLED.

Besides, Zhao's group studied new folded tetraarylethenes as well as tetraarylethanes by the McMurry coupling of

different diarylmethanones in 2016.[11] Non-doped devices fabricated

Table 1. Performance of non-doped blue and green OLEDs.

Compound	λ_{EL} Nm	[a]V_{on} V	[a]L_{max} cd m^{-2}	[a]CE_{max} cd A^{-1}	[a]PE_{max} lm W^{-1}	[a]EQE %	Ref.
2,5-mBTPE-TP	440	4.7	8 721	3.4	1.9	2.0	[7]
tPE-CBZ	441	4.8	7 500	1.3	1.3	-	[17]
Ph-BPA-BPI	448	2.5	-	3.6	3.7	4.6	[20]
mTPE-DPI	464	3.3	13 740	4.1	2.9	3.7	[16]
Py-BPA-BPI	471	2.2	-	10.9	10.5	5.6	[20]
2,5-BTPE-TP	492	3.3	24 096	6.8	4.07	2.7	[7]
5	496	4.6	3 886	2.1	1.0	-	[4]
TPE-4Py	496	6.5	1 678	3.1	1.0	1.3	[14]
2,5-BtPE-TP	508	3.1	35 380	6.4	3.9	2.3	[7]
TPE-CBZ	508	3.6	10 290	4.1	2.6	-	[17]
f-DPB-DFLE	512	4.4	49 030	6.6	3.0	2.5	[11]
TPE-TPAPBI	520	3.2	125 300	16.8	14.6	5.8	[19]
TPE-DB	521	4.9	38 430	6.5	-	2.3	[13]

[a] V_{on}: turn on voltage; L_{max}: maximum luminance; CE_{max}: maximum current efficiency; PE_{max}: maximum power efficiency; EQE: external quantum efficiency.

with the folded tetraarylethanes perform high luminance up to 49030 cd/m^2 and good electroluminescence efficiencies of 6.6 cd/A and 2.5%.

Tang and co-workers obtained high-performance deep-blue AIE OLEDs by combining the use of an anthracene core with two TPE as peripheral units.[12] The devices exhibit (i) low voltages of 2.75, 3.15, and 4.05 V at 1, 100, and 1000 cd/m^2, respectively, which are the lowest among deep-blue devices, (ii) luminance and power efficiency of 17721 cd/m^2 and 4.3 lm/W, respectively, which are the highest among deep-blue AIE OLEDs, and (iii) low efficiency roll-off, since the efficiency can remain 4.3 and 3.6 lm/W at the practical luminance of 100 and 1000 cd/m^2, respectively, which are much higher than previous deep-blue devices (> 200%)

The same research group also tackled another major concern for OLEDs efficiency, which is represented by the unbalance of charge carriers in the devices. Ideally, OLEDs architecture should ensure that injection and transport of electrons and holes are evenly facilitated. However, most of the organic electroluminescent materials are better hole-transporters (p-type materials) than electron-transporters (n-type materials). The introduction of electron-transporting functional groups into the p-conjugated system of the emitter is then a viable strategy to improve the charge balance. The incorporation into a TPE core of dimesitylboryl (DB) groups, which are inherently electron deficient, lowers the LUMO energy levels and thus enhances the electron affinities and electron-transporting abilities.[13] Devices fabricated by using TPE-DB as both light-emitting and electron-transporting layers exhibit green emission (λ_{EL} = 521-525 nm) with turn-on voltages between 3.9 and 4.9 V, luminance up to 38430 cd/m^2 and efficiencies of 13.5 cd/A and 4.6%, which are much better than those from the device with 1,3,5-tris-(N-phenylbenzimidazol-2-yl)benzene (TPBi) as the electron-transporting layer, demonstrating that TPE-DB is an efficient bifunctional material of light emitters and electron transporters for non-doped OLEDs.

Another chemical modification using TPE was proposed in 2017 by Li and co-workers, who designed a highly efficient blue emitter with an AIE effect achieved by combining a twisted TPE core and planar pyrene peripheries.[14] EL performances were achieved with a current efficiency up to 3.05 cd/A at 496 nm.

Similar to TPE, tPE is also a typical group with multiple rotatable single-bonds for realizing AIE properties. Limited by the twisted configuration of its three phenyl rings, tPE possesses a low conjugation and much bluer emission with a hypsochromatic shift as large as 1220 cm^{-1} compared with TPE. Therefore, tPE is considered as one of the ideal candidates for blue-OLED applications.[15] Zhang and co-workers designed two AIE blue emitters by integrating a tPE with one or two phenanthro[9,10-d]imidazole (PI) groups.[16] The PI unit is a wide-bandgap fluorophore, which can contribute to the desired high-energy emission of the compounds. Another attractive feature of the PI unit lies in its capability to transport both electrons and holes. The device with two PI units showed bright blue emission with a high luminance value of 13740 cd/m^2 and EL efficiencies of 3.69%, PE_{max} of 2.89 lm/W and CE_{max} of 4.13 cd/A.

Another important issue for the fabrication of efficient and stable OLED devices is the thermal stability. Recently, carbazole (CBZ) has drawn great attention due to its high thermal stabilities, charge-transport properties and luminescence. Tang and co-workers reported the use of two CBZ units attached on tPE and TPE cores.[17] The device constructed with the tPE-CBZ emitter presents a deep blue emission at 441 nm with a maximum luminance of 7500 cd/m^2, a maximum current efficiency of 1.286 cd/A and a maximum power efficiency of 1.339 lm/W, while the device using the TPE-CBZ emitter displays blue-green fluorescence at 508 nm with a maximum luminance, current efficiency and power efficiency of 10290 cd/m^2, 4.075 cd/A and 2.559 lm/W, respectively.

TPE and PI emitters possess also the advantage of being utilised in combination with donor (D) and acceptor (A) units with the aim of overcoming the problem of charge unbalance that we previously mentioned. Bipolar materials with an electronic donor−acceptor (D−A) structure are considered to be in favour of injecting and transporting both holes and electrons according to recent studies.[18] Two linear TPE derivatives modified with hole-transporting triphenylamine (TPA) and electron-transporting phenylbenzimidazole (PBI) groups have been recently reported and used as emitters in green AIE-OLEDs.[19] The device made using the D-A structure showed ultrahigh luminance of up to 125300 cd/m^2, and affords outstanding EL efficiencies of 5.8%, 14.6 lm/W and 16.8 cd/A, which are much superior to that of the device employing only the PBI-modified TPE emitter.

Table 2. Performance of non-doped yellow and orange OLEDs.

Compound	λ_{EL} Nm	V_{on} V	L_{max} cd m^{-2}	CE_{max} cd A^{-1}	PE_{max} lm W^{-1}	EQE %	Ref.
PDPBCE	537	3.8	59 130	6.43	-	-	[24]
2CzTPE	~ 540	2.8	5 400	2.8	-	0.9	[26]
(TPAP)$_2$PIO	546	4.2	21 890	7.8	5.1	2.2	[28]
PIPBT-TPE	552	3.7	38 100	10.6	7.5	2.3	[25]
BDPBCE	554	3.0	67 500	11.2	-	-	[24]
(TPA)$_2$PIO	555	4.0	18 830	7.1	4.3	2.0	[28]
(DPA)$_2$(CN)$_2$MPPS	557	3.7	32 050	4.6	3.9	1.6	[31]
Cbz-MI	563	5.88	18 303	12.9	-	3.7	[27]
BDTPE	566	5.1	1 978	2.87	-	-	[23]
3	566	3	-	-	-	-	[30]
(DPA)$_2$(MesB)$_2$MPPS	567	3.6	23 700	7.1	5.1	2.4	[31]
BP2TPAN	570	4.8	925	2.9	0.84	1.1	[32]
Cbz-MI(d)	584	5.85	73 915	13.8	-	4.1	[27]
PAC8	596	5.0	5 920	9.4	3.9	3.9	[33]
BBTPE	601	5.6	5 292	2.92	-	-	[23]

Adopting the same strategy, Lee and co-workers obtained two D−A emitters, by introducing rigid, planar phenanthrene or pyrene moieties to a TPA-modified PI core.[20] Both phenanthrene and pyrene based D-A systems show high photoluminescence efficiencies and strong charge-transfer characteristics, with excited-state dipole moments of 17.8 and 24.8 D, respectively. Non-doped blue OLEDs using them as emitters show high exciton recombination efficiencies of 36.2% for Ph-BPA-BPI and 39.2% for Py-BPA-BPI, which is far higher than that using the original PI emitter (19%). In addition, the deep-blue device based on the phenanthrene-modified emitter presents good colour purity with CIE coordinates of (0.15, 0.08) and high external quantum efficiency, current and power efficiencies of 4.56%, 3.60 cd/A and 3.66 lm/W, respectively. The pyrene-modified emitter affords a device with a very low turn-on voltage of 2.15 V, a sky-blue emission of CIE (0.17, 0.29), and maximum efficiencies of 5.64%, 10.9 cd/A and 10.5 lm/W, respectively.

Recently, a new class of emitters, named diaroylmethane boron difluoride complexes (DAM-BF2), has been attracting much interest as functional materials because of their easy preparation, high photoluminescence quantum yields, AIE ability, mechano-chromism and delayed emission. DAM-BF2 has also the emission colour changing property depending on its concentration in the matrix.[21] By employing various host matrices in the emissive layer, such as triazine, CBZ and TPA, AIE-OLEDs with avobenzone-BF2 (AVB-BF2) provide full-colour emission, covering the range from blue to green to red. As shown by Adachi and co-workers, the various emission colours of the devices can be easily tuned by manipulating the aggregation of AVB-BF2 with or without aggregation-induced exciplex formation

(AIEF) which provides the "triadic" exciplex between AVB-BF2 dimers and a host molecule.[22] Further, an AVB-BF2-based OLED using a CBZ derivative as the host matrix exhibited a high external quantum efficiency of 12.8%, which is based on TADF under the AIEF condition.

2.2. Yellow and orange AIEgens emitters

Different AIEgens have been used to generate yellow electroluminescent devices, and the properties of these OLEDs are outlined in Table 2.

Among the AIE-active cores, TPE derivatives with a donor-acceptor structure were used also to obtain efficient yellow AIE OLEDs.[23]

Two AIE-active compounds, BDTPE (4,4′-bis(diethylamino)-4′′-dimesitylboronotetraphenylethene) and BBTPE (4,4′-bis(diethylamino)-4′′,4′′′-bis(dimesitylboron)tetraphenylethene), combining the donor effect of the dialkylamine with the electron withdrawing strength of the dimesitylboron group, show yellow emission colour. The OLED obtained by using BDTPE as emitter displays turn-on voltage of 5.1 V, 1978 cd/m^2 at 16.2 V as maximum luminance and 2.87 cd/A at 10.5 V as maximum current efficiency. The presence of two acceptor groups in BBTPE shifts the emission peak of the corresponding device to lower energy, from 566 to 601 nm, by keeping good performance. In fact, the turn-on voltage slightly increases up to 5.6 V, while the maximum luminance and the maximum current efficiency rise to 5292 cd/m^2 at 16.2 V and 2.92 cd/A, respectively.

A dramatic improvement on the performance of yellow OLEDs employing very similar emitters based on TPE was

reached by Tang and co-workers.[24] By introducing the carbazole as donor instead of the dialkyamine in presence of one or two dimesitylboron group as acceptor, efficient yellow-greenish were obtained. Also in this case, the use of a symmetric structure allows bathochromically shifting the emission. Indeed, with the 3,3′-{1-[4-(dimesitylboryl)phenyl]-2-phenylethene-1,2-diyl}bis(9-ethyl-9H-carbazole) (PDPBCE) as emitter the device shows a maximum at 537 nm, with low turn-on voltage (3.8 V), high maximum luminance (59130 cd/m^2 at 15 V) and maximum current efficiency of 6.43 cd/A at 6.8 V. On the other hand, by employing the symmetric 1,2-bis[4-(dimesitylboryl)phenyl]-1,2-bis(9-ethyl-9H-carbazol-3-yl)ethene (BDPBCE) the emission peak shift to 554 nm, together with a decrease of the turn-on voltage to 3.0 V, the increase of maximum luminance at 67500 cd/m^2 at 15 V and 11.2 cd/A at 5.0 V as maximum current efficiency.

Different emission colours were obtained connecting TPE with phenanthro[9,10-d]imidazole in a linear configuration by changing the π-systems.[25] In particular, the insertion of 5-phenyl-benzo-2,1,3-thiadiazole (PIPBT-TPE) moiety as bridge allows obtaining yellow OLED with good performance. In fact, the device shows electroluminescent peak at 552 nm with maximum luminance of 38100 cd/m^2 and maximum current efficiency of 10.6 cd/A, and turn-on voltage of 3.7 V, with a power efficiency of 7.5 lm/W and an external quantum efficiency of 2.3%.

The versatility of TPE as AIEgen for OLEDs was demonstrated one more time by binding TPE and carbazole in linear configuration to tune the emission of electroluminescent devices. Grazulevicius and co-workers show the possibility to shift the emission of OLEDs from blue to yellow by modulating the aggregation-induced emission with the formation of exciplex just by adding hole-transporting and electron blocking layers in the device.[26] The orientation of the carbazole, bound selectively in position 3, 2 or 9, seems not to have a strong influence either in the emission or in the turn-on voltage, while became important in the brightness and current efficiency. The highest performance were obtained for green devices, while the best yellow device employing the 2-(4-(4-(1,2,2-triphenylvinyl)phenylethenyl)phenyl)-9-ethylcarbazole (2CzTPE) as emitter (λ_{EL} ~ 540 nm) has a turn-on voltage of 2.8 V, maximum luminance of 5400 cd/m^2 at 11 V, and 2.8 cd/A as current efficiency. However, the EQE remains very low (0.9%).

Besides TPE, other aromatic systems have been used as core of AIEgens emitting in the yellow-orange region (Chart 2).

Chart 2. AIE-active core alternative to TPE recently used for yellow-orange emission: maleimide (**4**), benzomaleimide (**5**), coumarin (**6**), phosphindole oxide (**7**) and silole (**8**).

For example, maleimide was also successfully used in combination with carbazole as donor to produce yellow OLEDs by Patil and co-workers. They show that the presence of two carbazole units on the maleimide in 3,4-bis(4-(9H-carbazol-9-yl)phenyl)-1-hexyl-1H-pyrrole-2,5-dione (Cbz-MI(d)) gave the best performance as bright yellow device with emission maximum at 584 nm, turn-on voltage of 5.85 V, EQE of 4.1%, maximum luminance of 73915 cd/m^2 and maximum current efficiency of 13.8 cd/A.[27] Interestingly, by increasing the length of the □-bridge with a second phenyl ring between donor and acceptor in the Cbz-MI, the emission shifts hypsochromically to 563 nm and the performance decreases,
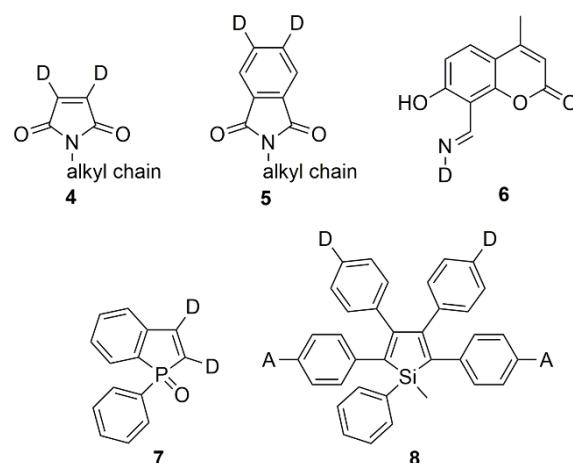
displaying a turn-on voltage at 5.88 V, lower maximum luminance (18303 cd/m^2), minor current efficiency (12.9 cd/A) and a slightly lower EQE (3.7%).

A slight change in the performance of yellow electroluminescent devices due to the increasing donor-acceptor distance was also observed by Tang and co-workers with different electron donor and electron withdrawing groups.[28] In this case, the phosphindole oxide acts as the acceptor unit bearing either two triphenylamine (TPA)2PIO or two phenyl-triphenylamine (TPAP)2PIO as donor substituents. Device fabricated with the longer π-bridge dye (TPAP)2PIO shows yellow emission at 546 nm with turn-on voltage of 4.2 V and EQE of 2.2%, while 21890 cd/m^2, 5.1 lm/W and 7.8 cd/A are the maximum luminance, the power efficiency and the maximum current efficiency, respectively. The use of the shorter π-system of (TPA)2PIO as emitter displays a slightly shifted yellow emission at 555 nm with turn-on voltage of 4.0 V, while the other performance are comparable with the abovementioned device (EQE of 2.0%, maximum luminance of 18830 cd/m^2, maximum current efficiency of 7.1 cd/A and power efficiency of 4.3 lm/W).

Recently, Qi and co-workers presented a coumarin-based Schiff base as AIE emitter for yellow OLED.[29] Due to the presence of Excited-State Intramolecular Proton Transfer (ESIPT) and TICT phenomena, the reported compounds appear very interesting for device application. However, the authors reported only data about doped OLED, which exhibits normal and tautomer ESIPT emissions maximized at 560 and 600 nm, respectively, turn-on voltage at 4.5 V and maximum luminance of 1675 cd/m^2 at 14 V.

Aryl amines were successfully used as electron donors in AIE dyes for devices emitting orange light. For example, triphenylamine as donor was also used by García-Frutos and collaborators in combination with azaindole as acceptor unit in the 5-(4-(diphenylamino)phenyl)-1-dodecyl-1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde (3).[30] The non-doped device exhibits low turn-on voltage of 3 V, and a broad EL emission at 566 nm, which becomes more intense upon increasing the bias from 0 to 18 V. Interestingly, the EL band is red-shifted with respect to the photoluminescence spectrum in thin film, which indicates that the hole-electron recombination leads to different emitting species.

Although silole-based chromophores have been applied in blue to yellow emitting electroluminescent devices, a recent study shows that siloles with an extended conjugation system

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can be employed as dyes for orange emitting devices.[31] The rare siloles functionalised with both donors and acceptors in 2,3,4,5-positions show twisted structures and good thermal stability. The presence of diphenylamino units as electron donor increases the hole injection and transport ability, while the two different electron-withdrawing groups (cyano for $(DPA)_2(CN)_2MPPS$ and dimesitylboryl for $(DPA)_2(MesB)_2MPPS$, respectively) allow the emission on the orange region. Non-doped OLEDs with $(DPA)_2(CN)_2MPPS$ and $(DPA)_2(MesB)_2MPPS$ as emitters

exhibit long wavelength emission with peaks at 557 and 567 nm, respectively, and turn-on voltage are as low as 3.7 and 3.6 V. Furthermore, the devices show maximum luminance of 32050 and 23700 cd/m², power efficiency of 3.9 and 5.1 lm/W, maximum current efficiency of 4.6 and 7.1 cd/A, and EQE of 1.6% and 2.4%, respectively.

Table 3. Performance of non-doped yellow and orange OLEDs.

Compound	λ_{EL}	V_{on}	L_{max}	CE_{max}	PE_{max}	EQE	Ref.
	Nm	V	cd m^{-2}	cd A^{-1}	lm W^{-1}	%	
PTNAA	615	4.6	23 931	13.7	9.6	7.1	[38]
BPPTA	625	4.1	21 673	11.8	8.9	-	[39]
NZ2AC	663	-	9 537	2.6	2.0	2.8	[37]
NZ2TPA	696	3.9	6 330	-	-	3.9	[36]
TPANSeD	730	5.2	-	-	-	2.7	[40][a]
NZ2mDPA	786	-	-	-	-	0.8	[42][b]

[a] Doped with TADF host. [b] Doped with CBP and Ir(bt)₂acac

Another highly twisted AIE-active compound for orange OLED, 2,2'-(([1,1'-biphenyl]-4,4'-diylbis(phenylazanediyl))bis(4,1-phenylene))bis(3,3-diphenylacrylonitrile) (BP2TPAN), was reported very recently by Wei and collaborators.[32] The particular conformation makes the dye suitable as mechanochromic luminogen and induces high thermal stability. However, the non-doped electroluminescent device emitting at 570 nm exhibits moderate performance, with turn-on voltage at 4.8 V, very low power efficiency of 0.84 lm/W, maximum luminance of 925 cd/m² and maximum current efficiency of 2.9 cd/A, while the EQE is 1.1%.

In 2017 Xue and co-workers reported a compound showing both mechanochromic and AIE properties suitable for solution-processed orange OLED.[33] The 9,10-divinylanthracene core of the 2,6-bis(diethoxyphosphorylmethyl)-9,10-bis(N-2-ethylhexylcarbazol-3-yl-vinyl-2)anthracene (PAC8) is known as starting material to obtain AIE luminogens, while the pendent groups increase the solubility in common organic solvents. The electroluminescent device shows an orange emission (596 nm) with turn-on voltage of 5.0 V, and maximum luminance of 5920 cd/m², together with a power efficiency of 3.9 lm/W, EQE of 3.9%, and an excellent maximum current efficiency of 9.4 cd/A, resulting the most efficient device among the solution-processed AIE-molecules and comparable to the most efficient vapour-deposited OLEDs.

2.3. Red and near infra-red AIEgens emitters

The simultaneous realization of high quantum yield and exciton recombination efficiency (η_r) remains a grand challenge in the quest for red and near-infrared (NIR) organic light-emitting diodes. The low photoluminescence quantum yields (PLQYs) are still the main shortcoming especially for most fluorescent NIR emitters, which directly lead to their low electroluminescence efficiencies. Typically, most red and NIR fluorescent emitters with donor and acceptor moieties exhibit a limited overlap between the highest

occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thus, leading to a substantially low radiative transition rate according to Fermi's Golden rule and therefore low PLQY values.[34] Such emitters also suffer from the intrinsic limitation of the energy gap law,[35] which describes an exponential increase in non-radiative rate and a decrease in radiative rate as the optical energy gap decreases when shifting towards the deep red and the NIR region of the light spectrum.

To date, suitable organic emitters include organic small molecules, conjugated polymers, and lanthanide and transition-metal complexes. Most organic red fluorophores usually consist of planar molecules with extended π-conjugation, such as rylenes, porphyrins and conjugated molecules that are substituted with an electron donor–acceptor (D–A) at the termini of the conjugated systems. Recently, several strategies have been proposed to realize high hr in pure organic dyes, exploiting charge-transfer states (CT) in such donor-acceptor (D-A) dyes (Chart 3). The features of red/NIR non-doped OLEDs fabricated with the reported compounds are summarized in Table 3.
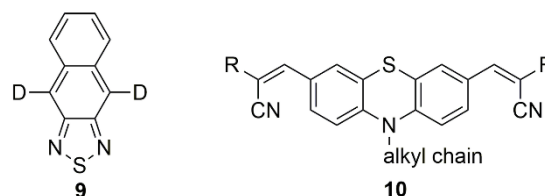

Chart 3. AIE-active systems for red and NIR non-doped OLEDs.

Yang and co-workers reported a highly efficient naphthothiadiazole derivative with PLQY up to 60% and this was attributed to the AIE characteristic of the compound.[36] In their work, a D-π-A-π-D type compound was designed with naphthothiadiazole (NZ) as acceptor and two triphenylamines as donor units, and the non-doped devices based on this emitter (NZ2TPA) exhibit excellent performance, achieving an EQE of 3.9% with the emission

peak at 696 nm and a high luminance of 6330 cd/m^2, with η_r up to 33%, which are among the highest in the reported non-doped NIR fluorescent OLEDs. Moreover, the device maintains a high EQE of 2.8% at high brightness of 1000 cd/m^2, with very low efficiency roll-off.

In the same year, they also reported a new red fluorescent emitter, named NZ2AC, incorporating an NZ unit electron acceptor core, a dimethylacridin unit electron donor, and a phenyl bridge into a D-π-A-π-D molecular architecture.[37] The non-doped OLEDs exhibit a deep-red emission at 663 nm, attributed to the AIE feature of NZ2AC, a low efficiency roll-off value of 18% at high brightness, with a luminance of 5000 cd/m^2 and a maximum EQE of 2.8%, corresponding to a maximum η_r of 93%, which are among the highest efficiencies at such high luminance for red/deep-red OLEDs.

However, conventional organic fluorophores undergo strong intermolecular π–π interactions in a highly concentrated or aggregated state, which lead to non-radiative decay of the excitons causing either weak emission or no emission in the aggregates. To overcome this limitation, Somanathan et al designed a class of organic luminophores with a structural combination of typical strong electron-donating phenothiazine and electrondeficient α-cyanostilbene with end-capped naphthalene, named PTNAA. The EL spectrum of such AIEgens showed a broad emission centred at 615 nm and the device showed a maximum luminance of 23931 cd/m^2 at 12 V, a maximum current efficiency of 13.7 cd/A, power efficiency of 9.6 lm/W and 7.13% EQE, with a low turn-on voltage of 4.6 V.[38]

In the same year, they also reported a novel multifunctional organic fluorophore consisting of two terminal attachments of push–pull moieties separated by a biphenyl free rotor named BPPTA and its copolymers. The OLEDs exhibited a maximum brightness of 21673 cd/m^2 at 16 V, whereas maximum luminous and power efficiencies of 12.43 cd/A and 9.04 lm/W were obtained, respectively, with a low turn voltage of 4.1 V.[39] Careful investigation revealed that the enhanced emission in the solid state was due to the formation of J-aggregates with a particular ordered supramolecular self-assembly. Moreover, the device with BPPTA functionalised with polyfluorene groups displayed pure and efficient white-light emission with CIE coordinates of (0.32, 0.33) and maximum luminance, current and power efficiencies of 15672 cd/m^2, 9.30 cd/A and 7.98 lm/W.

In recent years, many NIR emitters with high efficiencies have been designed and reported, also thanks to the breakthrough of the new radiative mechanisms. Nevertheless, it is a continual challenge for NIR organic fluorescent emitters to simultaneously realize high η_r and EQE in one molecule. It is often more accessible to fulfil these two requirements by assigning them to different molecules. The current strategy consists in using TADF materials as a sensitizing host to harvest triplet excitons, achieving high η_r, combined with conventional dopants with high PLQY to achieve highly efficient electroluminescence.

Qiao et al demonstrated high-efficiency NIR-OLEDs using a TADF host doped with a special naphthoselenadiazole emitter, TPANSeD.[40] The optimized devices without outcoupling enhancements display high EQEs up to 2.65% at 730 nm with η_r up to 45.7%, with a very small efficiency roll-off of 2.41% at 200 mA/cm^2, which are among the most efficient values for fluorescent OLEDs over 700 nm. Liao and co-workers set a new record for deep-red and NIR OLEDs based on TADF materials, with a high EQE up to 10.19% at 693 nm and a PLQY up to 63% and with a high EQE of 2.19% at 777 nm and a PLQY up to 17%, respectively.[41]

However, OLEDs with NIR emission beyond 750 nm are still far insufficient as compared with red-emitting systems. Especially, solution processed NIR OLEDs have not been reported, which provide a more cost-effective approach to developing novel OLEDs for mass production, as opposed to thermally evaporated devices.

Recently, Yang and co-workers, designed and developed a new fluorophore named NZ2mDPA, which was composed of a naphthothiadiazole acceptor core and two 4-methyl-N-phenyl-N-(p-tolyl)aniline moieties as the donors at the peripheral via direct linkage.[42] The optimized device, composed of 4,4′ -N,N-dicarbazolebiphenyl (CBP) as the host, Ir(bt)$_2$(acac) as the sensitizer, and NZ2mDPA as the emitter, achieved 786 nm emission with a EQEmax of 0.77%.

2.4. TADF AIEgens emitters

The introduction of the Thermally Activated Delayed Fluorescence (TADF) concept applied to OLED by Adachi in 2012[43] opened a new attractive research activity also in the field of the AIE chromophores. Common design of TADF dyes involve the combination of donor (D) and acceptor (A) units in a way that the HOMO and LUMO orbitals are lying separately on different moieties in a single molecule. With this strategy, the gap between singlet and triplet states (ΔE_{ST}) is very small (< 0.1 eV) allowing efficient thermally induced up-conversion from the triplet to the singlet state through reverse intersystem crossing (RISC) process, which generates the delayed fluorescence (see Figure 2). This approach allows increasing the internal quantum efficiency of the conversion of electricity into light to nearly 100%.

Figure 2. Schematic representation of the TADF phenomenon.
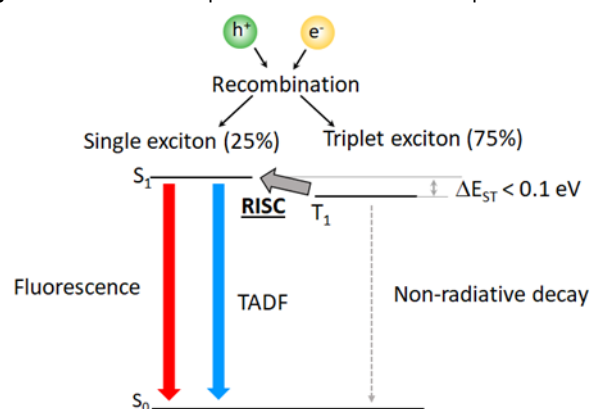
However, common TADF molecules can easily aggregate through π–π interactions, resulting in the ACQ phenomenon. The design of dyes combining AIE with TADF behaviour, sometimes indicated as AIDF, from aggregation-induced delayed fluorescence, appears as an efficient solution to overcome this limitation, as introduced first in 2015 by Xu, Zhang and co-workers.[44] The authors showed the importance of the asymmetric configuration (D-A-D') to reach the combination of the two phenomena. Afterwards, numerous researchers began to explore the application of AIEgens with TADF behaviour in electroluminescent devices.

Hereafter, we report the structure of dyes emitting at different wavelengths (Chart 4 and Chart 5) and the performances of the corresponding devices, which are summarized in Table 4.

2.4.1. Blue and green TADF AIEgens

As well for the general AIE non-doped OLEDs, the design and synthesis of blue-emitting devices remain challenging also by employing AIDF compounds.

Recently, Guo and co-workers showed that the isomer of the well-known blue TADF dye bis-[4-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]-sulfone (DMAC-DPS) obtained by linking the electron donor DMAC groups to the diphenyl sulfone (DPS) unit in meta position, exhibits AIDF properties and blue emission.[45] The non-doped OLED employing the bis(3-(9,9-dimethyl-9,10-dihydroacridine)phenyl)sulfone (mSOAD) achieves very remarkable performance as blue electroluminescent device with emission maximum at 488 nm and EQE of 14.0%. Besides, the turn-on voltage is 3.1 V, the maximum current efficiency and the maximum power efficiency are 31.7 cd/A and 28.4 lm/W, respectively.
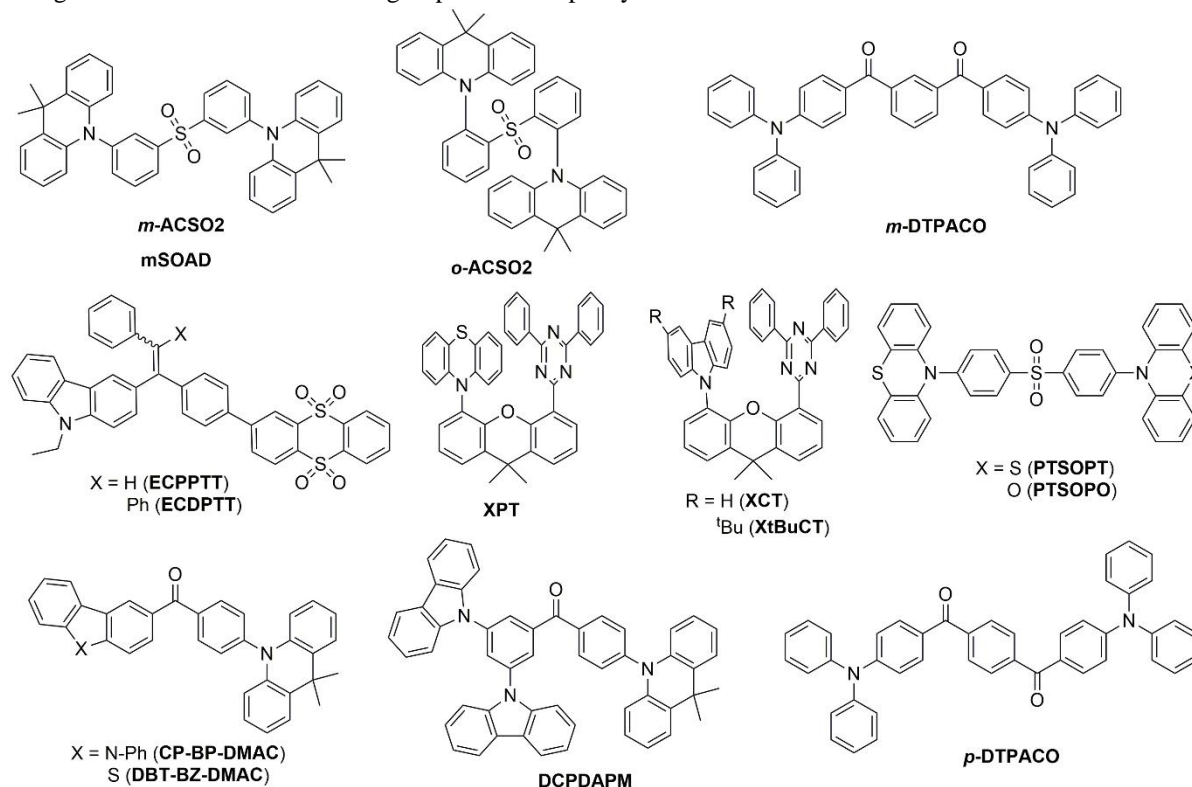

Chart 4. Chemical structure of AIDF dyes emitting blue-green.

The high performance of the AIDF OLED employing the isomer of DMAC-DPS was confirmed later by Yang and co-workers, which reported highly efficient sky-blue solution-processed OLEDs by using two different isomers.[46] Besides the isomers bis-[3-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]-sulfone (m-ACSO2) indicated as mSOAD by Guo and co-workers,[45] they prepare also the bis-[2-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]-sulfone (o-ACSO2) compound. Both molecules maintain good TADF properties with excellent solubility and AIE effect thanks to the large twisted angles between donors and acceptor unit. Device fabricated using m-ACSO2 exhibits the best performance as blue OLED (EL peak at 486 nm), with a turn-on voltage of 4.1 V, a maximum current efficiency of 37.9 cd/A, a maximum power efficiency of 23.8 lm/W and an EQE of 17.2%, thus showing better performance than the OLED obtained with DMAC-DPS. Interestingly, the performance data are different from the previous report, maybe due to the different materials used to fabricate the multilayer devices. By employing the other isomer o-ACSO2, the emission results slightly red shifted at 492 nm with an EQE of 5.9%, turn-on voltage at 4.4 V, maximum current efficiency of 14.1 cd/A, and maximum power efficiency of 7.8 lm/W.

Another sky blue OLED was reported by Zhang, Tao and co-workers[47] by using the 1,3-phenylenebis((4-(diphenylamino)phenyl)methanone) (m-DTPACO) as AIDF compound. The electroluminescent device shows EL maximum at 480 nm, with turn-on voltage of 3.9 V, maximum luminance of 10005 cd/m², maximum current efficiency of 4.8 cd/A, power efficiency of 2.8 lm/W and EQE of 2.4%.

An interesting strategy employed to have molecules showing AIDF properties was presented by Baldo, Swager and co-workers.[48] They used a U-shaped space-through architecture in which the π−π interactions mediates the through-space charge transfer because of the close proximity of donor and acceptor groups. The design involves a xanthene-based nonplanar molecule that cofacially organizes a donor and an electron-withdrawing group at controlled distance. In particular, the diphenyl-triazine acts as acceptor in combination with different electron donating substituents (phenothiazine for XPT, carbazole for XCT, and 3,6-di-tert-butylcarbazole for XtBuCT). The emission changed depending on the strength of the donor group, allowing tuning the device colour from blue to yellow (488 and 584 nm, respectively). Although the authors reported only data about doped OLEDs, the very innovative approach convinced us to mention it in this review anyway.

Blue-green OLED was obtained by Tang and co-workers by using the triphenylethylene as AIE-unit, a carbazole as donor and hole-transporting group, and thianthrene-9,9,10,10-tetraoxide as acceptor (ECPPTT).[49] The potential application of the dye as emitting layer is demonstrated by the performance of the non-doped OLED emitting at 494 nm, with turn-on voltage of

5.6 V, maximum luminance of 10090 cd/m^2 and maximum current efficiency of 3.437 cd/A. In the same article, the authors showed that the same donor-acceptor pair linked to the classical TPE as AIE-core (ECDPTT) displays a red-shifted emission, with EL maximum in the green region (517 nm). The performance of this device are lower than formerly reported, with higher turn-on voltage (5.8 V), and lower maximum luminance (7561 cd/m^2) and maximum current efficiency (2.478 cd/A).

Table 4. Performance of non-doped AIDF OLEDs.

Compound	λ_{EL} nm	V_{on} V	L_{max} cd m^{-2}	CE_{max} cd A^{-1}	PE_{max} lm W^{-1}	EQE %	Ref.
m-DTPACO	480	3.9	10 005	4.8	2.8	2.4	[47]
m-ACSO2	486	4.1	-	37.9	23.8	17.2	[46]
mSOAD	488	3.1	-	31.7	28.4	14.0	[45]
o-ACSO2	492	4.4	-	14.1	7.8	5.9	[46]
ECPPTT	494	5.6	10 090	3.437	-	-	[49]
G2B	500[a]	4.3[a]	-	11.3[a]	7.1[a]	4.8[a]	[54]
	500[b]	3.4[b]		14.0[b]	11.5[b]	5.7[b]	
CP-BP-DMAC	502	2.7	37 680	41.6	37.9	15.0	[51]
DBT-BZ-DMAC	508	2.7	27 270	43.3	35.7	14.2	[52]
G3B	513[a]	3.6[a]	-	8.7[a]	6.6[a]	3.6[a]	[54]
	516[b]	2.9[b]		7.7[b]	5.7[b]	2.9[b]	
p-DTPACO	517	3.9	7 354	10.8	8.2	3.7	[47]
ECDPTT	517	5.8	7 561	2.478	-	-	[49]
DCPDAPM	521	3.2	123 371	26.88	15.63	8.2	[53]
SBDBQ-DMAC	544	2.8	14 578	35.4	32.7	10.1	[57]
DBQ-3DMAC	548	2.6	29 843	41.2	45.4	12.0	[57]
CP-BP-PXZ	548	2.5	100 290	59.1	65.7	18.4	[51]
CP-BP-PTZ	554	2.5	46 820	46.1	55.7	15.3	[51]
DBT-BZ-PXZ	557	2.9	-	26.6	27.9	9.2	[56]
DBT-BZ-PTZ	563	2.7	-	26.5	29.1	9.7	[56]
DBQPXZ	564	3.4	20 167	24.9	19.6	8.8	[58]
SFDBQPXZ	584	3.4	21 102	24.3	22.5	10.1	[58]
PCZ-CB-TRZ	586	6.3	4 530	16.7	7.6	11.0	[55]
DFDBQPXZ	588	3.2	16 497	21.0	20.6	9.8	[58]
2PCZ-CB	590	4.4	-	19.9	11.2	9.2	[55]
SBDBQ-PXZ	608	2.4	21 050	10.5	12.0	5.6	[57]
DBQ-3PXZ	616	2.8	13 167	7.5	6.2	5.3	[57]
TPA-CB-TRZ	631	4.4	-	12.0	7.9	10.1	[55]

[a] Device A with TBPi layer deposited by vacuum evaporation. [b] Device B with TBPi layer deposited by spin coating.

In 2016, Lee and co-workers[50] described the application in non-doped green OLEDs of the pure organic AIE type emitters with TADF behaviour previously reported by Xu, Zhang and co-workers.[44] By comparing symmetric and asymmetric configuration of donor and acceptor groups, i.e. the use of one (phenothiazine) or two different donors (phenothiazine and phenoxazine) in combination with one central acceptor unit (bis-phenyl sulfone), the authors show that the asymmetry is the key characteristic to reach the AIDF effect also in device. Indeed, the non-doped film in OLEDs of the asymmetric PTSOPO provided higher current density, higher luminance and higher EQE than the symmetric PTSOPT. In particular, the non-doped PTSOPO device can reach maximum EQE of 17.0%, with green emission. However, the authors are not indicating values to allow a comparison between the performance of the fabricated devices and other reported OLEDs.

The asymmetric triad structure was also successfully explored by Tang and co-workers[51] to obtain OLEDs

emitting with different colours. The dye based on a D-A-D' configuration, where the D-A portion is made by 9-phenyl-9H-carbazole bound in position 3 to a benzoyl unit (CP-BP) and employing a 9,9-dimethyl-9,10-dihydroacridine (DMAC) as third substituent gives a blue-greenish OLED. Interestingly, the HOMO orbitals are localized on the electron-donating D part (DMAC) and the LUMOs on the benzophenone (BP) core and extended to another half to the carbazole moiety, allowing a reduction of the ΔE_{ST} compared to analogous molecules bearing a phenoxazine (PXZ) or a phenothiazine (PTZ) instead of DMAC (0.11, 0.45 and 0.33 eV for CP-BP-PXZ, CP-BP-PTZ and CP-BP-DMAC, respectively). The separated distribution of the frontier orbitals arises from the quasi-planarity between CP and BP and the perpendicular orientation of the donor substituent D', as confirmed by crystal structures. Moreover, the twisted phenyl ring at the 9-position of the carbazole hampers the close packing between molecules and weakens intermolecular interactions, thus reducing the ACQ effect on

film. The EL emission maximum is 502 nm, with low turn-on voltage (2.7 V), maximum luminance of 37680 cd/m^2, maximum power efficiency of 37.9 lm/W, maximum current efficiency of 41.6 cd/A, with EQE of 15.0%. It is worth noting the very low roll-off efficiency (0.2%), demonstrating the high performance of the non-doped blue-greenish OLED.

Another asymmetrical AIEgen based on the BP core bearing DMAC and dibenzothiophene (DBT) as donors (dibenzothiophenebenzoyl-9,9-dimethyl-9,10-dihydroacridine, DBT-BZ-DMAC) allowed obtaining efficient green OLED.[52] The non-doped device emits at 508 nm and turn-on at 2.7 V, with maximum luminance of 27270 cd/m^2, maximum current efficiency of 43.3 cd/A, power efficiency of 35.7 lm/W and EQE of 14.2%.

By changing the dibenzothiophene unit with two carbazoles in the D-A-D' structure presented before, the asymmetrical dye (3,5-bis-carbazol-9-yl-phenyl)-[4-(9,9-dimethyl-9H-acridin-10-yl)-phenyl]-methanone (DCPDAPM) maintains the combination of AIE and TADF properties, resulting in an efficient green OLED.[53] The non-doped device displays a maximum EL peak at 521 nm with turn-on voltage of 3.2 V. Additional interesting data (maximum luminance 123371 cd/m^2, maximum current efficiency 26.88 cd/A, maximum power efficiency 15.63 lm/W, and EQE 8.15%) confirms the excellent performance of the green OLED.
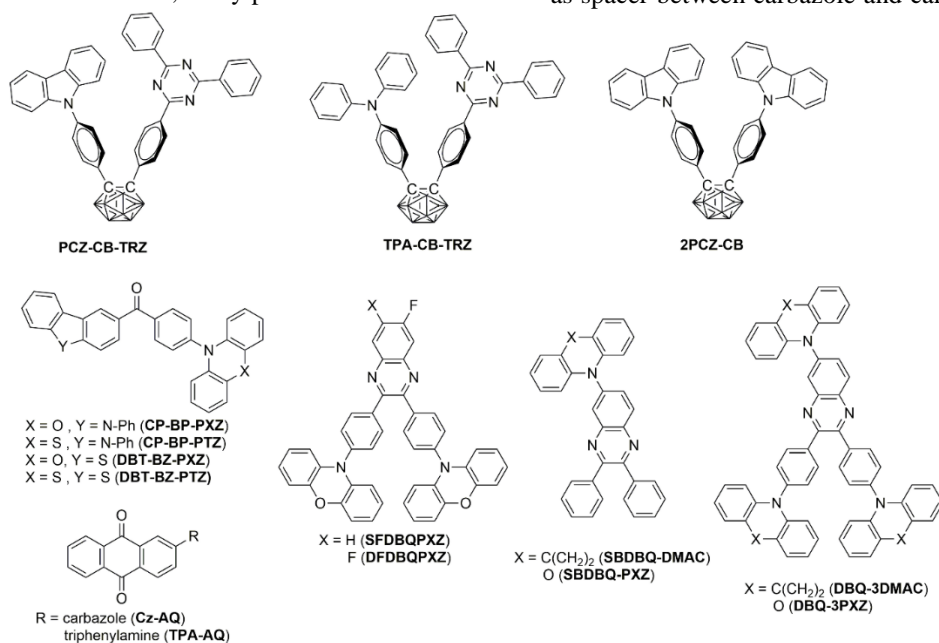
Fujita and co-workers reported on the solution-processed green devices obtained by using dendritic molecules based on BP core and carbazole.[54] Different dendrimers (GnB, n = generation = 1−3) are prepared, while only G2B and G3B were tested as emitting layer in electroluminescent devices due to the solubility of G1B in the solvent employed for the fabrication of devices. In fact, a key point of this research is

transporting layer TPBi = 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene, i.e. by vacuum deposition (device A) or by spin coating (device B). Interestingly, the two devices showed similar performance with both emitting layers, indicating the effectiveness of the fabrication process used. In particular, OLEDs with G2B emits at 500 nm with turn-on voltage of 4.3 and 3.4 V, maximum current efficiency of 11.3 and 14.0 cd/A, maximum power efficiency of 7.1 and 11.5 lm/W, EQE of 4.8% and 5.7% for device A and B, respectively. By employing G3B as emitting layer, the EL shifts at 513 nm (516 nm for device B) and the EQE decreases to 3.6% and 2.9% for device A and B, respectively. The other data for G3B-based OLEDs are 8.7 and 7.7 cd/A (maximum current efficiency), 6.6 and 5.7 lm/W (maximum power efficiency) for device A and B, respectively.

Besides the abovementioned sky blue emitter *m*-DTPACO, Zhang and Tao[47] showed that the OLED fabricated with the isomer *p*-DTPACO exhibits green emission (517 nm), with performance comparable with the blue OLED. In fact, the turn-on voltage is 3.9 V, the maximum luminance, maximum current efficiency, power efficiency and EQE are 7354 cd/m^2, 10.8 cd/A, 8.2 lm/W and 3.7%, respectively.

2.4.2. Yellow, orange and red TADF AIEgens

Several yellow OLEDs have been reported so far, some of them showing very high performance. For example, in 2016 Yasuda and co-workers reported efficient AIE-active compounds with triad structures (D-A-A') based on o-carborane as central unit and triphenyltriazine as second acceptor.[55] By using carbazole as D unit and a phenyl ring as spacer between carbazole and carborane (PCZ-CB-TRZ),

PCZ-CB-TRZ   TPA-CB-TRZ   2PCZ-CB

X = O , Y = N-Ph (**CP-BP-PXZ**)
X = S , Y = N-Ph (**CP-BP-PTZ**)
X = O , Y = S (**DBT-BZ-PXZ**)
X = S , Y = S (**DBT-BZ-PTZ**)

X = H (**SFDBQPXZ**)
F (**DFDBQPXZ**)

X = C(CH$_2$)$_2$ (**SBDBQ-DMAC**)
O (**SBDBQ-PXZ**)

X = C(CH$_2$)$_2$ (**DBQ-3DMAC**)
O (**DBQ-3PXZ**)

R = carbazole (**Cz-AQ**)
triphenylamine (**TPA-AQ**)

Chart 4. Chemical structure of yellow, orange and red emitting AIDF dyes

the strategy used for the preparation of OLEDs, which are fully solution processed organic multilayer fabricated by the orthogonal solvent approach. Two types of devices were prepared, depending on the deposition of the electron-

a highly efficient yellow OLED (λ_{EL} = 586 nm) with EQE of 11.0% was obtained in non-doped configuration. The other data of the device report a turn-on voltage is 6.3 V, maximum

luminance of 4530 cd/m^2, maximum current efficiency of 16.7 cd/A and power efficiency of 7.6 lm/W. The authors showed that also the symmetric compound with two carbazoles as donor groups linked to the carborane (2PCZ-CB) generates a yellow device with EL maximum at 590 nm. In this case, the turn-on voltage of the non-doped OLED is 4.4 V, the maximum current efficiency is 19.9 cd/A, power efficiency is 11.2 lm/W, with EQE of 9.2%.

Alternative triad structures reported by Tang and co-workers[51] based on 9-phenyl-9H-carbazole bound in position 3 to a benzoyl unit (CP-BP) as D-A pair in the D-A-D' configuration displayed higher performance. The dyes are alternatively bearing a phenoxazine (PXZ) or a phenothiazine (PTZ) as D'. The best performance was observed by using CP-BP-PXZ as emitter, which generates a yellow emission peaked at 548 nm with turn-on voltage at 2.5 V, high maximum luminance of 100290 cd/m^2, maximum power efficiency of 65.7 lm/W, EQE of 18.4% and maximum current efficiency of 59.1 cd/A. Likewise the greenish-blue device with CP-BP-DMAC described before, the current efficiency roll-off is only 1.2%, demonstrating the efficiency stability. The device using CP-BP-PTZ as yellow emitter (λ_{EL} = 554 nm) showed slightly lower performance, which authors associate to the reduced fluorescent quantum yield and increased ΔE_{ST} in neat film. Although the roll-off efficiency is 16.7%, the high luminance recorded is 46820 cd/m^2 with EQE of 15.3%, which remains a high-level performance for electroluminescent devices. The turn-on voltage remains low (2.5 V), while the maximum current efficiency and the power efficiency slightly decreases to 46.1 cd/A, and 55.7 lm/W, respectively.

Besides, by employing other D-A-D' compounds bearing PXZ or PTZ as D' unit, benzoyl as central acceptor and the planar DBT as D group as emitters, it is possible to observe yellow AIDF emission.[56] OLEDs incorporating DBT-BZ-PXZ and DBT-BZ-PTZ as emitting layer, display EL emission with peaks at 557 and 563 nm, respectively, with turn-on voltage of 2.9 and 2.7 V. The two devices exhibit similar performance, with maximum current efficiency of 26.6 and 26.5 cd/A, maximum power efficiency of 27.9 and 29.1 lm/W, and EQE of 9.2% and 9.7% for DBT-BZ-PXZ and DBT-BZ-PTZ, respectively.

Yang and co-workers employed quinoxaline derivatives as alternative acceptor unit in AIEgens with TADF behaviour. Yellow EL non-doped OLEDs were obtained by employing the 2,3-diphenylquinoxaline (DBQ) as acceptor bearing different number of DMAC as donor unit. In particular, devices using compounds with one or three DMAC substituents, i.e. 6-(9,9-dimethyl-9,10-dihydroacridinyl-10-yl)-2,3-diphenylquinoxaline (SBDBQ-DMAC) and 2,3-bis(4-(9,9-dimethyl-9,10-dihydroacridinyl-10-yl)phenyl)-6-(9,9-dimethyl-9,10-dihydrogen-acridine-10-yl)-quinoxaline (DBQ-3DMAC), showed yellow emission with peaks at 544 and 548 nm, respectively.[57] The turn-on voltage is quite low for both emitters (2.8 and 2.6 V), and the EQE are comparable (10.1% and 12.0%). The maximum luminance, maximum current efficiency, maximum power efficiency are 14578 and 29843 cd/m^2, 35.4 and 41.2 cd/A, 32.7 and 45.4 lm/W for SBDBQ-DMAC and DBQ-3DMAC, respectively.

The same research group reported the yellow OLED obtained incorporating the 10,10'-((quinoxaline-2,3-diyl)bis(4,1-phenylene))bis(10H-phenoxazine) (DBQPXZ) as emitting layer.[58] The non-doped device exhibits yellow EL with maximum at 564 nm, together with turn-on voltage of 3.4 V, a maximum luminance of 20167 cd/m^2, a current

efficiency of 24.9 cd/A, a power efficiency of 19.6 lm/W and an EQE of 8.8%.

The increase of the acceptor strength in the DBQPXZ molecule by introducing fluorine atoms on position 6 and 7 of the quinoxaline unit induces a bathochromic shift of the emission, thus allows observing orange EL in electroluminescent devices.[58] The non-doped OLEDs incorporating 10,10'-((6-fluoroquinoxaline-2,3-diyl)bis(4,1-phenylene))-bis(10H-phenoxazine) (SFDBQPXZ) and 10,10'-((6,7-difluoro-quinoxaline-2,3-diyl)bis(4,1-phenylene))-bis(10H-phenoxazine) (DFDBQPXZ) as emitting layer show EL emission maxima at 584 and 588 nm, respectively. The turn-on voltage is not changing (3.4 and 3.2 V), indicating that the efficiency of hole and electron injection is not influenced by the chemical modification of the dyes. The maximum luminance (21102 and 16497 cd/m^2), maximum current efficiency (24.3 and 21.0 cd/A), power efficiency (22.5 and 20.6 lm/W) and EQE (10.1% and 9.8%) of the two non-doped OLEDs indicate a more positive improvement by attaching only one fluorine atom.

If the quinoxaline core is linked with one or three PXZ units instead of the abovementioned DMAC, the EL of the non-doped devices is red-shifted at 608 and 616 nm in the case of one (SBDBQ-PXZ) and three PXZ units (DBQ-3PXZ), respectively.[57] The turn-on voltage seems to be independent from the nature of the donor attached to the quinoxaline core and the value remains similar to that recorded in compounds with DMAC (2.4 and 2.8 V for SBDBQ-PXZ and DBQ-3PXZ, respectively). The EQE of 5.6% and 5.3% indicates a very similar efficiency of the two non-doped OLEDs. Indeed, the performances are comparable in both devices, with a slight improvement using the mono-substituted dye: maximum luminance 21050 and 13167 cd/m^2, maximum current efficiency 10.5 and 7.5 cd/A, power efficiency 12.0 and 6.2 lm/W for SBDBQ-PXZ and DBQ-3PXZ, respectively.

The fabrication of red AIDF OLEDs is even more challenging than other colours and very few papers can be presented. One example is the work of Sun et al., based on the functionalisation of the anthraquinone with a triphenylamine unit, but they reported performance of doped device, which are not fitting with the focus of this review.[59]

The use of triphenylamine as donor in combination with o-carborane and triphenyltriazine in D-A-A' triad structure (TPA-CB-TRZ) to generate red emission was also presented by Yasuda and co-workers in 2016.[55] The EL emission of the non-doped device (λ_{EL} = 631 nm) is bathochromically shifted compared to the other carborane-based molecules reported as consequence of the higher donor strength of the substituent, with slightly lower efficiency (EQE = 10.1%). Interestingly, the ΔE_{ST} increases in the second compound (0.003 eV for PCZ-CB-TRZ vs. 0.146 eV for TPA-CB-TRZ), without remarkable change in the photophysical properties. The LUMO orbital is localized mainly on the triphenyltriazine unit, while the o-carborane seems to act as inert spacer. Besides, the turn-on voltage is 4.4 V, the maximum current efficiency is 12.0 cd/A and the power efficiency is 7.9 lm/W.

3. Summary and Outlook

Since the discovery of the AIE phenomenon, remarkable improvements have been made on the performance of non-doped electroluminescent devices. The recent results here reported illustrate the great effort made to enhance the

efficiency of pure organic non-doped OLEDs emitting different colours, including the near infrared region. In several cases, the donor-acceptor structure allows tuning the emission colour by varying the strength of the pair (stronger donor groups and/or more electron-withdrawing substituents).

However, the results are still not enough competitive for commercial application with the performance of metal-based phosphorescent devices. From this point of view, as mentioned in many articles, more efforts have to be directed to the optimization of the device design, for example by testing different materials in multilayer structures in order to create a better balance between charge transport and excitonic recombination on the emitting layer.

Nevertheless, the use of the new class of AIDF chromophores combining AIE with TADF appears a successful approach to overcome the limitation of EQE expected for OLEDs fabricated with fluorescent luminophores. In fact, the triplet to singlet up-conversion occurring in TADF process allows EQE exceeding the 10% with multiple dyes emitting at different wavelengths covering the entire visible spectrum from blue to red. Therefore, an increasing investigation on the design of novel AIDF chromophores is foreseen. However, synthesis, photophysical studies and application on devices have to been carried out together with computational analysis in order to increase the understanding of the AIDF phenomenon, which is still far to be completely comprehended.

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